Polymer Reaction Engineering
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Lecture – 34
Mode of Propagation

Welcome to this radical chain polymerization lecture. In this lecture, we will go into discuss about the different modes of propagation, see in polymer reaction engineering, there are 3 major steps: initiation, propagation and termination. So, in the previous lectures, we discussed about the concept of initiation with the help of various polymerization schemes initiate and in these schemes, we covered the different type of polymerization's steps, classification modes etcetera.

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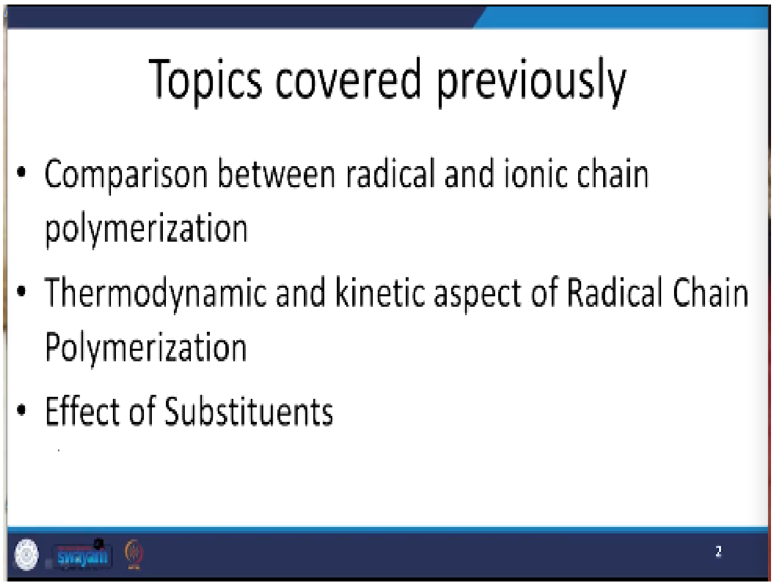

Topics covered previously

- Comparison between radical and ionic chain polymerization
- Thermodynamic and kinetic aspect of Radical Chain Polymerization
- Effect of Substituents

Apart from this, we performed the various comparative studies between the two polymerization schemes. Just for the example, in the previous lecture, we discussed about the comparative note between radical and ionic chain polymerization. Thermodynamics and kinetics, they play a very vital role in all kinds of chain polymerization or especially the radical chain polymerization step.

So, in the previous lecture, we discussed about the thermodynamic and kinetic approaches to this radical chain polymerization. Apart from this, we had a discussion about the effect of substitutes in the radical chain polymerization. So, in this particular lecture, we are going to start about the effect of propagation radical chain polymerization scheme. Now, let us have a brief look about that what are the different topics we are going to cover under the head of this particular lecture.

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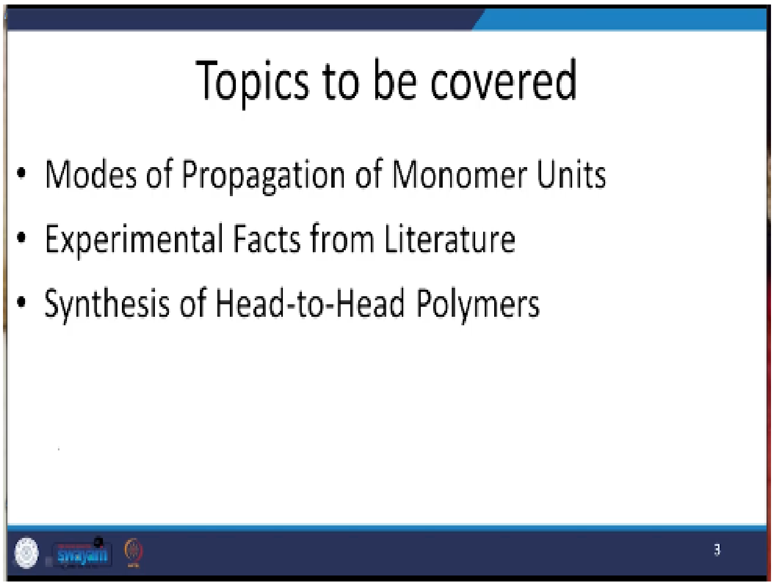

Topics to be covered

- Modes of Propagation of Monomer Units
- Experimental Facts from Literature
- Synthesis of Head-to-Head Polymers

One is the mode of propagation of a monomer unit. See in the previous lectures, we discussed about the concept of propagation. Here, the monomer units are attached to the either backbone or they combined to each other. So, that the chain length of these polymers may go on the higher side and subsequently the molecular weight of these polymer chains may become big and big. That is why we need to look a special attention.

Apart from this, we know that the molecular weight plays a very vital role in the property decided doing factor the polymerization scheme. So, based on this particular concept, we have to keep a close eye to this propagation step. So, that is why we will discuss about this propagation step in this particular chapter. Apart from this, we will have certain experimental facts which are duly enlisted in the literature and we will give you due reference to those literatures.

So, that you can have a look about those things in detail in due course of study. Then we will discuss about the various segments of head to head polymerization or head to head polymer synthesis. So, let us start about the modes of propagation of various monomer units. Now, see for vinyl group, the alpha carbon, they can either have one functional group replacing, maybe replacing by one hydrogen or 2 functional groups, maybe replacing both the hydrogen attached to it.

In both cases, there are 2 possibilities for chain propagation, maybe either on alpha carbon that is carbon 1 or on the beta carbon that is carbon 2. So, let us have about a brief example of this particular mode of propagation through this particular concept.

