Polymer Reaction Engineering
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Lecture – 32
Introduction to Radical Chain Polymerization

Welcome to the radical chain polymerization chapter. In this particular chapter, we are going to discuss about the radical chain polymerization. And we will discuss about the basic concepts of resonance because resonance is an integral part of polymer reaction engineering, then we will have a comparison between the radical and step growth polymerization. So, let us start with the radical chain polymerization.

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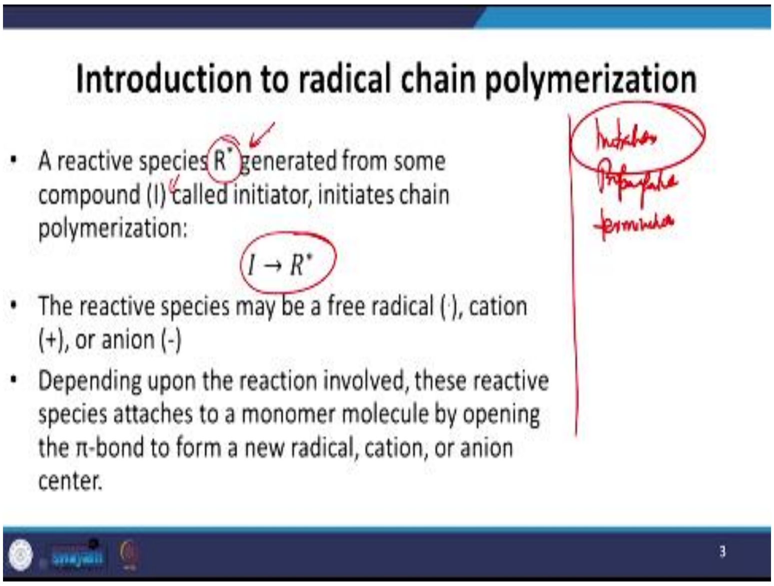

Introduction to radical chain polymerization

- A reactive species R^* generated from some compound (I) called initiator, initiates chain polymerization:

$$I \rightarrow R^*$$

- The reactive species may be a free radical (·), cation (+), or anion (-)
- Depending upon the reaction involved, these reactive species attaches to a monomer molecule by opening the π-bond to form a new radical, cation, or anion center.

Initiation
Propagation
termination

Now, a reactive species because, as we know that in all kinds of polymeric system, there is a reactive species and this reactive species initiate the polymerization reaction. So, reactive species, let us say in this case, R^* is generated from some compound I,

$$I \rightarrow R^*$$

which is usually called initiator and it initiates the chain polymerization like this. Now, if you recall that in the priorly, we discussed about the 3 stages of polymerization: initiation, propagation and termination.

Now, if you recall that not every monomer or not every molecule to participate in the polymerization reaction, the formation or the presence of either functional group, double bond or any kind of a reactive species is must for having the polymerization reaction take place.

Now, these reactive species whatever we are discussing maybe a free radical, maybe cation or maybe anion.

So, depending upon the reaction involved, now, these reactive species either attached to a monomer molecule, say by opening any phi-bond to form a new radical cation or anion centre.

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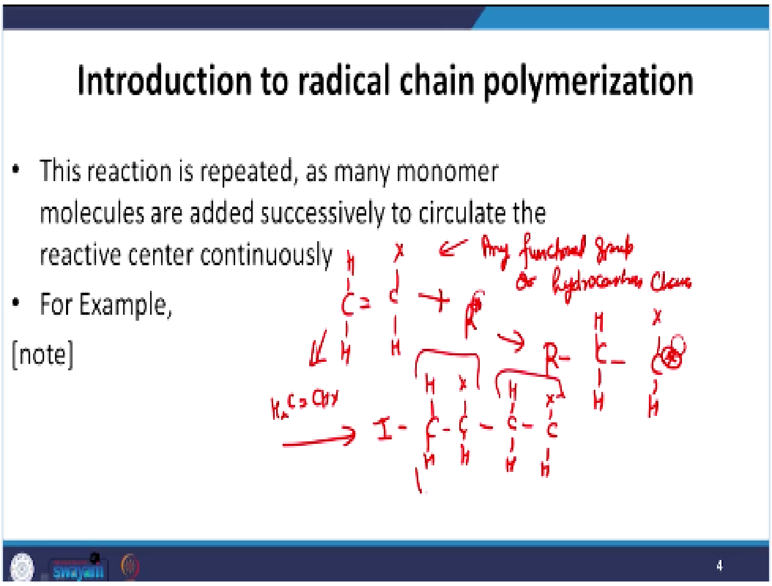
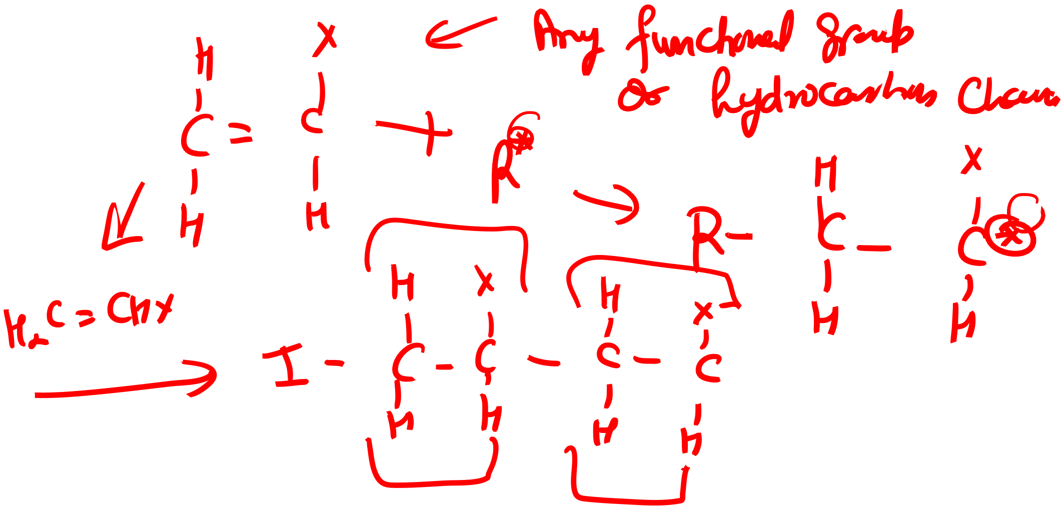


Introduction to radical chain polymerization

- This reaction is repeated, as many monomer molecules are added successively to circulate the reactive center continuously
- For Example,

[note]

Now, this reaction is usually whatever the reaction we are going to discuss is usually repeated as many monomer molecules are added successively or in sequentially to circulate the reactive centre continuously. Now, let us have an example of this particular approach.



We are having this particular molecule. Here, this x is any functional group or any kind of hydrocarbon chain. Now, it is related with this radical. So, it may form. Now, this is a transfer to here.

Now, if we keep on further increasing the chain, then this H 2 C CH x, this one may have like this. Now, these are the repeating units.

