Polymer Reaction Engineering
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Lecture – 58
Ionic Polymerization - III

Welcome to the next lecture of ionic polymerization. , before we proceed further, let us have a look at what we studied previously. We studied various classification scheme for ionic species, we discussed about the effect of solvents during the ionic polymerization. Apart from this we discussed the ionophores, the concept of ionogens, we discussed about the various ionic pair systems, we discussed about the covalent species.

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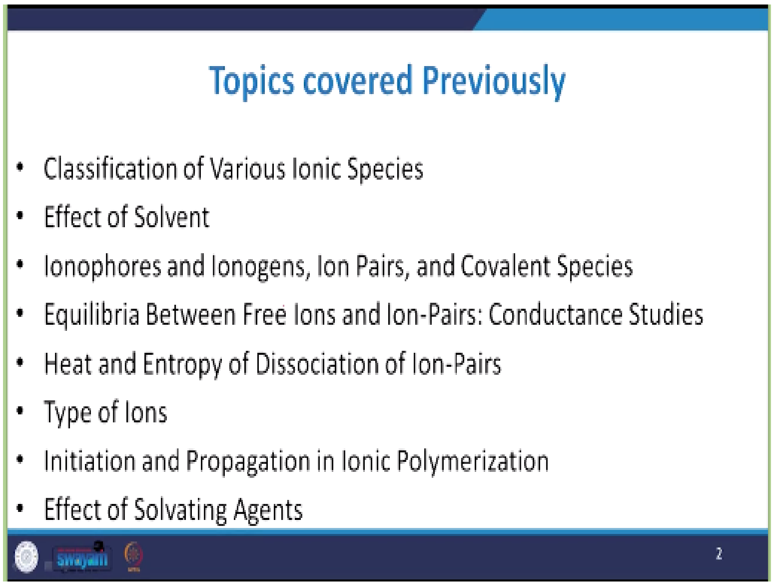

Topics covered Previously

- Classification of Various Ionic Species
- Effect of Solvent
- Ionophores and Ionogens, Ion Pairs, and Covalent Species
- Equilibria Between Free Ions and Ion-Pairs: Conductance Studies
- Heat and Entropy of Dissociation of Ion-Pairs
- Type of Ions
- Initiation and Propagation in Ionic Polymerization
- Effect of Solvating Agents

We had a discussion about the equilibria between the free ions and ionic pairs and we developed the mathematical equations related to the conductance studies. We discussed about the heat and entropy dissociation of various ionic pairs and describe the various type of ions. We had a discussion about the initiation and propagation in ionic polymerization and the effect of solvating agents in ionic polymerization.

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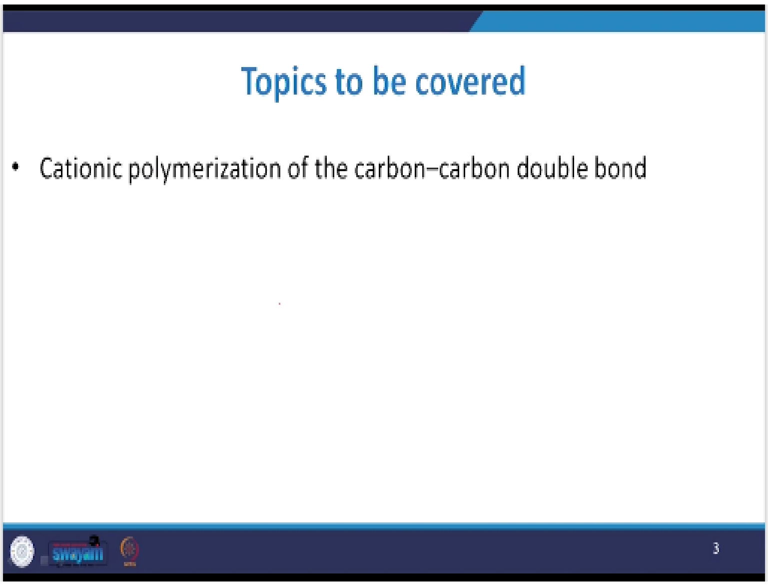

Topics to be covered

- Cationic polymerization of the carbon–carbon double bond

, in this particular chapter, we will discuss about the cationic polymerization of carbon carbon double bond. , this particular thing the cationic polymerization plays a vital role when we try to develop the industrial polymers for various specific uses.

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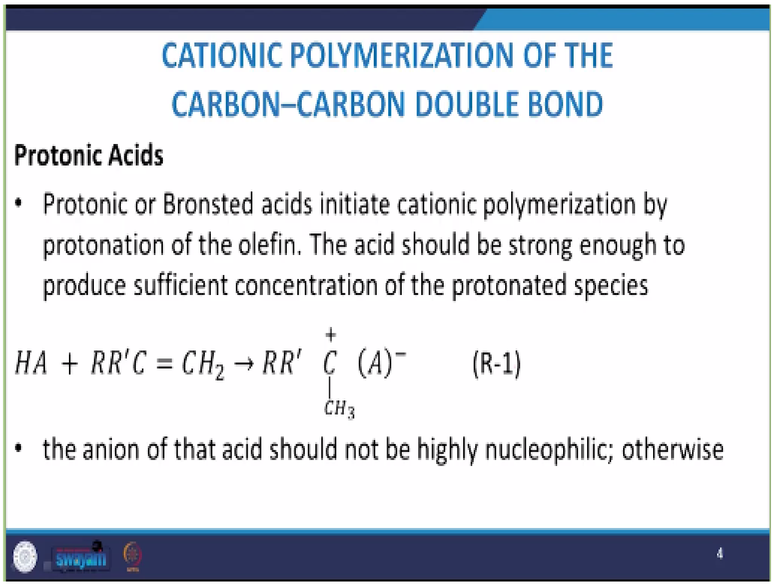

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

Protonic Acids

- Protonic or Bronsted acids initiate cationic polymerization by protonation of the olefin. The acid should be strong enough to produce sufficient concentration of the protonated species

$$HA + RR'C = CH_2 \rightarrow RR' \underset{\underset{CH_3}{|}}{\overset{+}{C}} \ (A)^- \qquad \text{(R-1)}$$

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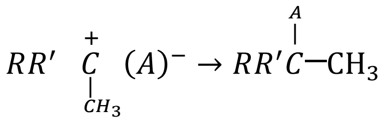
the anion of that acid should not be highly nucleophilic; otherwise it will terminate the protonated olefin by combination



$$RR'\underset{CH_3}{\overset{+}{C}}\ (A)^- \rightarrow RR'\overset{A}{C}{-}\mathrm{CH_3}$$

(R-2)

the ionic species usually do not exist as free ions but as ion pairs.

