Materials Science
Prof. S. K. Gupta
Department of Applied Mechanics
Indian Institute of Technology Delhi
Lecture 11
Polymers

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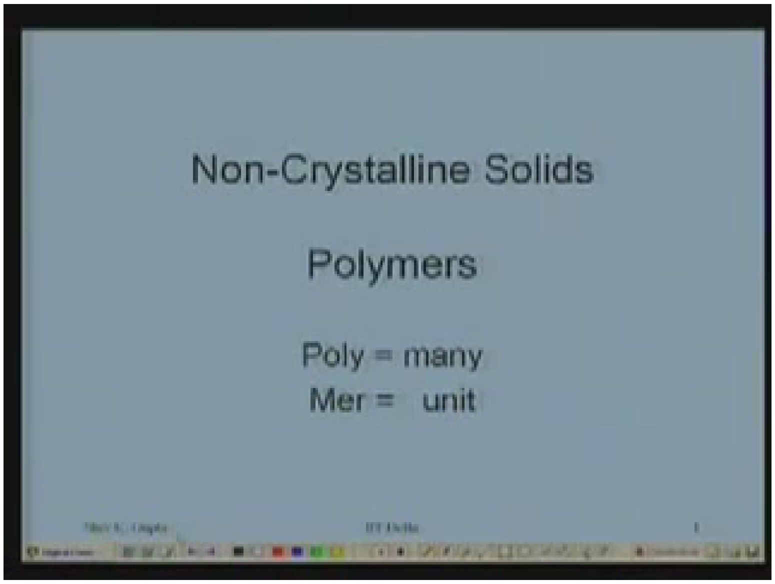

Non-Crystalline Solids

Polymers

Poly = many
Mer = unit

Well, in the last class we had begun to look at the polymers which are non-crystalline generally and we saw of these long chain polymers because network polymers there is no chance for us to get any crystallinity in them. And continuing with that we ended up the elastomers. We shall now look at the mechanical behavior of elastomers. Whereas you recall I said the elastomers are the polymers which behave like elastomers. They have the chain segments having translation mobility at room temperature. There is a natural tendency for binding and coiling that we express with the help of the monomer unit of polyisoprene.

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And there are few crosslinks. Here I show the crosslink is, in the lower picture the crosslinks are just one molecule or maybe one atom or something which is between the two chains like that. And here are smaller molecule or smaller chains which are the acting as crosslinks, the gray colors like this. Okay. So crosslinks can be made with the help of small molecule polymers as well, or smaller chains and it can also be made with the help of like I showed vulcanization of the natural rubber, we use sulfur. Okay.

So besides being the long chains they have to satisfy these conditions. There are few crosslinks, because in natural tendency we are binding and coiling and then the room temperature provides enough mobility to the chain segments. That is the translation mobility I am referring to because in solids oscillations are always present.

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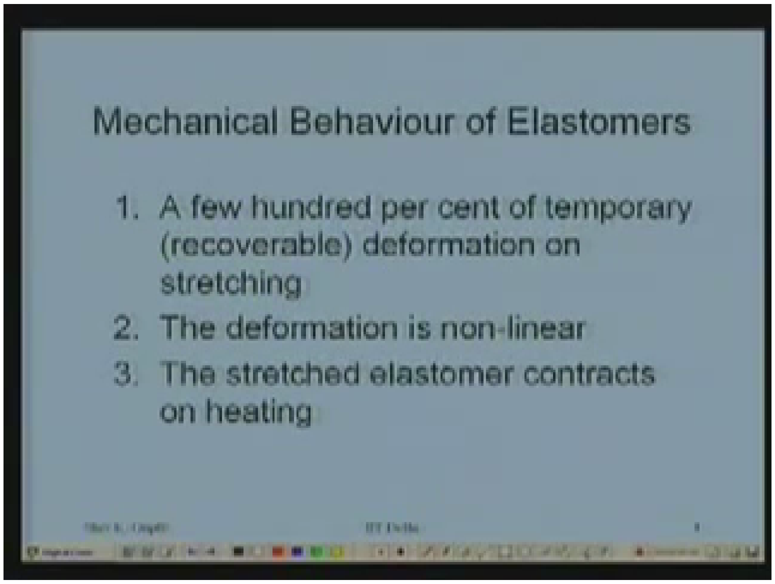

Mechanical Behaviour of Elastomers

1. A few hundred per cent of temporary (recoverable) deformation on stretching
2. The deformation is non-linear
3. The stretched elastomer contracts on heating

Now when we look at the mechanical behavior in elastomer, it is quite distinct from other materials which we will be talking about little later. If I have to test under stress or under force material like metal, steel and which is an alloy or copper or aluminum, I will get elastic elongation not exceeding 0.5 percent. It will be 0.2 percent, 0.15 percent, things like that. But here I get a few hundred percent of temporary deformation which is recoverable deformation.

Other words, when I remove the force the elastomer comes back to its original shape and size. After it was extended by the force to the tune of 400 percent, it comes back which is not the case in other metals and alloys or other solids. Secondly the deformation process is non-linear. Elastic behavior whether it is of steel or aluminum or any other material for that matter would be obeying the Hooke’s law. That is a linear elasticity, stress is proportional to the strain but here it is non-linear, it is not linear.

And the third defense with other materials is if you take a piece of aluminum or steel which is you apply the force and extend it and then you increase the temperature from room temperature to let us say 200 degree centigrade, then you will notice further elongation because of the thermal expansion. But in here if you increase the temperature by few degrees, you will find it starts to contract. So you will find that on heating a stressed elastomer contracts. This property has given rise to making rubber engines which converts the low heat, low grade heat at such slow temperatures and can be converted to mechanical energy.

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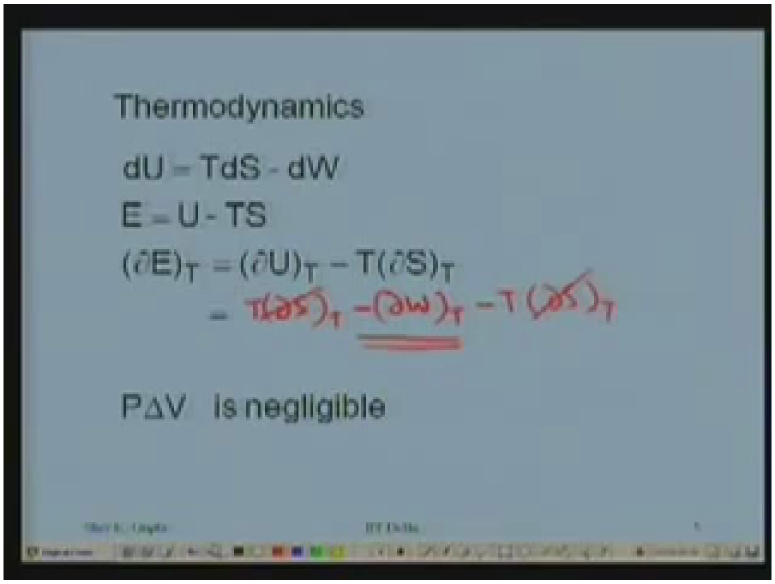

Thermodynamics

$dU = TdS - dW$

$E = U - TS$

$(\partial E)_T = (\partial U)_T - T(\partial S)_T$

$= T(\partial S)_T \underline{\underline{-(\partial w)_T}} - T(\partial S)_T$

$P\Delta V$ is negligible

Okay. So these are the defenses and we shall try to see these knowing the structure of the elastomer and looking at the thermodynamics, some of which we have already seen. Combined first and second law of thermodynamics can be written as dU is equal to TdS minus dW where TdS is a term which has the heat input and dW is the work done by the system. Heat is input to the system, work is done by the system and the difference of these is the increase in the internal energy of the, it is basically conservation of energy.

