Principles of Polymer Synthesis
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Lecture - 46
Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about the structure property relationship of polycarbonates in the previous class. In fact, we are right in a middle of it and we will continue that discussion in today's class.

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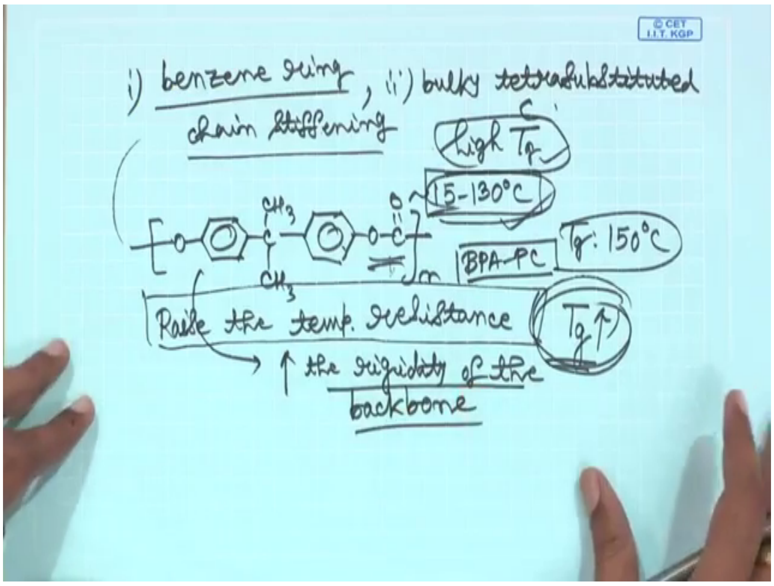

So, let us start at the point where you left in the in the last class ok. So, this is your structure; your basic structure of Bisphenol A polycarbonate and the question was; how can we improve the properties? So, the first thing that comes in mind is that simply try to raise the temperature resistance. So, that the glass transition temperature will be raised and so, the properties can be preserved up to a higher temperature because this has a glass transition temperature of 150 degree Celsius. So, why not try to increase the glass transition temperature.

So, if you look at the chemistry how can you increase the glass transition temperature, simply increase the rigidity of the backbone, you increase the rigidity of the backbone, you increase the glass transition temperature. So, of course, if you have a flexible chain as compared to these kind of rigid chains; that will have a lower glass transition temperature, we have discussed some of these things before. So, how can you then increase the rigidity of the backbone in order to have the basis structure?

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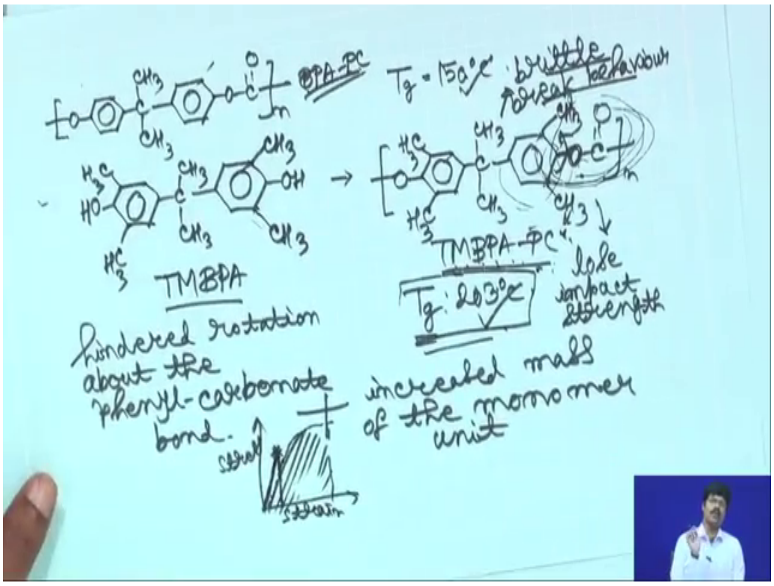

Allow me to draw the structure of your parent Bisphenol A polycarbonate once again ok.

So, now we want to increase the rigidity of this particular backbone because we want to increase the T g. So, the T g of this is around 150 degree Celsius. So, one approach could be to introduce more bulky substituent on this aromatic ring. So, you could potentially start with this derivative of Bisphenol A. So, this is your Bisphenol A and you substitute with 4 methyl groups.

