Principles of Polymer Synthesis
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Lecture 47
Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about the structure property relationship of bisphenol A polycarbonates and so mainly we have been talking about how to preserve the impact strength while we try to increase the thermal stability of the material. In other ways while we try to increase that glass transition temperature of the material.

So, just a quick recap if we go back to the script now, just a quick recap.

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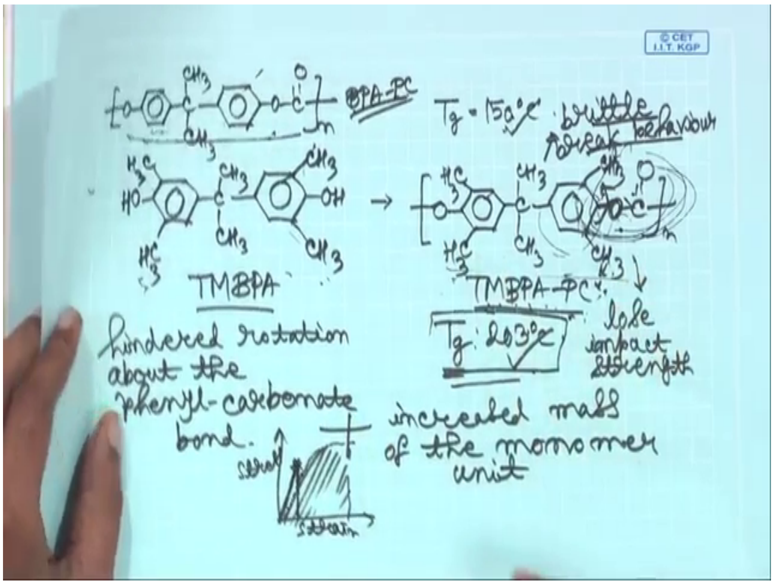

So, if we look at the bisphenol A poly carbonate the T g is quite low, I mean quite high but as far as what we expect, I mean if we want to increase if we have want to have very high thermal stability then it is moderate. So, we substitute 4 methyl groups in order to increase the rigidity of the poly carbonate.

So, we increase the T g no doubt, but the gamma relaxation temperature also is increased from minus 106 degrees and around about minus 160 degrees Celsius here to around plus 45 degree Celsius here. And we told the ratio of T g to T gamma actually determines that the impact strength will be retained or not.

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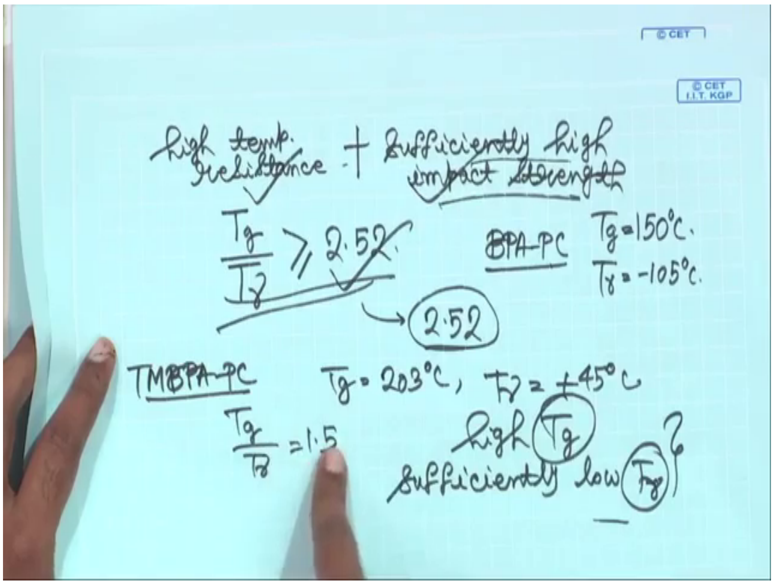

high temp. resistance + sufficiently high impact strength

$\frac{T_g}{T_\gamma} \geq 2.52$

BPA-PC $T_g = 150°C.$
$T_\gamma = -105°C.$

$\rightarrow \boxed{2.52}$

TMBPA-PC $T_g = 203°C$, $T_\gamma = +45°C$

$\frac{T_g}{T_\gamma} = 1.5$

high T_g
sufficiently low T_γ ?