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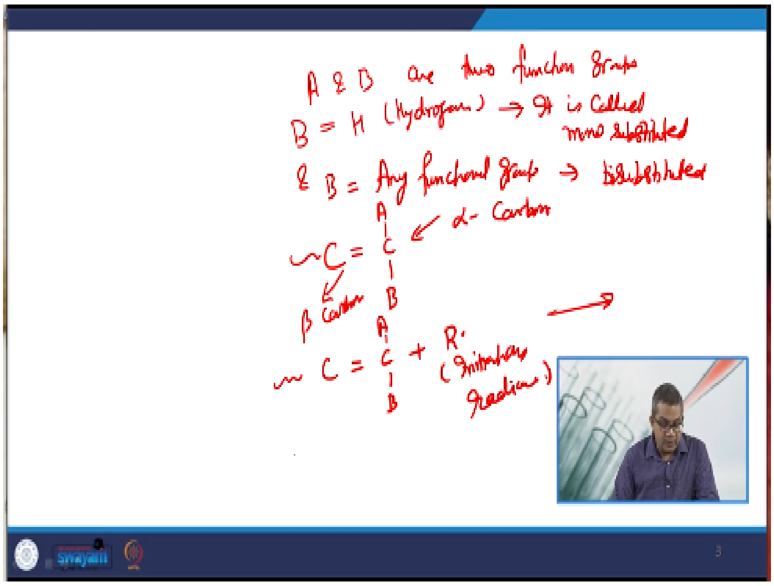
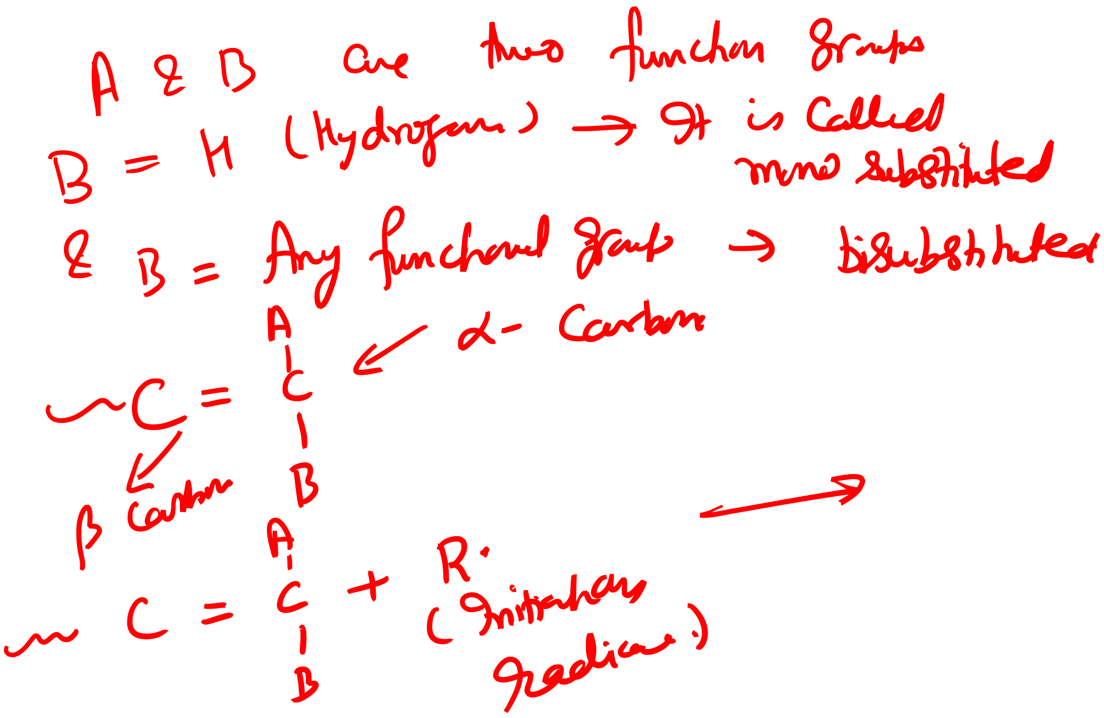


A & B are two function groups

B = H (Hydrogen) → It is called mono substituted

& B = Any functional group → bisubstituted



A & B are two function groups

B = H (Hydrogen) → It is called mono substituted

& B = Any functional group → bisubstituted

Now, let A and B, they are 2 functional groups. So, when B maybe replaced with the hydrogen, it is called mono substituted and B maybe any functional group, it is called bi-substituted. So, in this case, we may have this type of thing here, carbon, beta carbon and this one is alpha carbon. Similarly, this is your initiation radical, now, it goes to different cases.

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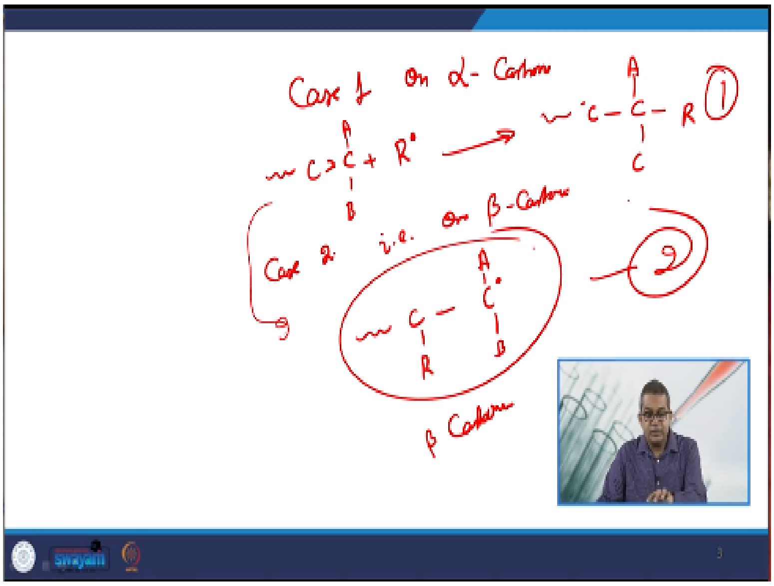

