Polymer Reaction Engineering
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Lecture – 33
Comparison with Ionic Chain Polymerization

Welcome to the next chapter of radical chain polymerization. And in this particular chapter, we are going to present a comparative study with ionic chain polymerization. Now, before we go into detail of this particular chapter, let us have a look at what we covered previously.

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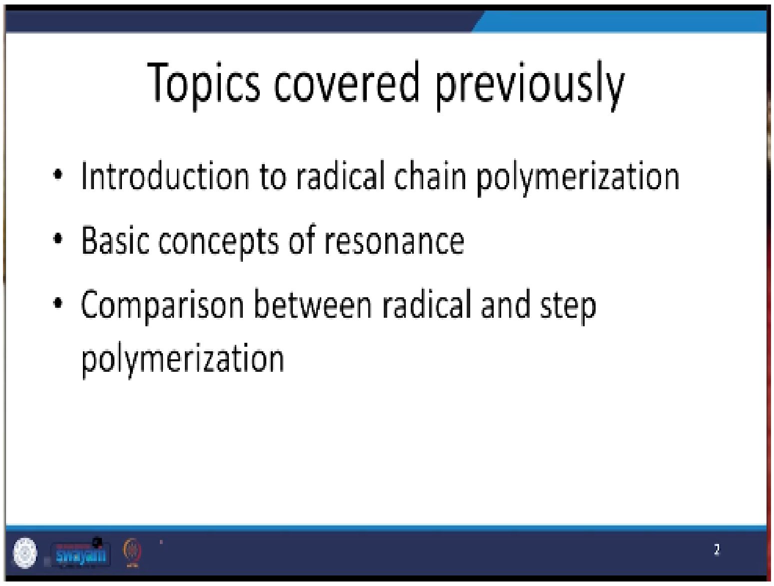

Topics covered previously

- Introduction to radical chain polymerization
- Basic concepts of resonance
- Comparison between radical and step polymerization

We had an introduction to the radical chain polymerization. Then previously, we discussed about various basic concepts associated with the resonance, then we perform a comparative study between the radical and step growth polymerization. And if you see that in the previous one, we discussed a detailed comparison between the radical and the step growth polymerization merits and demerits.

Now, in this particular chapter, we are going to discuss a comparative study between radical and ionic chain polymerization. Because, both things are extremely important when we discuss about the polymer reaction engineering, especially, with the perspective to the reactor aspect.

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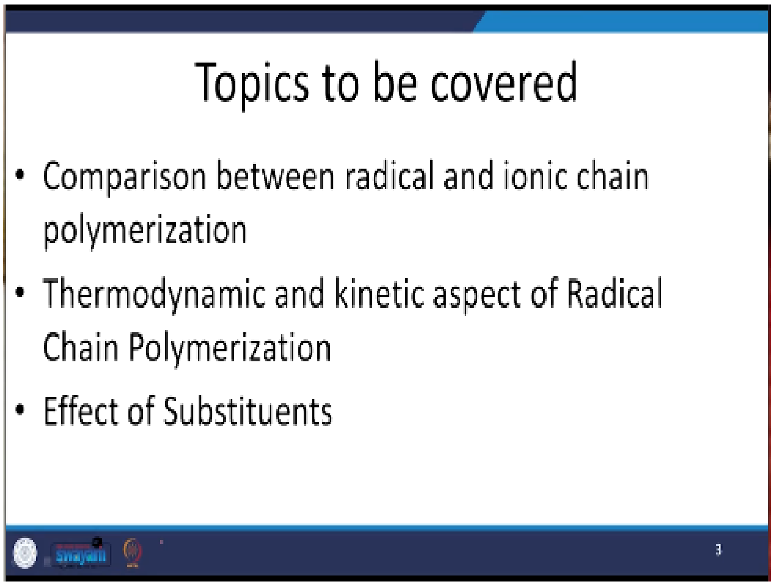

Topics to be covered

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

Then we will discuss about the thermodynamic and kinetic aspect of a radical chain polymerization, in light with the ionic chain polymerization and step polymerization. Then we will have a brief history about what are the effects associated with the various substitutes being added in during the course of polymerization. So, these 3 things, we are going to cover in this particular lecture. Now, let us have a look about a comparative note between the radical and ionic chain polymerization.

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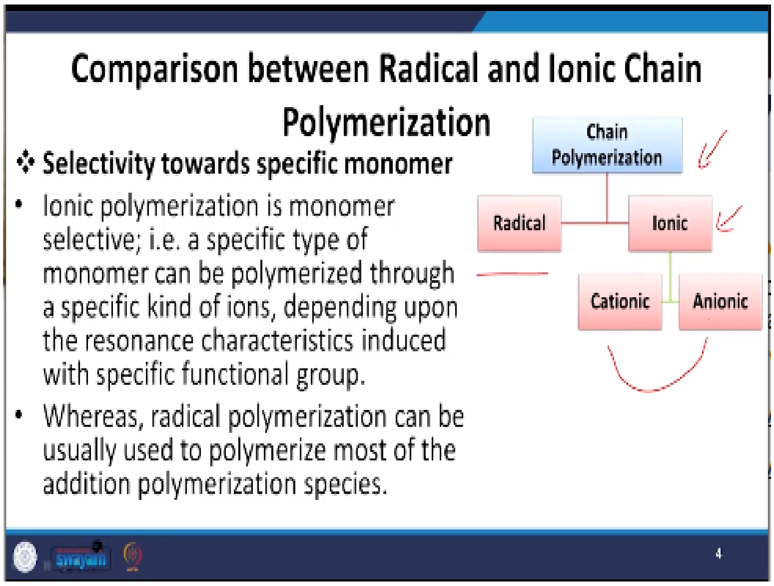

Comparison between Radical and Ionic Chain Polymerization

Selectivity towards specific monomer

- Ionic polymerization is monomer selective; i.e. a specific type of monomer can be polymerized through a specific kind of ions, depending upon the resonance characteristics induced with specific functional group.
- Whereas, radical polymerization can be usually used to polymerize most of the addition polymerization species.

We all aware about the basic concept note of radical polymerization as well as ionic chain polymerization. Now, here, we are going to discuss with respect to the selectivity aspect, now, selectivity towards a specific kind of monomer. Now, you see that in this particular figure, this chain polymerization is subdivided into 2 different streams. One is radical polymerization and another one is the ionic one.

And furthermore, the ionic polymerization or ionic aspect is again subdivided into 2 broad spectrum. One is the cationic one and second one is the anionic one. So, by this figure, the things should be clear in once mind. Now, let us have a look about the selectivity aspect with this, with the reference to this specific monomer. Now, ionic polymerization is a monomer selective polymerization.

So, based on the specific type of monomer, it can be polymerized through a specific kind of ions, those who are having the capability of promoting this polymerization. Now, this depends upon the resonating character which we discussed earlier in the different chapter. So, this induced this resonating character is induced with specific functional groups. So, if you recall that we discussed this particular approach in the previous lecture that, what are the different type of resonating characters?

And what is the impact of those designated character with respect to the functional group? Whereas, the radical polymerization, it can be usefully used to polymerize most of the addition polymerization species. So, this is a selective note with respect to the selectivity aspect, the specific monomer. And other thing is which is related to under the head of comparative note that is the propagating species.

Now, both radical and ionic polymerization process proceed in 3 steps. One is initiation, propagation and termination, which we had along discussion with respect to all 3 steps of polymerization process. So, both means radical and ionic chain polymerization, they use the different kind of propagating phenomena. And radical polymerization, the propagating specie is a free radical unpaired valence electron, while ionic polymerization, the propagating either they propagated either using the carbenium ion or through carbon ion.