And then we also define the Helmholtz free energy, E is equal to U minus TS. Elastomer is a solid and once again PV term is going to be negligible and therefore I can talk about the Gibbs free energy or the Helmholtz free energy. Here I am talking about the Helmholtz free energy which can be written as U minus TS. At a constant temperature when I try to differentiate this, I get delta E at constant temperature is equal to delta U at constant temperature minus T delta S at constant temperature. Temperature is constant. I do not have to differentiate that.

So now this number with constant temperature, I can write this from the combined first and second law. When I do that, it can be written as T delta S at constant temperature minus dW at constant temperature minus T delta S at constant temperature. First term and the third term cancel each other, I am left with this the middle term where W is the work done by the rubber or the system. With the minus sign in front it is the work done on the system.

At a constant temperature when I try to stretch the rubber, I apply the force of, the rubber elongates by a distance let us say delta L, not change the temperature, room temperature only. So work done by the force is of delta L. All right. That is what this minus dW would be at constant temperature. Since the condense system has already said this is negligible, this work is the work done by an external agency.

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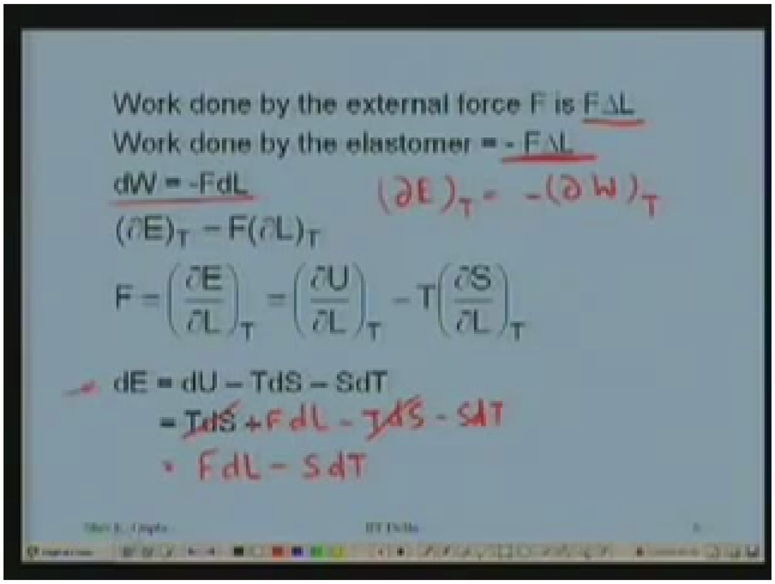

Work done by the external force F is $\underline{F\Delta L}$

Work done by the elastomer = $\underline{- F\Delta L}$

$\underline{dW = -FdL}$ $(\partial E)_T = -(\partial W)_T$

$(\partial E)_T = F(\partial L)_T$

$$F = \left(\frac{\partial E}{\partial L}\right)_T = \left(\frac{\partial U}{\partial L}\right)_T - T\left(\frac{\partial S}{\partial L}\right)_T$$

$$dE = dU - TdS - SdT$$
$$= \cancel{TdS} + FdL - \cancel{TdS} - SdT$$
$$= FdL - SdT$$

So that is what I said, the work done by the external force in extending the rubber by a distance delta L is F delta L. And the work done by the elastomer is minus of that because the work is done onto the elastomer in stretching it. So therefore work done by the elastomer, W we said is the work done by the elastomer, can be written as minus FdL. So delta you add because we are writing as a derivative. Right. We said delta E at constant temperature is minus delta W at constant temperature, previous slide. All right.

And dW is minus FdL, so I can write this minus and minus go away, become plus, now it is F delta L at constant temperature. Right, because we wrote that delta E at constant temperature is equal to minus delta W at constant temperature. This is the last slide if you recall. If I substitute that here, I get this F delta L at constant temperature. Well, this can be rewritten because I talked about this is only the total derivatives at a constant temperature which you can also say at a constant temperature, then it becomes a partial derivative.

F can be rewritten as at constant temperature, dE by dL. And E, I have already defined as U minus TS. So if I differentiate that, delta U, delta L at constant temperature, the right hand side, minus temperature is constant, T is constant, delta S by delta L at constant temperature. Well, if you write E, it is total derivative like dE, dU minus TdS minus SdT, because it is U minus TS. dU minus TdS minus SdT. dU can be written from the combined law, TdS minus dW and dW in this case should be written as minus FdL, so I make it plus and write it FdL. And then other terms, minus TdS minus SdT. So this TdS first term cancels with the third term here and I am left with this, FdL minus SdT. Is this clear? All right.

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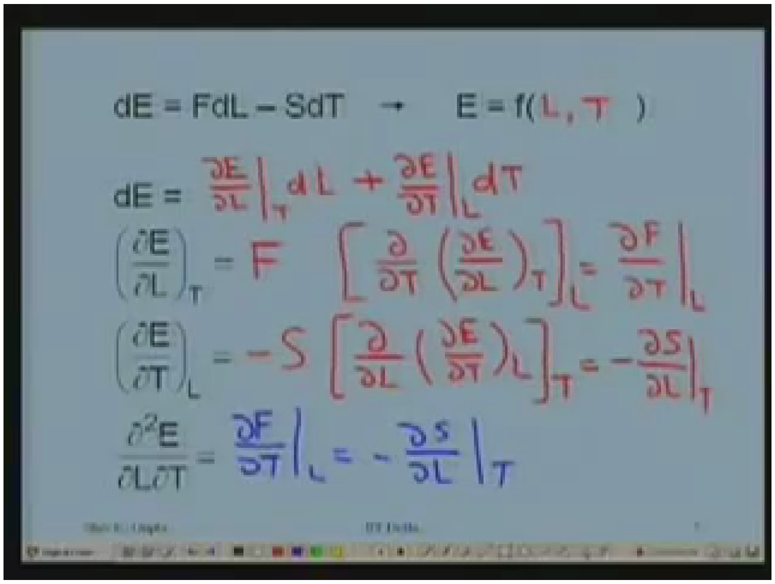

$$dE = FdL - SdT \rightarrow E = f(L, T)$$

$$dE = \frac{\partial E}{\partial L}\Big|_T dL + \frac{\partial E}{\partial T}\Big|_L dT$$

$$\left(\frac{\partial E}{\partial L}\right)_T = F \quad \left[\frac{\partial}{\partial T}\left(\frac{\partial E}{\partial L}\right)_T\right]_L = \frac{\partial F}{\partial T}\Big|_L$$

$$\left(\frac{\partial E}{\partial T}\right)_L = -S \quad \left[\frac{\partial}{\partial L}\left(\frac{\partial E}{\partial T}\right)_L\right]_T = -\frac{\partial S}{\partial L}\Big|_T$$

$$\frac{\partial^2 E}{\partial L \partial T} = \frac{\partial F}{\partial T}\Big|_L = -\frac{\partial S}{\partial L}\Big|_T$$

Now that is what we wrote, dE is equal to FdL minus SdT. This shows that E is considered, is total derivative written like this, is a function of L and temperature. If I have a variable which is a function of two other variables, this function can be differentiated and total derivative can be written as delta E, delta L at constant temperature into dT, plus…..