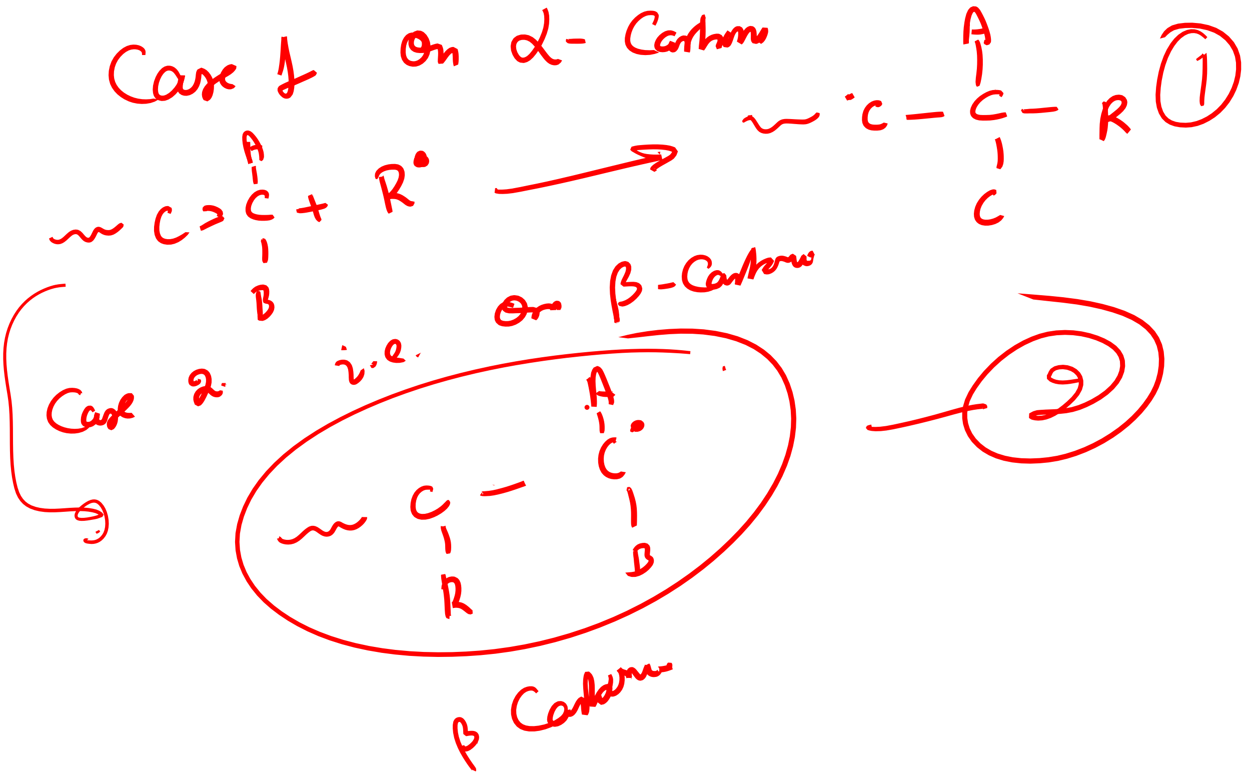

So, let us have first case and picture case 1 that is on alpha carbon. So, if it goes to alpha carbon, then this may be represented like this, you see my original reaction was this one, right. Now, similarly, if we consider the case number 2 that is on beta carbon. So, it will become, this may become like this. So, this is the case 2 where we are having this on the beta carbon.

Now, by this way, you can see or it clarifies the fact that this can propagate either to beta carbon or alpha carbon. Now, there can be 2 type of chain propagation as you see here. This is the one type and another one is the second type and either of both cases happen in a successful manner.

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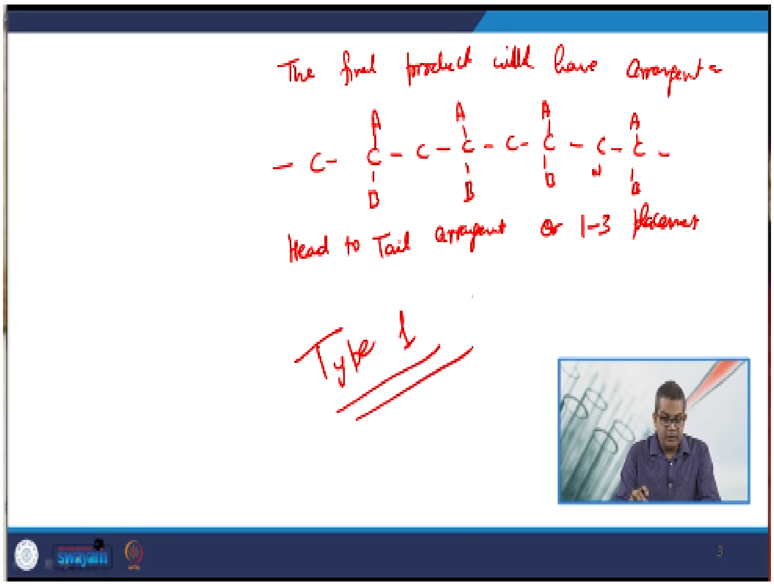
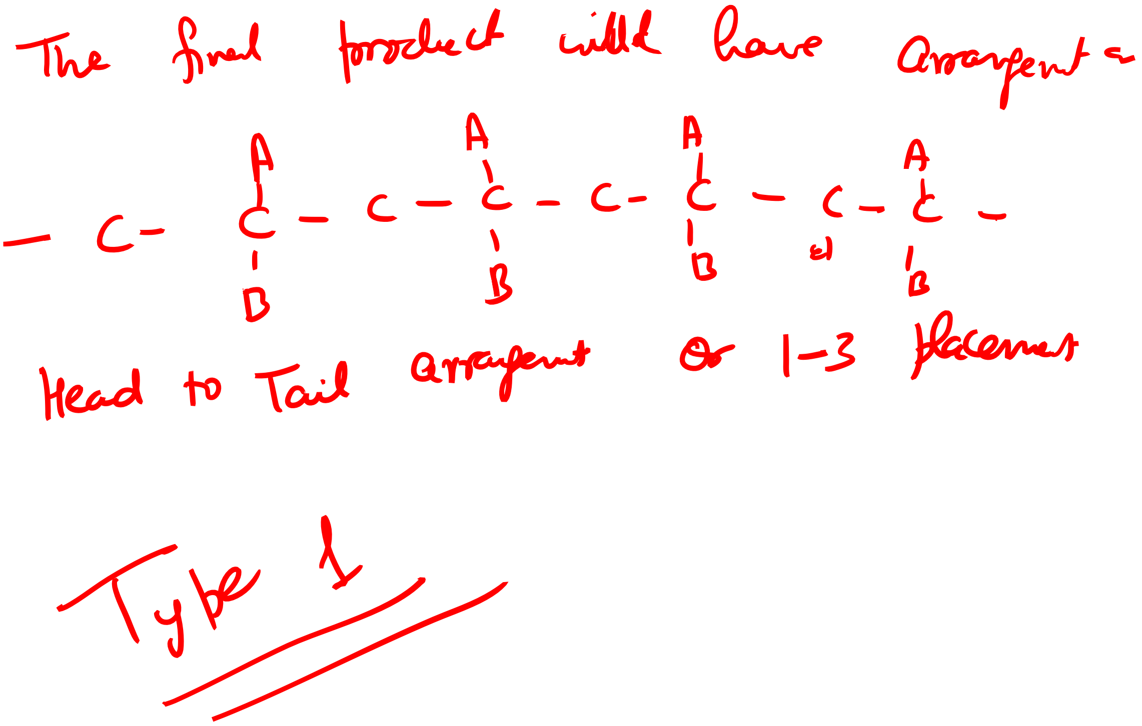