So, this will be tetra methyl Bisphenol A or I am just writing down this thing like TMBPA. So, if you react this tetra methyl substituted Bisphenol A with your carbonyl chloride, then what you will get you will get a polymer a a poly carbonate which has this structure just this structure and you will have these methyl groups present. So, you have increased the rigidity of the chain by this process because you have all these bulky substituents present in the system. So, this is TMBPA PC and this was BPA PC ok

So, this is Bisphenol A polycarbonate, this is tetra methyl Bisphenol A polycarbonate. So, did we increase the T g. In fact, yes experimental the T g is 203 degrees Celsius. So, we achieved; what we wanted to do, we increase the thermal stability from 150 degree Celsius 203 degrees Celsius simply by substituting these benzene rings with for methyl groups and increasing the rigidity of these chains. So, mission accomplished or is it first of all let us see why the T g has increased the reason could be that this phenyl carbonate bond if you look at this particular bond, the rotation the rotation around this bond is more hindered here because of the presence of these methyl groups.

So, the rotation about the final carbonate bond. So, you will basically have a hindered rotation about the phenyl carbonate bond plus you will have an increased mass of the monomer unit. So, these two things will combine to ensure that your polymer will have higher T g and not only that it will have a better hydrolytic stability, if you compare with your Bisphenol A simply because you have increased the you actually decreased the accessibility of this ester to water further by adding these methyl groups this was hydrophobic no doubt.

Now, we have added the methyl groups. So, it will also spherically it is now also hindered as far as the approach of a nucleophile is concerned to this ester. So, this becomes hydrolytically more stable with respect to your Bisphenol A all right, what is the disadvantage higher production cost more importantly even though you have increased the glass transition temperature this material will lose its impact strength, we talked about a troika of important properties, 1 high thermal stability, 2 high impact strength and 3 high transparency in the quest of increasing the thermal stability of the material, what you have done here is you have compromised the impact strength why we will come to it after, but the fact is that you lost the impact strength you have higher production cost we greed higher thermal stability, but you have lost the impact strength.

So, what happens is that this material? In fact, this material exhibits brittle break behavior, it cannot absorb large amount of energy before it breaks, it is stiffer no doubt, but it cannot absorb large amount of energy before he breaks and we have argued before that a material is stiffer that does not mean the material can absorb large amount of energy, before it breaks the material is stiffer that does not mean in other way that it will it will have high impact strength or high toughness ok.

Because I already told before that if you are plotting you know stress versus strain. So, initial linear portion if the slope is higher that will give you higher stiffness of the material that because the slope gives you the stiffness, but ultimately it may break here. So, the material will be brittle if a material is tougher, then what will happen is that that may have a little bit layer stiffness as shown by the lower slope of this linear part, but then they that can go further because the area under the curve of the under the stress strain curve that tells you how much energy it can absorb before it breaks.

So, you can see directly here the area under the stress strain curve is much lower even though the material is much stiffer that is exactly what happens here. So, the large commercial success of this tetra methyl Bisphenol A polycarbonate is not possible because it loses impact strength tremendously. So, it is a significant effect on its usage utility importance in industrial pass through industry perspective I mean in the context of industrial perspective.

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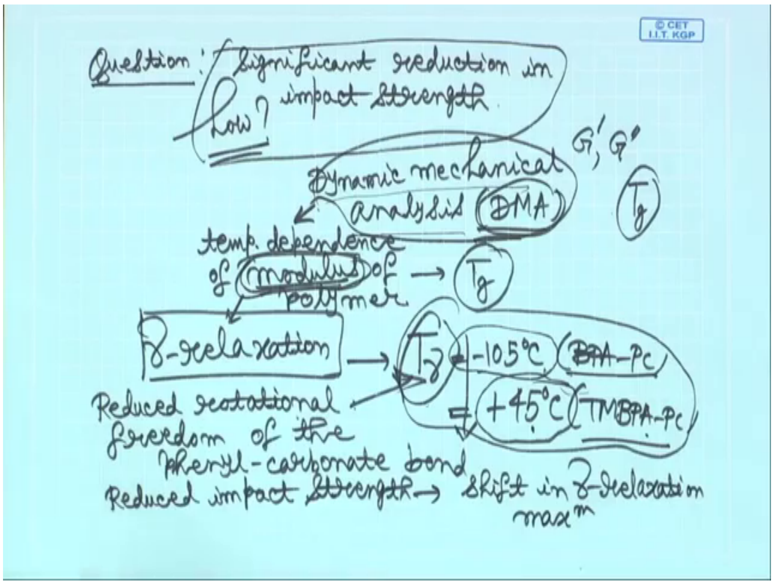