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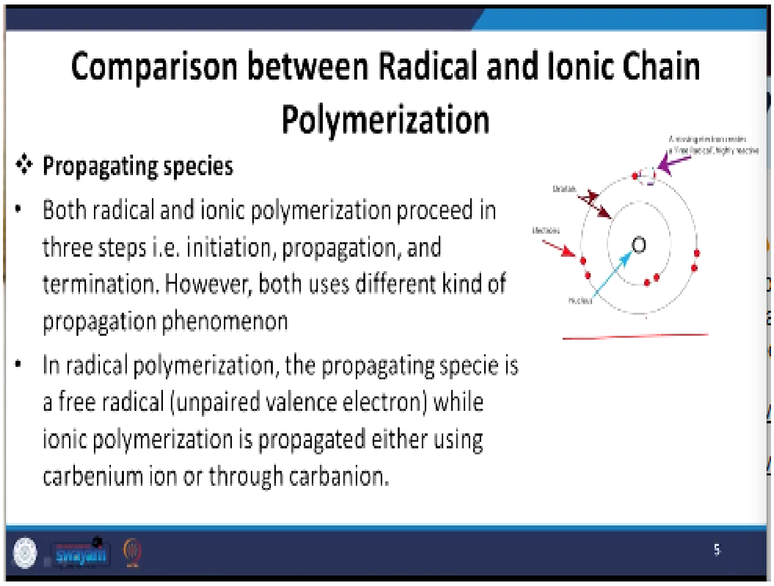

Comparison between Radical and Ionic Chain Polymerization

- **Propagating species**
  - Both radical and ionic polymerization proceed in three steps i.e. initiation, propagation, and termination. However, both uses different kind of propagation phenomenon
  - In radical polymerization, the propagating specie is a free radical (unpaired valence electron) while ionic polymerization is propagated either using carbenium ion or through carbanion.

So, you can see here, there are different approaches of molecular structure like nucleus, electrons, orbitals. Now, here, this particular point is very attractive respective to the free radical. Now, this is the missing electron here, if you recall the previous lecture where we discussed about the ionic as well as the radical concept. Here, the missing electron over here, it creates a free radical and that free radical is highly reactive in nature. So, this is the; you can say, the difference between the radical and ionic chain polymerization.

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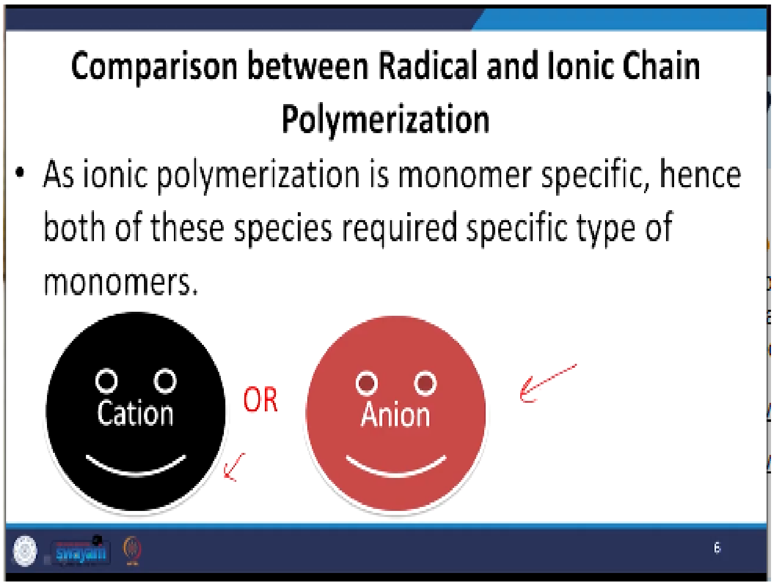

Comparison between Radical and Ionic Chain Polymerization

- As ionic polymerization is monomer specific, hence both of these species required specific type of monomers.

Now, as ionic polymerization is specific as both of these species required a specific type of monomer, maybe cation or maybe anion. So, that is very important thing which you need to be express, because they are very much monomer specific. So, whenever you require any kind of a specific polymer product, then definitely you have to be very choosy according to the monomer aspect.

And in that case, if you are going through the ionic polymerization route, you must remember that this particular route is monomer specific. Now, based on the type of monomer, we can differentiate between the radical and ionic chain polymerization.

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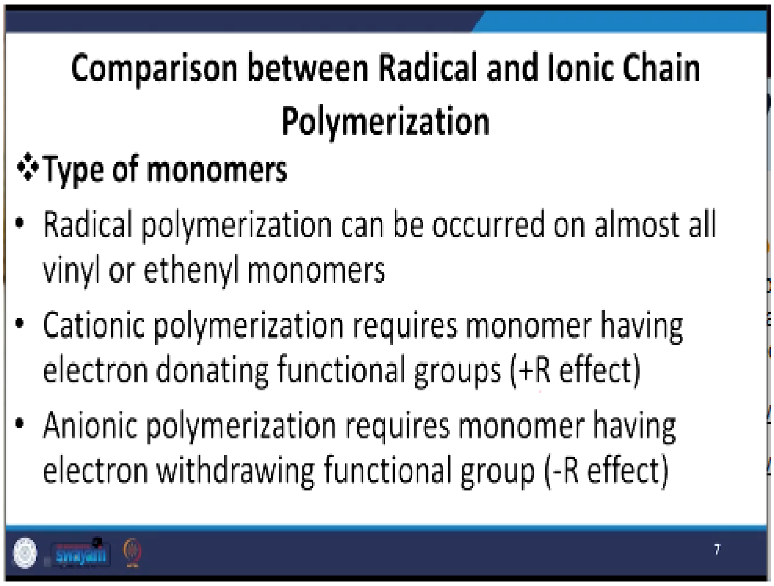

Comparison between Radical and Ionic Chain Polymerization

❖Type of monomers

- Radical polymerization can be occurred on almost all vinyl or ethenyl monomers
- Cationic polymerization requires monomer having electron donating functional groups (+R effect)
- Anionic polymerization requires monomer having electron withdrawing functional group (-R effect)

Radical polymerization it can be occur on almost all vinyl or ethenyl monomers. Whereas the cationic polymerization, they requires the monomer having the electron donating functional groups, which we discussed earlier, if you recall that it was plus R effect. And anionic polymerization, they require monomer having electron withdrawing functional group, if you recall that is minus R effect in the previous one.

So, this is a comparative note among radical cationic and anionic polymerization. Now, sometimes, another parameter which is having very important while discussing about the comparative note that is the effect of solvent polarity. Now, effect of solid polarity is again very integral part if you wish to distinguish between these 2 polymerization systems.

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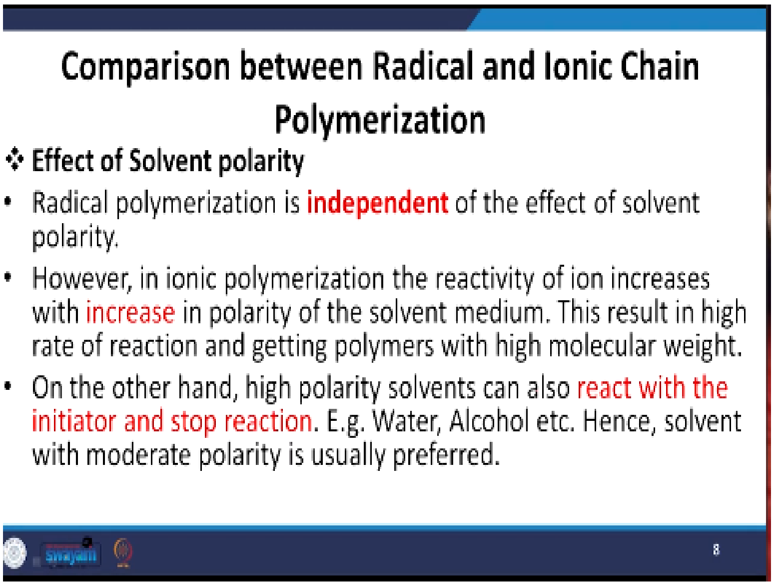

Comparison between Radical and Ionic Chain Polymerization

Effect of Solvent polarity

- Radical polymerization is **independent** of the effect of solvent polarity.
- However, in ionic polymerization the reactivity of ion increases with increase in polarity of the solvent medium. This result in high rate of reaction and getting polymers with high molecular weight.
- On the other hand, high polarity solvents can also react with the initiator and stop reaction. E.g. Water, Alcohol etc. Hence, solvent with moderate polarity is usually preferred.