The final product will have arrangement =

$-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-$

Head to Tail arrangement or 1-3 placement

Type 1



The final product will have arrangement =

$-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-C-\overset{A}{\underset{B}{C}}-$

Head to Tail arrangement or 1-3 placement

Type 1

So, the final product will have some arrangement as like this, you can see that this polymeric chain become more and more populated like this. So, this type of arrangement is also called head to tail arrangement or 1-3 placement. So, this is a very, you can say, the popular one and in this particular lecture, we will refer as type 1 type of arrangement.

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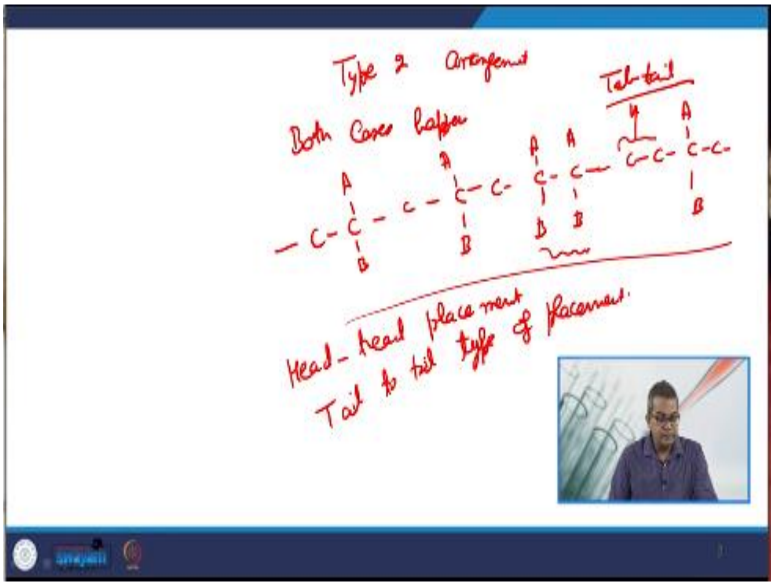


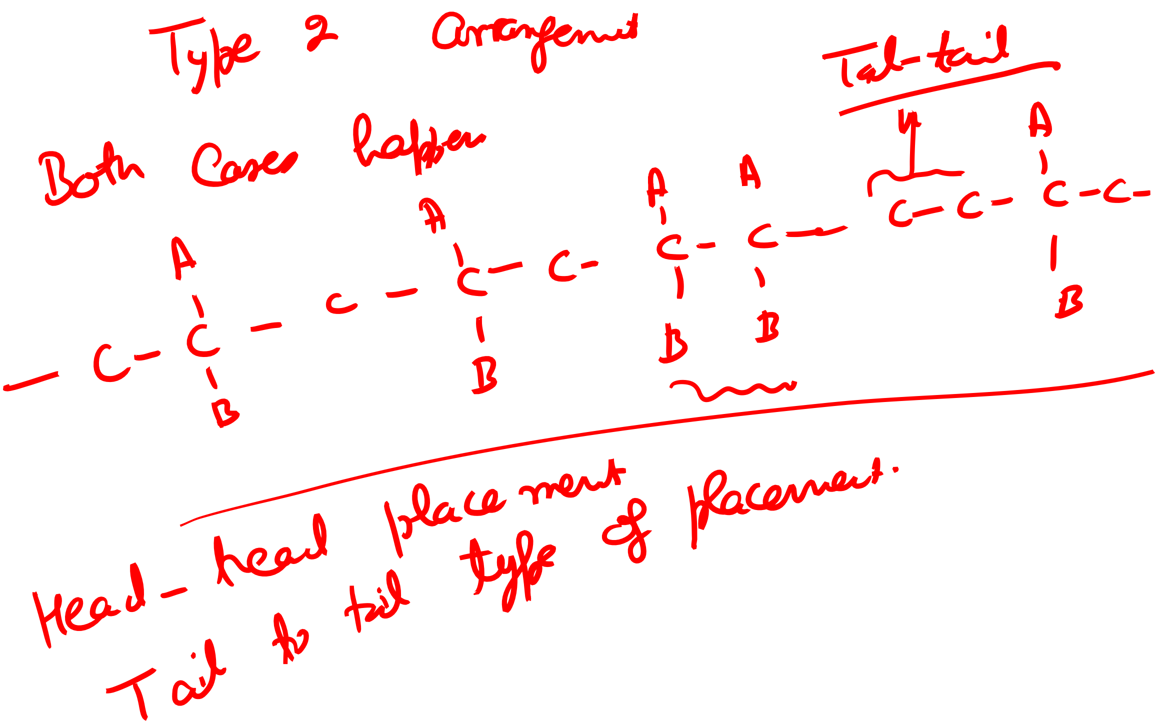
Type 2 Arrangement

Both Cases happen

Tail-tail

Head-head placement

Tail to tail type of placement.



Type 2 Arrangement

Both Cases happen

Tail-tail

Head-head placement

Tail to tail type of placement.

Now, let us have a brief look about the type 2 arrangement. Now, these both cases happen simultaneously developing an inversion condition. Now, this inversion condition is like this C’s, you can see over here the difference between these type 1 and type 2, it is clearly indicative that at this juncture, you can see this juncture, it is more prominent.