So, if you recall that in the previous lectures we discussed about the deadness of those active polymer chain. So, it made dead the polymetric chain so that the desired effect you may not be able to achieve those desired results.

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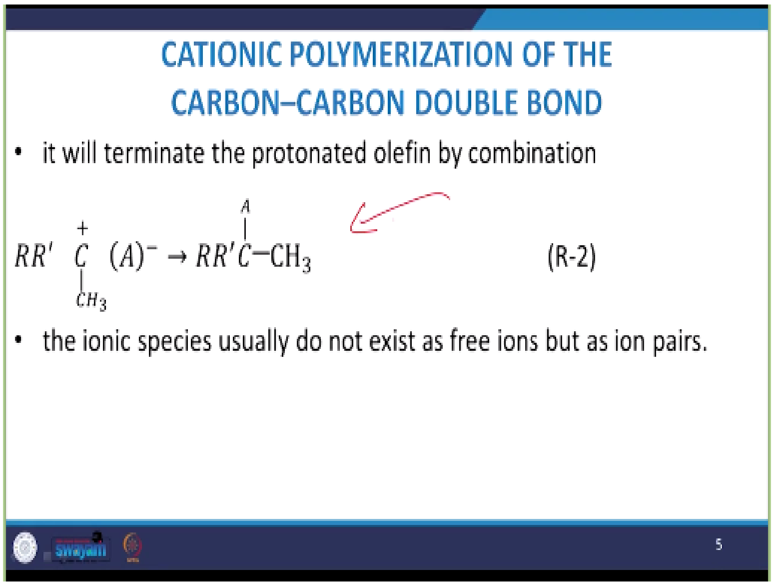

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

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So, this is one of the the example of this type of thing. , the ionic is species usually do not exist as a free ion, but as ion pair. So, if you recall that in the previous lecture, we discussed about concept of ionic pairs.

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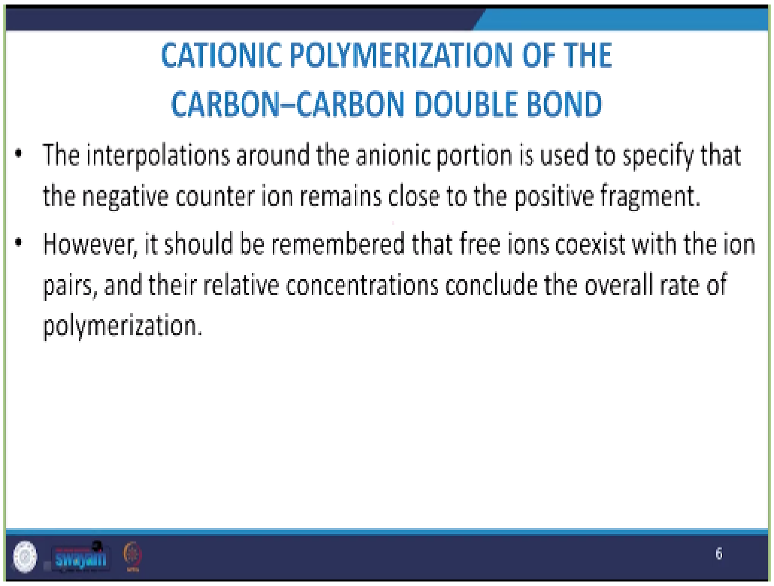

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

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, the interpolation around the anionic portion is used to specify that the negative counter ion remains close to the positive fragments. , however, it should be remembered that the free ion coexist with the ion pair and their relative concentration conclude the overall rate of polymerization. So, this usually this relative concentration play a very, very vital role in the overall rate of polymerization.

, let us have a look about the cationic initiator.

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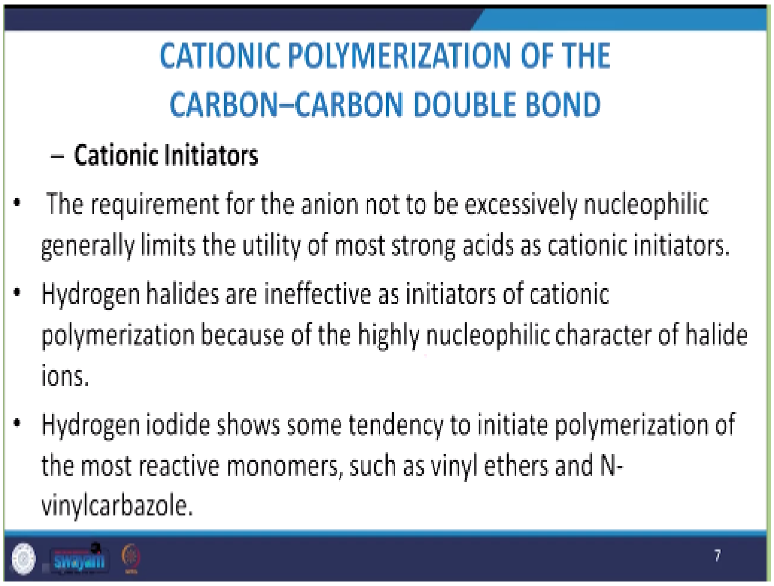

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

– Cationic Initiators

- The requirement for the anion not to be excessively nucleophilic generally limits the utility of most strong acids as cationic initiators.
- Hydrogen halides are ineffective as initiators of cationic polymerization because of the highly nucleophilic character of halide ions.
- Hydrogen iodide shows some tendency to initiate polymerization of the most reactive monomers, such as vinyl ethers and N-vinylcarbazole.

