Principles of Polymer Synthesis

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Lecture - 32

Synthesis of Industrial Polymers

Welcome back, today we are going to start talking about synthesis of industrial polymers. So, the topic of today which is going to be the continued theme for the rest of the course that is the synthesis of industrial polymers, I did not mention, what kind of polymers and what not because we will see as we go along.

There will be some step polymers that we will talk about and maybe some of the radical polymers the radical chain polymers that we will talk about. So, a quick recap of what has gone on in the past couple of weeks, close to maybe one and half weeks, we have talked about chemical reactors in general for simple chemical reactions, how the principles could be applied in order to design a chemical reactor and in order to choose the reactor that you would like to use, we also talked about selectivity of reaction and as a relationship to that what kind of reactors you could use.

We also talked about comparisons of different kinds of reactors when you have a specific conversion is mind and the reactors are operating at a specific at some specific temperatures defined by the operating conditions which one you will choose for higher conversion, so on and so forth for several such problems have been done and also we talked about what you call as simple mole balance energy balance and lots of problems we had we have done in order to consolidate those concepts and towards the end we talked about multiplicity of steady states; so on and so forth.

And this culminated to a problem on polymerization where we showed, how we can derive different steady states exothermic polymerization reaction and we of course, had simplified assumption that your kp that is the rate constant of propagation rate constant of termination those things do not change with conversion initiator concentration does not change with converse conversion neither does the initiator efficiency.

So, all those things, we have discussed and we have consolidated the concept of chemical reactors. So, now, is the time to move forward to the to the last topic as I had also mentioned in the concluding stages of the last class.

So, what we are going to do is we are going to talk about the structure mainly the structure property relationship of different kinds of commercial polymers, I mean in terms of also the synthesis, how we are going to synthesize those and more like the chemistry aspects of them and how the I mean differing structures of different polymers they will have effect on their corresponding properties at the end ok.

So, we start then if you remember from our very first class, we had talked about this classification of polymers and we talked about these commodity polymers.

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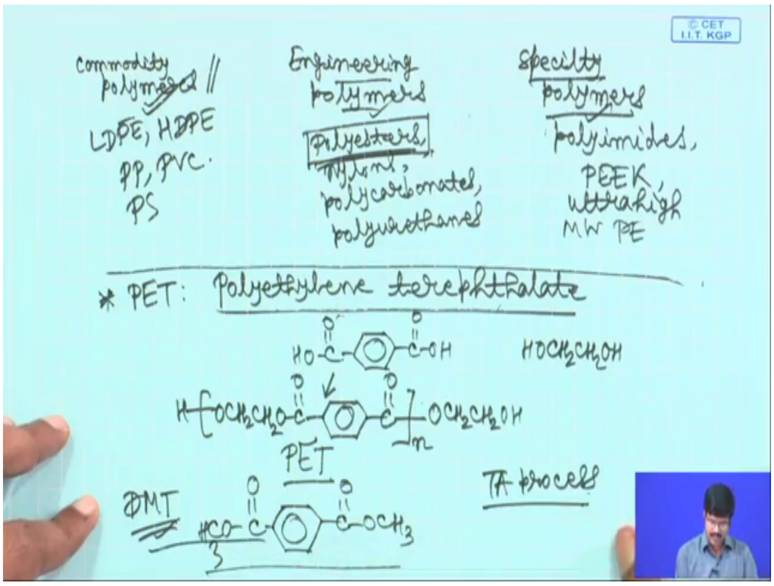

And engineering polymers and also specialty polymers specialty polymers and if you remember, we said that these are used for ordinary household applications and engineering polymers, they are actually used for higher end applications, they can withstand higher temperature specialty polymers they are more costly to prepare, but they are they can be used either even higher temperature even better mechanical properties than engineering and commodity polymers.

Commodity polymers are the lowest mechanical property lowest means I mean the say, for example, if you are looking at the quality of the mechanical property that you are looking for that mechanical property is lower here means it may be not very robust in terms of the stiffness or in terms of stability as a function of temperature so on and so forth.

So, those things we have discussed and we told say for example, here you have low density polyethylene high density polyethylene those are some of the examples polypropylene or PVC polyvinyl chloride like that or polystyrene engineering polymers it will be polyesters or say polyamides or nylons polycarbonate so on and so forth.