Now, in radical polymerization, it is independent of the effect of solvent polarity that is very important thing. And in ionic polymerization, the reactivity of ion increases usually with increase in polarity of the solvent medium. So, it is very selective about the solvent thing. Now, when it increases with the increase in the polarity of the solvent, now, this particular concept results in high rate of a reaction and getting polymers with the higher molecular weight.

So, this is a very important thing, while deciding that which polymerization scheme would you like to have on. On the other hand, if high polarity solvent, they can also react with the initiator and sometimes, they may stop the reaction. So, that is why it this particular thing is a very important while deciding; sometimes by mistake or by any experimental approach or head and tail method, sometime it may create a problem.

Because, these high polarity solvent may get associated with the initiator and your polymerization reaction will truncate without any initiation. So, these are the certain high quality solvent like water, alcohol etcetera. So, the solvent with a moderate polarity is usually preferred. So, that is another concept which we need to take into account.

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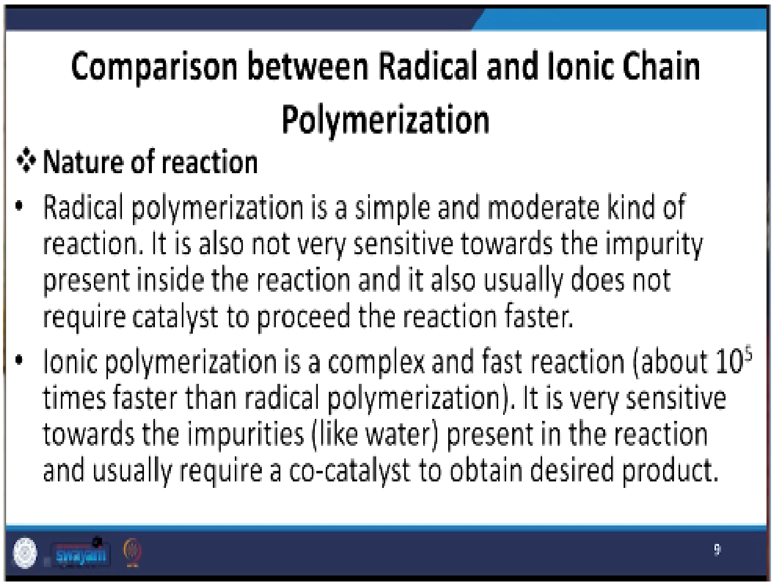

Comparison between Radical and Ionic Chain Polymerization

❖ **Nature of reaction**

- Radical polymerization is a simple and moderate kind of reaction. It is also not very sensitive towards the impurity present inside the reaction and it also usually does not require catalyst to proceed the reaction faster.
- Ionic polymerization is a complex and fast reaction (about 10^5 times faster than radical polymerization). It is very sensitive towards the impurities (like water) present in the reaction and usually require a co-catalyst to obtain desired product.

Another important factor is that that is the nature of reaction. Now, radical polymerization is a simple and moderate kind of a reaction. It is also not very sensitive towards the various impurities associated within the reaction mass or reactant etcetera. And it also usually does not require any kind of a catalyst to proceed the reaction faster. So, these are the things which are related to the radical polymerization.

Now, if you compare with any polymerization, which is a complex in nature and a very fast type of a thing about, you can say, 10 to the power 5 times faster than the radical polymerization. So, it is very sensitive towards the impurity like water, we discussed in the previous slide. Now, if it is present in the reaction, then it may kill the initiator and it may kill the entire desired polymerization process.

And ionic polymerization, it usually requires co-catalysts to obtain the desired product. So, this is the comparative note with respect to the nature of reaction. The termination's step also plays a very vital role if we wish to compare between these 2 polymerization system.

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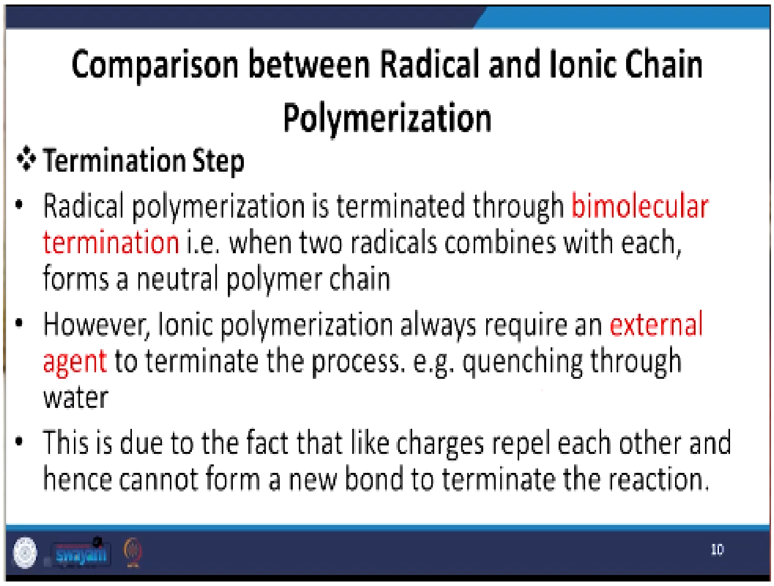

Comparison between Radical and Ionic Chain Polymerization

❖ **Termination Step**

- Radical polymerization is terminated through bimolecular termination i.e. when two radicals combines with each, forms a neutral polymer chain
- However, Ionic polymerization always require an external agent to terminate the process. e.g. quenching through water
- This is due to the fact that like charges repel each other and hence cannot form a new bond to terminate the reaction.

Now, in radical polymerization is usually terminated through any kind of bi-molecular type of termination protocol. Now, to more precise or to explain all those things, so, when the 2 radicals combined with each other to form a neutral polymer chain. So, this is the radical polymer and this is the radical polymer if they combined together, then they truncate the polymerization reaction.

However, the polymerization or ionic polymerization always require an external agent that is important thing to terminate the process. Sometimes, maybe with the help of a quenching with water, because you see that water because of the polarity of the water, it may react with the initiator to stop the reaction. So, sometimes, it may require to quench with water or sometimes the addition of water or any kind of a solvent may play a vital role.

Now, this concept is just can be explained with the help of a small thing that this is attributed to the fact that like charges, they repel each other and hence, cannot form a new bond to terminate the reaction. It is just like that both of them, they are having like charges and they cannot come together. So, they are far away and that is why, they promote to the termination aspect of the polymerization reaction.

Another, so, therefore, the ionic polymerization is also termed as the living polymerization. Now, if we add more and more monomer to the reaction mass, then it will again start propagating in a similar manner. Now, let us have, by this way, we discuss about a comparative note between the radical and ionic polymerization. Now, let us have a look about the thermodynamic and kinetic aspect of radical chain polymerization.

Now, the condition that any specific monomer, it can be transformed to polymer depend on the aspects of both thermodynamic and kinetic visibility. In the previous lectures, we discussed about the impact of thermodynamic character with respect to the exothermic and endothermic and the kinetic behaviour of various kinds of polymerization reaction. So, these 2 aspects plays a very vital role in every kind of polymerization reaction and that is why the radical chain polymerization we are going to discuss over here.

So, under any and all condition of a reaction, polymerization will be impossible, unless it passes that thermodynamic feasibility tests, there are various thermodynamic equations associated with this type of a concept. So, if it fails in the thermodynamic feasibility test, then there is no point to carry out any kind of a polymerization reaction under the given heads.

So, thermodynamically a feasible chemical reaction is a chemical reaction or a reaction, which will proceed in forward direction result to a decrease in free energy that is the Gibbs free energy of the system. This means that a monomer will only convert to the polymer, if a free energy changes delta G. Delta G is the Gibbs free energy. Delta G is negative that is the universal factor that needs to be accounted.

Now, negative Gibbs free energy is the desired condition of any chemical reaction to proceed, but polymerization can only occur if a reaction is kinetically feasible, we have discussed a broad spectrum of kinetic study of these polymerization processes. So, in other words, chemical process or reaction is feasible, when a chemical process proceeds at a realistic phase. So, one handles with the theoretical aspect; another one handles the practical aspects.

So, the feasibility again is tutored by this kinetic approach. So, the polymerization of a very large variety of unsaturated monomer is usually thermodynamically feasible. A very specific condition of reaction are often needed to achieve kinetic feasibility in order to achieve a particular polymerization. So, that is the very foremost a very important part which we need to encounter.