Student: dL sir.

Professor: dL sorry, you are right. It should be possible for me to, and plus delta E, delta T at constant length into dT. If I compare this expression with this expression, I get delta E, delta L at constant temperature is nothing but……and if I compare the second term delta E, delta T at constant length is equal to minus of S. Right. I try to work out the second derivatives like this, delta square E, delta L, delta T. It can be brought from here by differentiating this number, delta

E, delta, delta T, delta E, delta L at constant temperature. Whole thing is differentiated at constant length here.

That means I have to differentiate this this right hand side with respect to T at constant length and that becomes equal to delta F, delta T at constant length. Similarly from here I can get this derivative as delta, delta L of delta E, delta T at constant length and put this at constant temperature. That means I must differentiate the right hand side with respect to length at constant temperature, minus S delta L at constant temperature.

So this becomes equal to from there, delta F, delta T at constant length and is also equal to minus delta S, delta L. This is something equivalent to Maxwell's relation which we have done in gases in thermodynamics. But the important thing what we notice here is this second derivative, once I write force, with change in force with change in temperature at constant length, I maintain the constant length of the elastomer, change the temperature, see what is the change in force required to achieve that.

Similarly here it is entropy which is related to the length of the elastomer at a constant temperature. Now the importance of getting this information is the first derivative in the left I can experimentally measure. I can measure force, I can measure temperature, I can measure length. So therefore I can measure these and you will be performing these out of this first set of minus, the second set of experiments. We will be doing one experiment on this.

But if you look at the right hand side, delta S, delta L, you cannot measure entropy with respect to length, you cannot measure entropy at a temperature. There is no easy way of measuring entropy of the rubber. But when it comes to seeing the arrangement of chain segments which are coiled, which are crosslinked, how are they placed in the given volume, you can find out the number of configurations and you can model out the configuration entropy.

Since it is a constant temperature, there will be no change of thermal entropy. So you can model out the configuration entropy, from there you can write down this derivative delta S by delta L at constant temperature. So modeling can be done, that is the right hand side. Verification of the model can be done by measuring the left hand side through the experiment. That is the great advantage of getting this relationship. And that is what I need to show you now next.

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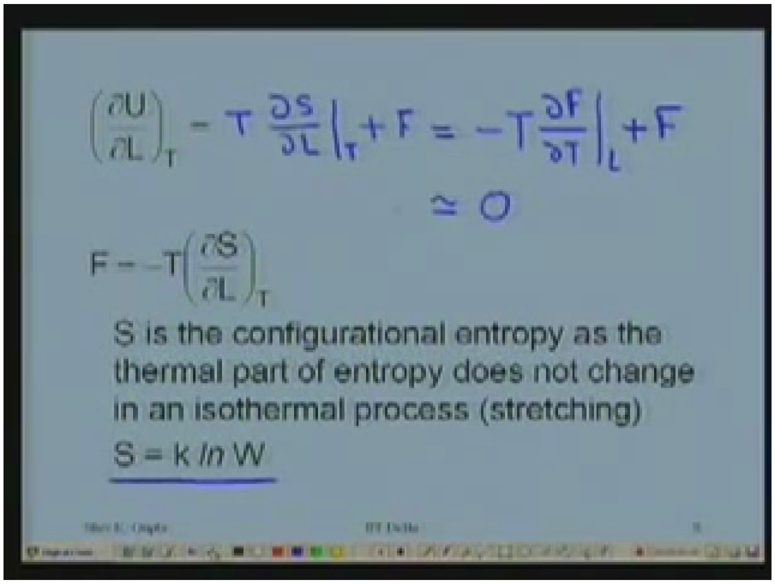

$$\left(\frac{\partial U}{\partial L}\right)_T - T\frac{\partial S}{\partial L}\Big|_T + F = -T\frac{\partial F}{\partial T}\Big|_L + F$$

$$\simeq 0$$

$$F = -T\left(\frac{\partial S}{\partial L}\right)_T$$

S is the configurational entropy as the thermal part of entropy does not change in an isothermal process (stretching)

$S = k\ ln\ W$

While in an experiment it is also possible for to measure the change in internal energy at a constant temperature elastomer. And if you write this, it turns out to be U is TdS, so it turns out to be constant temperature, it is T delta S delta L at constant temperature minus dW which is the work done on the rubber, delta L by delta at constant temperature will come this. That is the combined first and second, I have differentiated already.

Experimentally when we measure, I cannot measure this as I already told you. What I will be measuring experimentally is minus of T times delta F, delta T at constant length plus F. Because delta S, delta L at constant temperature is equal to minus delta F, delta T at constant length. And this also you will measure in an experiment because this is measurable in experiment. This is measurable, that is measurable and that turns out to be approximately 0. Of course you will get that within your experimental errors.

“Professor-student conversation starts.”

Student: Sir, what is force on the…..?

Professor: Force, is the force applied on the elastomer. See you have, take a rubber band, you stretch, you are applying some force to stretch it. If you do not apply that force, it comes back to its original shape. And we are talking about the thermodynamics when the rubber is already stretched after applying some force. And it is the thermodynamics of stretched elastomer we are working out.

“Professor-student conversation ends.”

Okay. So once this is 0, it can be rewritten this from here as F is equal to minus T delta S, delta at constant temperature or it can be written as F is equal to T delta F delta T at constant length. Here it is the minus sign, there it is plus sign. And in here S is the configurational entropy because I am maintaining the temperature constant. There is no change in the thermal entropy. And the stretching we are doing isothermally and if the configurational entropy we had written earlier, S is equal to k log W. This W is not the work here. W is the number of configurations. Right? And this number of configurations have been modeled, it has been worked out for us. I shall not go into the details of that.

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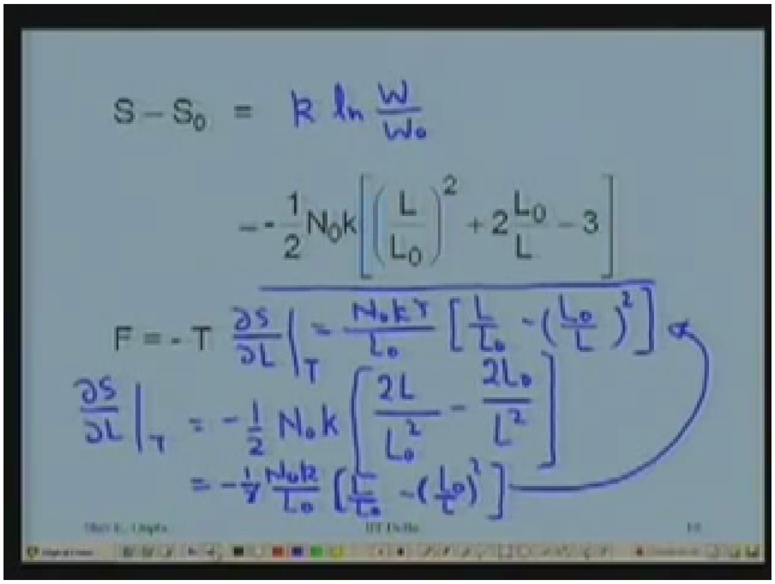

$$S - S_0 = k \ln \frac{W}{W_0}$$

$$= -\frac{1}{2} N_0 k \left[\left(\frac{L}{L_0} \right)^2 + 2 \frac{L_0}{L} - 3 \right]$$

$$F = -T \left. \frac{\partial S}{\partial L} \right|_T = \frac{N_0 k T}{L_0} \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right]$$

$$\left. \frac{\partial S}{\partial L} \right|_T = -\frac{1}{2} N_0 k \left[\frac{2L}{L_0^2} - \frac{2L_0}{L^2} \right]$$

$$= -\frac{1}{2} \frac{N_0 k}{L_0} \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right]$$