Cationic Initiators

, cationic initiators are equally important as compared to the protonic initiator. , the the requirement for the anion not to be excessively nucleophilic generally limits the utility of most strongest as cationic initiator. , hydrogen halides are usually ineffective as initiator of cationic polymerization, because of highly nucleophilic character of halide ions.

So, that must be very selective things when we discuss about the nucleophilic character of various compounds. , hydrogen iodide this shows some tendency to initiate the polymerization of the most reactive monomers like vinyl ethers or N-vinylcarbazole etcetera. So, it it seems some tendency. apart for this Lewis acids also play a very important role in the cationic polymerization.

Lewis Acid

There are various Lewis acids is being used to initiate the cationic polymerization and generally at low temperature with the formation of high molecular weight polymer in high yields. These include metal halides (e.g., $AlCl_3$, BF_3, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$) and their organometallic derivatives (e.g., $RAlCl_2$, R_2AlCl, R_3Cl).

Lewis acid are most important means of initiating cationic polymerization. Alumunium boron tin, titanium halides these are the most frequently used Lewis acid. So, this this this, this promotes the cationic polymerization. , initiation by Lewis acid is almost or you can see the always requires to proceed much faster in presence of either proton donor referred as sometimes referred as protogen.

Sometimes, you may call the water, hydrogen halide, alcohol and carboxylic acid as a proton donor. Sometimes, carbocation donors catiogens they are also required such as alkyl halides. One of the best example is t-butyl chloride, tri phenyl methyl chloride and esters, ethers, or anhydrides. So, they play a vital role.

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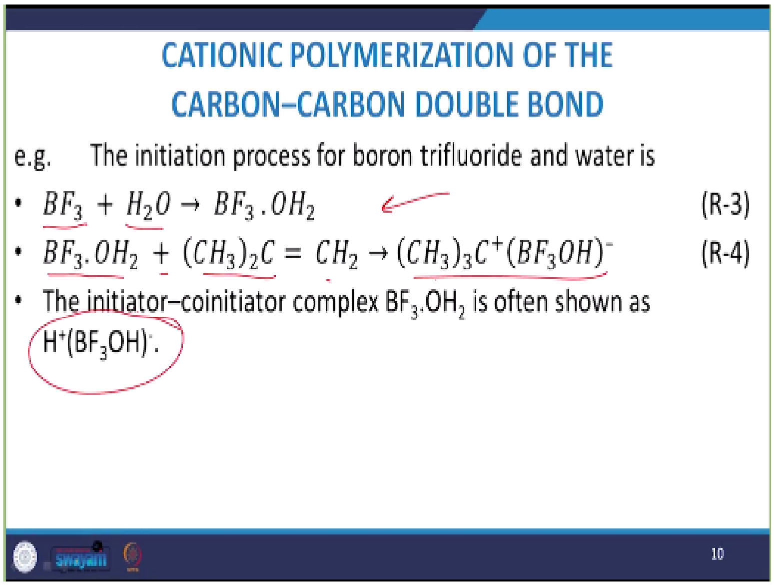

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

e.g. The initiation process for boron trifluoride and water is

- $BF_3 + H_2O \rightarrow BF_3.OH_2$ (R-3)
- $BF_3.OH_2 + (CH_3)_2C = CH_2 \rightarrow (CH_3)_3C^+(BF_3OH)^-$ (R-4)
- The initiator–coinitiator complex $BF_3.OH_2$ is often shown as $H^+(BF_3OH)^-$.

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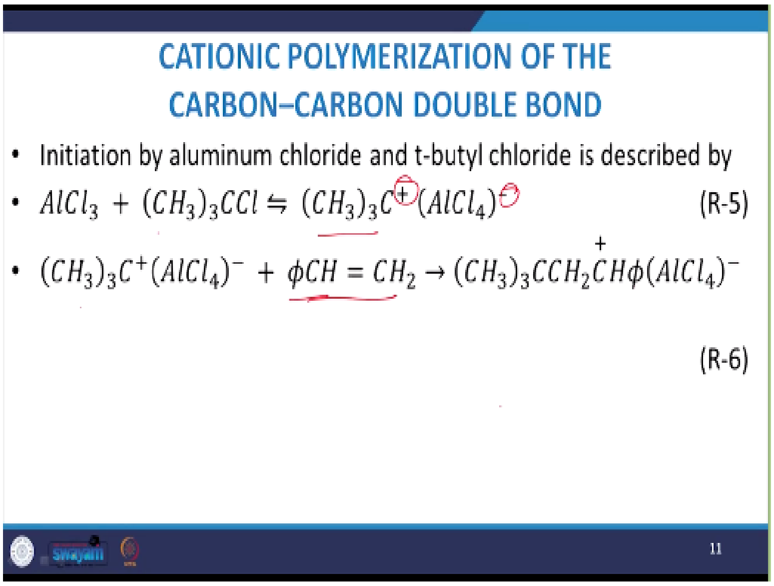

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- Initiation by aluminum chloride and t-butyl chloride is described by
- $AlCl_3 + (CH_3)_3CCl \leftrightharpoons \underline{(CH_3)_3C}^{\oplus}(AlCl_4)^{\ominus}$ (R-5)
- $(CH_3)_3C^+(AlCl_4)^- + \underline{\phi CH = CH_2} \rightarrow (CH_3)_3CCH_2\overset{+}{C}H\phi(AlCl_4)^-$

(R-6)