Polyurethanes like this and specialty polymers say polymides, it could be polyimides or poly ether, ether ketone ultra high molecular weight polyethylene ultra high ultra high molecular weight polyethylene like this ok.

So, what we are going to start with is we will start with the preparation of polyesters today and what I have chosen for this particular class is polyethylene terephthalate which is your pet this is poly ethylene terephthalate ok. Now, this polyethylene terephthalate as you can understand this is an ester and this is an ester of terephthalic acid and ethalene glycol, then what you get is polyethylene terephthalate and the structure will be this like this at the end, you have OH and then CH2; CH2 this is the alcohol part.

It is very important to write to be able to write down the structure correctly and here, this is the acid part, it could of course, end with an acid, but for reasons, we will discuss after basically on both sides, you will have the alcohol remember in this case, the ends cannot react with themselves if you are using one of the amine axis.

So, this is your pet polyethylene terephthalate. Now there are basically two processes which can be used to synthesize this particular polymer one process is DMT process, DMT stands for dimethyl terephthalate. So, basically your starting material here is the methyl ester of terephthalic acid ok. So, this is the methyl ester, you react the terephthalic acid with methanol and you will get the methyl ester.

This is a starting material. So, that is why the name is there that is a dimethyl terephthalate process and another process is your terypthalic acid process you start with terephthalic acid. So, that is TA; that is terypthalic another process is TA or terephthalic acid process. So, first we are going to talk about this dimethyl terephthalate process.

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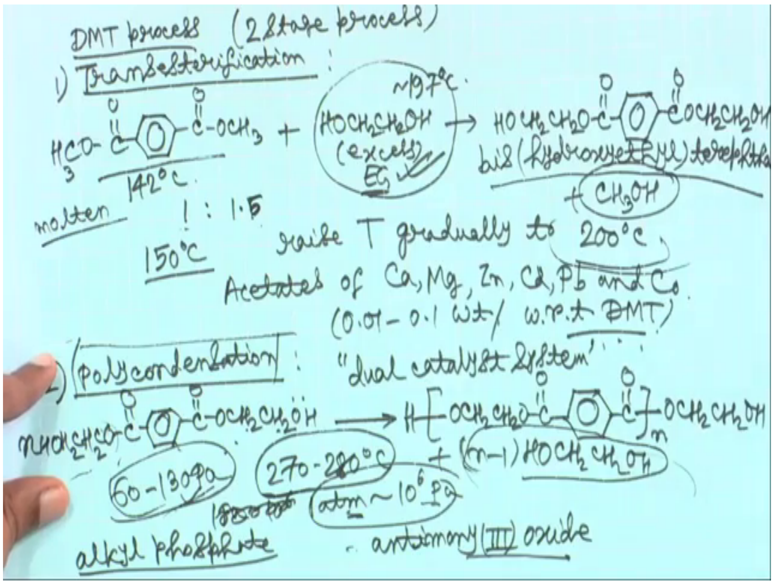

So, basically this DMT DMT dimethyl terephthalate process this is a 2 stage process, the first stage is what you call a trans-esterification trans-esterification. So, here you are doing an ester exchange reaction. So, you start with your dimethyl terephthalate as I told this is where the name is derived from. So, you start with your dimethyl terephthalate you react, this with ethylene glycol.

Basically you are using an excess of ethylene glycol EG ethylene glycol. So, what will happen is that this ethylene glycol will replace the methanol in this ester that is why it is a trans-esterification process the alcohol part of the ester is replaced by another alcohol. So, that the methanol is liberated.

So, basically what you will get is this particular product HCH2 CH2O CO ok, this is the product that you will get. So, this is this hydroxy ethyl terephthalate, this hydroxy ethyl terephthalate ok. So, this is used in excess the alcohol is used in excess and here your methanol is also produced and this methanol has to be continuously distilled off in order for the reaction to progress towards this side importantly the molar ratio of your DMT to EG the molar ratio is basically one is to 1.0 around 1 is to 1.5.