So, the question; so, let me frame this question here how do we explain this significant reduction in impact strength. So, you have a significant reduction in impact strength. So, the question is how to explain this. So, in order to find out the answer we have to do what you call as dynamic mechanical analysis dynamic mechanical analysis or DMA.

So, basically, this particular process it determines you know the temperature dependence of modulus of polymer I mean this modulus that I am going to talk about I mean you remember there is something called Young’s modulus, this is something different of course, because Young’s modulus, it tells you the stiffness of the material the slope of the linear part of the of the stress strain curve blah blah blah. So, it is another kind of module as I am going to talk about. So, this is temperature dependence of the modulus of the polymer and this also gives you an estimate of T g.

So, if you now let me let me explain to you ok, before we go to explain the experimental result further because we have not even gotten to the experimental result we are talking about the analysis itself. So, this is dynamic mechanical analysis this actually tells you I mean this a I can give you a mechanical analogy that if you take your material and if you shake this material at different frequencies at different temperatures, this is just a mechanical analogy to explain to you what is dynamic mechanical analysis.

So, you take your material and you shake the material and this frequency of shaking you change say 1 per second, 2 per second, 3 percent frequency you can change this frequency of shaking and secondly, also what you can do is that as you go along doing this you can change the temperature also and through this particular process you can find out what are the different molecular motions that are being affected by this particular shaking. So, you know when it is shaking, it is absorbing some energy and what are the molecular motions that are responsible for this absorption of energy.

Now, the modulus that I was talking about basically here you are going to talk about two kinds of modulus one is elastic modulus or storage modulus and another is loss modulus. So, elasticity typically you see, for example, if you are talking about linear elasticity you stretch a material and if it is a linear least let us say we are talking about say Hooke's law, if you have a linearly elastic material if you are stretching it what happens is that it it stores the energy of course, your stress is proportional to strain it may or it may not be proportional also then it will be non-linear whatever.

So, elasticity means when you are applying some force it is storing that energy and then when you are releasing it is uti utilizing that energy and that is also a reason of course, why your rubber band becomes cold so on and so forth, if you touch it on the lip and then you just release it then it will become cold it takes that sensation for you to understand that it becomes colder because it does some work.

Now, elastic modulus directly relates to how much energy is stored, now a material may not be a perfectly elastic material, a material may have some elastic property as well as a viscous property you know when you have a liquid you apply some force, it modifies itself in order to be accommodating to that force it just distributes that force into the material. So, that it does not store that energy it just dissipates that energy. So, that is something that that is signified by the viscous nature of the material.

Now when you have a solid which have a perfectly elastic solid it just stores all the energy that you put now there is a kind of material that is somewhere in between the two that is viscoelastic material which will have both elastic property as well as viscous property; so, both the property of the solid as well as the property of the liquid. So, what happens is that when you apply some force to the material it can store some energy which will be signified or which will be given by a corresponding storage modulus or you know elastic modulus and then some of the energy it can also dissipate just like it is a viscous material.

So, that part that dissipation part will be given by lost modulus because it is lost you are not storing that energy cannot use it. So, that is a lost modulus. So, basically you will have two kinds of moduli a 2 modular; one is your storage modulus or elastic modulus and is loss modulus and when you are doing this dynamic mechanical analysis basically you are setting a particular frequency for example, and then you are following how these storage modulus and the lost modulus they change as a function of temperature that is the idea here.

Now, something that you need to keep in mind here is that the glass transition temperature is also given by this particular kind of experiments and without going it doing much at all we will first go into some data here if you look at the PowerPoint slide here.