If this ratio is higher or equal to 2.52 then you will have high impact strength. In the quest of increase in the T g if you also increase the T gamma then what can happen is that this ratio may become lower than this. In fact, for tetrameter substituted bisphenol A starting material this ratio is 1.5.

So, the T g although it goes up to 203 degrees Celsius a full 53 degree Celsius higher than your parent bisphenol A polycarbonate even then your T gamma goes up to plus 45 degree Celsius. So, this ratio is lower. So, you lose impact strength. So, what we told is that in order to solve this problem we can rigidify the main chain in order to increase the thermal stability no doubt, but do not try to effect this rotation, do not try to hinder this rotation around the phenyl carbonate bond.

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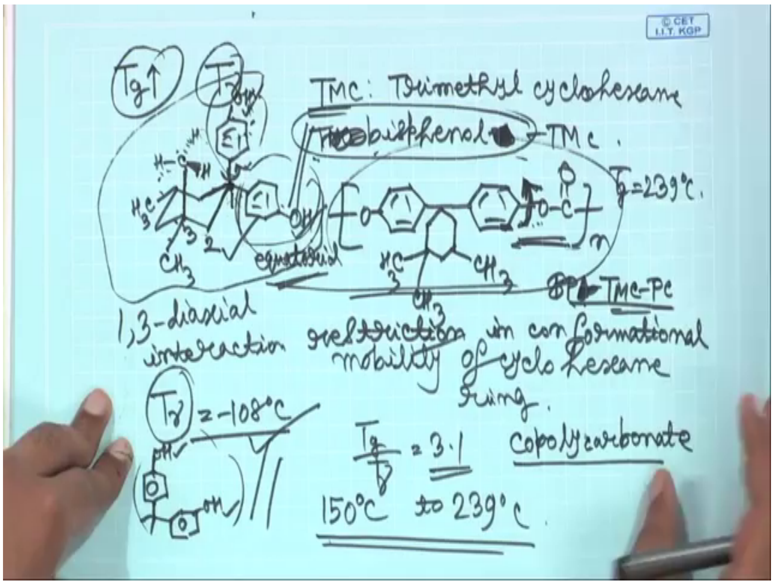

If you do not hinder this rotation then your T gamma or the gamma relaxation temperature remains relatively unaffected, but your T g increases tremendously because of the restriction of mobility of the cyclohexane ring plus the restriction of this phenyl ring rotation because of this 1 3 diaxial interaction. So, ultimately then you have a high T g to T gamma ratio. In fact, for this material you will have a T g to T gamma ratio which is 3.1 quite high. So, you have both high thermal stability as well as high impact strength of the material.

So, basically then this is your BPA bisphenol and BP instead this is not bisphenol A. So, this is bisphenol TMC PC polycarbonate. So, this bisphenol TMC polycarbonate can be produced in the same way as you produce your bisphenol A polycarbonate ok. So, the same interfacial polymerization process you could use. So, you can you can react this monomer the sodium salt of this monomer, you can react it phosgene and you can get your bisphenol trimethyl cyclohexane polycarbonate, also this phenolic O H group and the phenolic O H group or bis of bisphenol A.

So, if you look at this molecule and if you look at this molecule where you have two methyl groups, these phenolic groups here in bisphenol A and the phenolic groups in this bisphenol trimethyl cyclohexane they have a similar reactivity. So, what you can do is that they since they are comparable react reactivity you can actually prepare copoly carbonates from them. You can actually prepare copoly carbonates. So, you mix them together during the copolymer preparation and then you will have both this monomer as well as this monomer present in the polymer. And you can change the relative ratio of them depending on how you start with depending on the relative ratio of the monomers in the starting copolymerization mixture you can introduce these two components in different ratios in this polymer backbone.