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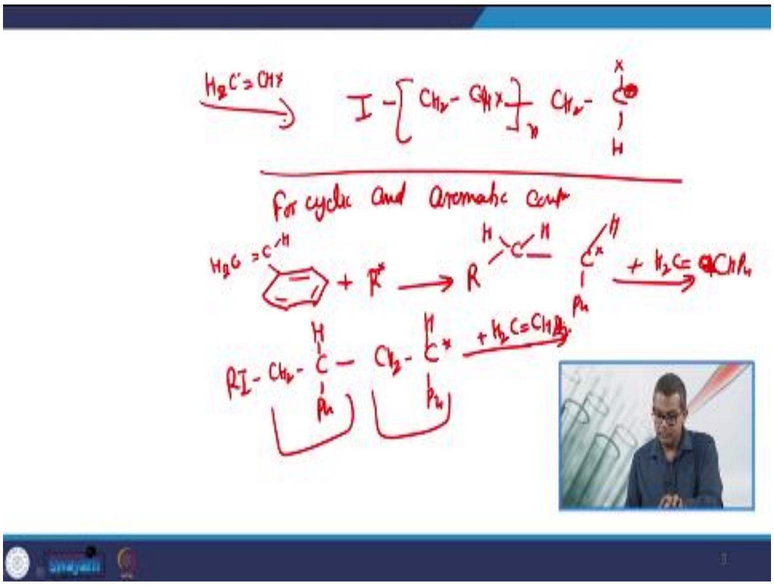
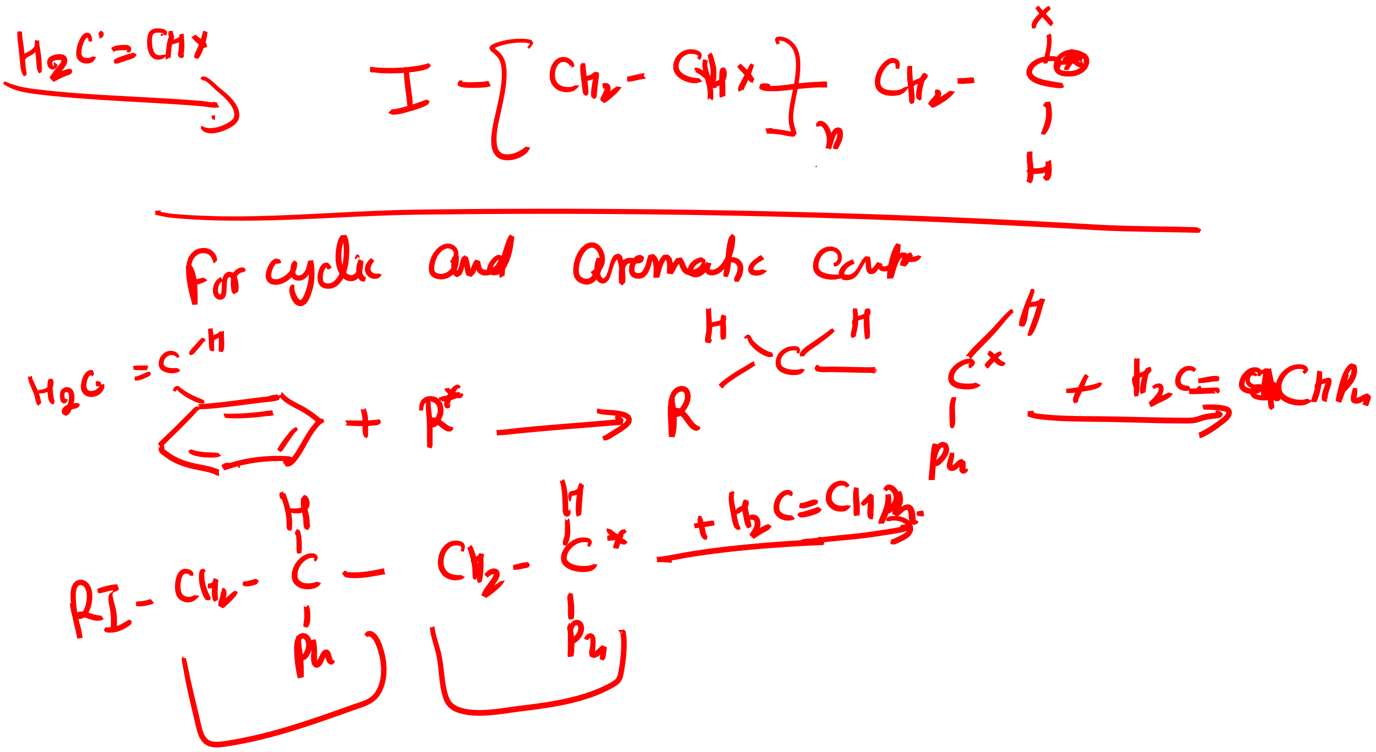
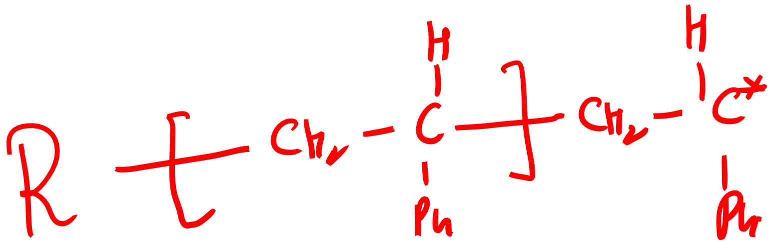


Now, if we keep on moving the things in the same direction, then we may have again, that is so, this is you can say, the stages of various polymerization and we may take another example of this particular approach for cyclic and aromatic compound.



And aromatic compounds like, we may have. Now, you will see that here, we are performing that thing opening and approach. Further, if we go ahead with that, then phenol ring, Ph stands for phenol ring.

Now, you see here, these 2 are the repeating units. Now, if further we carry out up to the nth molecule level, then this may become, now, this is my polymer.



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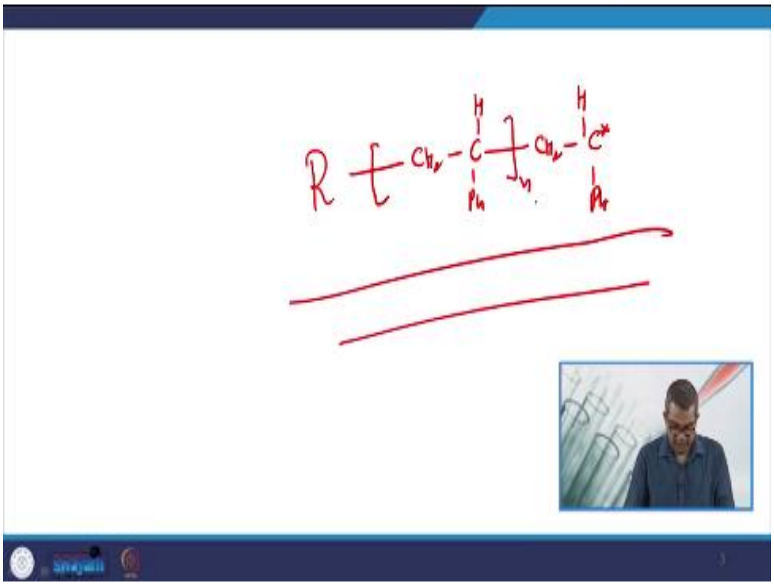

So, this is again you see that this is the basic the genesis of radical chain polymerization. Now, at some stage, polymer growth is terminated by the degradation and if you recall that we discuss about initiation, propagation and termination, and sometimes, it may be terminated chain growth; may be terminated by the degradation of any kind of reactive centre by an effective reaction, sometimes it depends on the form of reactive centre and precise condition of any reaction.

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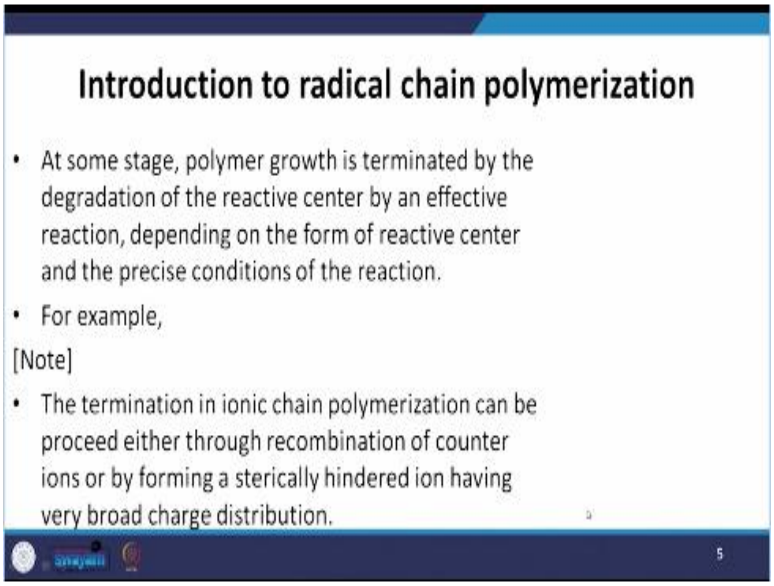


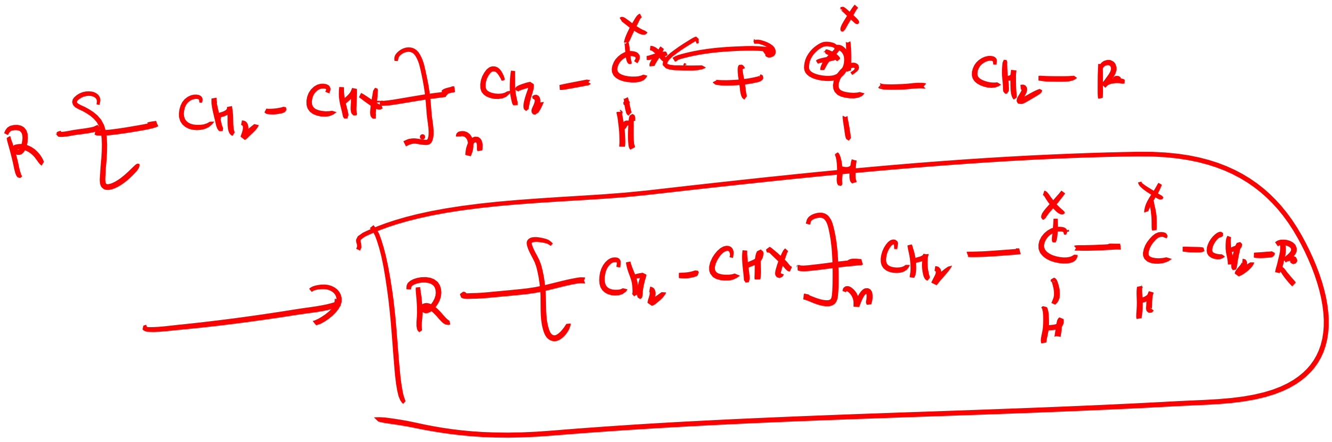
Introduction to radical chain polymerization

- At some stage, polymer growth is terminated by the degradation of the reactive center by an effective reaction, depending on the form of reactive center and the precise conditions of the reaction.
- For example,

[Note]

- The termination in ionic chain polymerization can be proceed either through recombination of counter ions or by forming a sterically hindered ion having very broad charge distribution.

Now, let us have a look about this thing. If we take the previous example, now, the chain can be terminated through another reactive centres like here we are having this polymer with us CH 2 CH x.