Now, here, this is B, this is you can see referred as tail to tail type of arrangement. So, these 2, you can see that by this way, mean both the types, we are having the placement of different monomer chain. Now this type of placement is also called the tail to tail or head to head placement. Either you can say, head to head placement or it is tail to tail type of placement.

So, this is the way through which you can represent the things. Now, in real situation, both type 1 and type 2 type of placements, they can occur together. However, it is found that the steric and resonance effect developed in case 2, which we discussed in the previous slide. The head to tail placement usually preferable over this kind of propagation scenario. Now, the developed resonance effect in case 2, this increases the stability of radical. Hence, you can say more similar kind of radicals are present in the reaction mass.

If you talk about the case number 1, the functional groups, they are not present in conjugate pair, if you recall we discussed this conjugation aspect in the previous lecture. So, they are not present in the conjugate pair. Hence, the resonating effect cannot be seen. Therefore, the approach like subsequent attachment of propagating radical to un-replaced carbon referred as beta carbon of monomer molecule is much less sterically impeded compared to the alternative carbon approach that is alpha carbon if you recall the slide number 2, so, alpha carbon.

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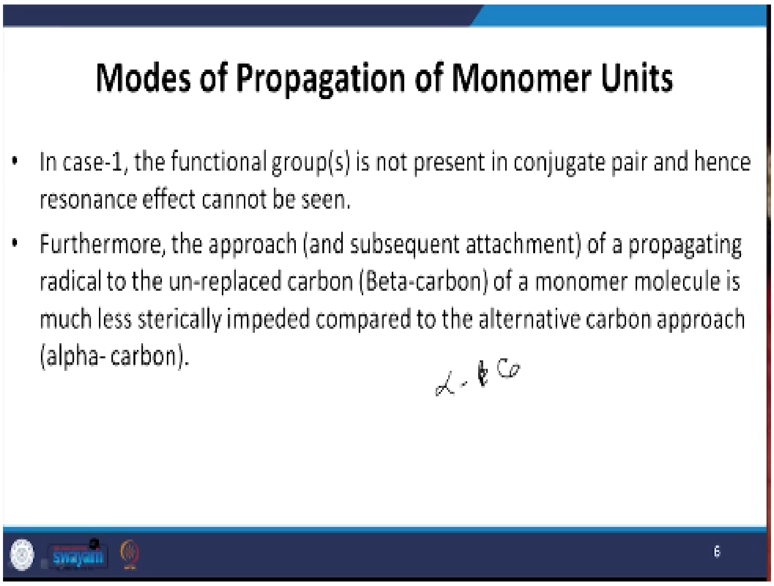

Modes of Propagation of Monomer Units

- In case-1, the functional group(s) is not present in conjugate pair and hence resonance effect cannot be seen.
- Furthermore, the approach (and subsequent attachment) of a propagating radical to the un-replaced carbon (Beta-carbon) of a monomer molecule is much less sterically impeded compared to the alternative carbon approach (alpha-carbon).

α - β Co

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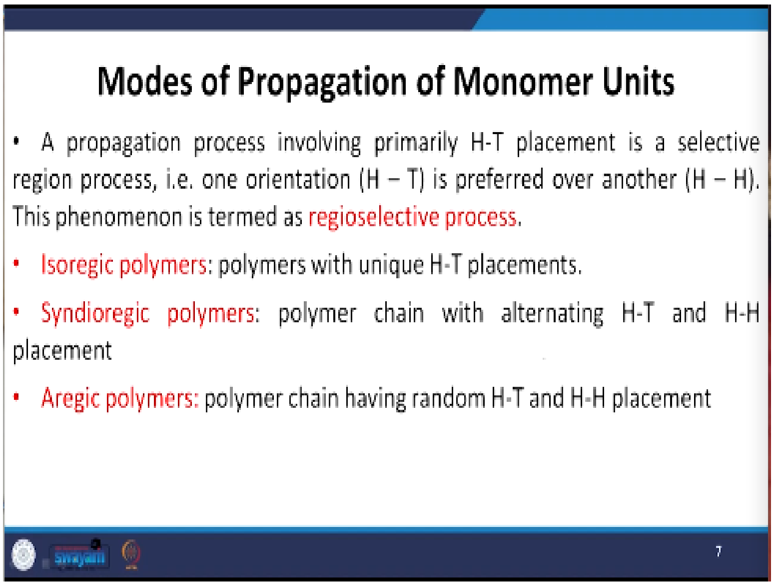


Modes of Propagation of Monomer Units

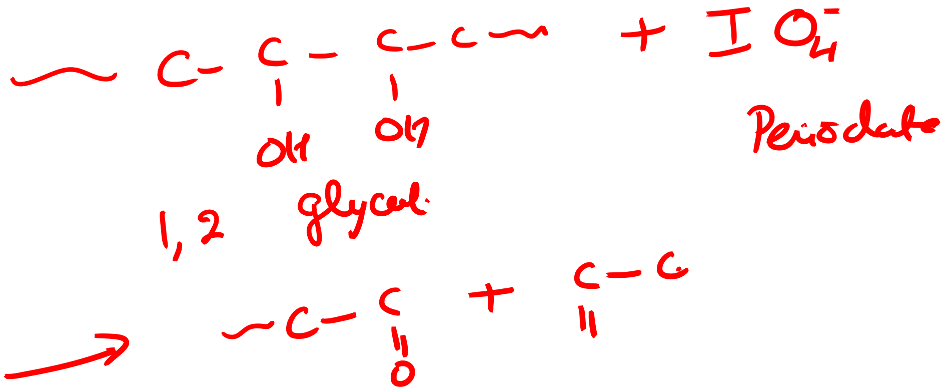
- A propagation process involving primarily H-T placement is a selective region process, i.e. one orientation (H – T) is preferred over another (H – H). This phenomenon is termed as regioselective process.
- Isoregic polymers: polymers with unique H-T placements.
- Syndioregic polymers: polymer chain with alternating H-T and H-H placement
- Aregic polymers: polymer chain having random H-T and H-H placement

Now, a propagation process usually involves primarily head to tail type of a placement, it is the selective region process that is one orientation of head to tail is preferred over another thing of head to head. Now, this phenomena is termed as regioselective process. There are certain other process is like isoregic polymers, these polymers with a unique head to tail placement.