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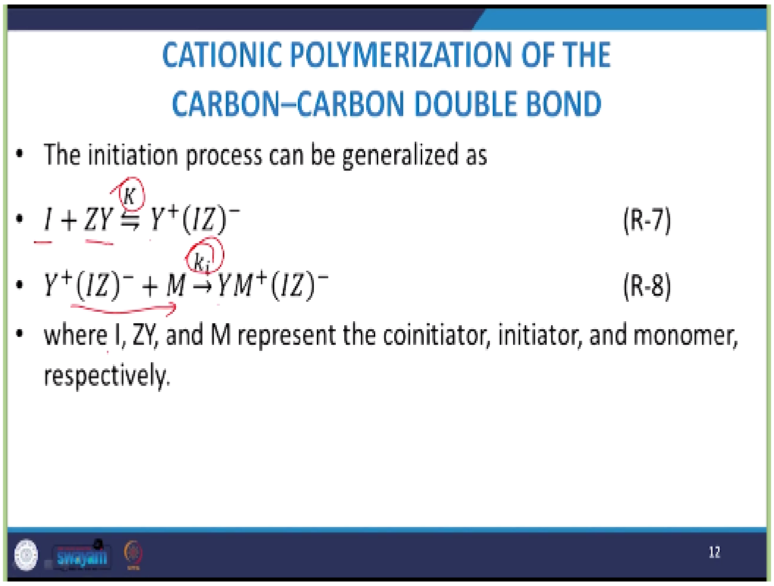

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- The initiation process can be generalized as
- $\underline{I} + \underline{ZY} \overset{\textcircled{K}}{\leftrightharpoons} Y^+(IZ)^-$ (R-7)
- $\underline{Y^+(IZ)^- + M} \overset{\textcircled{k_i}}{\rightarrow} YM^+(IZ)^-$ (R-8)
- where I, ZY, and M represent the coinitiator, initiator, and monomer, respectively.

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where I, ZY, and M represent the coinitiator, initiator, and monomer, respectively.

So, this is the basic chemistry behind this initiation process. , initiation by a combination of a Lewis acid and protogen or cationogen has the advantage over initiation by Bronsted acid that the anion IZ$^-$ is far less nucleophilic than A$^-$. , this prolongs the effect life of propagating carbocation allows the propagation to proceed to the higher molecular weight.

, initiation by the combination of an alkyl halide and the Lewis acid this can be achieved by using the hydrogen halide and a Lewis acid. So, the alkyl halide thus produced in situ by addition of hydrogen halide to monomer followed by the reaction with the Lewis acid. , usually there is an evidence that Lewis acid initiate a slow polymerization in some cases or some system, but very rarely or not in the most of the system.

, usually these this slow polymerization system by a self ionisation process, in addition to the coinitiation process. , self ionisation process is again very crucial or very important in the cationic polymerization. , people have suggested the two mechanism for the self initiation.

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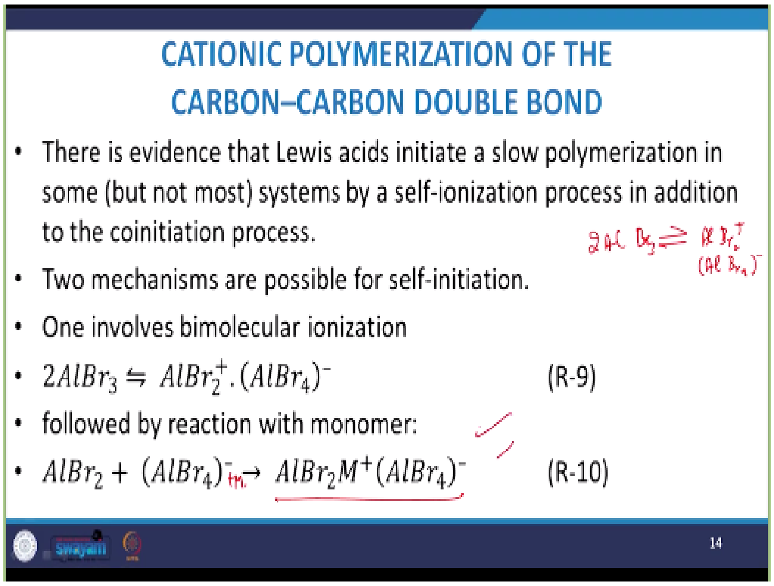

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- There is evidence that Lewis acids initiate a slow polymerization in some (but not most) systems by a self-ionization process in addition to the coinitiation process.
- Two mechanisms are possible for self-initiation.
- One involves bimolecular ionization
- $2AlBr_3 \leftrightharpoons AlBr_2^+.(AlBr_4)^-$ (R-9)
- followed by reaction with monomer:
- $AlBr_2 + (AlBr_4)^- \xrightarrow{M} \underline{AlBr_2M^+(AlBr_4)^-}$ (R-10)

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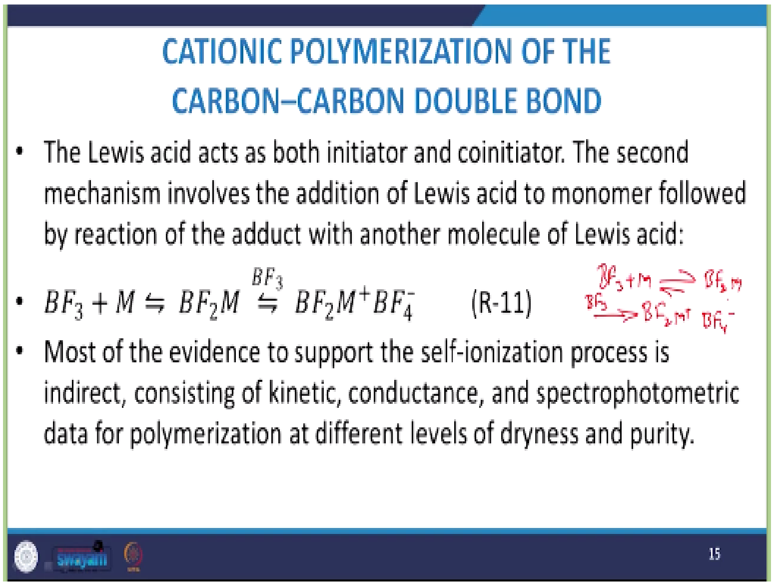