I will talk about the reason why it is 1 is to 1.5 and not 1 is to 2, I mean you can think about, it basically you have only one molecule of this and if you are putting 2 molecules of this, then you can have a balanced equation. So, basically two molecules of this reacts with one molecule of this to replace 2 molecules of methanol, but for reasons, I will mention after you are using 1 to 1.5 this is the first point.

Secondly the melting point of dimethyl terephthalate is around 142 degrees Celsius, but what you do is you do the reaction in a situation where your DMT is molten, it is in molten condition so; that means, you start with a temperature which is higher than 142 degree Celsius. So, I have the specific values with me. So, basically you start the reaction at 150 degree Celsius you start it at 150 degree Celsius and then you raise the temperature gradually to 200 degree Celsius.

Of course you are doing these reactions under nitrogen atmosphere so on and so forth because it presents oxygen in the systems I mean afterwards the polymer that is produced and all those can have degradation so on and so forth and this reaction is done under normal pressure you are not using high pressure and all and initially you are using 150 degree Celsius which is higher than 142. So, you are working in a molten condition and then you are raising the temperature gradually.

Of course, you could ask why we are not going directly to 200 degree Celsius and why you increasing the temperature gradually one reason is that you want to avoid sublimation of dimethyl terephthalate and that is the reason why you directly do not apply a very high temperature you start with low temperature and gradually you go to high temperature.

Now, one other point that we should mention here that you have to use a catalyst in order to have a reasonable rate of this transesterification reaction; so, you know that why it is transesterification why you are doing a high temperature because you also want to distill off the methanol and you want these to be in a molten condition ok.

So, this kind of reasoning is very important. So, you will see throughout the rest of the course this kind of reasoning we will try to provide wherever possible the explanations and we will try to correlate the structures with the properties that come like that; now the catalysts that you are going to use here because if you do not use catalyst the reaction does not progress even to a satisfactory yield even at this temperature, then you need very high temperature which is not practical for this situation because then these can decompose at those temperatures.

So, basically in order to do the reaction at what we call a moderate temperature, we use catalyst and these catalysts are typically there are acetates of calcium magnesium zinc cadmium lead and cobalt and typically they are used at 0.01 to 0.1 weight percent with respect to your dimethyl terephthalate, and the goal here is to observe quantitative conversion of your DMT into your base hydroxy ethyl or the product here in this case because if you have a methyl ester group present that can interfere with a subsequent reaction because this is not here polymer, you see this is not yet your polymer, you are still not arrived at the polymer this is the first step of the reaction.

Now, the second step of the reaction is poly condensation. So, you have obtained this bis hydroxy ethyl bis hydroxymethyl terephthalate and then you do a poly condensation of this product in the same container. So, basically this is what happens you have your bis hydroxy ethyl terephthalate. So, look at the name and the structure, it is easy to remember this name from the structure if you apply the logic.

So, CH2 CH 2 oh yes. So, n number of these molecules; so, they will react and they will produce ultimately your product which is your det and n minus 1 molecules of ethylene glycol will be liberated.

Now, how this reaction progresses basically you can visualize this, this is also kind of ester exchange reaction. So, basically the same alcohol is exchanging with the same alcohol I mean the same structure of the alcohol is exchanging with another alcohol. So, ultimately what you will see. So, maybe one of these molecules can react with another of these molecules through this oxygen. So, what will happen is that. So, this will basically attack another molecule over here and liberate say one molecule of ethylene glycol.

So, basically then you have extended the chain. So, if you envisage a reaction of one molecule of this with another molecule of this from this alcohol site. So, what will happen is that this alcohol will attack the ester linkage of another molecule and liberate this alcohol. So, basically instead of now one aromatic unit you have a chain which has two aromatic units so on and so forth.

So, ultimately, it can go on and on like that and it can have what you call as poly condensation because ethylene glycol is removed at each step. So, this is the; this is why we call this poly condensation. So, you see that there are two steps involved here trans-esterification and poly condensation reaction. Now, what you do is that after the trans-esterification reaction is complete whatever excess of ethylene glycol was there that you have to remove the ethylene glycol boiling point is around 197 degree Celsius.