Net, S minus S0 can be written as k natural logarithm of W by W0. Right? So this is the reference state. W0 is for the reference state. S is the stretched rubber state and W is the state of the stretched rubber. All right. So that is the configurational, difference in the configuration entropy, which I will get delta S. When I differentiate them, S0 is the reference state, is going to be constant. So I can always talk about, when I differentiate this, I have been differentiating basically the S.

So this model has been worked out for us. I am not going to work it details, and somebody searched, it was done. Of course, some assumptions are involved in here. And from the formula which you got, F is equal to minus T times delta S, delta L at constant temperature. I can differentiate this with respect to length at constant temperature and see what do we get. So this derivative, delta S, delta L at constant temperature from expression, minus 1 by 2 N0k, Boltzmann constant, it is L square when they differentiate it becomes 2L divided by L0 square. When I differentiate this, it becomes minus 2L0 by L square and constant does not give me anything, that gives me 0. All right. So this you can further simplify. I do not have a place to that.

I can take L0 out, then what it gives me is minus of 1 by 2, N0k by L0. And 2 also is taken out, so this 2 will cancel out there. I have been left with 1, will be L by L0 minus L0 by L whole square it would be. As it is different way of writing also. And when we go back to this F, I have to multiply it by minus T. This minus sign will also go and T will come in the numerator. So F will be equal to N0kT by L0 , in bracket L by L0 minus L0 by L whole square.

So this is where I get from here. That is my F. Now I have related the force to the original length of the elastomer, stretched length of the elastomer and the T, the temperature. Applied force, stretching of the elastomer and temperature, these have been related. This is called the equation of state of the elastomer.

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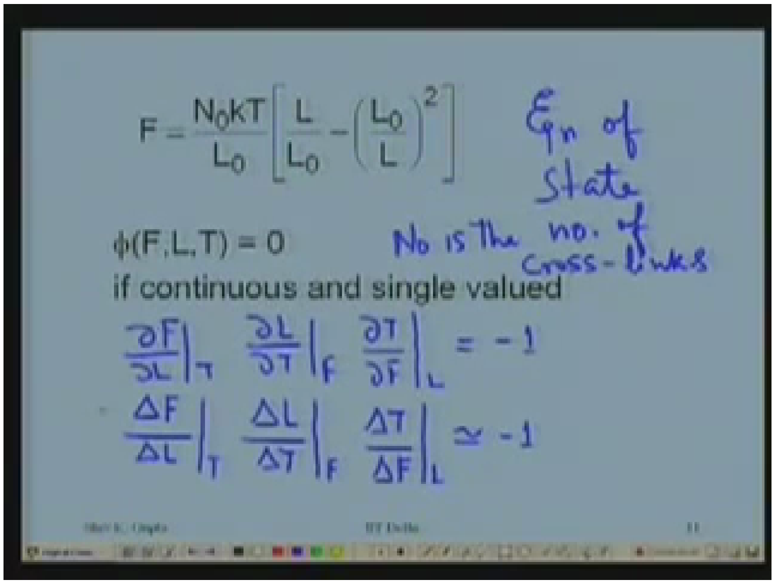

$$F = \frac{N_0 kT}{L_0}\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$ Eqn of State

$\phi(F,L,T) = 0$ No is the no. of cross-links

if continuous and single valued

$$\left.\frac{\partial F}{\partial L}\right|_T \left.\frac{\partial L}{\partial T}\right|_F \left.\frac{\partial T}{\partial F}\right|_L = -1$$

$$\left.\frac{\Delta F}{\Delta L}\right|_T \left.\frac{\Delta L}{\Delta T}\right|_F \left.\frac{\Delta T}{\Delta F}\right|_L \simeq -1$$

That is what you have got, F is equal to N0kT by L0, L by L0 minus L0 by L whole square. If this is the equation of state of the elastomer, any equation of state must be single value and continuous. For the simple reason my rubber is not an imaginary item, my rubber does not evaporate, my rubber is there where it is. When I apply a force a little more, little less, it is there. So therefore it must be a continuous and single valued function. This can be rewritten as a function of force, length and temperature. N0 in here is the number of crosslinks in the given piece of the elastomer.

N0, I think should have defined, is the number of crosslinks. It is not the number of place. And if you say N0 by L0, is the number of crosslinks per unit length of the elastomer given to you in the original state. Okay. So this is, has to be continuous and single valued function, it must satisfy from the calculus a relationship that is delta F, delta L at constant temperature multiplied by delta L, delta T at constant force into delta T, delta F at constant length. And the product should be minus 1. All right.

This if you want to work out as an experimental test state, you will not be able to get derivatives like this. But what you will be able to get is delta F, delta L, maintain a constant temperature, apply some incremental force. You have already stretched the rubber and apply some incremental force, find out what is the increase in length. We got this derivative approximately. Then what you do is increase the temperature. Right. Do not change the force, whatever force you had applied. Find out what is the change in the length. And as I said rubber would contract. This should be a negative number. Force is not changed. Right, you got that.

Once you have done this, now bring it back to the original length which was there after applying the force delta F. Means whatever it has shrunk or contracted by, you extend it by the same amount at the increased temperature. So that shall give you delta T, delta F. You have to know how much force you have to apply to come back to the length which was there after applying the stretching, come back to there. So multiply these products, it should come approximately minus 1, because it is not the limit tending 0, you have not worked it. That will say the yes, this is a continuous and a single valued function. Okay.

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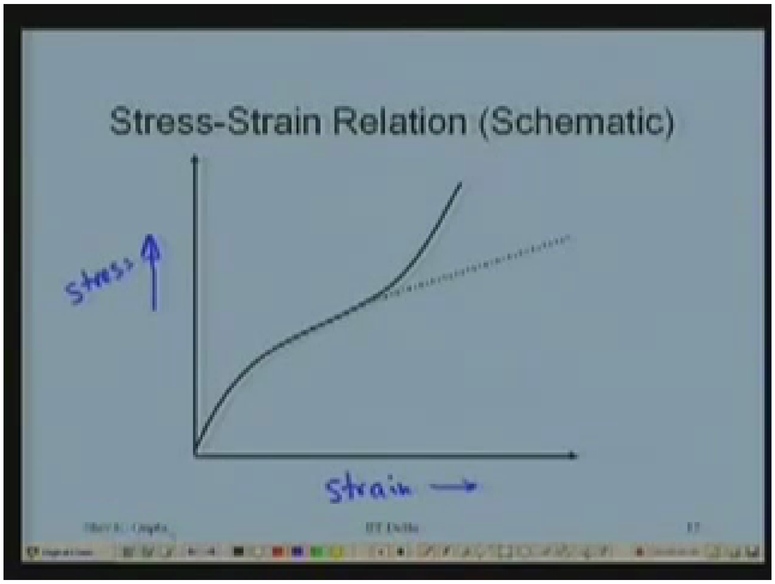
Stress-Strain Relation (Schematic)

This equation of state which is here available, if it is plotted, the stress and force divided by the area of cross-section and the strain onto the elastomer here, it is non-linear, that is what you work out. And what the equation of state gives us is this path which goes beyond here, dot dot dot dot, goes on. But what happens? After about a few hundred percent of elongation, it starts to deviate from this equation of state and it goes in this direction where it becomes more and more steep. All right. That is all what we have to see what it is. We have to explain that.