Now, while radical cationic and anionic initiators are used in chain polymerization. They cannot be use of used in discriminately as these 3 initiations forms do not function for all monomers. So, you cannot take the things for granted, because sometimes, it may not be feasible to use with the line that this will be applicable for all monomers. It is not. So, monomer exhibit varying degree of selectivity as we discussed in the previous where we were having different type of solvent.

So, they exhibit a varying degree of selectivity regarding the type of reactive centre that will cause the polymerization. So, these are the additional factors which one should look into while carrying out any kind of polymerization process. Most monomer with a radical initiator may undergo polymerization through varying rates monomer. However, they show the high selectivity against ionic initiator, because of the availability of those ions in the initiator.

So, many monomer with the cationic initiator, they do not polymerize whereas other made not polymerized with anionic initiator. So, this particular approach is a case sensitive approach. So, based on the different type of a scenario, it can be achieved.

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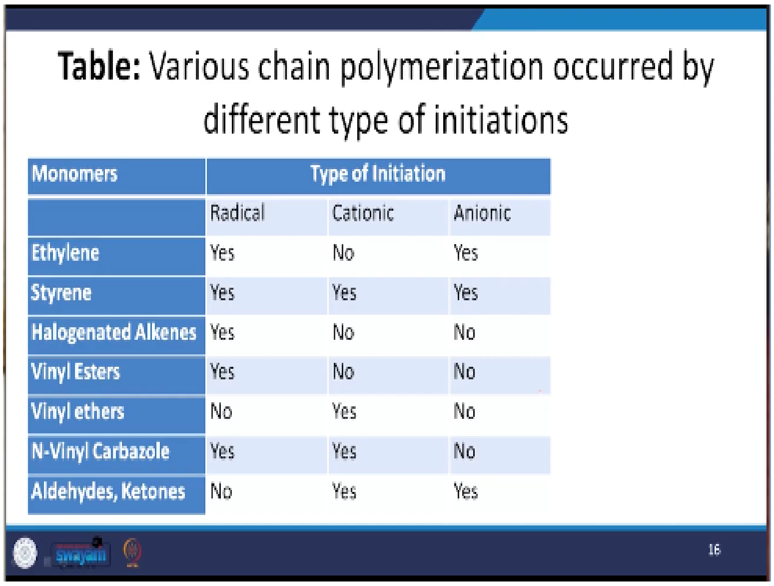

Table: Various chain polymerization occurred by different type of initiations

Monomers	Type of Initiation		
	Radical	Cationic	Anionic
Ethylene	Yes	No	Yes
Styrene	Yes	Yes	Yes
Halogenated Alkenes	Yes	No	No
Vinyl Esters	Yes	No	No
Vinyl ethers	No	Yes	No
N-Vinyl Carbazole	Yes	Yes	No
Aldehydes, Ketones	No	Yes	Yes

Now, the form of initiation that introduce polymerization to high molecular weight polymer of a different monomers are indicated in a different table. Now, you see here, there are a various chain polymerization occur by the different type of initiator, you see, one column reflects the different type of a monomer. Then there are the classes of initiation processes. Like ethylene, it can go with the radical polymerization, but cationic, it is not at all feasible and anionic, it is visible.

Similarly, styrene this monomer works for all type of protocols whether radical cationic and anionic. Similarly, halogenated alkenes, they are very selective; they work with the radical type of initiators, but they are not comfortable with the cationic and anionic. Similarly, vinyl esters, vinyl ethers, they are having their own parameters of selectivity. So, different types of initiators are being used, similarly, N-vinyl carbazole and aldehydes, ketones, etcetera.

So, before we proceed further, we must have this type of information with us in a handy form. So, that we can design our polymerization process accordingly. Now, if you see that the table the monomers those who are having plus R or minus R effect, like here, this effect, they are containing the functional group favours the cationic and anionic polymerization respectively.

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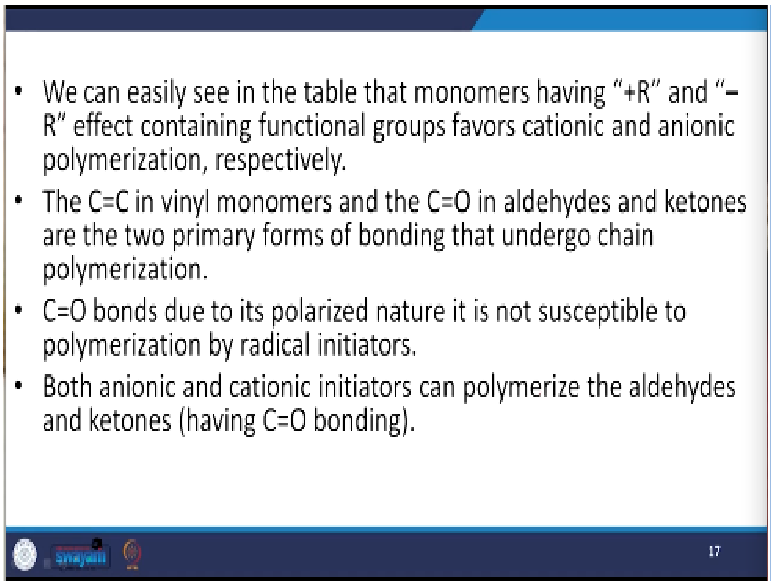

- We can easily see in the table that monomers having "+R" and "–R" effect containing functional groups favors cationic and anionic polymerization, respectively.
- The C=C in vinyl monomers and the C=O in aldehydes and ketones are the two primary forms of bonding that undergo chain polymerization.
- C=O bonds due to its polarized nature it is not susceptible to polymerization by radical initiators.
- Both anionic and cationic initiators can polymerize the aldehydes and ketones (having C=O bonding).

Now, if, we go for the carbon-carbon double bond in vinyl monomers here in the table, then C O double bond in the aldehyde and ketone are the 2 primary forms of bonding that undergo chain polymerization. Now, similarly, C O double bond due to its polarized nature, it is not susceptible to polymerization by the radical initiators. See, that is because, it is very again case sensitive sometimes it may not be feasible and sometimes it may be feasible.

Now, both anionic and cationic initiators can polymerize the aldehydes and ketones. Obviously, they must have C double bond O bonding with them.

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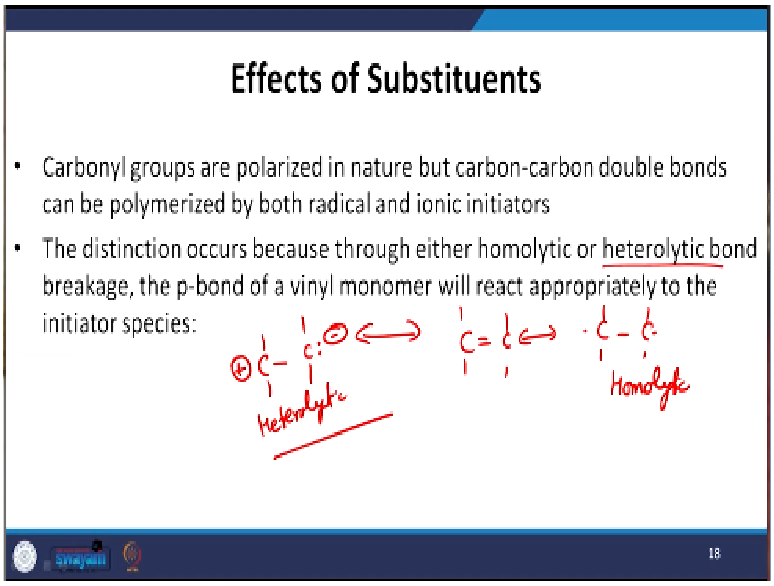
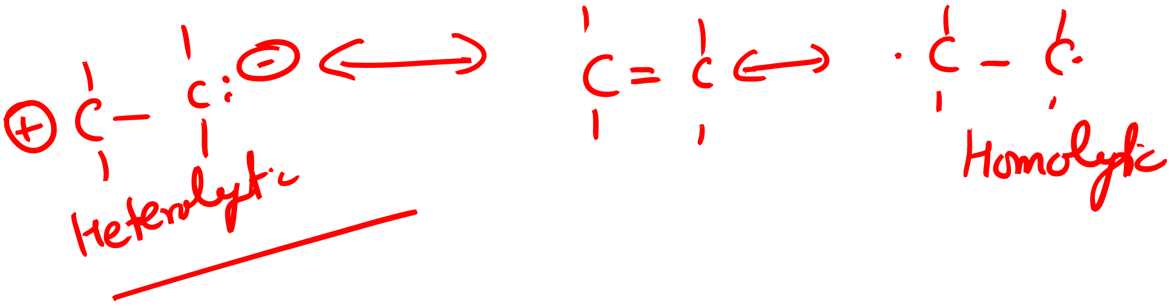