So, what you do is that you gradually increase the temperature from 200 to 250 degree Celsius once the trans-esterification reaction is complete the first step is complete you gradually increase the temperature to 250 degree Celsius and then you distill off all of this ethylene glycol residual whatever ethylene glycol was there unreacted that you distill off and afterwards what you do is that you further increase the temperature to around two seventy to 280 degree Celsius and you apply a reduced pressure; that means, you apply vacuum to the system.

So, it is basically 60 to 130 Pascal that is the pressure that you have here. So, one Pascal is close to you know 10 to the power actually one atmosphere is close to 10 to the power 6 Pascal. So, you have some idea. So, this is atmospheric pressure is around 10 to the power 6 Pascal's. So, we have some idea of how much you have to reduce the pressure and under this condition also, you are creating this ethylene glycol to the system that also have to continuously distill off and you can use.

Of course, a catalyst to accelerate this reaction in principle the same catalyst that you have used for trans-esterification reaction the first step would be used here also, but the problem here you have already gone to very high temperature and at these temperatures the presence of those catalysts your calcium acetate or magnesium acetate or zinc acetate those can actually decompose your product.

So, the thermal stability of your product can be compromised in presence of the trans-esterification catalysts that you have used in the first step. So, what you do is you use what you call as a dual catalyst system; that means, for the second step when you are going to the second step what you do is the catalyst that was used in the first stage that is still in the reaction mixture that is deactivated.

So, you deactivate by addition of an alkyl phosphate. So, you have deactivated your catalyst for the first reaction now for the second reaction what you do is you add antimony oxide which will act as the catalyst for the poly condensation reaction. So, this is the overall process of poly condensation. So, you see some of the details are important here and you will stop the reaction, when the desired melt viscosity is reached because depending on the viscosity of the product you can use for a specific application and and all.

Now, this poly condensation reaction that you are talking about in order for this reaction to be rapid whatever ethylene glycol that is produced has to be quickly removed and this is something that you can achieve by using a good stirrer to have an intensive mixing because when you have intensive mixing that increases the polymer melt surface area also and so that gives you more chance for this liberated ethylene glycol to diffuse out and go into I mean diffuse out and get distilled out.

So, that is why what you do is your studying is very very important. So, that you increase the polymer melt surface area because the temperatures 270-280 degree Celsius that you are using your polymer will be a in a molten situation molten state. So, whatever ethylene glycol has come out if you have the melt surface higher the distillation will be easier for the ethylene glycol.

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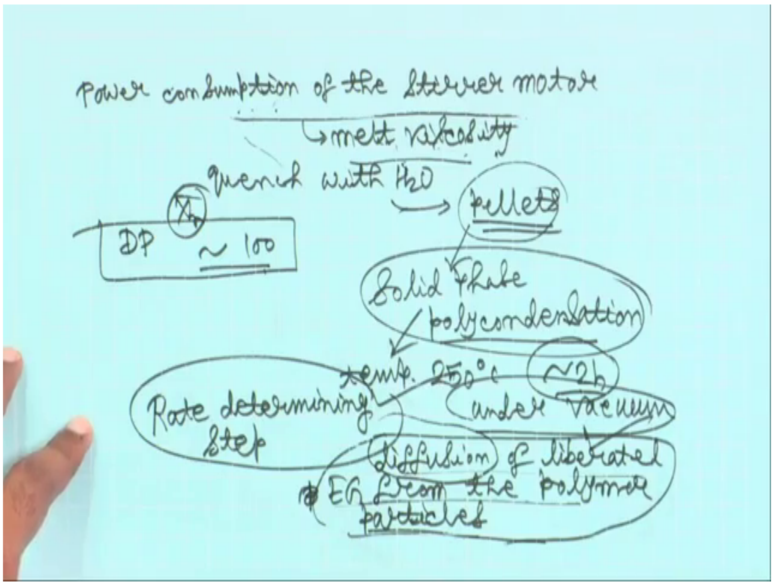

Now, how do you know you have reached the desired melt viscosity the power consumption of the stirrer motor the power consumption of the stirrer motor that will give you an adequate indication of the melt viscosity because it will consume more and more power if the melt viscosity is increasing, I mean if this viscosity reaction mixture is increasing.