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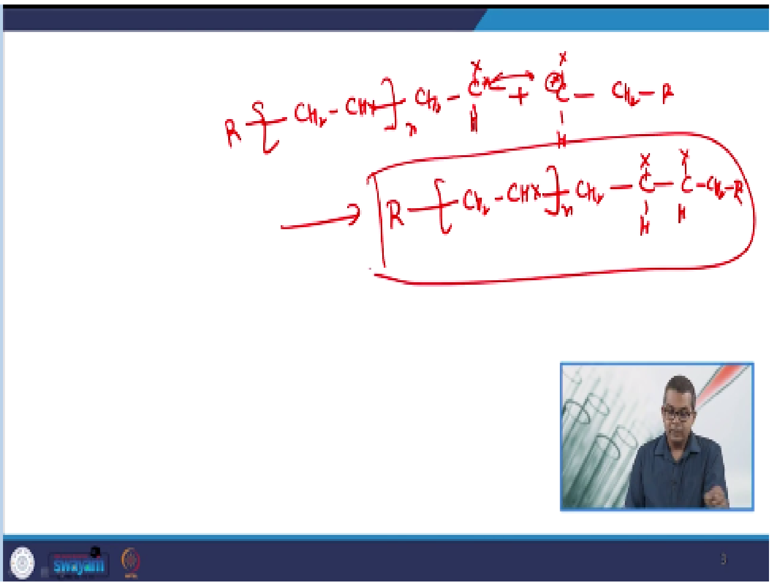

Now, this is another reactive centre. Now, here, this chain is auto terminated with the help of this reactive centre. So, both of them may combine together to truncate the reaction and that is why you may be at the stage of completion of this polymerization reaction. Now, this is the way through which you can truncate this further polymerization. So, this is my entire polymer. So, that termination in ionic chain polymerization, it can be proceed either through recombination of counter ions like this.

We have discussed in the previous example or by forming a sterically hindered ion having very broad chain distribution.

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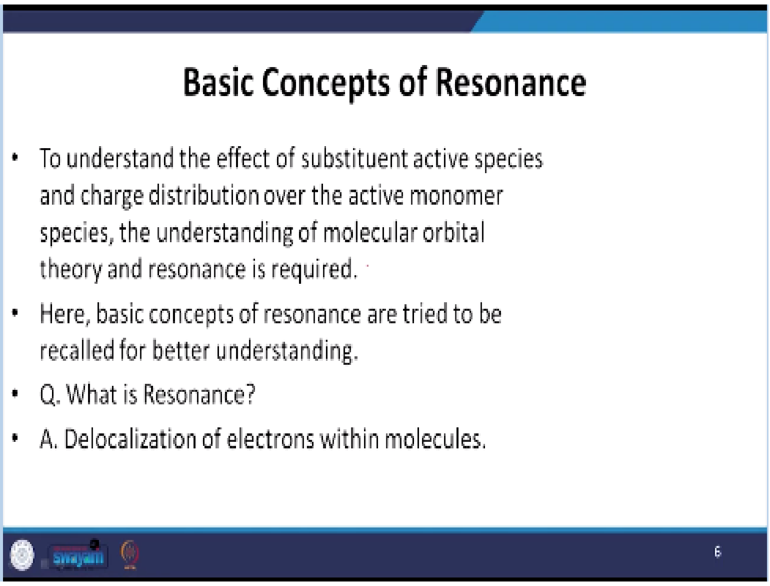


Basic Concepts of Resonance

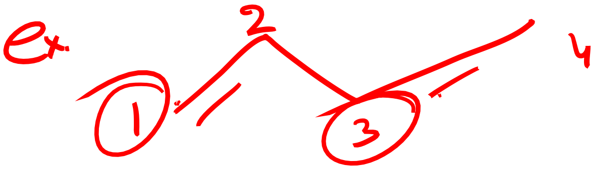
- To understand the effect of substituent active species and charge distribution over the active monomer species, the understanding of molecular orbital theory and resonance is required.
- Here, basic concepts of resonance are tried to be recalled for better understanding.
- Q. What is Resonance?
- A. Delocalization of electrons within molecules.

Now, to understand this particular effect, substituent active species and sometimes, the charge distribution over the active monomer species, the understanding of a molecular orbital theory or a resonance is required that is why the second point in this approach was the discussion about the resonance. Now, here, the basic concept of resonance, they tried to be recalled before understand that there are certain FAQs or frequently asked to question which are related to this resonance concept that what is the resonance.

We discussed about the phi system. Now, this resonance is usually a delocalization of electrons within molecule sometimes, this type of approach. Now, another thing is that what is its effect? People may ask that what are their effects? Now, the basic effect of these resonating concept is to increase the stability of the molecule with respect to the polymeric system.

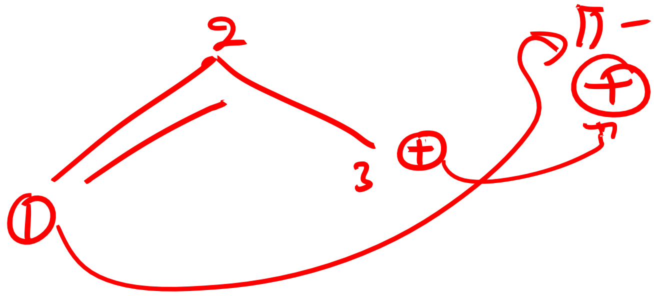
Sometimes, we may ask that what are conjugates or what is conjugate? So, there are 2 subjects usually in different alternate positions maybe a b c, d or a and c, and similarly b and d both are the conjugate to each other. So, this facilitates the formation of stable system within the polymer system. Now, what are the requirement of resonance in any molecule? This is again very broad question.

① π- π Conjugate



π bonds at position ①
& ③

② π- Cation Conjugate



π - bond @ Position①

⊕ Charge at position ③

Now, the things is that I mean sometimes it may refer to as a prerequisite for resonating system in any kind of molecule, so, the molecule must have a conjugate system. So, let us ask about that what are the different type of conjugate systems. So, I will discuss about a couple of things before we discuss further. Now, here, there are a couple things related to the conjugate system.

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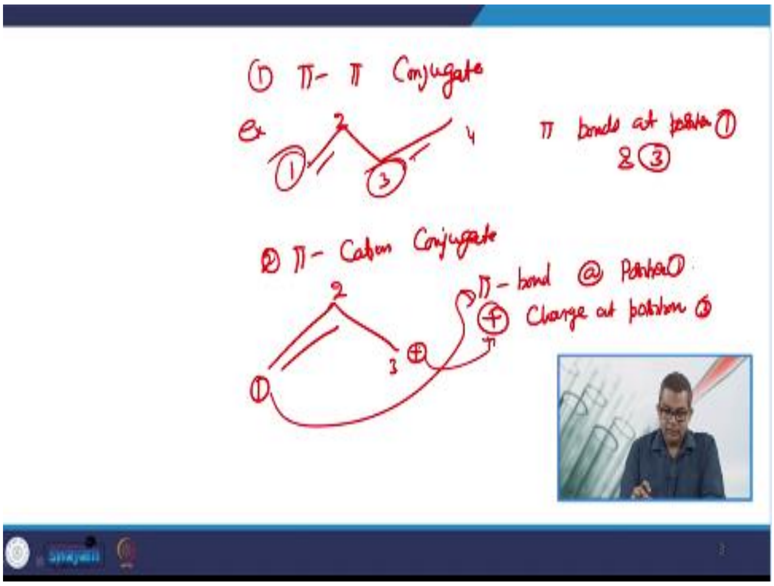


① π- π Conjugate

Ex

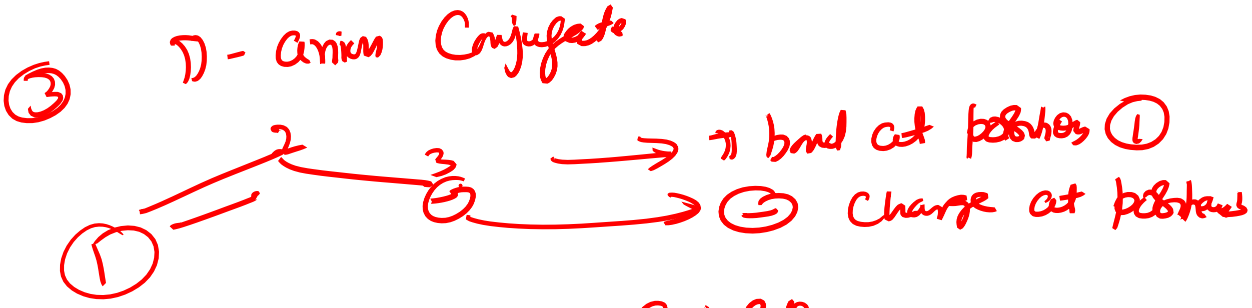
π bonds at position ① & ③

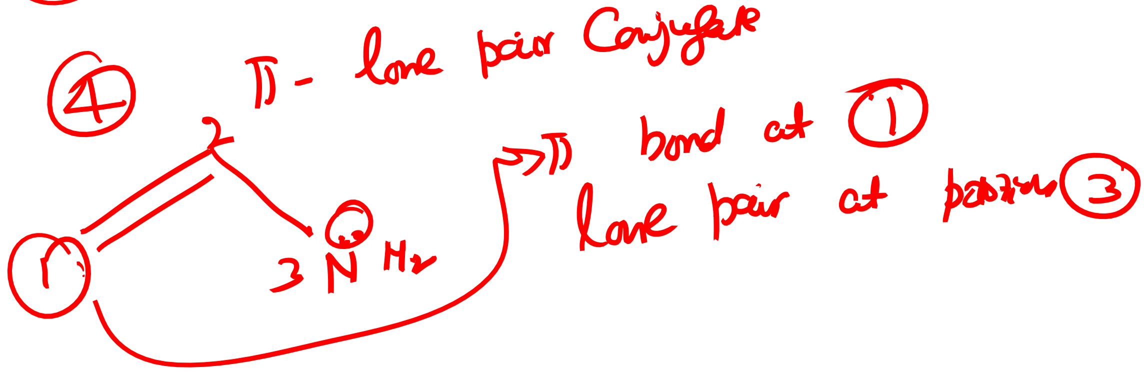
② π- Cation Conjugate

π - bond @ Position ①

⊕ Charge at position ③

One is the phi-phi conjugate. Now, the example is 1, 2. Now here, the phi bonds at position number 1 and position number 3. Another is the phi cation conjugate that is a second approach. Now, here, the pi bond, this is the pi bond at position 1 and discharge at position 3.