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- The Lewis acid acts as both initiator and coinitiator. The second mechanism involves the addition of Lewis acid to monomer followed by reaction of the adduct with another molecule of Lewis acid:
- $BF_3 + M \leftrightharpoons BF_2M \overset{BF_3}{\leftrightharpoons} BF_2M^+BF_4^-$ (R-11)
- Most of the evidence to support the self-ionization process is indirect, consisting of kinetic, conductance, and spectrophotometric data for polymerization at different levels of dryness and purity.

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$\xrightarrow{BF_3} BF_2M^+ \; BF_4^-$

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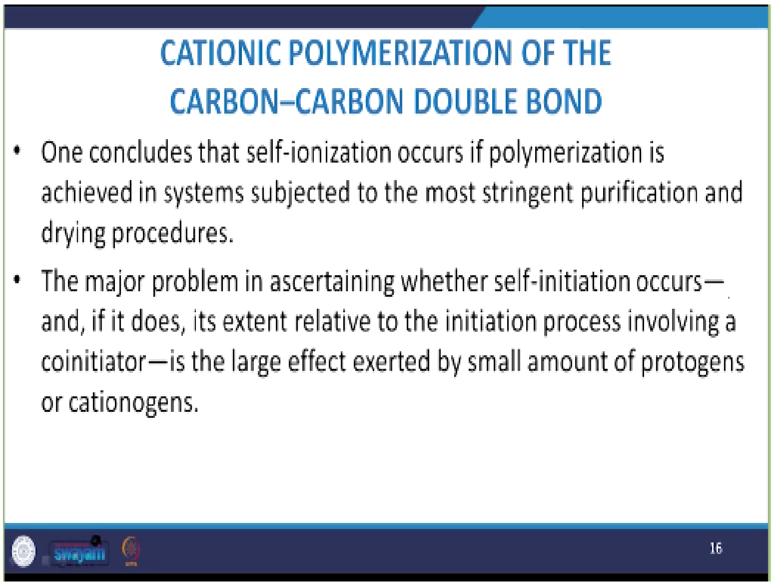

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- One concludes that self-ionization occurs if polymerization is achieved in systems subjected to the most stringent purification and drying procedures.
- The major problem in ascertaining whether self-initiation occurs—and, if it does, its extent relative to the initiation process involving a coinitiator—is the large effect exerted by small amount of protogens or cationogens.

So, one can conclude that the self ionisation occurs if polymerization is achieved in system that is subjected to the most stringent purification and drying protocols. The major problem which people may face in ascertaining whether the self initiation occurs and if it does its extent relative to the initiation process involving a coinitiator. , this is the large effect exerted by the small amount of protogens or cationogens.

Thus for example, water concentrations of 10^{-3} M are sufficient to increase the initiation rate by a factor of 10^3 for $TiCl_4$ and $AlCl_3$ in $CH2Cl_2$.

Sterically hindered pyridines (SHP) are generally active proton scavengers but do not react with Lewis acids or carbocations; in other words, steric hindrance cuts down on the reactivity of the nitrogen toward electrophilic species larger than protons.

The presence of SHP results in complete inhibition of polymerization in some systems but only lowered reaction rates in other systems.

Activity of initiator-coinitiator complex

The activity of an initiator–coinitiator complex is dependent on its ability to donate a proton or carbocation to the monomer, which, in turn, depends on the **initiator, coinitiator, solvent, and monomer**.

The extent of formation of the initiator–coinitiator complex (i.e., the value of K) and its rate of addition to monomer (i.e., the value of k_i) generally increase with increasing acidity of the Lewis acid coinitiator.

Lewis acidity for different metals generally **increases with increasing atomic number** in each group (vertical row of periodic table):

Ti > Al > B; Sn > Si; Sb > As

For any metal, Lewis acidity **increases with increasing oxidation state**,

for example, **$TiCl_4 > TiCl_2$**

Ligands increase Lewis acidity in the order:

F > Cl > Br > I > RO > RCOO > R

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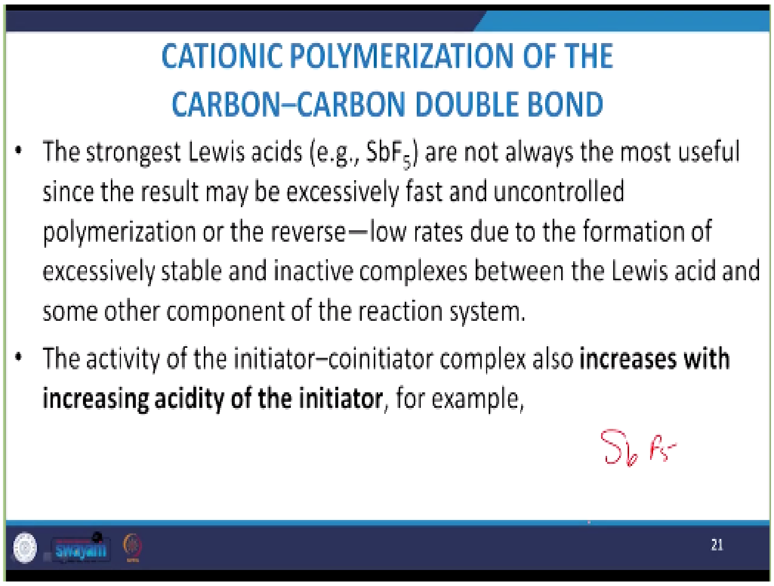

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- The strongest Lewis acids (e.g., SbF_5) are not always the most useful since the result may be excessively fast and uncontrolled polymerization or the reverse—low rates due to the formation of excessively stable and inactive complexes between the Lewis acid and some other component of the reaction system.
- The activity of the initiator–coinitiator complex also **increases with increasing acidity of the initiator**, for example,

SbF_5

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The activity of the initiator–coinitiator complex also **increases with increasing acidity of the initiator**, for example,

hydrogen chloride > **acetic acid** > **nitroethane** > **phenol** > **water** > **methanol** > **acetone** in the polymerization of isobutylene with tin(IV) chloride

A word of caution regarding these generalizations—the order of activity of a series of initiators or coinitiators may differ depending on the identity of the other component, monomer, solvent, or the presence of competing reactions.