So, there is a relation between the two and so, from this power consumption data you can actually find out the melt viscosity and when you have reached the desired melt viscosity you can stop it. So, what you do is that you have a vacuum. So, you release the vacuum by replacing it with nitrogen. So, you put some nitrogen inside the system and then under the pressure of this nitrogen, you expel the melt out of the system and afterwards, what you do is that the melt you can quench with water quench with water and you can make pellets out of the polymer.

Now, something that you have to keep in mind here in this particular process the degree of polymerization or the Xn bar; Xn bar the degree of polymerization that you can reach is only about 100. Now in order to obtain a higher degree of polymerization, what you have to do is that these pellets you have to subject them to solid phase poly condensation solid phase poly condensation, you have to subject them to solid phase poly condensation.

I mean what you do is that in the solid phase itself you further do the poly condensation you go to temperatures up to you heat it up to temperatures of 250 degree Celsius for around 2 hours and under vacuum of course, under vacuum because remember that when the poly condensation is progressing an ethylene glycol is being liberated that has to be removed from the system.

So, you go to high temperature keep for a certain time this has been standardized and the rate determining step the rate determining step for the solid phase poly condensation is basically the diffusion of liberated ethylene glycol which is a byproduct of course, liberated ethylene glycol from the polymer particles because they have to come out. So, it is a solid phase reaction. So, they have to diffuse out of the polymer particles and the and this rate is the slowest of all the rates that are involved in this reaction.

So, this is the rate determining step and the rate of diffusion of course, then will depend on the size of the particles of the polymer all right. So, this is in a nutshell the reaction that that is used to prepare poly ethylene polly polyethylene terephthalate. Now, let us come back to this particular reaction, again, the trans-esterification, I told that we are using 1 to 1.5 and not 1 to 2 in actuality you would expect I would use 1 to 2.

Now, keep in mind if you are using one to two you are going to get only this product as a stoichiometry demands 2 molecules per 1 molecular, this you are going to get only this product; however, if you are using less than that stoichiometry requires a 1 to 1.5, you will get something else also and with this product you are going to get some oligomers which are very same structure as the as the polymer.

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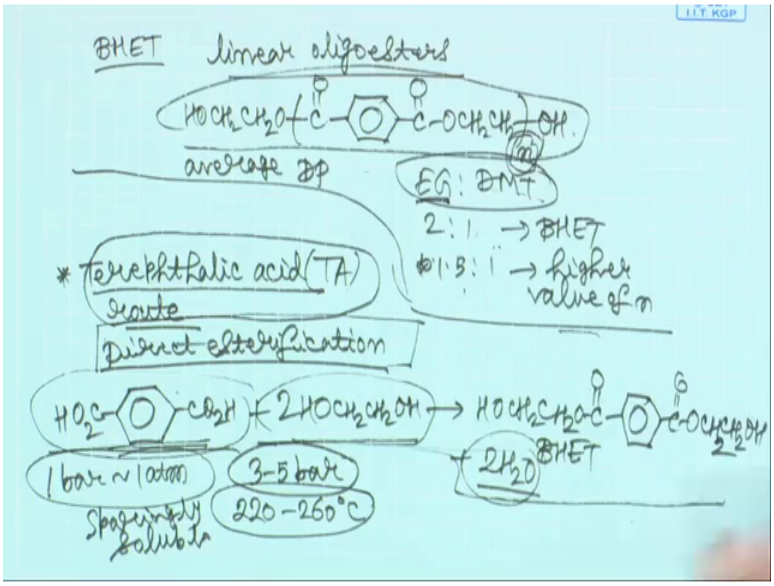

So, what you will get other than your these hydroxy ethyl terephthalate also what you will get is that you will get some linear oligo esters of the general formula like this. So, basically I mean you will still have some of these to react with because if you just reacted 2 molecules with this then this will be the product that is produced, but if you have taken this less then what will what will happen is that the proportion of this part the acid part might increase in the product.

So, along with this particular product you will also get some of these particular product which is a linear oligo ester of course, this is the same formula as your as your as your product which is your polyethylene terephthalate, but basically this is not a polymer this is linear oligomers this n value is small. So, you will have some degree of polymerization to start within the transesterification step itself.