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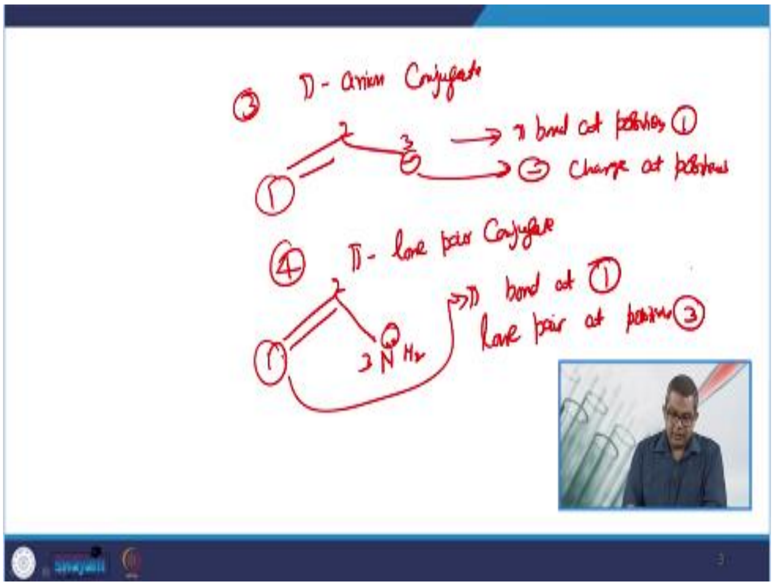

③ π- anion Conjugate

→ π bond at position ①

→ ⊖ Charge at position

④ π- lone pair Conjugate

→ π bond at ①

lone pair at position ③

Another is, the third one is phi-anion conjugate. Now, the example is now here, 1, 2, 3. So, the phi bond that position 1 and this is negative charge at position 3. Now, fourth one is phi lone pair of conjugate so, 1, 2. Now, here, the phi bond at position number 1 and lone pair you see here, lone pair at position number 3.

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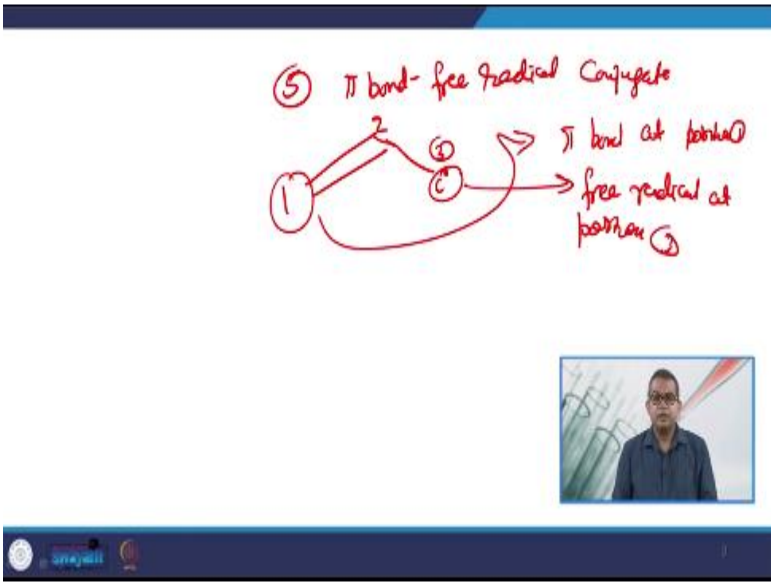
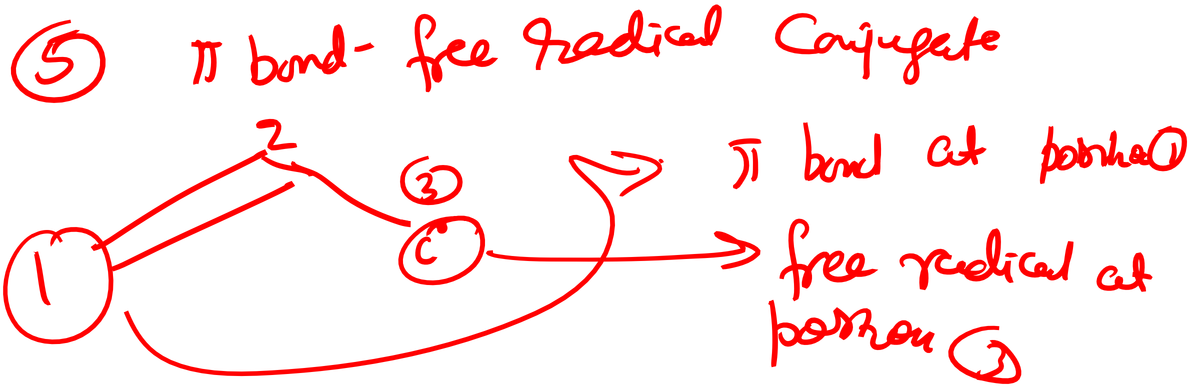


⑤ π bond- free radical Conjugate

π bond at position①

free radical at position ③



⑤ π bond- free radical Conjugate

π bond at position①

free radical at position ③

And other is, the fifth one is phi bond free radical conjugate. So, this is 1, 2, 3. So, you see that here, this is the phi bond at position 1 and here this is the free radical at position number 3. So, this is the different type of the resonating concepts.

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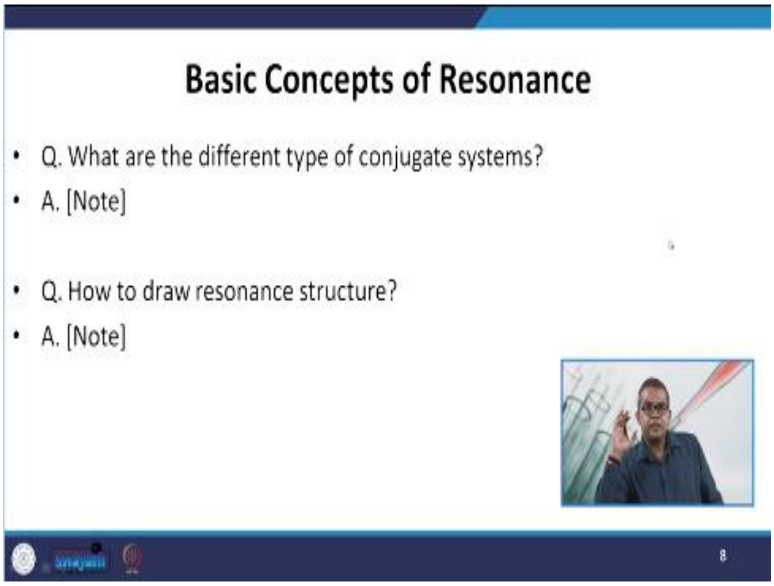

Basic Concepts of Resonance

- Q. What are the different type of conjugate systems?
- A. [Note]

- Q. How to draw resonance structure?
- A. [Note]

Now, another thing is that the question arises that how we can draw the resonating structure. This is again a very typical type of thing. Now, again one basic question is that how to draw the resonance structure. Now, previously in the previous question, we studied that how what are the different type of conjugates system and they are very useful in any kind of a polymeric system.

Then based on this and in the sequence, then the question is that how we can draw any kind of resonating structure. So, let us have a brief about this approach.

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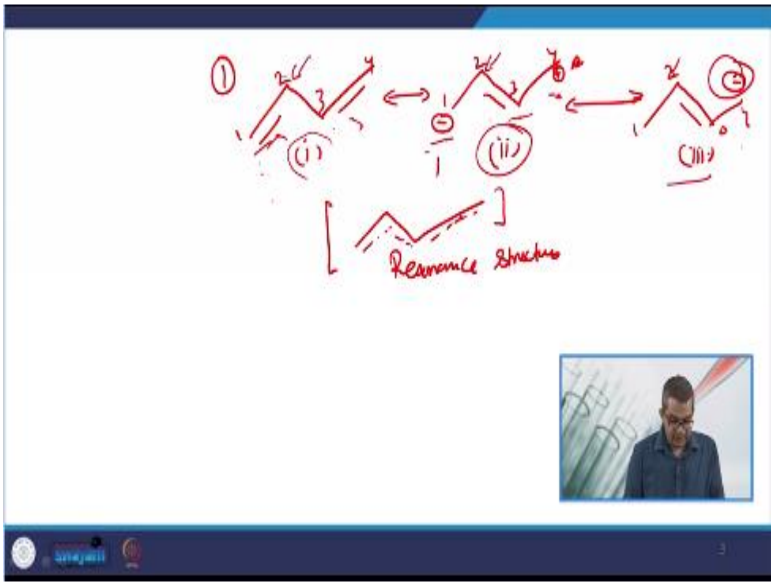
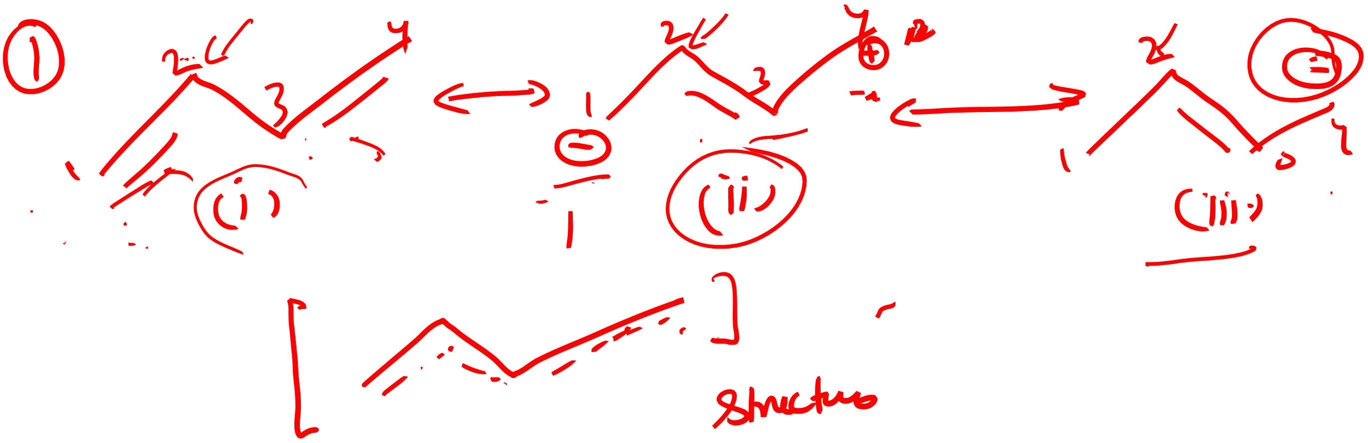