Simply because these alcohols these phenolic O H groups here, they have same reactivity very similar reactivity to the phenolic O H groups in this bisphenol A. And of course, if you have different proportions of these in the polymer you can also modulate your glass transition temperature according to your needs and that glass transition temperature you can have anywhere between 150 degree Celsius to 239 degrees Celsius, because if you have only homo polycarbonate based on this which is bisphenol trimethyl cyclohexane homo polycarbonate which will have a glass transition temperature of 239 degrees Celsius. Homo polycarbonate based on bisphenol A itself will have a glass transition temperature of 150 degree Celsius,

So, if you just now, make a co-polycarbonate with different relative ratios and accordingly they will go into the polymer also. So, your T g can be varied somewhere between these two depending on what you want. So, in fact, the dependence of this class transition temperature or T g on the comonomer ratio is reflected quite well in the empirical fox relationship.

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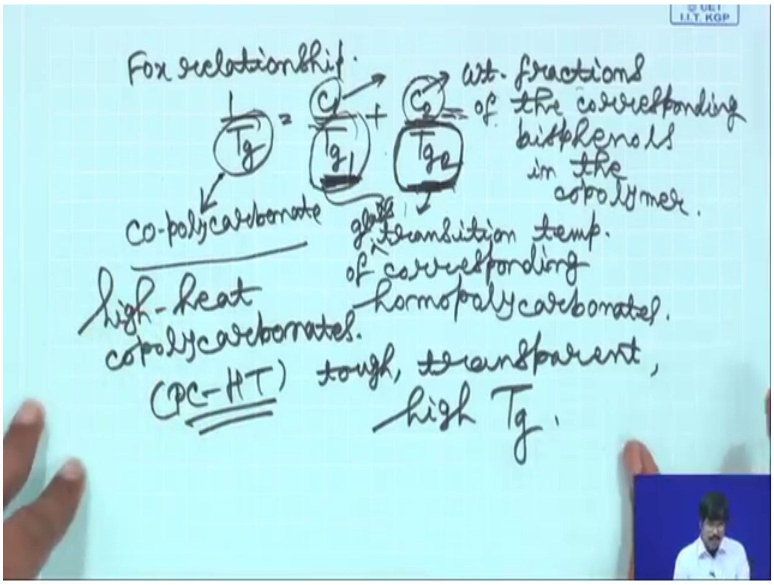

Fox relationship.

$$\frac{1}{T_g} = \frac{C_1}{T_{g1}} + \frac{C_2}{T_{g2}}$$

wt. fractions of the corresponding bisphenols in the copolymer.

co-polycarbonate

glass transition temp. of corresponding homopolycarbonates.

high-heat copolycarbonates. (PC-HT) tough, transparent, high Tg.

So, the fox relationship is this 1 by T g is equal to C 1 by T g 1 plus C 2 by T g 2, where this T g 1 and T g 2 their glass transition temperatures of the. So, this is their glass transition transition temperatures of corresponding homo polycarbonates, homo poly carbonates, and C 1 and C 2 they are basically the weight fractions, weight fractions, weight fractions of the corresponding bisphenols in the copolymer.

So, this may be bisphenol A this may be the bisphenol trimethyl cyclohexane and this is the corresponding glass transition temperature their homo polymers. So, weight fractions of the corresponding bisphenols in the copolymer and then this T g is basically the T g of your co polycarbonate this is how you can get your T g co polycarbonate. So, this is the, so, let us say this T g 1 is for bisphenol A polycarbonate. So, this 150 degrees Celsius this T g 2 is for bisphenol transmittal cyclohexane polycarbonate homo poly.

So, both are homo polymers. So, this is basically how much 239 degree Celsius. So, you change this ratio depending on what weight fraction you want for the corresponding monomer to go into the copolymer and then from this relationship you can find out what will be that glass transition temperature of the corresponding co-polycarbonate.

And these are examples of a class of polycarbonate also called high heat co-polycarbonates high heat co-poly carbonates, so polycarbonate H T like that. And these materials are tough they are transparent and they have high T g as a matter of fact the commercially available products that reflect the technical requirements they are usually expressed by what you call as the vicat softening temperature.