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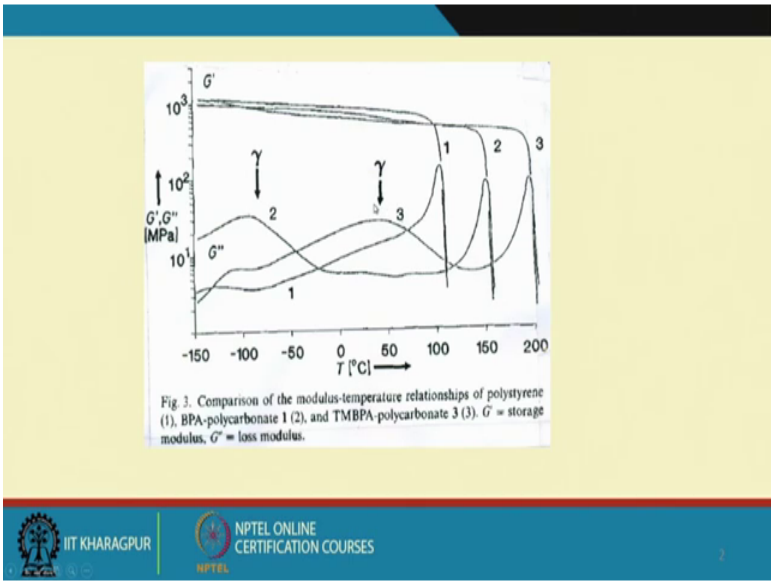

Fig. 3. Comparison of the modulus-temperature relationships of polystyrene (1), BPA-polycarbonate 1 (2), and TMBPA-polycarbonate 3 (3). G' = storage modulus, G'' = loss modulus.

So this will take some explaining although a part of it, I have already explained. So, you are plotting this G prime, this G prime is basically your storage modulus which is typically higher than your loss modulus which shows that the material is viscoelastic and this is G double prime. Now these curves are designated as 1, 2, 3 because for example, the one when you are saying one, it has 2 sets of curves.

So, one is G prime and another is your G double prime. So, this is your G double prime for the set of curve which is one. Now what is one let us find out comparison of modulus temperature relationships of polystyrene ok. So, this one is basically polystyrene. So, the G prime is somewhere here this goes like this and that these drops around this point and this G double prime is here which is designated by one and it goes like this. So, this is the set of curves that that results from polystyrene.

Now, Bisphenol A polycarbonate which is of importance to us which is two, the G prime follows almost the same path, but it actually falls down at a higher temperature this is the temperature which signifies your T G because these G prime signifies kind of the stiffness of the material and. So, when you go beyond T G the stiffness drops because you are losing that stiffness you are losing the mechanical the material properties and your segmental motion has started to play more role the chains have become more flowy so on and so forth. So, the G prime drops. So, that so that is why this experiment the dynamic and dynamic mechanical analysis can tell you about the glass transition temperature also. So, you see that for Bisphenol A polycarbonate, it is around 150 degree Celsius and interestingly, there is a bump somewhere here which is very important we will talk about it after and when you are talking about your tetra methyl Bisphenol A polycarbonate again G prime is very very similar, it goes down at a higher value of temperature two hundred which tells you the glass transition temperature is around 50 degrees Celsius higher than your parent Bisphenol A polycarbonate and this is your loss curve. So, this is 3.

So, your G prime is not much different except for the fact that the point at which it it falls down that signifies the T G and you can see polystyrene has a lower T G and b p d Bisphenol A polycarbonate has a T G 150 and when you have tetramethyl substitution the T G is around 200, the loss modulus though is very important to keep in mind you will see here, say for example, the lost modulus this is the curve number two which is the lost modulus for Bisphenol A polycarbonate this shows a peak here.

So, this indicates what you call as some kind of relaxation. Now this is called in this case gamma relaxation and this signifies that there is some kind of motion maybe involving two or three atoms that kind of motion. So, this shows that there is an absorption of energy around this particular temperature. So, around minus 100 degree Celsius you have some peak. So, there is still some motion that is there in the material in the in the in the chain a little bit a small number of atoms that are involved in that motion much below glass transition temperature.

So, typically, if you think that everything is rigid below glass transition temperature, then think again because this is not always true, of course, at the glass transition temperature, what happens that maybe 50 or 60 atoms in the backbone, together, they will start to have all them all their motions freed up at a higher temperature. So, that you have a big effect on G prime, but even much lower than glass transition temperature, you still can have motions. So, this is segmental motion a big segment has started to become has started has been freed from rigidity they have started to have motions.