Effects of Substituents

- Carbonyl groups are polarized in nature but carbon-carbon double bonds can be polymerized by both radical and ionic initiators
- The distinction occurs because through either homolytic or heterolytic bond breakage, the p-bond of a vinyl monomer will react appropriately to the initiator species:

Now, let us have a look about the effect of a substituent. Now, carbonyl group, they are highly polarised in nature, but the carbon-carbon double bonds, it can be polymerized by both radical and ionic initiator. Now, the distinction occurs because through either homolytic or heterolytic bond breakage and the phi-bond of a vinyl monomer that will react appropriately to the initiator species. Let us have a look about these carbonyl groups.



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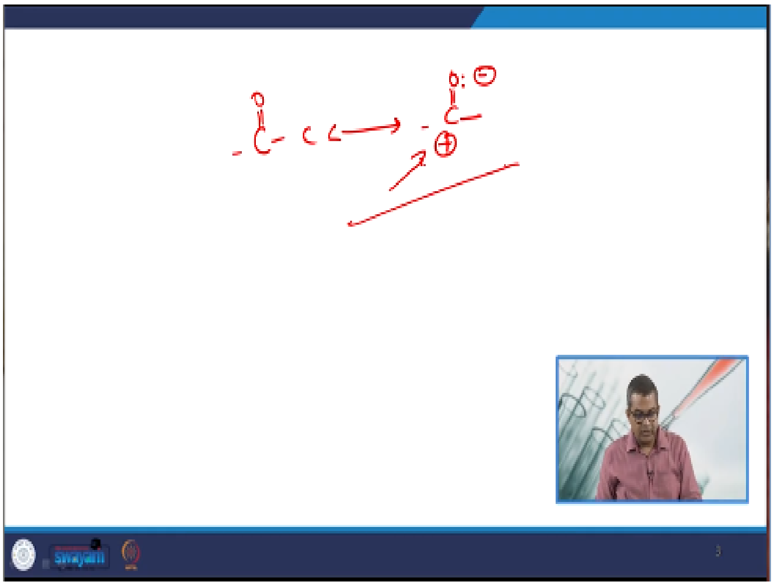

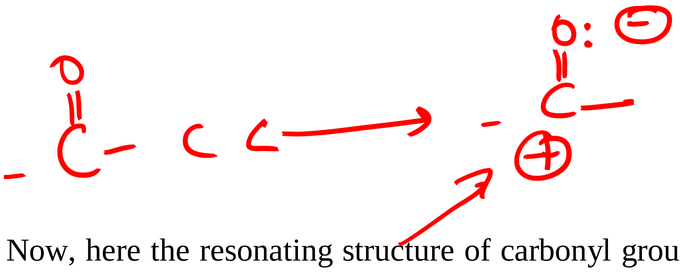

Now, here the resonating structure of carbonyl group is given as C double bond over C, you can see here, the plus double bond O. Now, here you see nothing, now, we can see the polarised nature in such a functional group. So, this is again a crucial thing while we go to this particular approach. Now, let us have a look about the effect of substituent. Now carbonyl groups they are polarised in nature, that is why we discussed but the carbon-carbon double bond can be polymerized by both radical and ionic initiators.

The distinction occurs because either through the homolytic or heterolytic bond breakage and sometimes phi-bond play a very vital role, like in the vinyl monomer. They react appropriately to the initiator species. Now, let us have a look about this particular approach. Now, here these bonds are here, now, you see this is, this one is homolytic and this one is heterolytic.

So, what we are discussing here that is the heterolytic and homolytic you can see over here that how they are playing a vital role while deciding the effect of substitute. Sometimes, the carbonyl group which are polarised in nature, now, the inductive and resonating characteristics of vinyl monomer, they decides whether the radical or ionic polymerization will occur or not, maybe with respect to the cationic or anionic approaches.

Now, the substituents effect usually, they demonstrates itself through its alteration of the electron cloud density, the double bond and its ability to stabilise the possible formation of either radical ion or cation approaches. Now, there are other things which are attributed related to the electron donating functional groups. Now, these electron donating functional groups, they increases the electron density over carbon-carbon double bond of the system. Now, this may lead to facilitate the cationic polymerization of the monomer.

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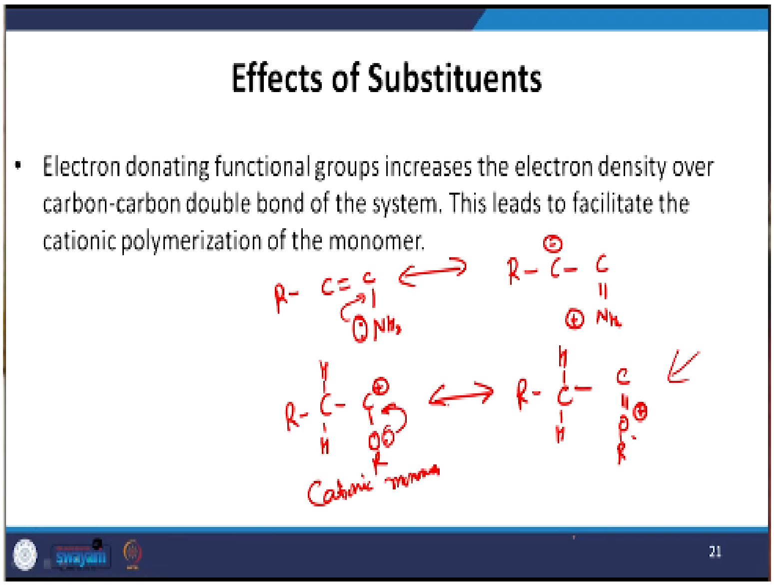
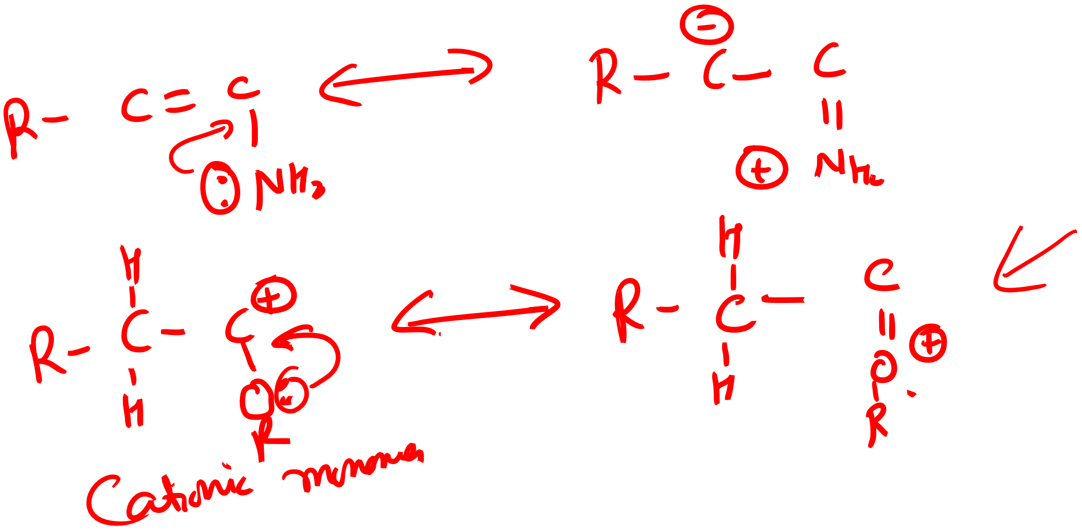


Effects of Substituents

- Electron donating functional groups increases the electron density over carbon-carbon double bond of the system. This leads to facilitate the cationic polymerization of the monomer.