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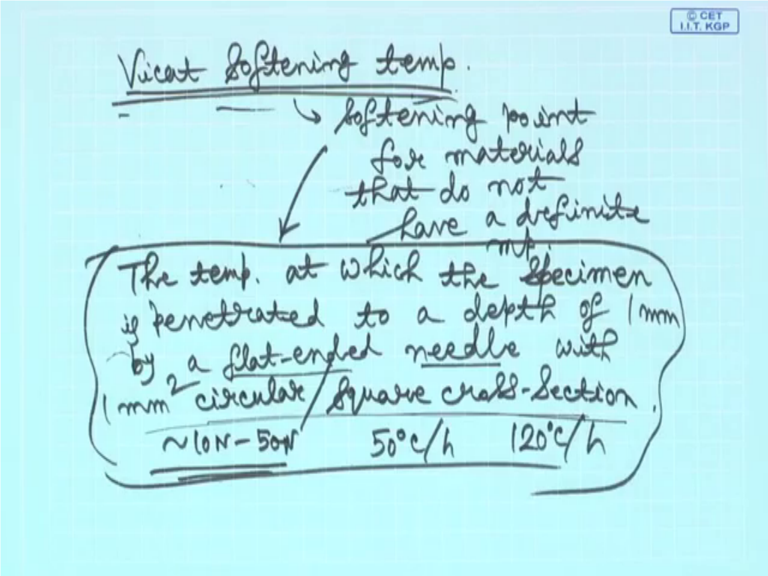

Vicat Softening temp.

→ Softening point for materials that do not have a definite mp.

The temp. at which the specimen is penetrated to a depth of 1 mm by a flat-ended needle with 1 mm^2 circular / square cross-section.

~10N – 50N 50°C/h 120°C/h

So, that is vicat softening temperature. So, their utility is usually expressed by this vicat softening temperature which is directly related to the amount of co monomer present in the system. So, if you look at the power point presentation here, you will see if you go to the slide please the power point presentation you will see that the vicat softening temperature is plotted as a function of the comonomer content.

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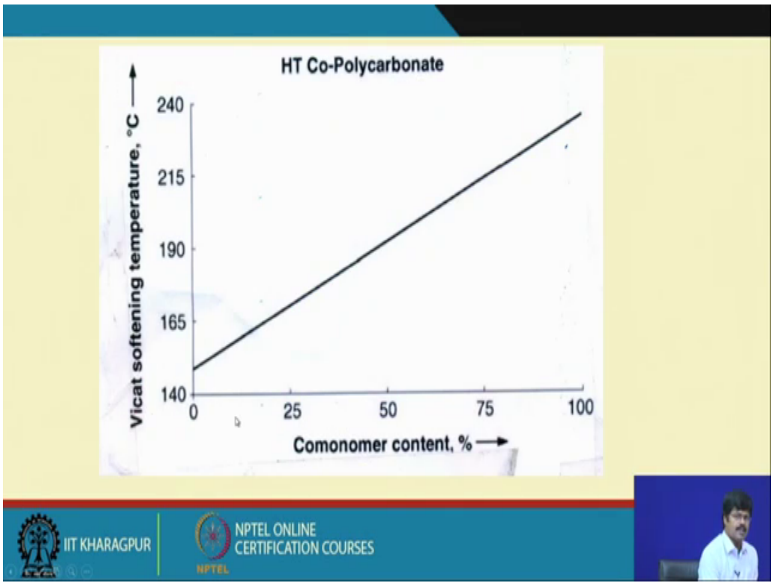

So, depending on how much of the relative amount of the different comonomers this vicat softening temperature or the temperature at which the material is softened or the temperature at which the mechanical properties are lost that can be plotted as a function of the comonomer content. So, this is of course, this keeps the utility of the material because beyond this temperature the material cannot be used. So, you use at a temperature which is lower than that, and this temperature may be typically slightly lower than your glass transition temperature. So, this has a linear relationship with comonomer content you see this is the this is the you know what we told this is high heat co-polycarbonate or PC HT we already talked about this.

So, let us come back to our script. So, basically this temperature will determine the soft ending point for materials which do not have a definite melting point ok. So, softening point for materials which do not have a definite melting point. So, basically this is like you know how do you determine this the temperature at which the specimen is penetrated to a depth of 1 millimeter by a flat ended needle with 1 millimeter square circular or square cross section and you are using a load of around 10 Newton, 250 Newton and specific heating rate say 50 degree Celsius per hour or 120 degree Celsius per hour.