So, that is the point at glass transition temperature, but much below glass transition temperature also, you can have motion of 2 or 3 carbon atoms together maybe a rotation a slight rotation around the phenyl, around the phenyl carbonate bond. So, those kind of rotations or small motions those can absorb energy.

So, those are not completely rigidify it at a temperature lower than glass transition temperature. So, those are called they have different names for relaxation for polycarbonates this is called gamma relaxation. So, you see that for Bisphenol A polycarbonate your gamma relaxation this point, it is around minus somewhere here, it is around minus 105 degree Celsius, it is it is a range, it is not exactly a particular specific point. So, this is for Bisphenol A polycarbonate, when you substitute with tetra methyl 4 methyl groups, what happens your T G goes up from here to here, as you can see from the G prime goes up around 50 degree Celsius, but the gamma relaxation point which was here for Bisphenol A polycarbonate it has come.

Now, to this point which is close to 45 degree Celsius; so, this gamma relaxation temperature also goes up probably because you have actually introduced some restriction around the phenyl carbonate bond by introducing two more methyl groups and introducing steric hindrance. So, that directly effects the rotation and that directly effects your gamma relaxation temperature. So, now, you have to go to a considerably higher temperature. So, before it was at minus 105 degree where this rotation was possible, now only at plus 45 degrees this rotation is possible. So, this is your gamma relaxation.

Now, let us come back to our script and try to explain this little bit further. So, what we have seen there is a result of dynamic mechanical analysis where you are plotting both elastic or storage modulus and loss modulus as a function of temperature which gives you an idea of T G and which also keeps you an idea of what you call as gamma relaxation involving maybe 2 or 3 atoms, together the motion of that and that motion is not frozen at a temperature lower than glass transition temperature unlike the popular belief for quite some time.

So, this gamma relaxation this happens the temperature of gamma relaxation let us say is T gamma, it is around minus 105 degree Celsius for Bisphenol A polycarbonate, it goes up to around plus 45 degree Celsius for tetra methyl substituted counterpart huge change. So, reduced rotational freedom of the phenyl carbonate bond; that is responsible for such a huge increasing because that rotation. Now in order to affect that rotation, you have to go to much higher temperature before you could affect that rotational minus 105 degrees.

Now, you need to go to this much high temperature. So, this temperature shift in the gamma relaxation is substantially larger than the temperature shift for glass transition temperature because here it is close to around hundred 50 degrees difference from BPA PC to TMBPA PC, the T gamma, but T G is only around 50 degree difference. So, that effect on this gamma relaxation is huge. Now the decreased impact strength of this tetra methyl substituted counterpart with respect to the unsubstituted Bisphenol A polycarbonate can be directly related to this increase in the temperature of gamma relaxation somewhat intuitively can understand that when you are giving an impact to the material, it has to absorb some energy and yet it has to distribute that absorbed energy in the material and this possibly happens.

Because you put some energy and there might be slight rotation here or slight rotation they are of the bond and you can absorb some energy and if you stop that you cannot you know absorb and distribute this energy. So, it is an intuitive way to understand to correlate the relaxation, it is called relaxation because it is a change in the shape of the lost modulus you know the liquid, for example, when you put some energy to it or force to it just takes the shape that you are forcing it to take; that means, it is the distributes the energy. So, this is kind of relaxation it is not like it is storing that energy or whatever. So, that way you put some energy and maybe it is relaxing by rotating slightly that phenyl carbonate bond, but now if the rotation is hindered you have to go to higher temperature. So, that is the impact strength also is substantially affected this is a way to look at it. So, this T gamma.

Now, this is true for Bisphenol A polycarbonate materials it is not always it thumbs rule for all kinds of materials now this has been observed. So, so, the reduced impact strength the reduced impact strength is a direct result of the shift in gamma relaxation maximum the T gamma increases. So, from here then you can actually formulate some kind of rule that. So, you want high temperature.