Usually in a series of initiator or coinitiator, sometimes it may differ depending on the identity of other component monomer, solvent or the presence of other competing reactions. So, sometimes the intermediates they play a vital role sometimes some byproduct may create, so, all these things need to be addressed during this particular process. And especially when you decide or when you discuss the activity of those initiator or coinitiator.

Initiation through Halogen

Chlorine, bromine, and iodine act as cationogens in the presence of the more active Lewis acids such as trialkylaluminum or dialkylaluminum halide.

The initiating species is the halonium ion X^+ present in low concentration via the equilibrium reaction between Lewis acid and halogen.

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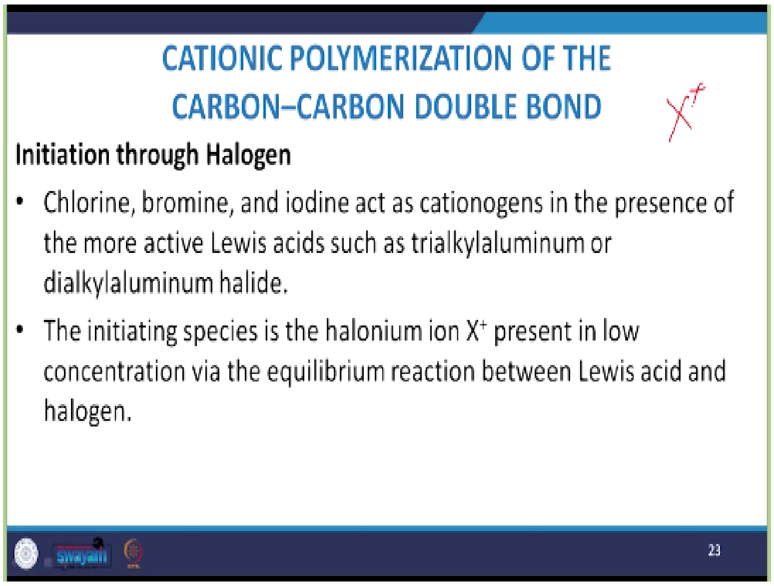

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

X^{+}

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Iodine is unique among the halogens in that it initiates polymerization of the more reactive monomers (styrene, vinyl ether, acenaphthylene. N-vinylcarbazole) even in the absence of a Lewis acid.

Iodine is not the actual initiator in this system. Iodine adds to the double bond to form a diiodide that eliminates hydrogen iodide.

So, the mechanism is quite simple that it adds a double bond, then the dio di-iodide form and that eliminates the hydrogen iodide. , this hydrogen iodide is generated by this process act as the cationogens with iodine acting as the Lewis acid to form the initiating system. , see, when we talk about this hydrogen iodide, this is not the efficient initiator because iodide ion is too nucleophilic and you see that we have discussed this particular thing in the previous slide.

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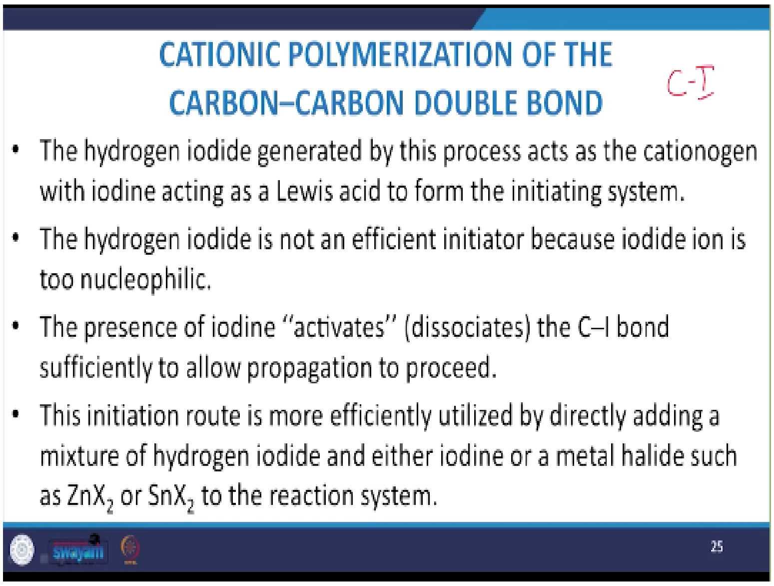

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

C-I

- The hydrogen iodide generated by this process acts as the cationogen with iodine acting as a Lewis acid to form the initiating system.
- The hydrogen iodide is not an efficient initiator because iodide ion is too nucleophilic.
- The presence of iodine "activates" (dissociates) the C–I bond sufficiently to allow propagation to proceed.
- This initiation route is more efficiently utilized by directly adding a mixture of hydrogen iodide and either iodine or a metal halide such as ZnX_2 or SnX_2 to the reaction system.

The hydrogen iodide generated by this process acts as the cationogen with iodine acting as a Lewis acid to form the initiating system. The hydrogen iodide is not an efficient initiator because iodide ion is too nucleophilic. The presence of iodine, this activates or sometime dissociates the the C-I bond sufficiently to allow the propagation to proceed. So, sometimes when you look into the after initiation if you look into the propagation then you need to look into this particular aspect. This initiation route is more efficiently utilised by directly adding a mixture of hydrogen iodide and either iodine or metal halide sometimes referred to as ZnX_2 or SnX_2 to the reaction system.