Like, there are several things which we need to address. One is, one approach is that we are having this type of resonating structure that put us like this, then another resonating structure is like this, then another resonating structure is like this. So, if we put the things in a sequential manner, then this may be like this, you see. This is the resonance structure and this example of 1,3-beta time, the electron at phi bond at 1 and 3 position repel each other.



So, this will result the shifting of electron either at position number 1 as shown in this thing like this, both are in the repulsive manner so, this one or the position number 4 as represented here. So, these are 1, 2, 3, 4; let me clarify this thing 1, 2, 3, 4. So, 1 and 3 here, 1 and 3 position, they repel each other, so, that this will result the shifting of electron either within it may acquire at this juncture minus and plus or may acquire like this.

So, therefore, the electron at position number 2 and 3, I will try to fill the vacant space by joining a new bond at the position number 2. So, here there will be an opportunity to get the things done with respect to the; now, there is a possibility of both positive and negative charge at position number 1 and 4 and hence, no charge will be located at the final resonance structure.

Now, as this phi bond is moving from position 1 to 4 here, there will be an equal possibility of phi bond at all place, which can be shown or which we have already shown in this dotted lines. Similarly, we may have another approach that is the example number.2 Let me have a blank sheet Again.

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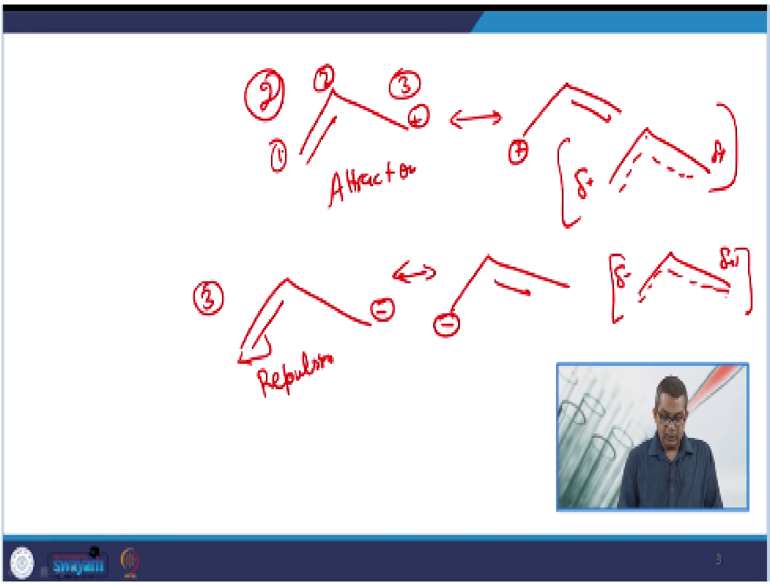

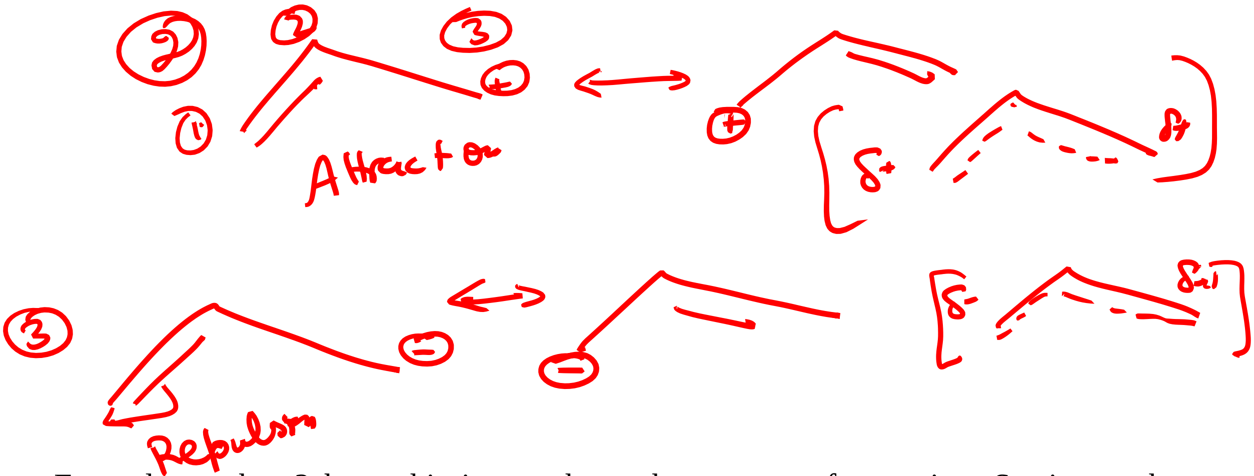

Example number 2 here, this is now here, the concept of attraction. So, it may become; remember 1, 2 and 3; these are the positions, so, this may become like this or sometimes resonating structure can be represented like this here. So, this is my resonating structure for this particular approach. Similarly, let us have another example of a repulsion. Now, here, you see, this may requires the negative charge and the resonating structure would be like this.

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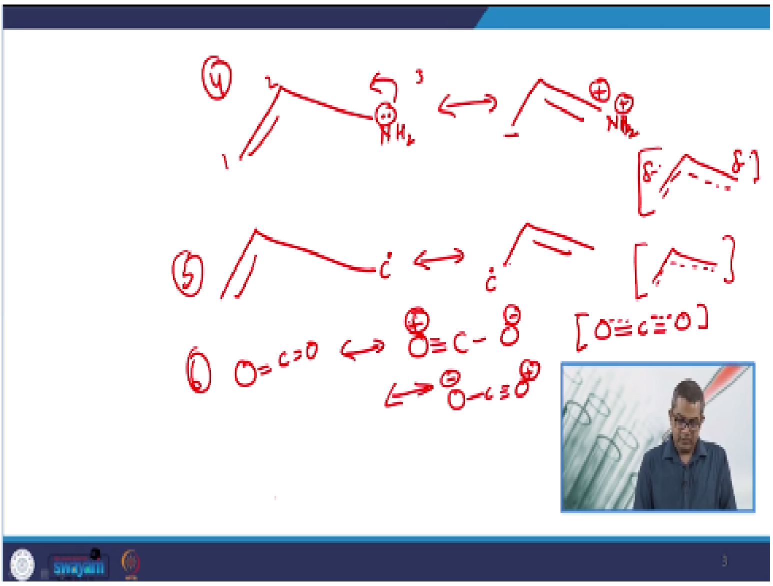

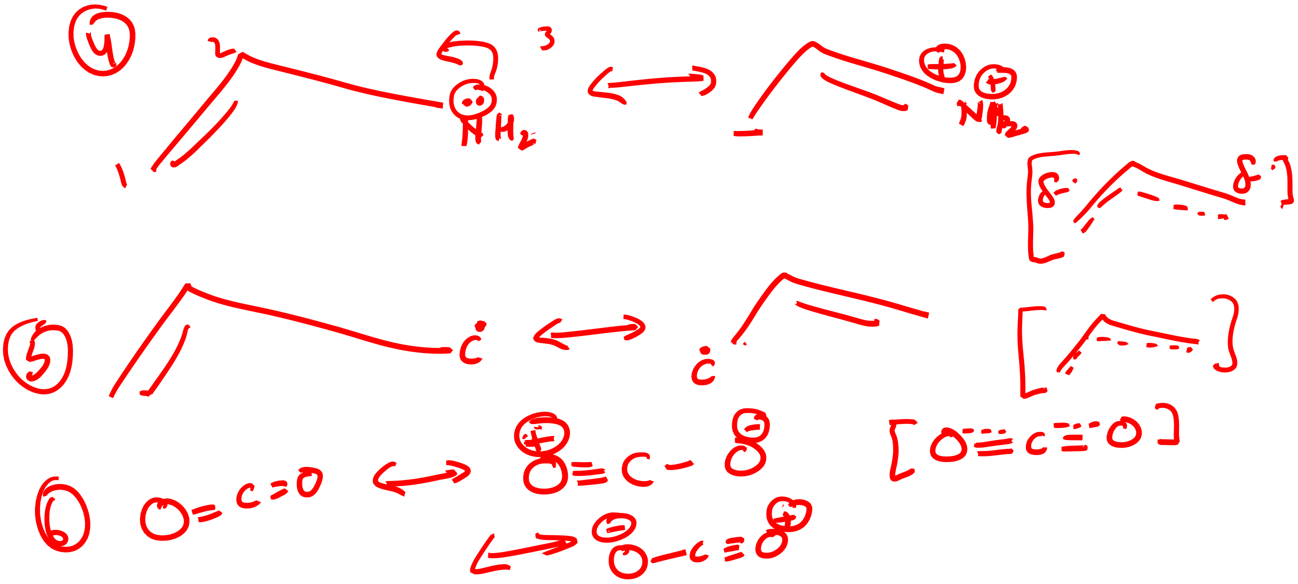

Another example of this one is; if you recall that, here we are having the lone pair. This may have a tendency to move like this, in that case like this. Similarly, another example, we may take another example like this; another example if you take this these 2 double bonds like. We may have; now the charges like this here, the positive; this one becomes the negative. So, it may become like this. Dotted line represents the resonating structure or sometimes, you may represent another form like this one.