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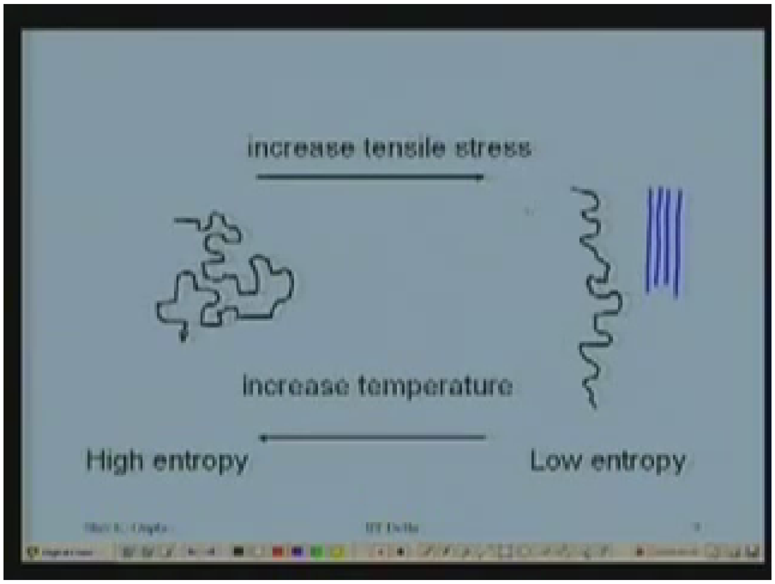

Go back to earlier picture here. Initially what is given to us is in coiled state the rubber is lined. Whatever maximum possible coiling can take place is taking place already. Configuration entropy is the maximum at this stage. Now when I stretch it, coiled states of the chain start to get uncoiling. On increasing the tensile stress or the force, they try to straighten out. But complete straightening is not possible, why? Crosslinks are there between various chains. They do not allow them to move very far off from each other and chain segments are able to translate here.

Yes, it is possible for them to translate along with slightly and therefore re-exist to get some straightening. The ultimate state, if it is possible for you to get to the straightened state, is this where all chains are lined parallel like this. What shall be the configuration entropy then? 0. In that state the configuration entropy would be 0. So you are decreasing the configuration entropy when you apply the stress like this. Right.

Now what happens? When you are in this state, your stretched state when it is uncoiled to some extent, there are secondary forces which come into play to maintain them in that state. With besides the primary crosslinks and secondary forces are van der Waals forces. It is important for you to understand because we know that configuration entropy is not a function of temperature. But when I talk of the configuration entropy, I must, I have to talk about the number of configurations belonging to the same energy.

What I am demonstrating here is now this stretched piece of rubber when I increase the temperature, what happens? These secondary forces which are there between the chains, van der Waals forces these weaken or you can say they break. Right? So since one of the forces which is holding them in this configuration is gone or reducing in strength they try to coil back because the primary crosslinks are trying to take them back.

The applied force is tried to straighten it out. And then to maintain them in that state are being helped by the van der Waals forces. Out of the two forces, van der Waals forces and applied stress, applied force, van der Waals forces have become weak and therefore the crosslinks try to turn it back to coil, so the length decreases. This way when we increase the temperature, we go to the configuration, coiled state configuration, more coiling, higher entropy state.

All right. So the point which I am trying to make here is configuration entropy is not a function of temperature but by changing the temperature, by increasing the temperature in here what you have done is you have changed the energy which belongs to the secondary bonds, the van der Waals forces. That energy is being increased, so you go back to, because that is the force which is holding the this configuration. It is now no more available and therefore it goes to the state and it contracts back.

It is not a very large contraction. You will be doing the experiment, you will see that, it contracts. It is good enough to say it contracts and we can make use of it. In rubber engines we do use this property of the rubbers. All right. Now when I talk about this, I have uncoiled this and during the process of uncoiling coiled chain is uncoiled, I have not stretched any of the carbon-carbon bonds. It is only bent and therefore coil is formed, so I just uncoiled. There is not stretching of primary bonds.

“Professor-student conversation starts.”

Professor: Would there be a change in internal energy? I am talking about it constant temperature, no increase in temperature here, not this.

Student: No change.

Professor: There would be no change in the internal energy. And that is assumption which we have made in working out this equation of state which I showed you. I said delta U, delta L at constant temperature is 0. That you also try work out in your experiment, it comes out to 0 approximately. Right.

“Professor-student conversation ends.”

So that is the basic underlying assumption that there is stretching, there is only uncoiling of the coiled chains, there is no change in the internal energy of the elastomer. Now what happens? You are, as I said you are not able to reach that state. What primary crosslinks are going to stop you? You cannot translate them permanently and make them completely straight. Once you reached that stage, now if you want to stretch it, what would happen?

You would start stretching the primary bonds, primary crosslinks are also primary covalent bonds. You start stretching them and that means you are tending towards Hook's law where the modulus of elasticity is very high and that is what I was trying to say what happens.

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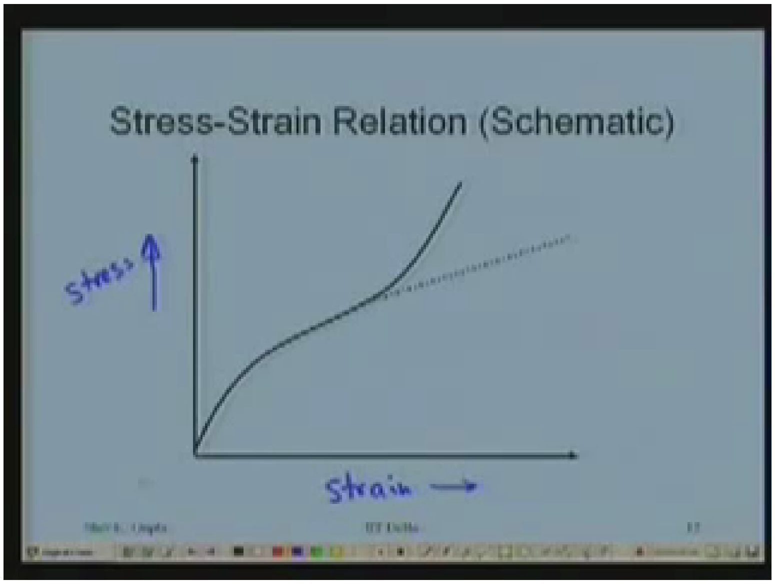
Stress-Strain Relation (Schematic)

Go back. When you reached here, the primary bonds gets start, starts getting stretched and this becomes steeper and steeper and steeper where the Hook's law will be obeyed. And if you do further anything, it may break. That can happen. So this is the part of the equation of state which you worked out under the assumption that there is no change in internal energy when a piece of elastomer is stretched. It is merely uncoiling of the coiled chains. Is the point understood?