See, similarly, syndioregic polymers, these polymers chain with the alternating head to tail and head to head placement. If you see that we discussed in detail about these head to head or head to tail type of thing. So, you can see, there are different permutation and combination for orienting these chains. And whenever this type of things occur, the property of the developed polymer is usually changing drastically.

Third one is that aregic polymers, these polymers are having the random head to head and head to tail placement. So, there are 3 different places where in one, you may have a unique head to tail placement. And the second one, you may have alternate head to tail or head to head placement. And the third one where you may have head to tail and head to head placement in a random order.

So, in all 3 type of a situation, you may experience the different kind of properties. Let us have a look about some experimental facts, which we collected from various literature and this may be very much useful for you, if you wish to have a further study in this kind of scenario. Now, there are so many researches have been conducted by various renowned researchers to understand the chain propagation pattern. Most of these research, they confirmed about the discussed point.



Now, one thing is that the occurrence of not more than 1 to 2, head to head placement in different polymer of vinyl esters such as polyvinyl acetate. This was determined by the polymer hydrolysis with the help of vinyl alcohol and periodic oxidation of 1-2 glycol units. So, acetol, they discussed this thing and they find out some interesting results. And that is these results are attributed in this particular slide that they find out that, this one, the 1- 2 glycol. Now, this one, this periodate, they gives. So, this is one part of the literature.

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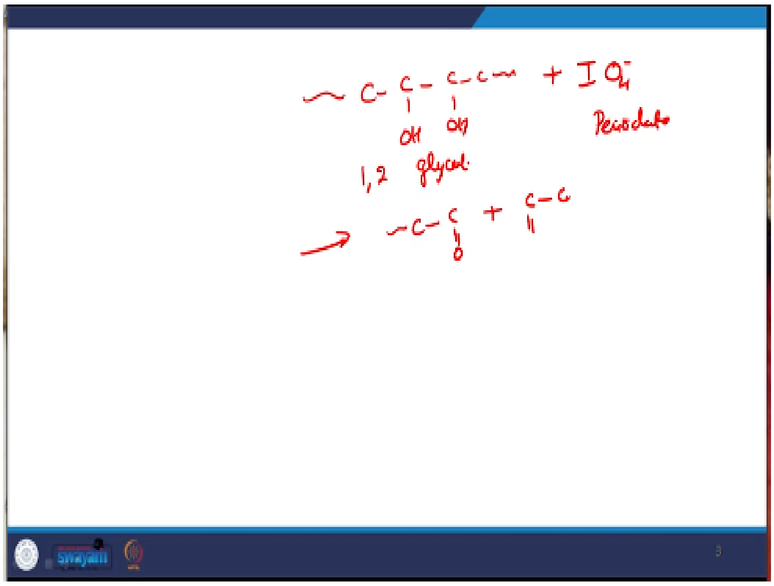

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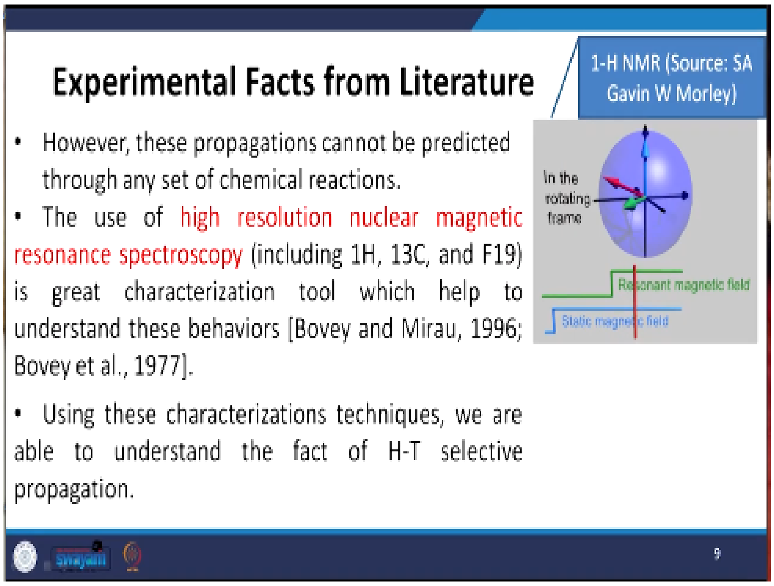

Experimental Facts from Literature

- However, these propagations cannot be predicted through any set of chemical reactions.
- The use of high resolution nuclear magnetic resonance spectroscopy (including 1H, 13C, and F19) is great characterization tool which help to understand these behaviors [Bovey and Mirau, 1996; Bovey et al., 1977].
- Using these characterizations techniques, we are able to understand the fact of H-T selective propagation.

1-H NMR (Source: SA Gavin W Morley)

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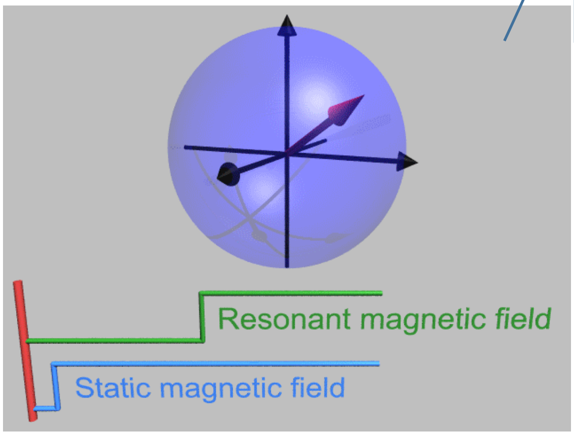
(Video Starts: 14:56) And other thing is that these propagations cannot be predicted through any set of chemical reactions and we see that we have developed some rotating pattern. Now, the use of high resolution NMR nuclear magnetic resonance spectroscopy, this including 1H, 13C, F19. They have found a reasonable good approach for characterization of these type of developed polymer.



1-H NMR (Source: SA Gavin W Morley)

So, by this way, it is extremely helpful to understand the behaviour of whatever polymer being generated in due course of time. Now, using these characterization techniques, we can understand the fact of the head to tail selective propagation. Now, this is some brief concept of NMR **(Video Ends: 15:51)**.