Let us have a look about this particular approach in detail. The first example is this one. Here, we are having this lone pair of electron which is transferred over here. Now, this may become like this. Similar, the second example is; this is the lone pair which is transferred to here or this is cationic monomer. Now, the functional group, this allows the delocalization of charge therefore, the stabilising the cationic and propagating species of resonance. Now, similarly, we can see this particular approach in various aromatic systems.

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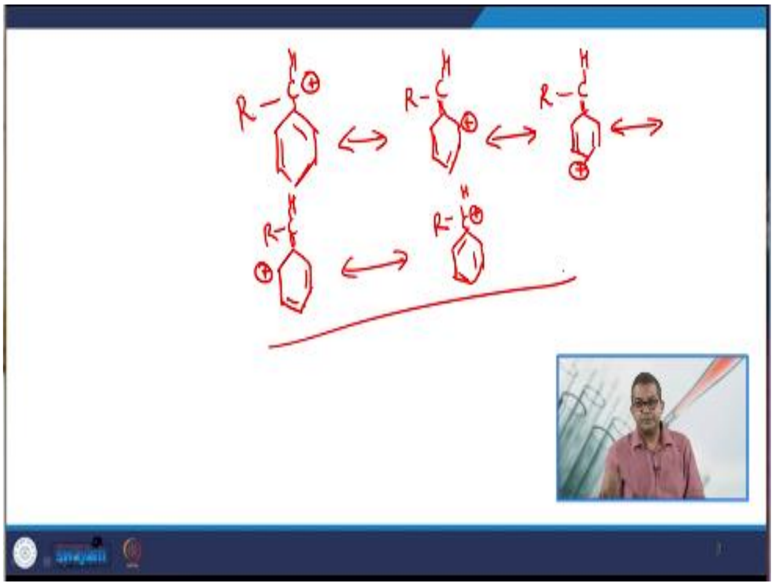
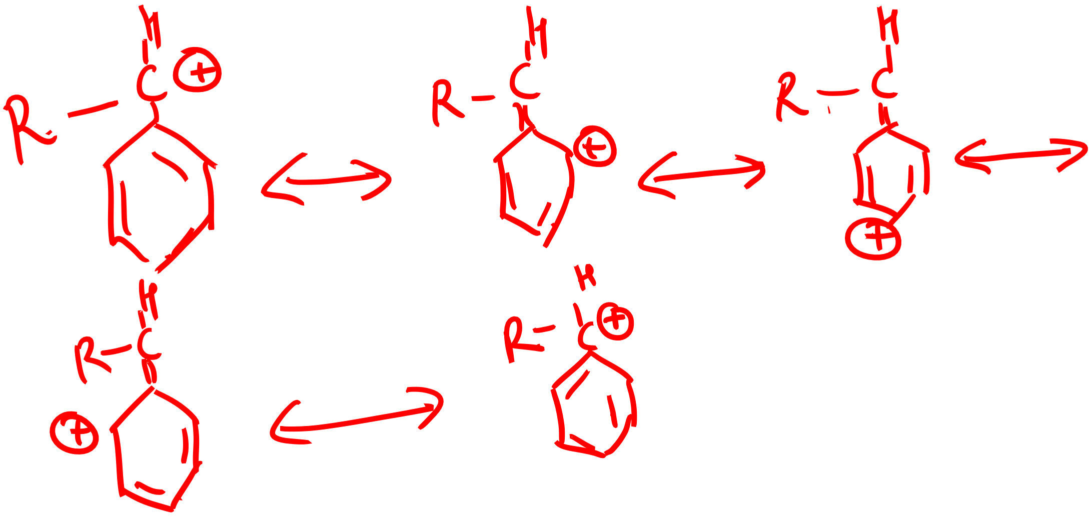
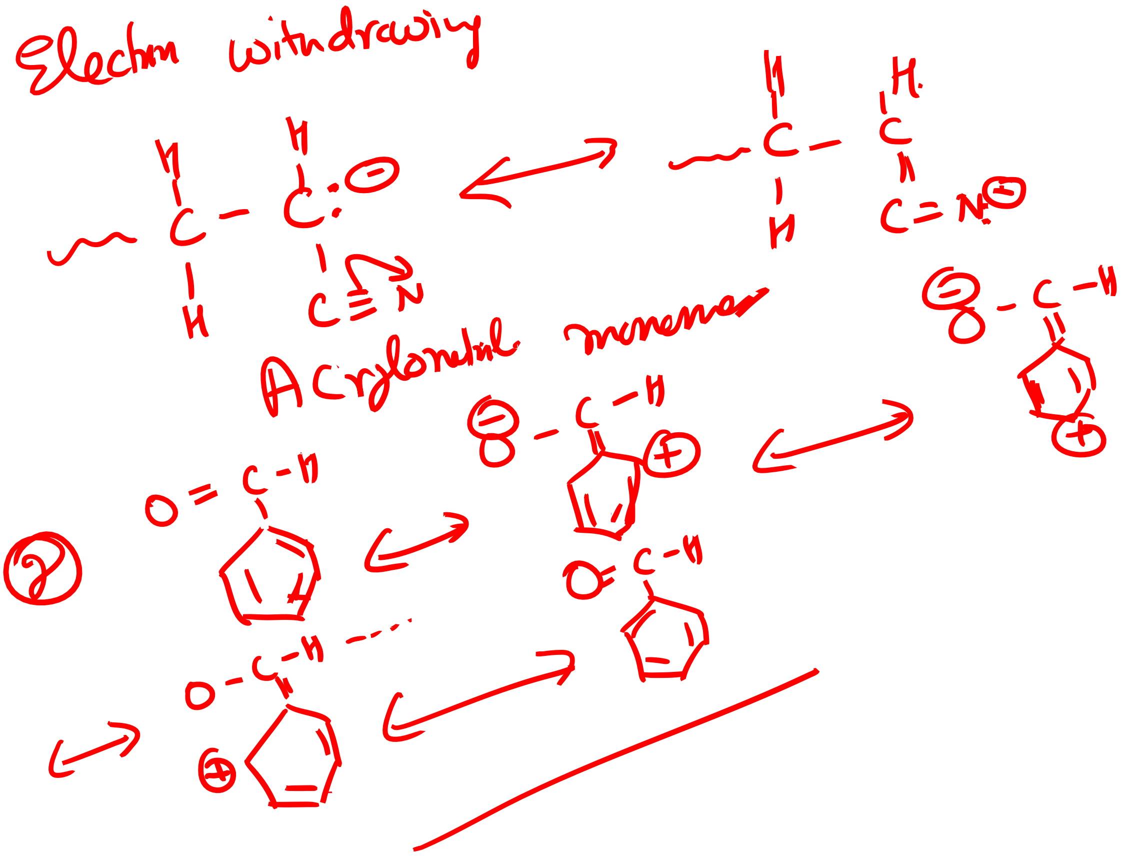




Here, you can see, this is the aromatic type of approach phenol ring. Now, this is having the resonating structure or you can form the transfer of charge with respect to. Now, here, you see that this positive charge is moved over here. Now, another condition if you recall that we discussed this particular approach in the resonating structure thing, now, here, you see that this positive charges localised over here.

So, this is another approach with respect to the resonance and other thing. Now, sometimes, the electron withdrawing is also plays a very vital role while discussing this particular approach. And specifically would like to discuss with the help of acrylonitrile approach which is if you see that in the previous example, we discussed all those things.



Now, alkoxy substitute, they allow the positive charge to be localised. If the substituent is not present that is in the ethlyne, the positive charge on the single alpha carbon atom will be localised. Now, we discussed this particular approach if you see that the example number 2 here, where the involvement of alkoxy group contribute to the carbocation stabilisation through delocalization of a positive charge between 2 atoms, the carbon and oxygen.

Now, sometimes, the alkyl group usually play a very vital role, they are having a very poor effect in promoting cationic polymerization. Now, it is only the 1-1 diol alkene then undergo the cationic polymerization. Similarly, if you see the electron withdrawing functional group, they decreases the electron density over the carbon-carbon double bond. We will discuss this thing the equation.