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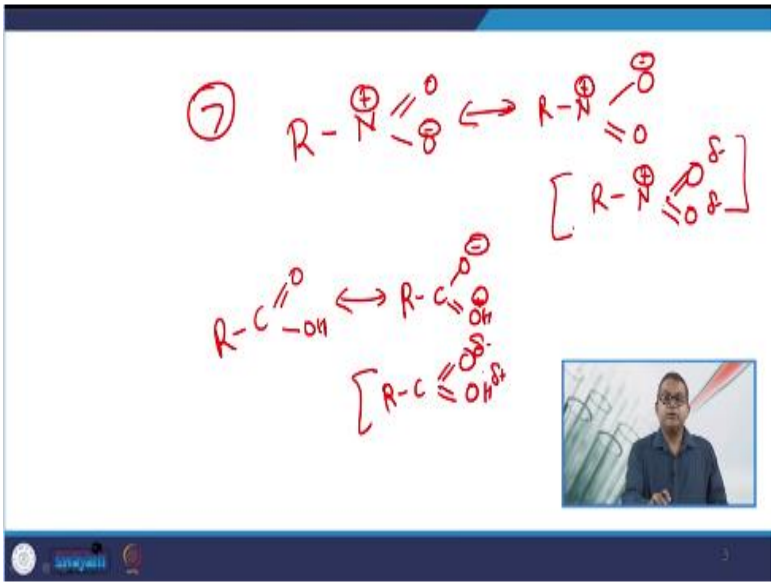

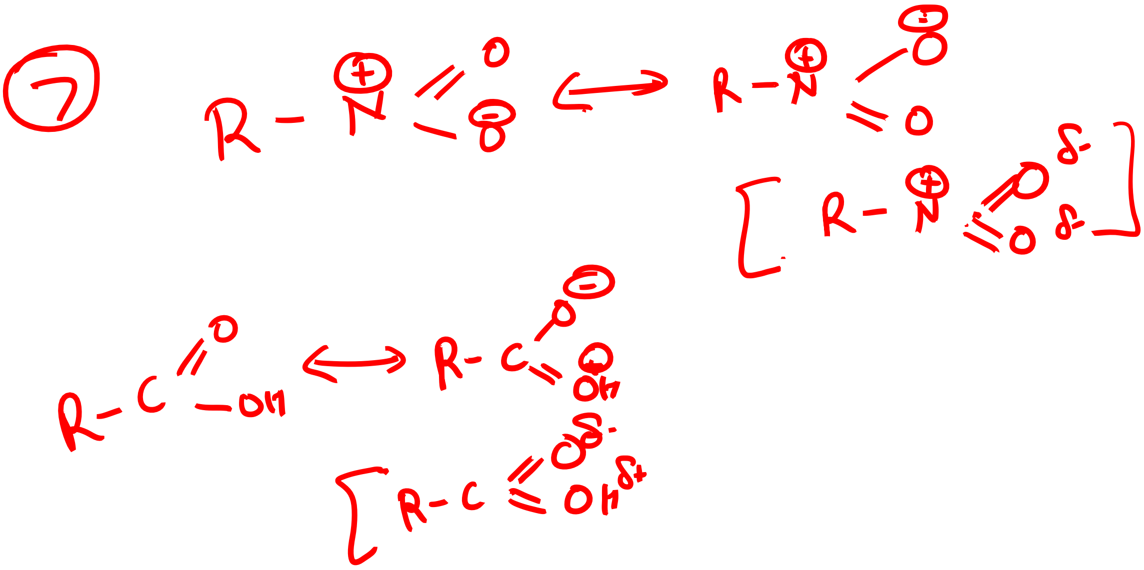

Now, again, we may have another example, notice example number 7 that is R. Now, let us take another example of this type of approach, this is again my, now, there is again shifting of these things. Now, you see here, this requires the negative charge and this requires the things, there is a transfer of things over here and the resonating structure becomes. Let us take another example, this is R CO OH. This is the structure.

Now, the resonating structure becomes. So, these are the various structures as I discussed that how we can draw the various kinds of resonating structures in this particular approach.

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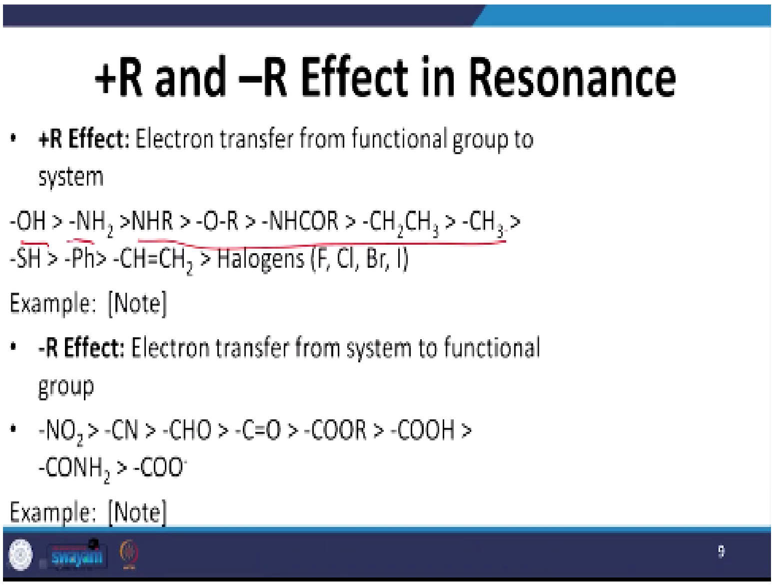

+R and –R Effect in Resonance

- **+R Effect:** Electron transfer from functional group to system

-OH > $-NH_2$ >NHR > -O-R > -NHCOR > $-CH_2CH_3$ > $-CH_3$ > -SH > -Ph> $-CH=CH_2$ > Halogens (F, Cl, Br, I)

Example: [Note]

- **-R Effect:** Electron transfer from system to functional group
- $-NO_2$ > -CN > -CHO > -C=O > -COOR > -COOH > $-CONH_2$ > $-COO^-$

Example: [Note]

Now, there is a concept of plus R effect that is plus R and minus R effects in the resonance structure that is positive and negative resonating effects.

- **+R Effect:** Electron transfer from functional group to system

-OH > $-NH_2$ >NHR > -O-R > -NHCOR > $-CH_2CH_3$ > $-CH_3$ > -SH > -Ph> $-CH=CH_2$ > Halogens (F, Cl, Br, I)

Example: [Note]

- **-R Effect:** Electron transfer from system to functional group
- $-NO_2$ > -CN > -CHO > -C=O > -COOR > -COOH > $-CONH_2$ > $-COO^-$

Now, this plus R deals with the electron transport from functional group to the system. Like here, you see that OH that how what should be the sequential order for the transfer of these kind of functional groups to within the system. Let us have another example of this particular approach that is the plus R effect.