Photoinitiation by Onium Salts

Aryldiazonium ($ArN_2^+Z^-$), diaryliodonium ($Ar_2I^+Z^-$), and triarylsulfonium ($Ar_3S^+Z^-$) salts, where Z^- is a nonnucleophilic and photostable anion such as tetrafluoroborate (BF_4^-), hexafluoroantimonate (SbF_6^-), and tetraperfluorophenylborate [$(C_6F_5)_4B^-$], and hexafluorophosphate (PF_6^-), are effective photoinitiators of cationic polymerization. Aryldiazonium salts have limited practical utility because of their inherent thermal instability. Diaryliodonium and triarylsulfonium salts are very stable—so stable that their mixtures with highly reactive monomers do not undergo polymerization on long-term storage.

Some of these initiators have found commerical application in the photo crosslinking of epoxy resins through cationic polymerization.

Diaryliodonium and triarylsulfonium salts act as photoinitiators of cationic polymerization.

So, sometimes the photon of photonic energy being used to induce or initiate the cationic polymerization, but you require certain energy levels certain level of actuation to initiate that particular reaction.

Photolytic celeavage of an Ar─I or Ar─S bond yields a radical–cation that reacts with HY to yield an initiator–coinitiator complex that acts as a proton donor to initiate cationic polymerization.

$Ar_2I^+(PF_6^-) \xrightarrow{hv} Ar_2I.^+ (PF_6^-) + Ar\cdot$ (R-12)

$Ar_2I.^+ (PF_6^-) \xrightarrow{HY} ArI + Y\cdot + H^+(PF_6^-)$ (R-13)

$Ar_3S^+(SbF_6^-) \rightarrow Ar_3S\cdot^+ (SbF_6^-) + Ar\cdot$ (R-14)

$Ar_3S\cdot^+ (SbF_6^-) \xrightarrow{HY} Ar_2S + Y\cdot + H^+(SbF_6^-)$ (R-15)

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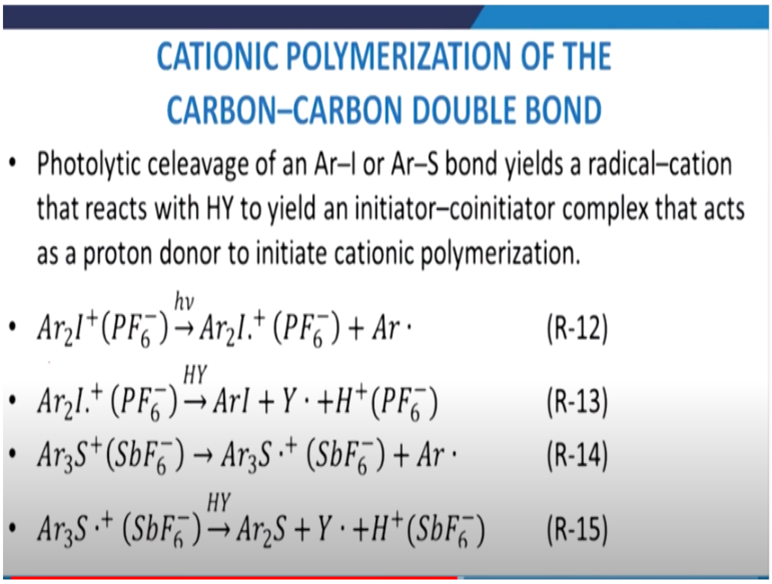

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

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- $Ar_2I.^+ (PF_6^-) \xrightarrow{HY} ArI + Y\cdot + H^+(PF_6^-)$ (R-13)
- $Ar_3S^+(SbF_6^-) \rightarrow Ar_3S\cdot^+ (SbF_6^-) + Ar\cdot$ (R-14)
- $Ar_3S\cdot^+ (SbF_6^-) \xrightarrow{HY} Ar_2S + Y\cdot + H^+(SbF_6^-)$ (R-15)

So, if you see this particular reaction here, these two with the help of this photoelectric effect they form the various complexes over here and then they subsequently they may have react with the monomer to initiate these cationic polymerization or to be more precise the the with respect to the carbon carbon double bond. This HY this may be a solvent or some other deliberately added substances sometimes like alcohol or sometimes this may have a water with reliable hydrogen.

Overall the overall the process is photo electrically induced, the redox reaction between the carbon radical and HY. Interestingly, the same result has been achieved thermally without the photolysis by coupling the appropriate reducing agent, sometimes ascorbic acid or copper benzoate with the dry aryl odium salt. So, this people have achieved this type of a thing with some alternate routes.

By spectral response usually referred as the absorption wavelength, absorption coefficient, quantum yield, photosensitivity etcetera. And the thermal stability of this onium salt photoinitiator this can be altered by modifying the structure of aromatic group in the cationic portion. , sometimes this particular approach is useful for doctored polymers that means, the you can change the chain you can change the the various groups by either grafting or by some other means.

So, the choice of the anion in the onium salt alter its behaviour in polymerization by altering the identity of initiating species. So, cationic photoinitiators they are used in coating, printing inks, adhesives, sealant, photoresist applications, where you can use sometimes these kind of photoinitiators are used to crosslink the things so that the mechanical strength among the polymeric chain or the surfaces can be improvised.

So, they are having a very wide application in in due course of time. , sometimes people may refer the other applications these are involved the vinyl ether polymerizations or sometimes the ring opening polymerization of epoxy monomers. So, as we were discussing that these may a create a creature of the doctored polymers. , there are some differences between the radical and cationic photopolymerization.