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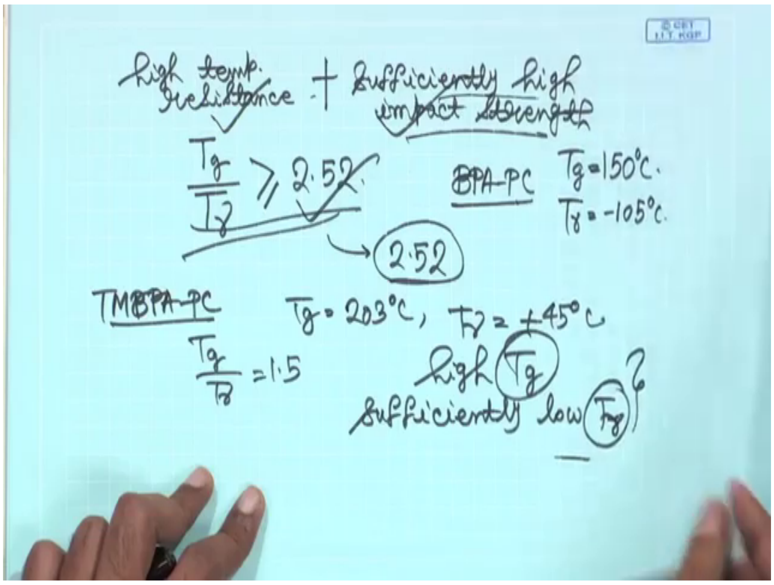

Resistance of course, you want high T g that that is that you already achieved and along with that you want sufficiently high impact strength which you could not achieve when you substitute it with 4 methyl groups on the benzene ring you lost the impact strength.

Now, in order to have the combination of both what you need to have is that this ratio of T g to T gamma this ratio should be greater than equal to 2.52. So, if you are looking at Bisphenol A polycarbonate what is this ratio for that T g is around 150 degree Celsius and your T gamma is around minus 105 degree Celsius. So, this ratio if you look at this ratio that ratio is somewhere around 2.52.

So, that meets this criterion. So, your material has high impact strength if you go to tetra methyl Bisphenol A polycarbonate then your T g goes up no problem around I think 203 degree Celsius to be exact and around 53 degree Celsius higher , but your T gamma also goes up to plus 45 degree Celsius. So, this ratio now drops and this ratio actually becomes equal to 1.5.

So, there could be some kind of empirical rule you could develop that this ratio of T g to T gamma has to be greater than equal to 2.52. So, then this is the design principle if you want to improve the property of BPA PC Bisphenol A polycarbonate then of course, you have to introduce some rigidity into the material which increases the T g and at the same time, you do not want to affect the T gamma that is the gamma relaxation temperature because that ratio has to be greater than or equal to 2.52 in order to create a rigid material, what you did in this case you substituted two four methyl groups in the benzene ring and that increased your T g no doubt, but the T gamma also increased significantly. So, that the ratio now became lower around 1.5. So, that is the material lost the impact strength.

So, a technologically valuable polycarbonate with high T g should have sufficiently low T gamma. So, that this ratio is higher than 2.52 then you will have a technological important polycarbonate which is a substantially higher on enhanced property with respect your BPA polycarbonate all right. So, what can we do then we want to increase the T g.

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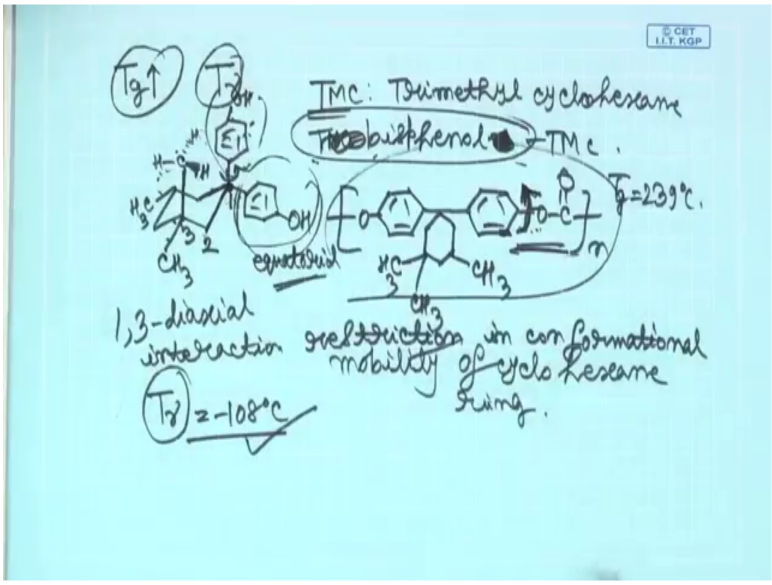