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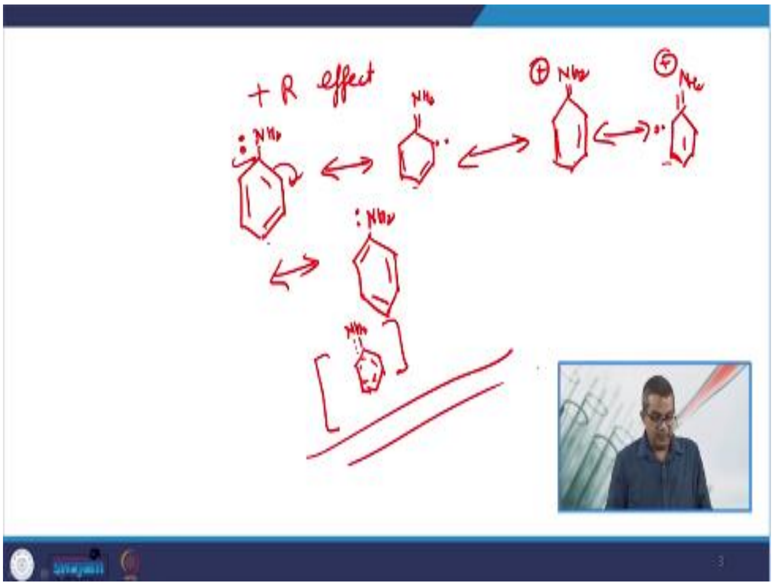
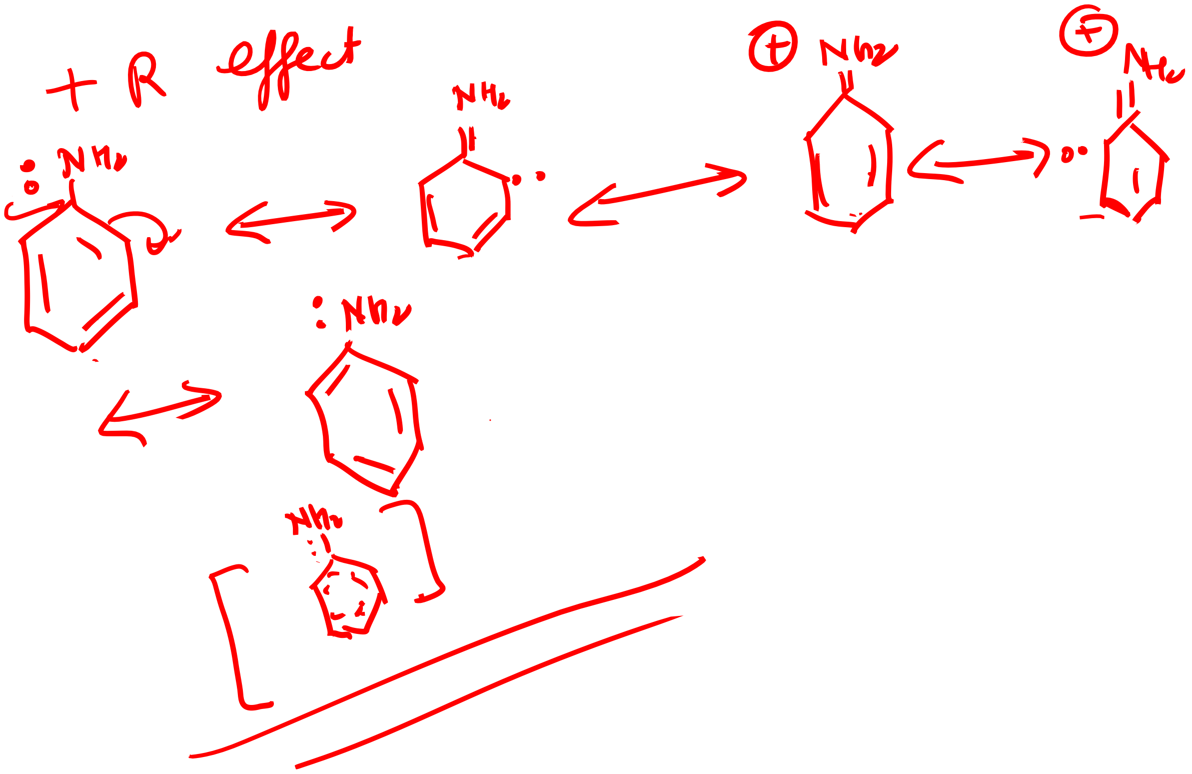
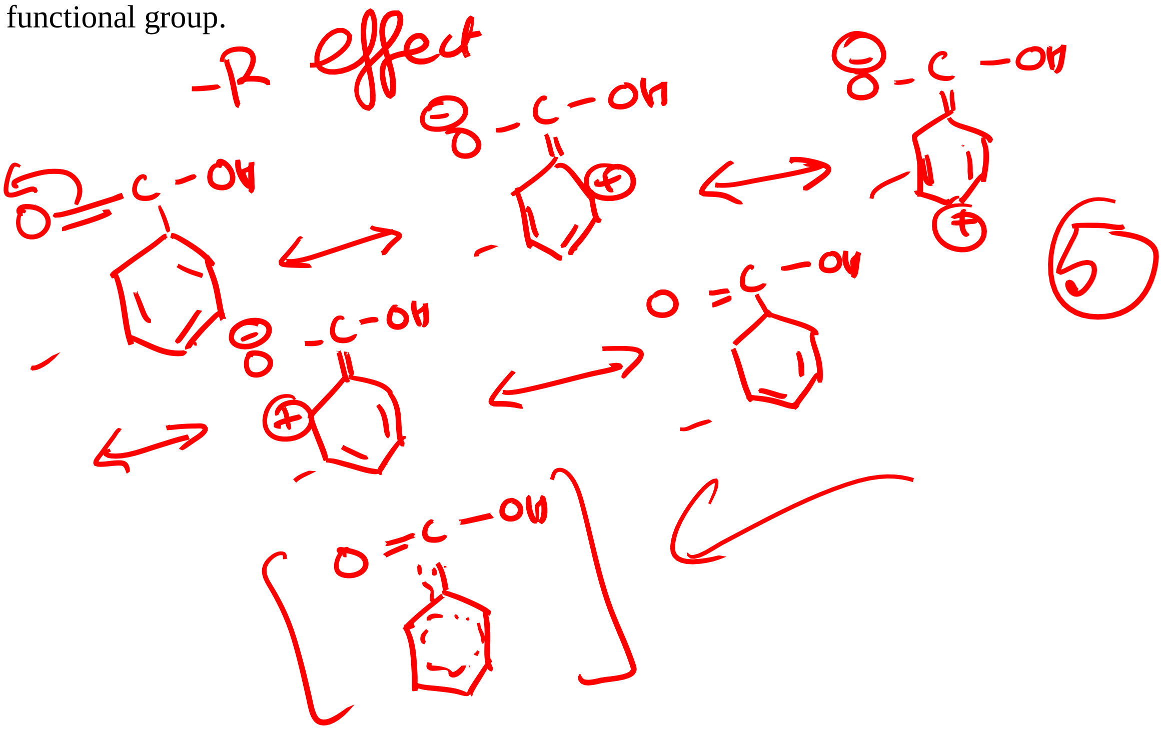




Now, you see that this is the lone pair. Now, this is shifted to this one over here. Now, you see now, here that this becomes a double bond and a lone pair is over shifted over here. Now, here and you see the how this lone period is shifted to the various positions as per the requirement. So, you see that there are 5 resonating structures in and around. So, you may need to look all the possibilities of these resonating structures 1, 2, 3, 4 and 5.

So, these are the various effects attributed to plus R effects. Now, let us have an example of negative R effect. Now, electron transfer from system to functional group. There is a difference;

transfer from functional group to system. Now, we are taking the transfers from system to functional group.



The sequential order in this category is already mentioned in this screen that NO 2, CN, CHO, C double bond O, COOR etcetera.

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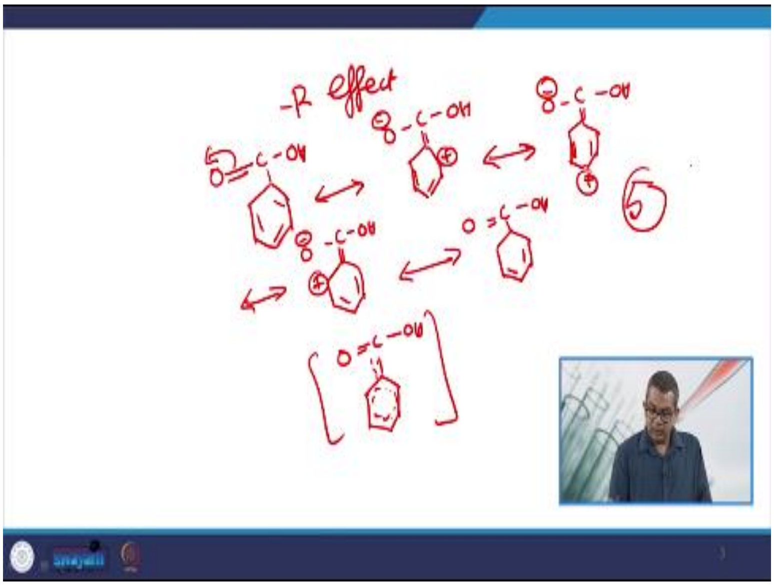

Let us have a look about the one example to explain the things for this one. That is the; now, see here, this is again our subject. Now, this transfers to this oxygen and the resonating structure becomes like this, this one. Now, these are the 5 resonating structure and overall, you can write like this just in a generalised manner if you were willing to write. So, overall just putting all these things, so, there are overall 5 resonating structure 1, 2, 3, 4 and 5. And if you wish to put this is the overall one.

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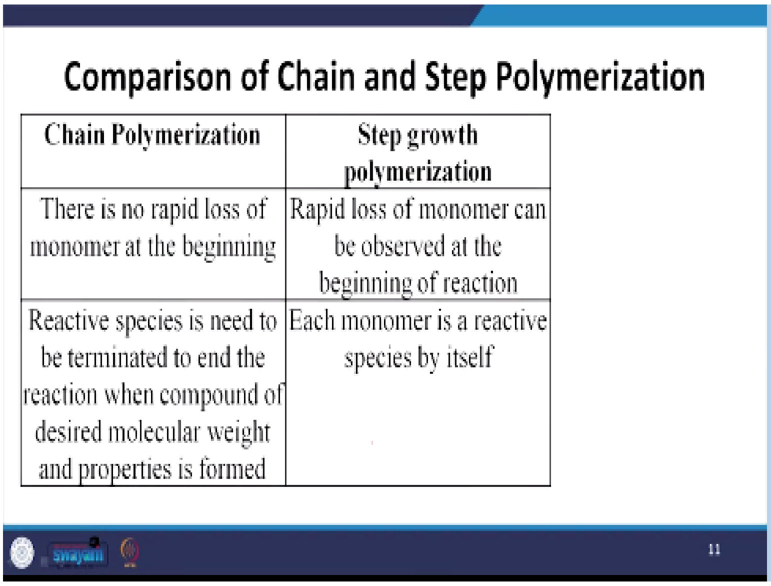

Comparison of Chain and Step Polymerization

Chain Polymerization	Step growth polymerization
There is no rapid loss of monomer at the beginning	Rapid loss of monomer can be observed at the beginning of reaction
Reactive species is need to be terminated to end the reaction when compound of desired molecular weight and properties is formed	Each monomer is a reactive species by itself

So, by this way, we studied about the various kind of resonating structure and based on this particular discussion, if we try to make a comparative statement respect to the chain and step polymerization, you see that in chain polymerization, the formation of high molecular weight polymers from unsaturated monomers is possible whereas, in the step growth polymerization, the formation of a polymer from bi-functional or multifunctional monomer is possible.