Now, this because the decreases a carbon-carbon double bond which result in the development of a parallel partial positive charge over the carbon atom. Therefore, such monomers usually they are facilitated by anionic polymerization. Let us have a look about all this particular approach related to the electron withdrawing.

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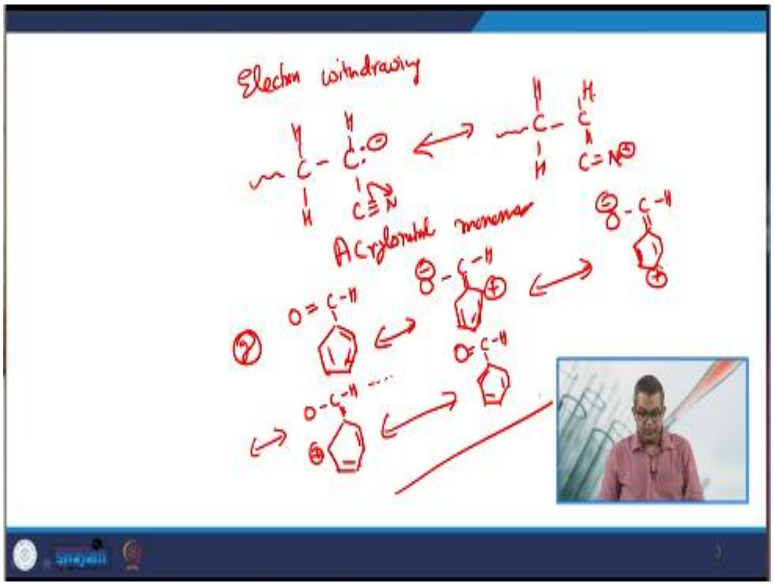

Now, here you see, there are 2 examples. One is this acryonitrile monomer. Now, here, this is shifting towards this one. Now, this is, the second example is attributed to the phenyl ring. Now, you see here this, the localization of the charge with respect to the electron withdrawing. Now, another resonating structure is like this. So, you see this, these are the different approaches over here you can see, the concept of electron withdrawing over the period of time.

And other thing is that stabilisation of propagating carbon ions happens by the delocalization of negative charge over the nitrile group or alpha carbon and nitrogen. Now, alkenyl or phenol substitutes if you have seen this previous figure, which we discussed that, while inductively electron withdrawing can be resonating stabilises, the ionic propagating species in the same way as in a cyano group.

So, therefore, if you see that the monomers such as styrene or 1, 3-betadine, they can undergo both anionic and cationic polymerization. So, if you see the previous table where we discussed about the selectivity of these type of polymerization step, these 2 are the best example, those performed the both anionic and cationic polymerization in their respective approaches. Let us have a look about these approaches in detail.

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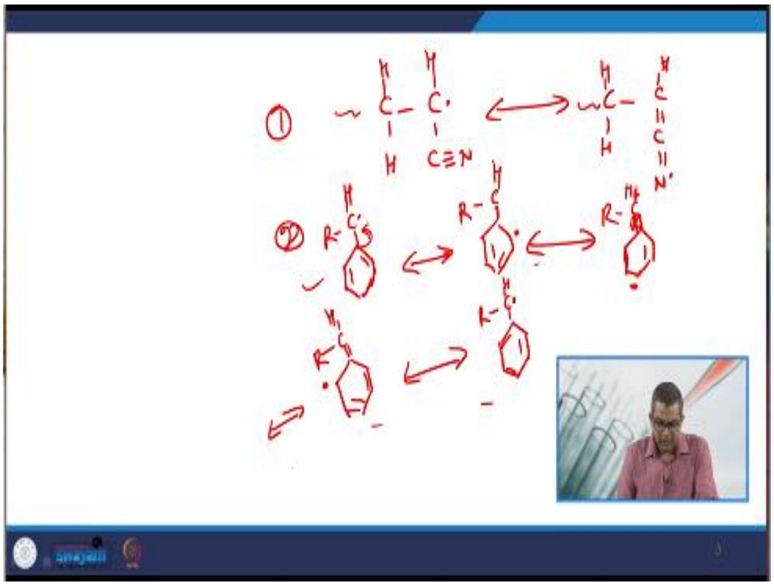
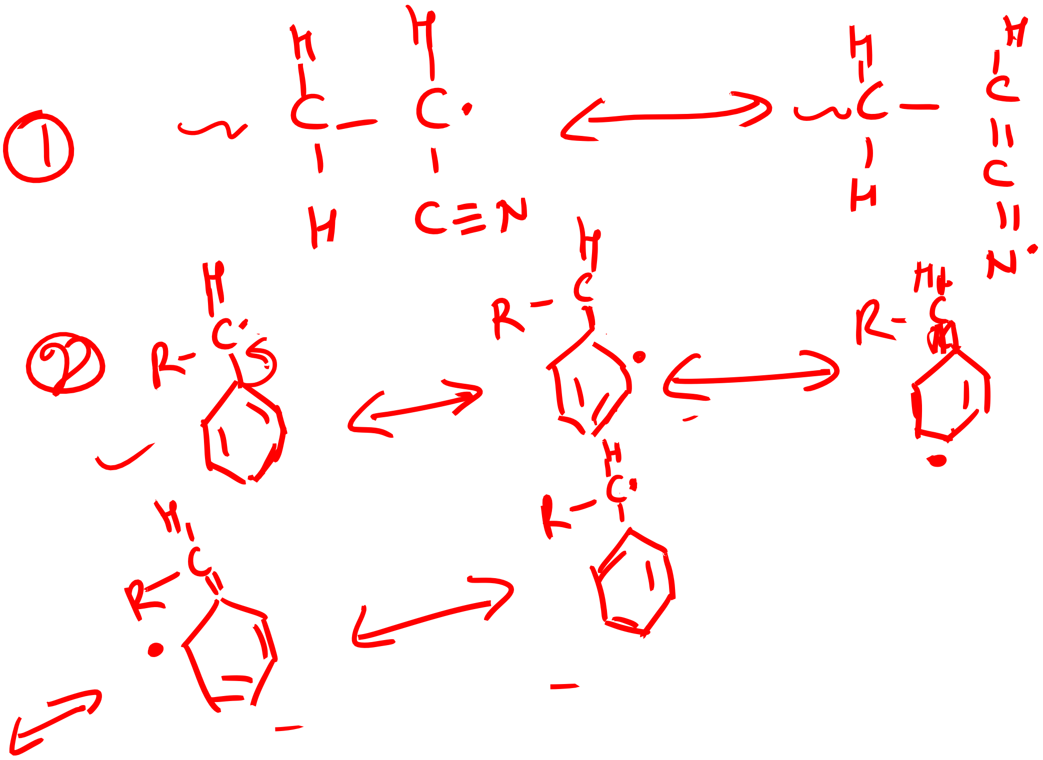


This is related to the attributed to the radical resonance. Now, here, the first example carries with; this is cynao group, it is a very popular polymerization reaction especially used for different kinds of industrial applications. Now, this is the first example and second one if you see the phenyl ring over here and different types of resonating restructure if you recall that in the previous lecture, we discussed.



There are 5 different type of resonating structure which are possible for to carry out these polymerization reactions. Now, this is the third one. Now, if you see and the fourth one, here, this is a charge which is being relocated over the period of time, radical being relocated. Now, see 1, 2, 3, 4 and 5, these are the things.