So, basically this is an experimental process through which you determine the vicat softening temperature. So, what you do is that you put a flat ended needle on the top of the of the of the material and this needle the end of it has a specific defined cross section and then you are putting a load on the material on the on the at the end of the needle. And so what happens is that it is on the surface of the material and when you increase the temperature the material becomes softer and softer.

So, the temperature at which the material is penetrated to a depth of one millimeter that is the temperature which you tale as a softening temperature which you signify as the softening temperature ok.

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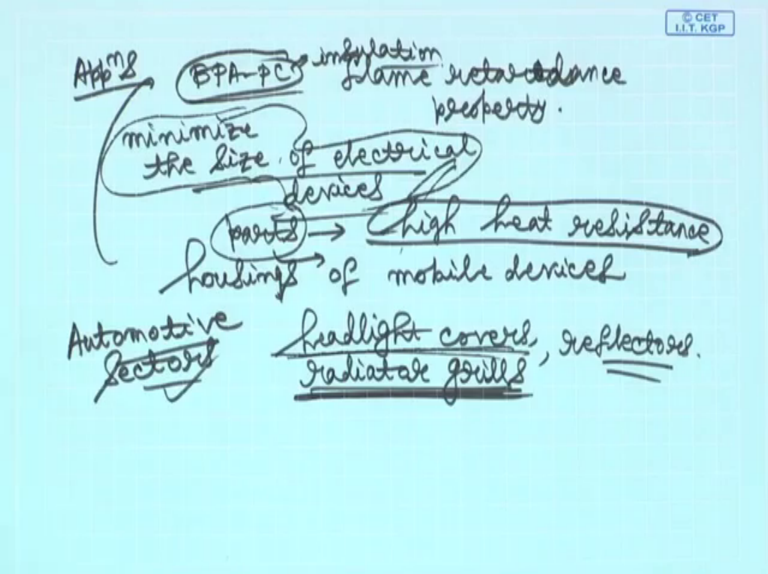

App^{ns} BPA-PC insulation
flame retardance
property.

minimize
the size of electrical
devices

parts → high heat resistance

housings of mobile devices

Automotive
sectors

headlight covers, reflectors.
radiator grills

So, basically then the applications of these materials if you are looking at; so already you now understand the structure property relations the intricate details of that why you need aromatic units while you need certain substitutions at one position and not in another position so on and so forth. So, typically they have outstanding. So, BPA bisphenol A poly carbonates they are outstanding electrical insulation good flame retardants property good flame retardants property they have high heat resistance.

Now, you know when you are trying to minimize the size of electrical device devices minimize. So, these are good insulation insulation also electrical insulation properties ok. So, when you are trying to minimize the size of your electrical devices what you need are parts with high heat resistance. That is because when you are going to small size I mean when you are trying to reduce the sizable electrical devices the different parts that you are using they are also going to a smaller size and the thickness of these parts also has to be reduced and that is why you need high heat resistance for these parts.

And you can use this phenyl a polycarbonate based materials for that ok. They can be used for housings of mobile devices for example, all also in flat panel displays or T v sets so on and so forth.

And some of the other usages; So, this is electrical sector some of the other usages could be in automotive sectors also automotive sectors, because these are lightweight materials. So, what you can do is that this bisphenol A polycarbonate based materials you can use say for example, as and also their transparent. So, you can use that headlight covers in the in the radiator grills, radiator grilles. Now, this particular application is because of the high temperature resistance headlight covers because they are transparent material they can be also used to as deflectors so on and so forth. So, depending on what kind of usage you want you would want a specific property high heat resistance or hot or high transparency high impact resistance so on and so forth, all right.

So, the final thing that we want to talk about here is the flame retardant property of these materials, flame retardant property.