“Professor-student conversation starts.”

Professor: All right. That is, now if that is so, if I give you a piece of rubber, what you have an eraser and ask you put a weight of 10 kgs on it, measure the contractions or the change in size and then heat it, will all the thermodynamics you have done will work there? Will it work if I give you a piece of (eras), you have seen the piece of eraser, put a 10 kg weight on it?

Student: (())(37:33)

Professor: Why will it not work?

Student: Internal Energy (())(37:36)

Professor: Yes. The configurations are already there, the maximum possible coiling is there. When I put the force, (compre) compressive force, I am not stretching the elastomer but I am trying to bring atoms closer. So I am affecting the primary bonds. So internally change will not be 0 in such a situation. It is not uncoiling of the coiled chains and there is no question of further coiling of the coiled chains. They are already coiled, right. So therefore on compression this analysis which we have done will not be valid because of the assumption that there is no change in the internal energy of the elastomer. Is that clear? Good.

“Professor-student conversation ends.”

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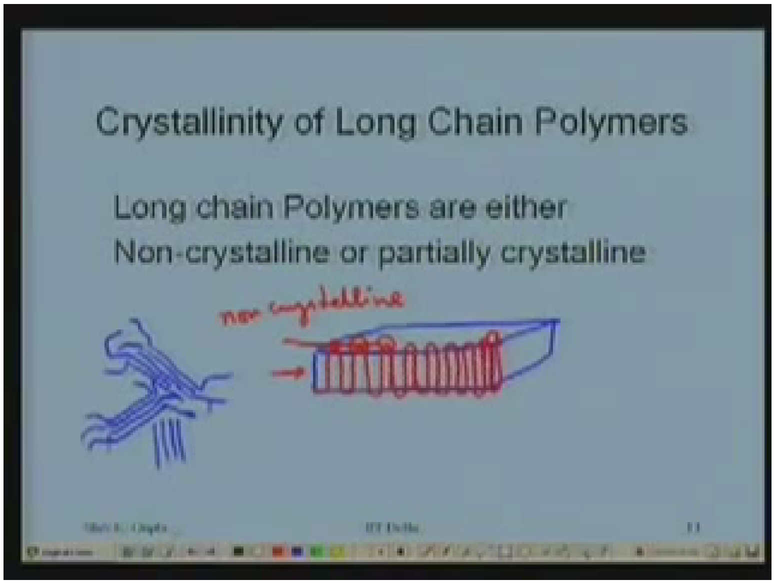

Crystallinity of Long Chain Polymers

Long chain Polymers are either
Non-crystalline or partially crystalline

Now we shall look at the long chain polymers, can they be crystalline? I started with these structures, non-crystalline. Most of the time they are non-crystalline. But particularly a network polymer I said I can never crystallize it. It is always non-crystalline structure. And same is true about the long chain polymers, they are most of the non-crystalline. But it is possible for us to have partially crystalline long chain polymers. Right.

Partial crystallinity, let us see what I mean by partial crystallinity. Let us say in this small volume, I have a few chains which are stuck parallel to each other. But since they are not of the same length, at the ends they do not remain parallel to each other because they are not of the same length. Then maybe another place, another set of chains are parallel arranged but their ends again will cause problems because they are not of the same length and so on and so forth.

So there are some volume of the metal where the chains are aligned parallel, they are crystalline ordered arrangement. Rest of this is non-crystalline volume. That is why the partial crystallinity. If there is possible to have all chains of the same length and all parallel, yes, we will get 100 percent crystalline material which is not the case, which is never the case. The other way they can arrange themselves if have very long chain, in a let us say a rectangular block like this, which is of course the thin block, these chains and then it can go back into the solid region.

So this region you see they are all parallel. In this region they have accepted the folds, the chain segments are all parallel, that becomes a crystalline region. Only non-crystalline region at the folds. These folds become non-crystalline. And we have seen such kind of, this kind of structure, that kind of structure we have seen in polyethylene itself. Layers, for layers, layers of layers, that means these chains arrange like this. They can be pilled now because between the one layer like this and the second like that, there will be only van der Waals forces. One can be pilled over the other easily. Pilling can take place.

And here some like, something like this is also seen in the flower patterns, that they are partial regions which are crystalline and other regions are non-crystalline. So this is how this crystallinity if at all is seen, is like this, it is partially crystalline. 100 percent crystallinity is not possible for a simple fact that no two chains are of the same length. Okay.

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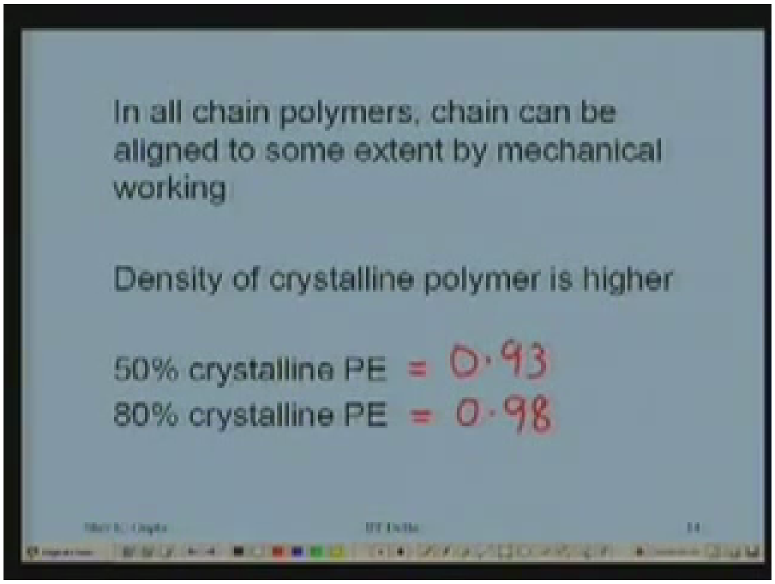

In all chain polymers, chain can be aligned to some extent by mechanical working

Density of crystalline polymer is higher

50% crystalline PE = 0·93
80% crystalline PE = 0·98

And we can also try to align these chains by doing some mechanical working. I just talked about it yesterday briefly. Cut a small strip from a container or this carrier bag of polyethylene, try to stretch it. If start with a transparent material, after stretching you will see that it becomes opaque. It is now, it does not remain transparent any more. We are trying to straighten out the chains by doing this. And also this is becoming little more rigid. When the chains straighten out, straightened out chain will be kind of a fiber where the chains are parallel. You try to stretch further. So initial stretching you will find is easy for you but later on you will find it becomes difficult for you to stretch it and that becomes opaque.

That is kind of working you can do and if you the working, chains can get aligned. That is one way of doing this. And we have seen that when we want to see how much crystallinity is present in a polymer, we can measure it density, which is going to be more dense and which is going to be less dense. In non-crystalline region all chains are exact, 100 percent non-crystalline. They are not going to fill the space efficiently, density would be lower. And when the all the chains are parallel, they feel the space more efficiently, density would be higher.