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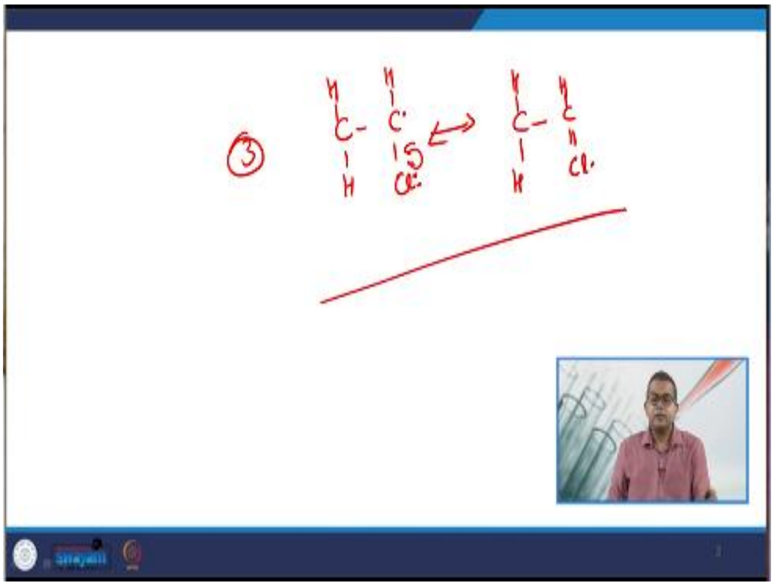
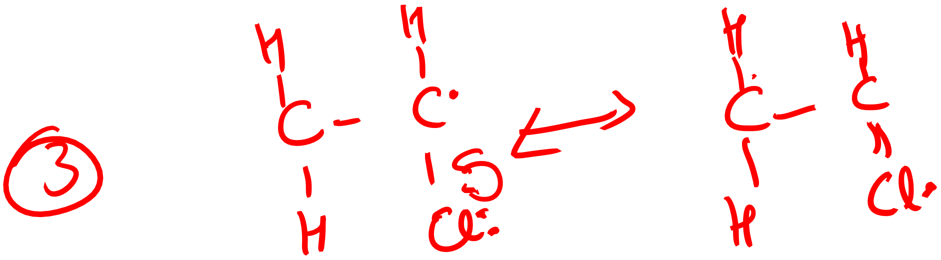


Another best example, which you can see and clearly visible example, which is more relevant to the system is like this. And now, here, you see that this is the example of radical resonance. So, these are the 3 examples, they are attributed to this type of polymerization step.



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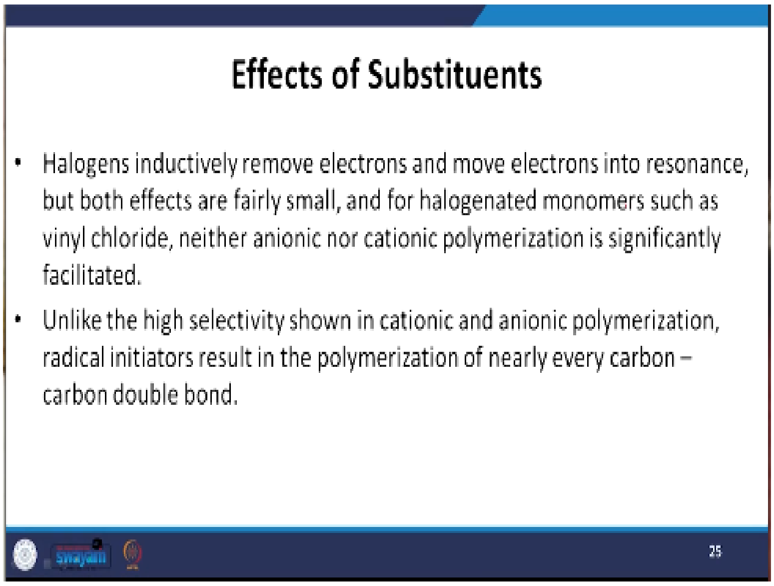

Effects of Substituents

- Halogens inductively remove electrons and move electrons into resonance, but both effects are fairly small, and for halogenated monomers such as vinyl chloride, neither anionic nor cationic polymerization is significantly facilitated.
- Unlike the high selectivity shown in cationic and anionic polymerization, radical initiators result in the polymerization of nearly every carbon – carbon double bond.

Now, in the third example, you see that we introduced the halogens. So, halogen inductively removed the electron. If you see that, they removed the electrons and move electrons to the resonating structure, but both effects are fairly small. And if you see that the halogenated monomers such as vinyl chloride, neither anionic nor cationic polymerization, they are significantly facilitated.

So, unlike the high selectivity which was shown in this previous figure, the cationic and anionic polymerization, the radical initiators such as polymerization of nearly even carbon-carbon double bond are always possible.

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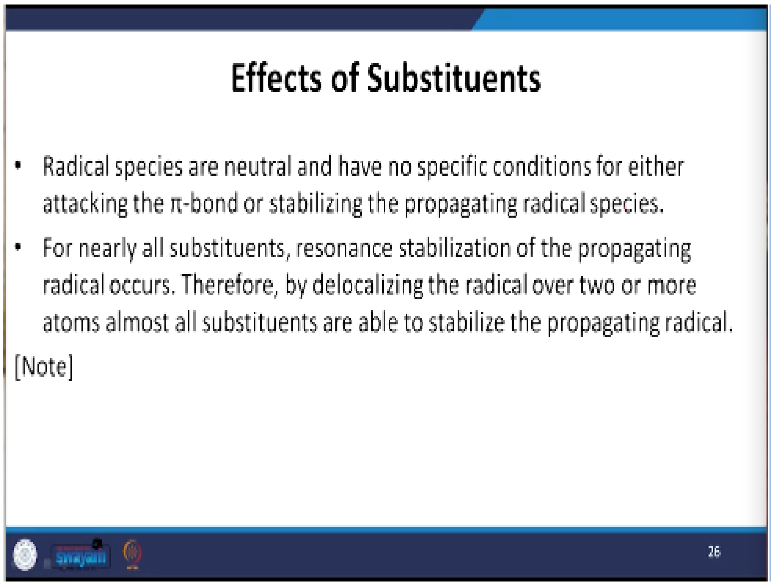

Effects of Substituents

- Radical species are neutral and have no specific conditions for either attacking the π-bond or stabilizing the propagating radical species.
- For nearly all substituents, resonance stabilization of the propagating radical occurs. Therefore, by delocalizing the radical over two or more atoms almost all substituents are able to stabilize the propagating radical.

[Note]

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So, when we talk about the radical species as usually they are neutral in nature and they have no specific conditions for either attacking of phi-bond or stabilising the propagating reactors. So, they are not having very specific conditions need for. So, for nearly all substituent, the resonance stabilisation of the propagating radical occurs. So, therefore, by delocalising the radical over 2 or more atoms, almost all substituent are able to stabilise during the propagating reactor.

So, we were having 4, 5 different type of things related to the you see that there are 5 different type of resonating structures. So, you can use all those things as per the choice.

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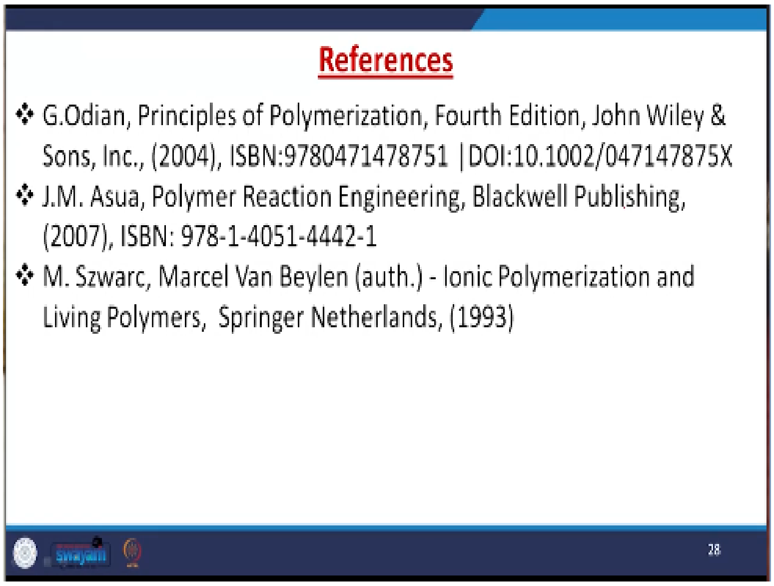

References

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Now, by this way, we are concluding this particular lecture and we discussed about the various thermodynamic and kinetic studies to give a competitive node between the polymerization scheme and discuss about the various resonating correctors of these polymer radicals. If you wish to have the studies, then you can have a look of all these references which are listed in this particular slides. Thank you very much.