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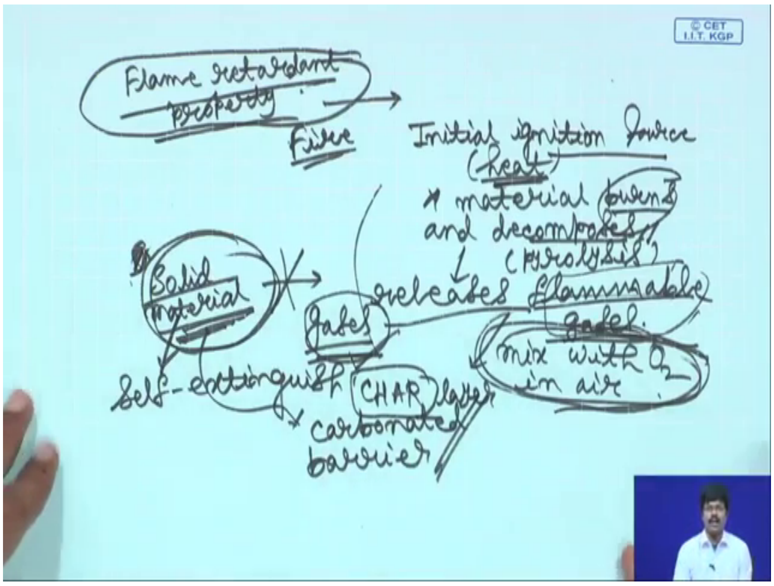

So, you know these kind of materials means materials which are which show these kind of flame retardant properties they are useful because you do not want they will limit the devastating effects of fires.

So, basically what happens is that when you are having a fire typically you have an ignition source initially you have an ignition source, initial ignition source. Now, and then maybe you, so maybe you are heating the system or whatever. So, this is the source and then what happens is that the material that you have this material will burn and when it burns and then it decomposes when it burns it decomposes.

So, this is actually your pyrolysis. So, initially you need some ignition source and then the material will start to burn and it will decompose and when it decomposes it will release flammable gases flammable gases and these flammable gases they get mixed up with oxygen in air and they will start to burn. So, this fire then could be quite self sustaining after you know because that also increases the heat so on and so forth a material burns further and it decomposes and further flammable gases are released.

Now, one of the ways in which a fire retardant could work there are different ways one of the ways in which it could work is that you know it could stop the feeding of the combustion process because when it is this combustion is going on you know that it is releasing more heat you know the flammable gas mixes with oxygen and it burns it releases more heat. And then what happens to your material burns further and it is releasing more and more flammable gas so on and so forth. So, you want to stop that feeding. So, what you can do is that you can this material that you have this solid material this one you stopped its decomposition to this flammable gases.

So, then the fire will not get any fuel and it will stop. So, basically your solid material it will self extinguish, if you can stop the formation of these gases and what you can do is that maybe this flame retardant material can form a carbonated barrier a carbonated barrier over this solid material preventing you know contact between the flame and the underlying material it can prevent the contact between the flame and the underlying material first of all. Secondly, it can stop the decomposition of this material. So, that no more flammable gas is released this is one of the ways in which it can be done.

Secondly, what can be done also you can use a kind of flame retardant materials which can basically you know it can release inert gases which can mix with these flammable gas and oxygen and continuities and can reduce the diversity effect of the fire.

So, what is done for bisphenol A polycarbonate is this part. So, basically a carbonated barrier or what you call as a CHAR, a CHAR layer is being formed on the surface of this bisphenol A polycarbonate. And so the flame cannot reach the bisphenol A polycarbonate and it does not decompose after and the flammable gas is not released. So, the way it is done is the is the following is through the following process.

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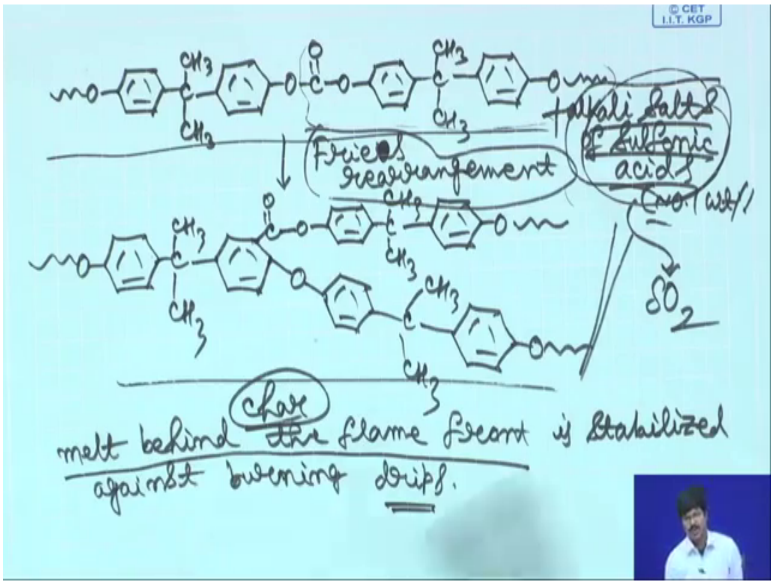