We do not want to increase the T gamma ok, let us try this let us look at trimethyl. So, TMC is try to trimethyl cyclohexane, let us look at TMC trimethyl cyclohexane based bisphenol a as the starting material ok. So, cyclohexane. So, trimethyl cyclohexane. So, one hydrogen here one hydrogen at the back of the page one hydrogen coming out of the page in front and then you have another two methyl groups here. So, you have trimethyl cyclohexane all right. In fact, it is not Bisphenol A because instead of acetone you have these two bonds you remember let me draw the full structure and then you will understand.

So, here you have OH. So, in Bisphenol A at this carbon this tetra substituted carbon you had two methyl groups instead of two methyl groups you have now substituted those two methyl groups with two arms of a cyclohexane ring; that is all. So, this is trimethyl. So, this is bisphenol trimethyl cyclohexane basically. So, this particular molecule; so, this is bisphenol trimethyl cyclohexane, if you use this for the preparation of a polycarbonate what will be the structure of the polycarbonate the polycarbonate the structure will be something like this and here there are two methyl groups.

Instead, those two groups are basically two arms of the cyclohexane ring and you have a CH 3 here CH 3 here and you have a CH 3 here. So, this material is quite rigid the restriction in the molecular mobility arises from the fact that there is a restriction in the conformational mobility of a cyclohexane ring restriction in conformational mobility of cyclohexane ring also this phenyl ring, it can rotate like this right this phenyl ring can rotate around this bond, but this rotation of this phenyl ring is also hindered because of one three diaxial interaction.

So, this position is one this position is two this position is three. So, at three position I have a methyl group here these these hydrogens can interfere with a rotation of this phenyl group because of this one three diaxial interactions because this phenyl is a di is an axial position this phenyl is equatorial position for this carbon. So, this an equatorial position equatorial this group this group is axial and this methyl is also axial because of this one three diaxial interactions because this phenyl is at one position this methyl is at 3 position, the rotation of this phenyl group is also hindered.

This is the first thing. Secondly, the cyclohexane mobility is also restricted conformational mobility that is the reason why you will have a rigidity more rigidity introduced into this system as compared to your your typical Bisphenol A say for example, this if you compare this with this material this will become more rigid and that is why the T g or the glass transition temperature will also go up. In fact, the T g goes up to 239 degree Celsius. So, if you compare that with for example, your parent Bisphenol A polycarbonate the T g is around 150. So, huge increase if you compare that with your parent your dimethyl substituted for the tetra methyl substituted Bisphenol A polycarbonate, this was only 203 degrees 53 degree Celsius increase here, it is almost hundred degree Celsius increase. So, your T g has increased what about T gamma or the or the relaxation temperature gamma relaxation temperature.

So, basically what happens is that your T gamma remains relatively unchanged if you compare with your Bisphenol A polycarbonate unlike your tetra methyl substituted one where the T gamma increased to plus 45 degree Celsius from the parent polycarbonate where the T gamma was minus hundred and seven degree Celsius approximately here in this material the T gamma is minus 108 degree Celsius does not change at all almost why is that. So, because the mobility of this carbonate group around the phenyl ring the final carbonate phenyl oxygen bond this mobility is not affected, the T g is increased because it becomes highly rigid, but the mobility around this bond is not affected because you are not putting any steric hindrance here.

Since the mobility is not affected and since this mobility is directly this is the T gamma your T gamma does not change. So, then the design principle is that make the molecule rigid, but do not hinder the rotation around the phenyl oxygen bond which you did by the way of putting methyl groups here and that is why the T gamma increased tremendously to plus 45 degree Celsius decreasing that ratio of T g to T gamma and decreasing the impact strength. So, now, you have a material which has a high impact strength as well as high thermal stability. So, what we will do is the we will stop here today and in the next class we will continue to discuss some more implications of what we have already stated today about the T gamma and T g. So, until then;

Thank you and goodbye.