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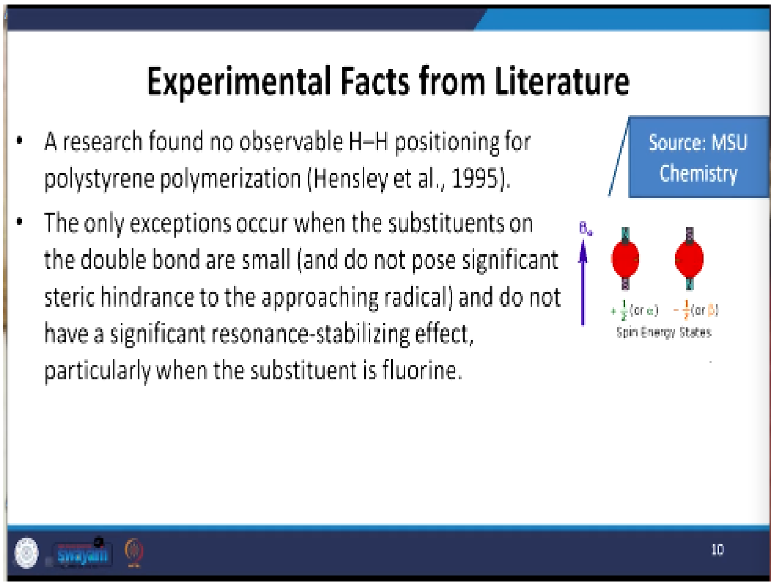

Experimental Facts from Literature

- A research found no observable H–H positioning for polystyrene polymerization (Hensley et al., 1995).
- The only exceptions occur when the substituents on the double bond are small (and do not pose significant steric hindrance to the approaching radical) and do not have a significant resonance-stabilizing effect, particularly when the substituent is fluorine.

Source: MSU Chemistry

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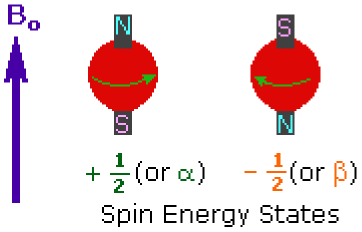

Now, another thing is that research found no observable head to head positioning for polystyrene polymerization and that is attributed to the Hensley in 1995. The only exception occur when the substituents on the double bond which we discussed small that is they do not pose any kind of significant steric hindrance to the approaching radical. And they do not have a significant resonance stabilising effect particularly when the substituent is fluorine. So, it is very case sensitive type of thing.

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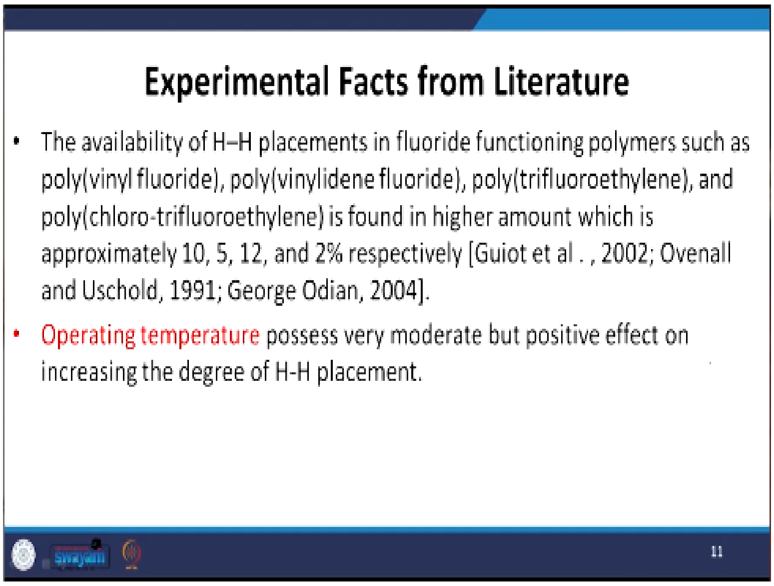

Experimental Facts from Literature

- The availability of H–H placements in fluoride functioning polymers such as poly(vinyl fluoride), poly(vinylidene fluoride), poly(trifluoroethylene), and poly(chloro-trifluoroethylene) is found in higher amount which is approximately 10, 5, 12, and 2% respectively [Guiot et al . , 2002; Ovenall and Uschold, 1991; George Odian, 2004].
- Operating temperature possess very moderate but positive effect on increasing the degree of H-H placement.

The availability of head to head placement in fluoride functioning polymers such as polyvinyl fluoride, polyvinylidene fluoride etcetera. Now, they are found at a higher amount which is approximately 10, 5 and 2% respectively. So, Guiot et al and Odian et al, they found this availability of head to head placement in different fluoride functioning polymers. Sometimes, people considered about the rule of operating temperature.

So, operating temperature possesses very moderate, but positive effect on increasing the degree of head to head placement. So, this reflects the positioning of this particular concept. Now, another approaching part is that the head to head content in polyvinyl acetate increases from say, 1 to 2% when the temperature usually rises from 40 to 100 degrees Celsius.

So, the increase of say, PTFE polytetrafluoroethylene, they rises from 10 to 14% when the temperature rises from minus 80 to 80 degrees Celsius. So, George Odian, he discussed and he find it out very useful thing that the increase or decrease in the temperature of any kind of a polymerization reaction, sometimes play a very significant role in synthesising the different type of polymers.

Another thing is that when we talk about the head to head polymer, so, several polymers they composed entirely of head to head placement, they were purposely synthesis to determine if they are major variation in the properties compared to the head to head placement polymers. Now, such polymer synthesis involves choosing a suitable monomer for the specific head to head placement.

Now, this particular example was set up by the Kawaguchi in 1985 and later on, it was modified by vogl in 2000. The head to head PVC is obtained by 1-4 poly 1-3 betadine chlorination, we will take this particular concept as an example.