So what you find is in polyethylene, when I take a 50 percent crystalline polyethylene, its specific gravity is 0.93 and when it is 80 percent, it is 0.98. So by measuring and there is a linear variation of density and the percent crystallinity. So once measure, make these measurements, it is possible for us to say after measuring the density of polyethylene, how much crystalline it is.

So with this small kind of differences in density, one is called the high density polyethylene, other is called the low density polyethylene. You have high density polyethylene bags, you have the low density polyethylene bags. All these things are available. Right.

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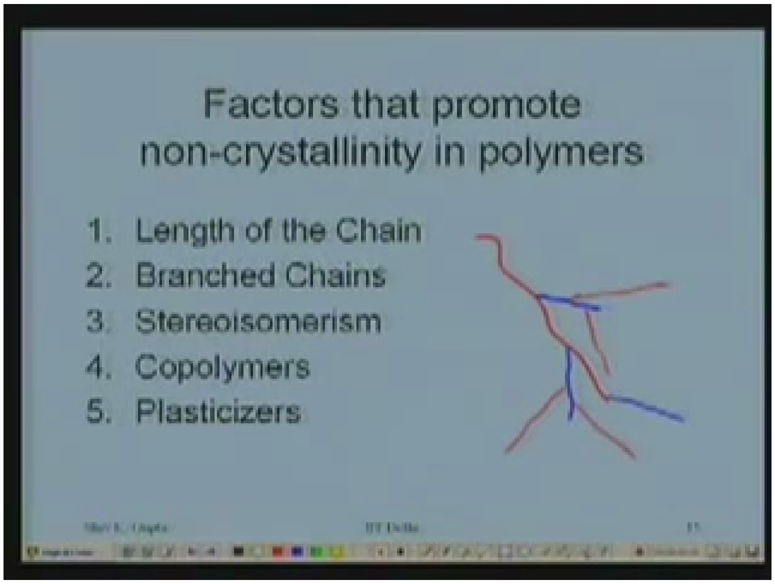

Factors that promote non-crystallinity in polymers

1. Length of the Chain
2. Branched Chains
3. Stereoisomerism
4. Copolymers
5. Plasticizers

Now I just talked about the chain lengths not being equal, I shall look at the factors that promote non-crystallinity in these long chain polymers. First of all, is the length of the chain. Longer the chain, means on an average, some would be longer than that, some would be shorter than that, there will be large variation of chain lengths. And there will be more entanglement of chains and there will be more crystallinity, non-crystallinity. It will not become crystalline if the chain lengths are long. Similarly chains can get branched. I will show you structures of branched chain.

What I mean is suppose I have a chain like this, when I say it is branched, there may be a branch going out from here, a branch going out from here and further from here the branch could go out like this. Like in a tree you have branches. Such a chain can you align parallel to each other? Certainly not. Branching can also be achieved sometimes by eradiating the polymers to gamma rays or x-rays, it can be achieved.

So that is when sometimes we want to make the material non-crystalline purposely, so is more appliable, more soft, we do that. Then stereoisomerism is the arrangement of side groups, R1, R2, R3, R4, I talked about in the space. Let us first have a look at that, then we shall come to the copolymers and plasticizers.

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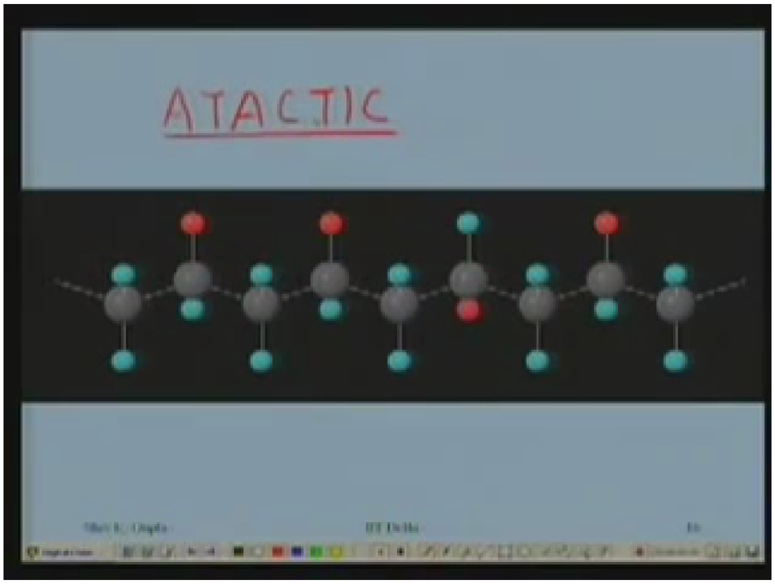

ATACTIC

Arrangement in space, here I have, I am showing let us say, this is a, okay, PVC. One atom is chlorine, other three are hydrogen. Red one is the chlorine let us say. This is coming on this side, that side, that side, is coming randomly. There is no regular arrangement. Such an arrangement is called, and generally we have this atactic arrangement of the side groups. They are randomly arranged and this can never give me a periodically repeating pattern. Crystallinity is not possible, improve the non-crystallinity. By its presence there will be non-crystallinity in polymers. All right. Let me show the next one. Okay. I suddenly crossed I think two of them.

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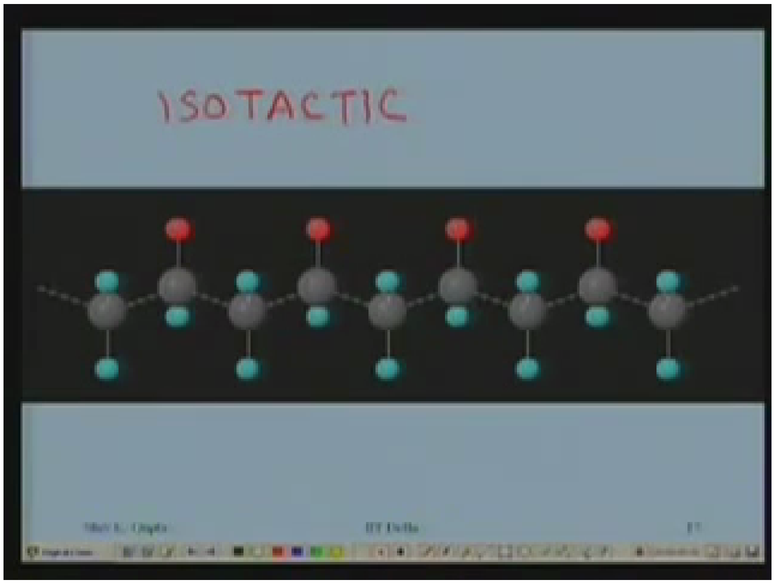

ISOTACTIC

All right. Let us go this. This is one where chlorine ones are always on the same side, it can provide me a periodically repeating pattern and can improve the crystallinity, is called isotactic arrangement. This can improve the crystallinity.