Similarly, in chain polymerization, the polymer growth is occurred by attachment of a single monomer at a time; here, in the step growth polymerization, the oligo bar is formed first, which then combined together to form the polymer chain. So, these 2 are the basic differences between the chain polymerization and step polymerization. Another thing is that in chain polymerization, there is no rapid loss of monomer at the beginning.

Whereas in step growth polymerization, there is a rapid loss of monomer, you can observe at the beginning of the reaction. Similarly, in chain growth polymerization, the reactive species are needed to be terminated to end the reaction usually the termination step and this is a carbon compound of desired molecular weight and properties is formed. In the step growth polymerization, each monomer is a reactive species by itself.

So, it is a very crucial point for carrying out this step growth polymerization. In chain growth polymerization, the required initiator should be there. So, it required an initiator to start the reaction.

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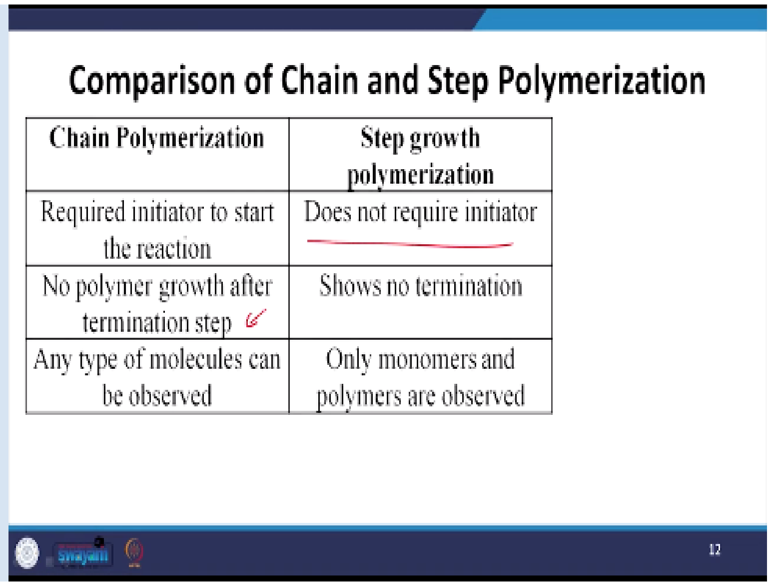

Comparison of Chain and Step Polymerization

Chain Polymerization	Step growth polymerization
Required initiator to start the reaction	Does not require initiator
No polymer growth after termination step	Shows no termination
Any type of molecules can be observed	Only monomers and polymers are observed

Whereas there is no such type of requirement in a step growth polymerization. It can occur at same. In chain growth polymerization, no polymer growth after you have one termination's step but step growth polymerization on the contrary, it shows no termination step. And in chain growth polymerization, you can observe any kind of molecule, any type of a molecule. Whereas in step growth polymerization, only monomers and polymers, you can see in this particular approach.

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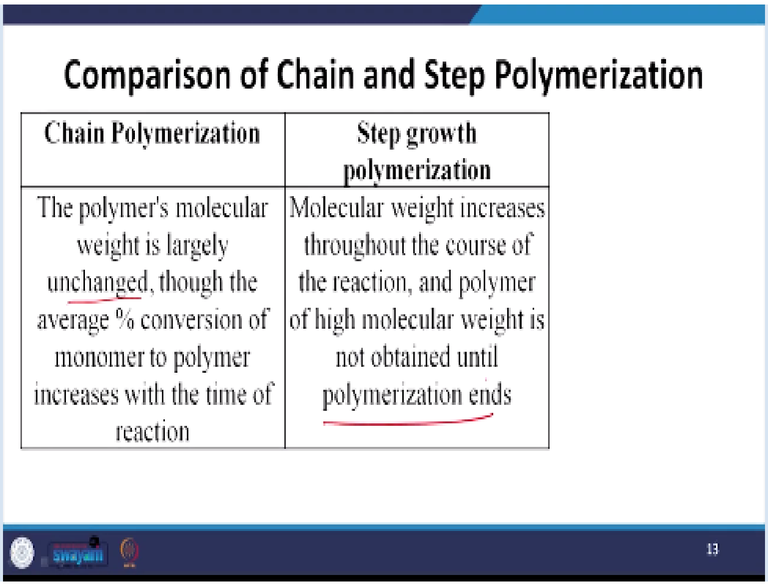

Comparison of Chain and Step Polymerization

Chain Polymerization	Step growth polymerization
The polymer's molecular weight is largely unchanged, though the average % conversion of monomer to polymer increases with the time of reaction	Molecular weight increases throughout the course of the reaction, and polymer of high molecular weight is not obtained until polymerization ends

Now, in chain growth polymerization, the polymers molecular weight is largely unchanged, though the average percent conversion of a monomer to polymer increases with respect to the time. In step growth polymerization, the molecular weight increases throughout, no doubt, the course of the reaction, the polymer of high molecular weight is usually not obtained until the polymerization ends. So, you can see that all depends on the chain type of structure.

Another comparison between both of polymerization protocols are: the chain growth polymerization, they are relatively low reaction time is required to get high molecular weight polymer whereas, in step growth polymerization, the longer reaction times are sometime important for carrying out higher conversion percentage as well as a higher molecular weight.

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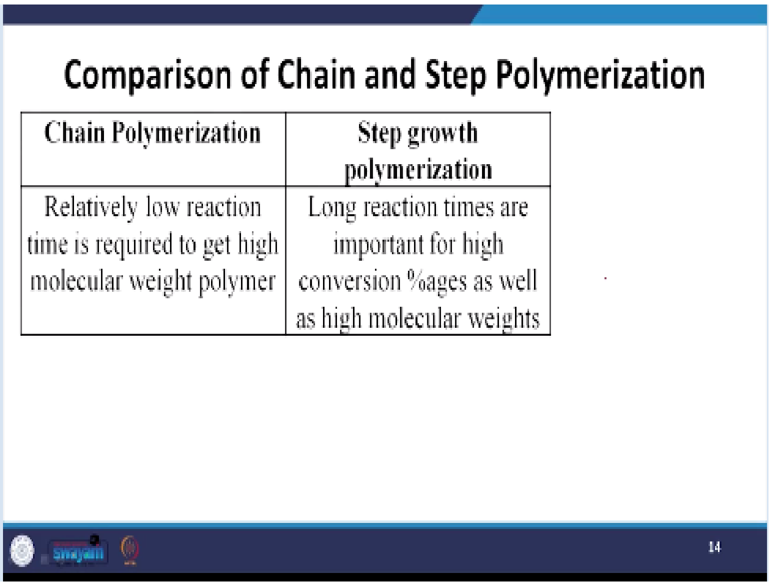

Comparison of Chain and Step Polymerization

Chain Polymerization	Step growth polymerization
Relatively low reaction time is required to get high molecular weight polymer	Long reaction times are important for high conversion %ages as well as high molecular weights

So, by this way, we carry out a brief comparison between the step growth and chain growth polymerization.

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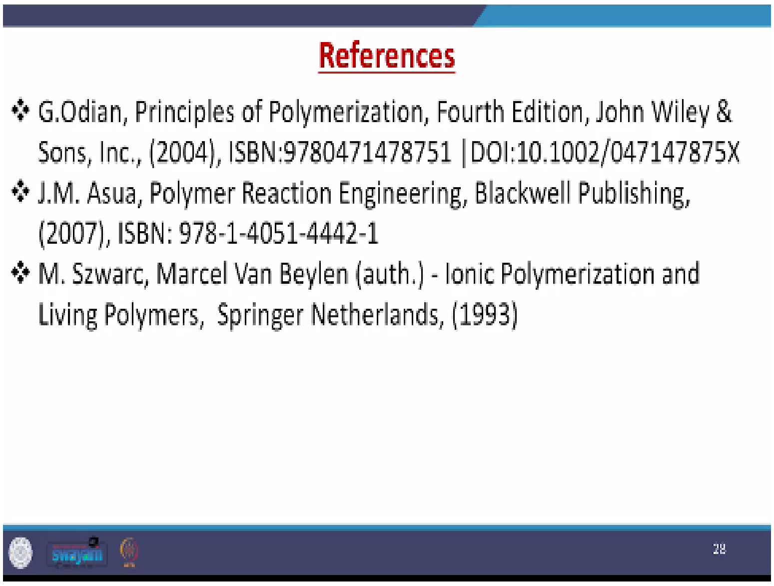

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So, at the outset, in this particular lecture, we discussed about radical polymerization. We discussed about the various types of resonating structures, different types, how we can have a different type of resonating structure, especially related to the polymerization process. Then we had a brief study about the comparative note on the distinguishment between the chain and the step growth polymerization. So, thank you very much for your attention.