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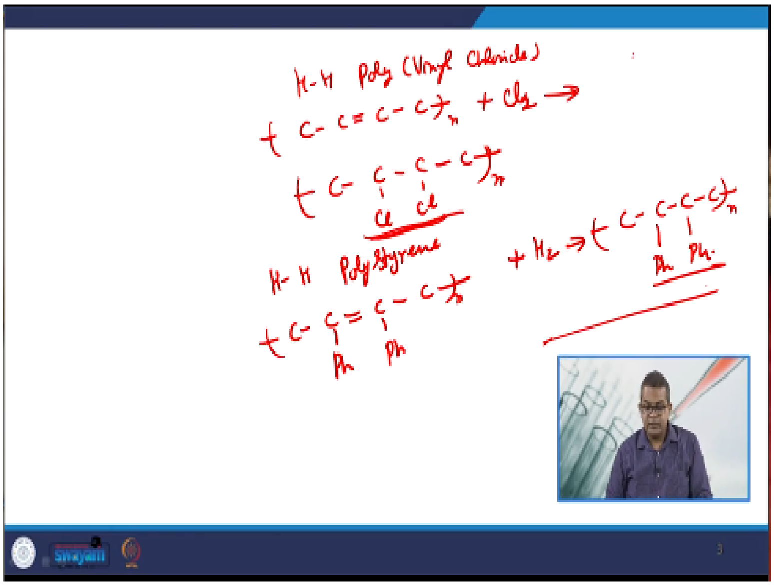

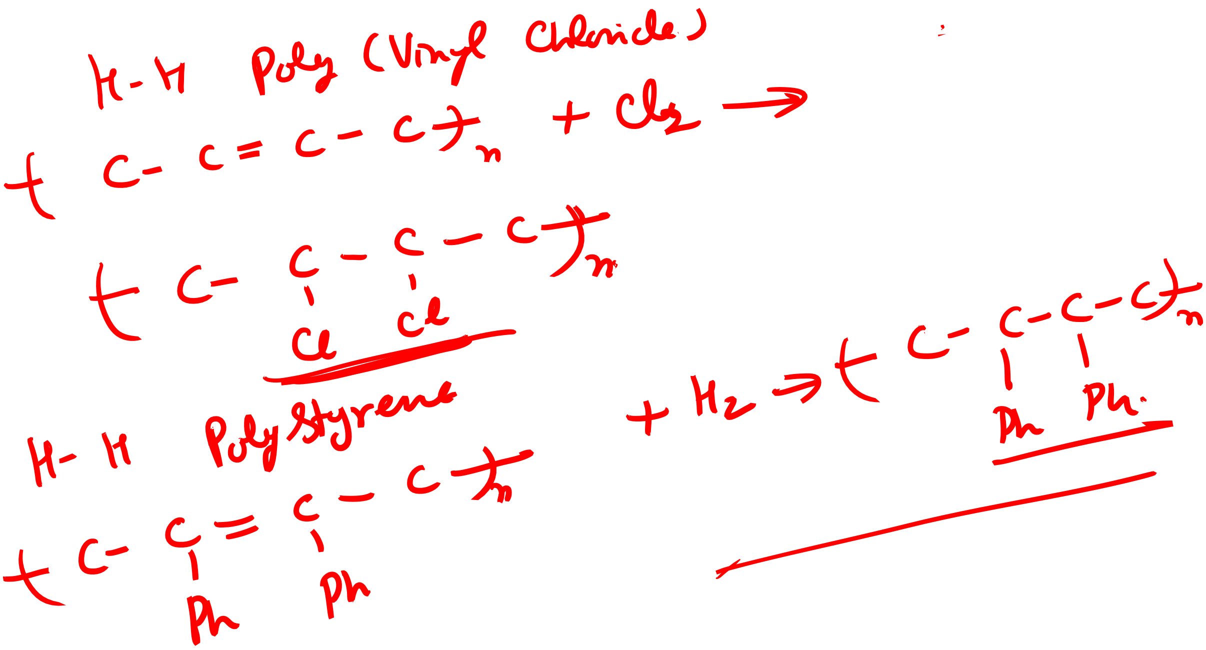

Now, this is head to head poly vinyl chloride. Now, you see, now, you can see the formation of this. Now, similarly, if you see that we discussed about head to head polystyrene. Now, this is the polystyrene. This is the phenyl ring which we are not going to show. Now, perform this hydrolyses, it may give you, now here, you see the synthesis of these 2. So, this is you can see that this is the head to head PVC and this one is the head to head polystyrene.

So, this is again a good concept to be addressed while taking into consideration of this particular approach in detail. Marshall et al, they compared the head to head and head to tail polystyrene by thermally stimulated discharge using the depolarisation technique and high dielectric strength. So, they observed that head to head placement as compared to head to tail placement with the help of this high dielectric strength.

So, depending upon the type of properties required for a particular application, these variation, you can obtain in this type of synthesis.

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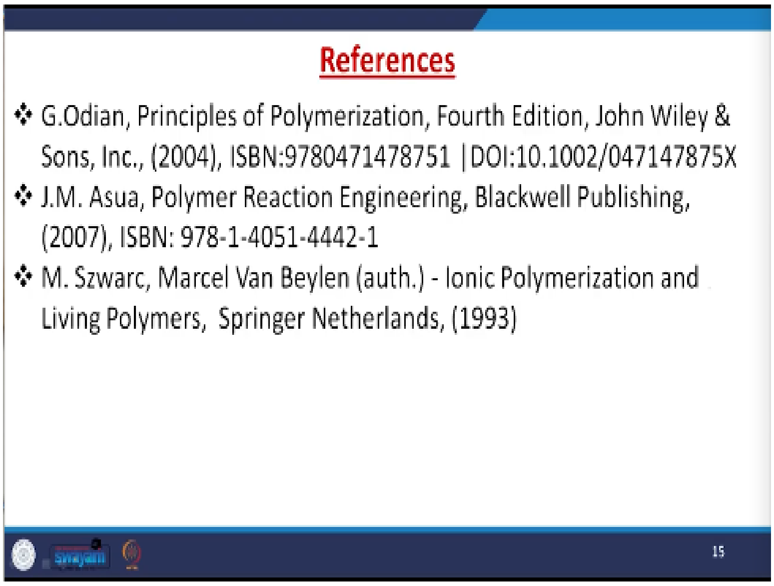

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Now, in this particular brief lecture, we discussed about the head to head and head to tail formation and polymerization protocols and we carry out certain literature approaches in this aspect. Now, we have listed very important literature for the further reference of these concepts. Thank you very much for paying attention.