So, that is the reason why you are not using one to two you are using say one to one point five now. So, this linear oligo esters will be produced and the average degree of polymerization average degree of polymerization of this linear oligo ester that is produced in the first step that is trans-esterification step that will be depending on the ratio of ethylene glycol to di methyl terephthalate that you are using.

If you are using two to one which we are not using in this case you will get only bis hydroxy ethyl terephthalate you will only get bis hydroxy.

Bis hydroxy of this means there are two units of this that is why it is bis and this is hydroxy ethyl. So, bis hydroxy ethyl and this is a terephthalate ester linkage. So, that is bis hydroxy terephthalate. So, you will get only bis hydroxy terephthalate. Now if the number of moles of ethylene glycol is lower than 2 times the moles of TMT; that means, say 1 to 1.5 if you are using say then you will get a higher value of m higher value of n.

So, instead of 1 to 2, if you are using 1 to 1.8, then you will get some n value if you are using instead of 1 to 1.8 you are using one to one point five then you will get higher n value so on and s forth.

So, you will get something like what you call as a pre polymer that you can subject to further poly condensation step in the next process, the same reaction mixture you are increasing the temperature and slowly you are distilling away all the unreacted ethylene glycol that was present because the boiling point is a 197 degree Celsius and after that you are you are also destroying the catalyst that you have used in the first day because that will compromise the thermal stability of the product and you are adding another catalyst that is why it is a dual catalyst system that you are using ok.

So, these are some of the main important parts that I wanted to talk about now we can of course. So, this is your dimethyl terephthalate acid route another route that we can talk about is terephthalic acid route I told you that there are 2 routes one is the DMT route dimethyl terephthalate another is terephthalic acid route.

Now, this route was initially not used because economic processes to produce pure terephthalic acid were not available initially that is why people are using DMT. Now, DMT is not a direct process because you know you are using a trans-esterification in the first step. So, this terephthalic acid route is something that is that the people are using much more. Now, that we have all these economic processes to prepare the terephthalic acid.

So, something that you have to keep in mind is that in this particular reaction that you do you are using a direct esterification route you are using a direct esterification route. So, which is nothing but; reacting your terepthalic acid. So, this is your terethalic acid you react with your ethylene glycol and you get your bhet which is your; I mean instead of transesterification you are using a direct esterification as route to obtain your this hydroxy terephthalate.

Now, why we will use this terephthalic acid root and not terephthalate route we will tell you after the advantages of this route afterwards. So, you directly get your bhet and in this process. So, two molecules of this can react and two molecules of water can be evolved water you have to remove by distilling out.

Now, this particular process that you are you are you are using here one difference here is that this terephthalic acid you are not using any other solvent right you are using this plus this. So, terephthalic acid has a sparing solubility it is not soluble to a large extent in ethylene ethylene glycol.

So, this direct esterification route if you are going to do you have to use a high pressure around three to five bar of pressure you have to use just to compare it with your normal atmospheric pressure one bar is approximately equal to one atmosphere. So, 3 to 5 bar of pressure you have to use and you are basically using a high temperature in the range of 220 to 260 degree Celsius; in order to do these direct esterification step compare this with your transesterification step that you used for the synthesis of bhet in the first step of the DMT process from the dimethyl terephthalate this process this reaction temperature was much lower.

You start with 150 degree Celsius, you go to 200 degree Celsius the reaction temperature now is much higher 220 to 60 degree Celsius the pressure that we used here was normal atmospheric pressure, here you are using three to five atmospheric pressure simply because you are using die instead of dimethylene instead of sorry instead of dimethyl terephthalate you are using terepthlic acid this reactant remains the same.

So, the solubility is also important now in this case here this melts and it made forms a homogenous mixture now in this case, this particular material terephthalic acid, it has sparing solubility it is sparingly sparingly soluble. So, you need to go to high pressure go to high temperature in order to effect this reaction.

So, what we will do is that we will stop here today and we will continue the discussion of the terephthalic acid route in the next class because this is not the end of the terephthalic acid route this is just the first step. So, we will continue here after the discussion of this and. So, the topic remains the same we will keep talking about the synthesis of different step growth polymers and our time is up for the day.

So, we will see you in the next class until then.

Thank you and goodbye.