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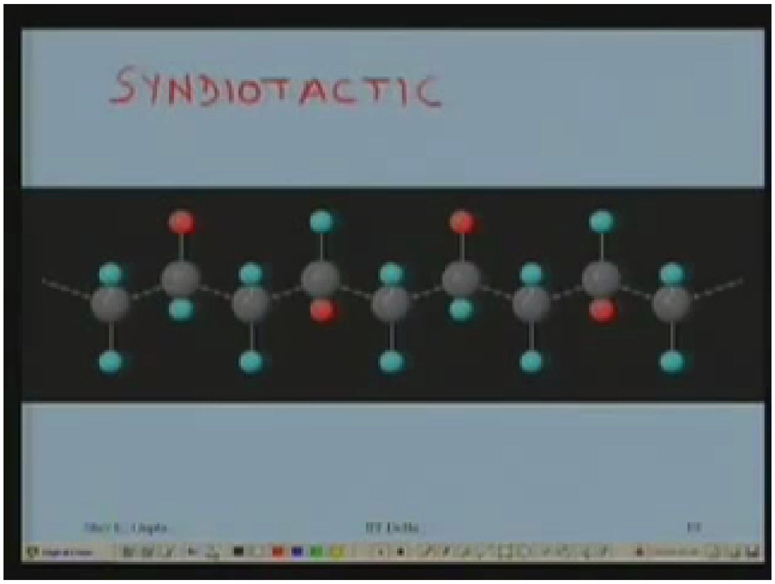

SYNDIOTACTIC

Now the third possibility, chlorine comes alternately above, below, above, below, like that. This can also improve the crystallinity. This is called syndiotactic arrangement. And this stereoisomerism is also called tacticity. Okay. So the syndiotactic can also give rise to crystallinity, improved crystallinity. All right.

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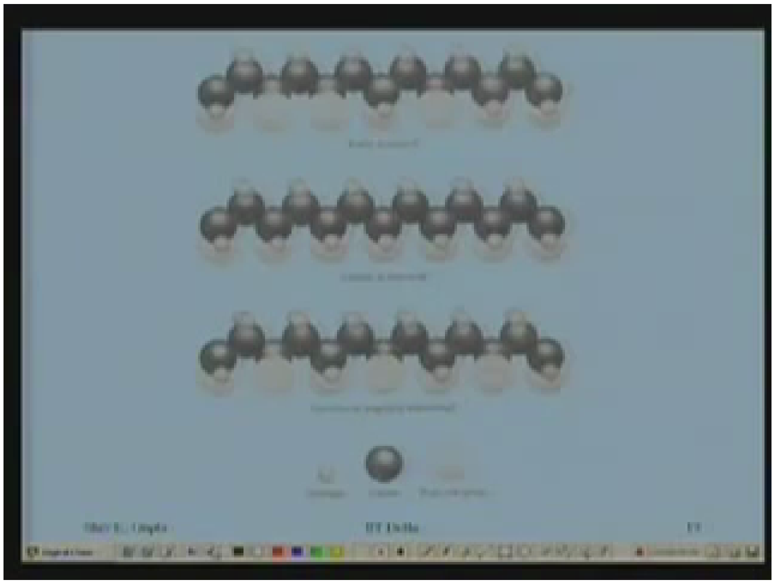

Next in the list was copolymers. Copolymer means I have another polymer present in the long chain. Long chain by itself is a polyethylene I having between polyvinyl chloride. Here I am showing a, well these are the arrangements which I just showed, atactic arrangement, isotactic arrangement and syndiotactic arrangement. That is I just showed, is the same thing. It is not so colored but let us go to the copolymers.

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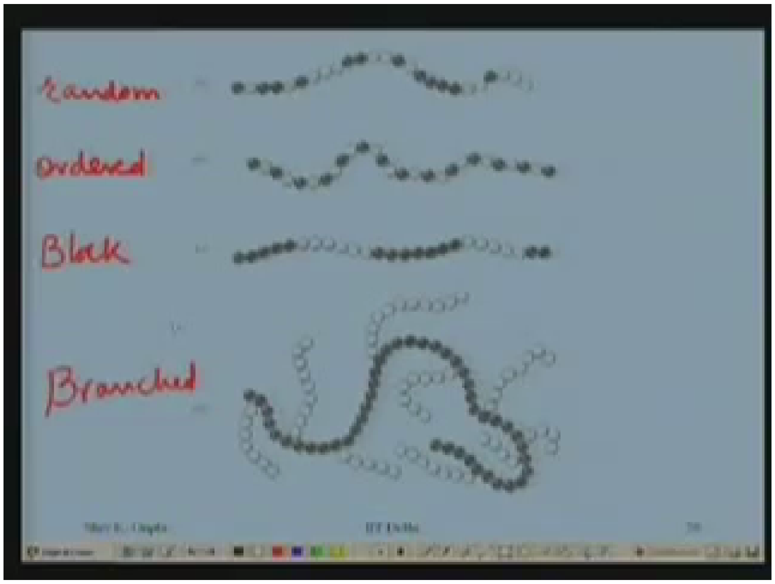

Yeah. These as a monomer of let us say of polyethylene and the white one is a monomer of polyvinyl chloride let us say. Black is polyethylene monomer and white is the, or the uncolored one is the polyethylene. So polyvinyl chloride and polyethylene, they are growing monomers randomly distributed, it is called the random copolymer. I cannot find any periodicity in this. It cannot give me crystallinity, that will rather improve the non-crystallinity of the polymer.

When it is present, alternately polyvinyl chloride, polyethylene, polyvinyl chloride, polyethylene, so on and so forth, this is an ordered one, difficult to obtain this. But if it is there, chances of improved crystallinity would be there. In here I have a block of polyvinyl chloride, another block of polyethylene. Other words, these are long chains, not one monomer or two monomers, large number of monomers there. So this is called the block copolymer.

This is also not likely to give me because segments having the length of the polyvinyl chloride, the polyethylene length and polybag they are not of the same length, they are the segments of different lengths. And just now I talked about the branched chains, here I show you the branched copolymer. This is a polyvinyl chloride, on the sides are branched through the polyethylene chains like this. Only thing is one hydrogen is removed and suddenly you put a chain there. Okay.

And that is becomes the branched copolymer. Copolymer, two of them are existing together. If you look at what I talked about the alloys, this is something similar to substitutional solid solution. This is something similar to substitutional solid solution. Okay. All right. The last one we talked about is the presence of plasticizers.

Plasticizers are low molecular weight additives put in the polymer. So by their presence what they do is they increase the distance between chains. Once the distance between chains is increased, their translation mobility improves. And therefore my polymer becomes more appliable, more soft. As I told you yesterday, PVC is a rigid material but the PVC pipings are tubes we use for watering the gardens. It is very soft. We add some plasticizer to it to make it appliable, more soft.

Similarly you have heard of the cellulite films, the photography you do, the films you use. Basically cellulose is very rigid material, wood consists of cellulose chains which are bound by some glue which is called lignin. This is a rigid material. Only when add camphor to it, we can make it soft and appliable, so it is like a negative film. If this negative film, you keep it in the open air for about a month, you will find that it becomes very rigid and crisp.

If you try to fold it, it will crack. The camphor has evaporated and that appliability is gone. Camphor when it present, it was present, it has increased the chain length or distance between the chains, that is a cellulose chains and it has become soft and appliable. Right. So that is what happens to the garden hose also, it keeps lying in the summer in the lounge itself. You will find that in the sun, the plasticizer evaporates very fast. It comes to the surface and just goes because it is a low molecular weight material and just simply evaporates.

And what is left material is a rigid material, so it cracks with use. That seasoning takes place, that is a role of plasticizers. It is similar to what is the role of modifiers, the impurities in silicon like soda and lime. They lower the viscosity, means soft, make soften the glass. Similarly here they make the more appliable and more soft plastics by addition of these plasticizers. Thank you.