melt behind ~~the~~ char flame front is stabilized against burning drips.

So, basically you have your bisphenol A polycarbonate it can undergo what you call as a fries f r i e s, fries rearrangement at this high temperature and the product is something like this it is kind it is a cross linked material. So, you will have. So, this will go here.

So, basically you will have this C double bond oxygen O C CH 3 CH 3 like this and here you will have. So, you had the chain here. So, you basically have another chain that has come into the situation and so this is a rearrangement and this rearrangement will basically produce a cross linked material and this cross linked layer is basically the CHAR layer it is a carbon osseous layer that forms on the surface of your bisphenol a polycarbonate and then.

So, what happens is that the this material is stabilized this melt behind the flame front is stabilized against the burning drips melt behind. So, it is molten at these high temperatures the melt behind the flame front. So, this charge layer forms over this melt. So, this melt behind the flame front is stabilized against burning drips.

So, what typically is done is that to this material you add some alkali specific alkali salts of sulphonic acid. So, typically around 0.18 percent and this low content of additive does not affect the transparency of the polycarbonate or the mechanical property of the polycarbonate. But what it does. So, it is alkali salt of sulphonic acid at this high temperature of the flame front what happens is that. So, basically it is a potassium salt of sulphonic acid it decomposes and it produces sulfur dioxide and this sulphur dioxide is a powerful catalyst for this cross linking reaction or this fries rearrangement reaction.

So, this catalyzes this fries the arrangement reaction at this high temperature this small amount of this additive is added in your parent BPA poly carbonate and this actually catalyzes by reedy by releasing sulfur dioxide this cross linking reaction and then the melt is stabilized from the reach of the burning drip or the flame front.

So, that is the principle through which these primary property of the BPA polycarbonate works. For some other kind of materials the mechanism might be different it might release some inert gas in nitrogen or whatever to dilute your flammable gas or burning gases, but this mechanism for BPA polycarbonate is different like these the fries rearrangement.

So, with this we have finished the details of the structure property relationship of BPA polycarbonate and with this discussion we are also coming to the end of this course. So, we have had in the in the first part of this course we have discussed you know the principle of basically the synthesis of polymers in different ways same polymerization and then we have talked about step polymerization and what not maybe the you know co polymerization the principles of those in great details, we had talked about.

And in the second part we started with the chemical reactors and we discussed about different simple chemical reactions in terms of the design of the chemical reactors through our design equations of chemical reactors and then came the polymerization reactions and how we can correlate there is something called ignition temperature or something called extinction temperature so on and so forth.

What are the different stable steady states for say a continuous stirred tank reactor are those things we discussed, whether to use a passive reactor or a continuous stirred tank reactor for a polymerization it depends on whether it is a straight polymerization or a radical chain growth polymerization and so on and so forth. And then in the final part we have discussed in some detail the synthesis of different commercially important step growth polymers and then we also talked about followed it up by discussing in depth the structure property relationships what kind of structures can generate, what kind of properties and how you can basically engineer these different structures in view of those properties.

So obviously, I hope you have now, understood the importance of understanding these structures and how you can generate the properties because if you do not understand the structures you cannot generate the properties. And if you do not understand how you can synthesize the structures you cannot get to the structures in the first place.

So, I hope with this conclusion you have had a overall holistic view of you know the synthesis of polymers and their applications.

So, thank you for your attention for this course and I wish you the best of luck for the exams.

Thanks.