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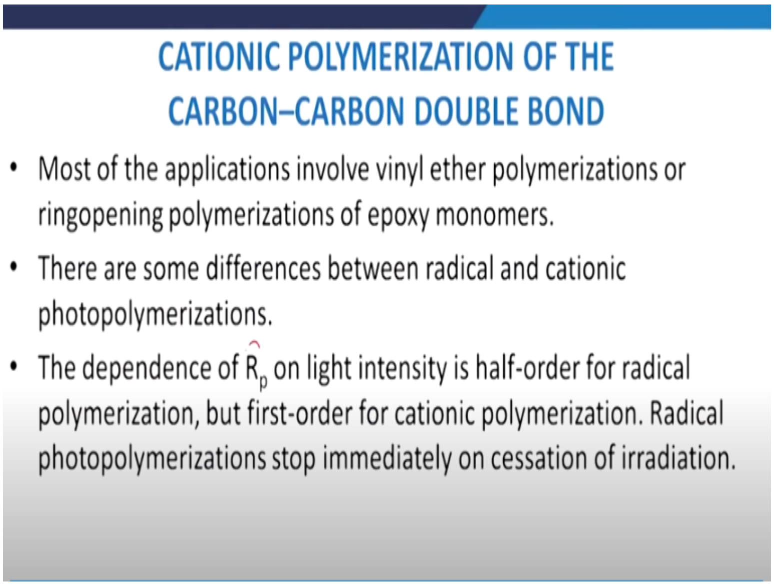

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- Most of the applications involve vinyl ether polymerizations or ringopening polymerizations of epoxy monomers.
- There are some differences between radical and cationic photopolymerizations.
- The dependence of $\overset{\frown}{R}_p$ on light intensity is half-order for radical polymerization, but first-order for cationic polymerization. Radical photopolymerizations stop immediately on cessation of irradiation.

that dependence on R_p on the light intensity of is usually half order of radical polymerization, but first order for the cationic polymerization, the radical polymerization is stopped immediately on cessation of irradiation. So, this is the you can say the hairline difference between the radical and cationic photopolymerization. A more strict cationic photopolymerization once initiated, they continue in the absence of light because most of the reaction system chosen are living polymerization.

If you recall that we discussed the living polymers, living polymers and dormant polymers. So, usually, when we talk about this cationic polymerization, then especially under the aegis of photopolymerization, then we have to look into these living polymerization concept too. ,

Electroinitiation

Electrolytic or electroinitiated polymerization involves initiation by cations formed via electrolysis of some component of the reaction system (monomer, solvent, electrolyte, or other deliberately added substance)

May be attributed to the monomer, solvent, electrolyte or other deliberately added substances. xSo, the initiation in the presence of perchlorate, ion, perchlorate ion is again a very important for this cationic initiation. So, perchlorate ion usually proceeds by oxidation of perchlorate followed by the hydrogen abstraction.

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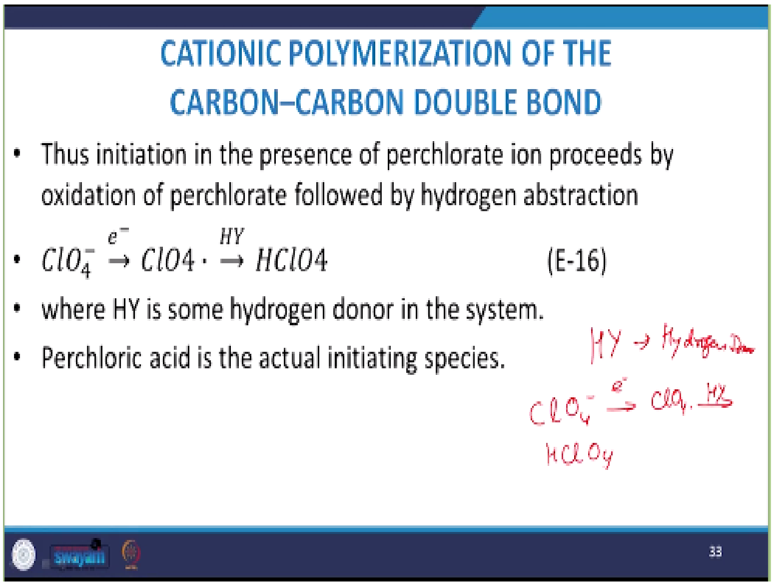

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- Thus initiation in the presence of perchlorate ion proceeds by oxidation of perchlorate followed by hydrogen abstraction
- $ClO_4^- \xrightarrow{e^-} ClO4\cdot \xrightarrow{HY} HClO4$ (E-16)
- where HY is some hydrogen donor in the system.
- Perchloric acid is the actual initiating species.

HY → Hydrogen Don

$ClO_4^- \xrightarrow{e^-} ClO_4\cdot \xrightarrow{HY}$

$HClO_4$

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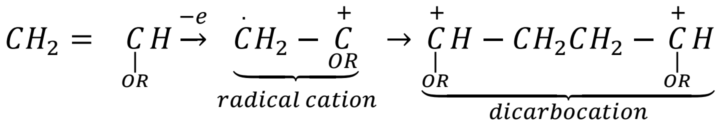

$$CH_2 = \underset{OR}{\underset{|}{C}}H \xrightarrow{-e} \underbrace{\dot{C}H_2 - \overset{+}{\underset{OR}{C}}}_{radical\ cation} \rightarrow \underbrace{\overset{+}{\underset{OR}{\underset{|}{C}}}H - CH_2CH_2 - \overset{+}{\underset{OR}{\underset{|}{C}}}H}_{dicarbocation}$$ (E-16)

This monomer radical cations, usually they are formed by electron transfer from monomer either to the anode or to a polynuclear aromatic compound. Usually when we talk about this electro initiated then propagation is usually proposed to proceed via carbocation formed by the dimerization of radical cation. Remember this is slightly different what we discussed in previous slides previous concept that is the radical because electron transfer from monomer maybe either to the anode or any kind of a polynuclear compound.

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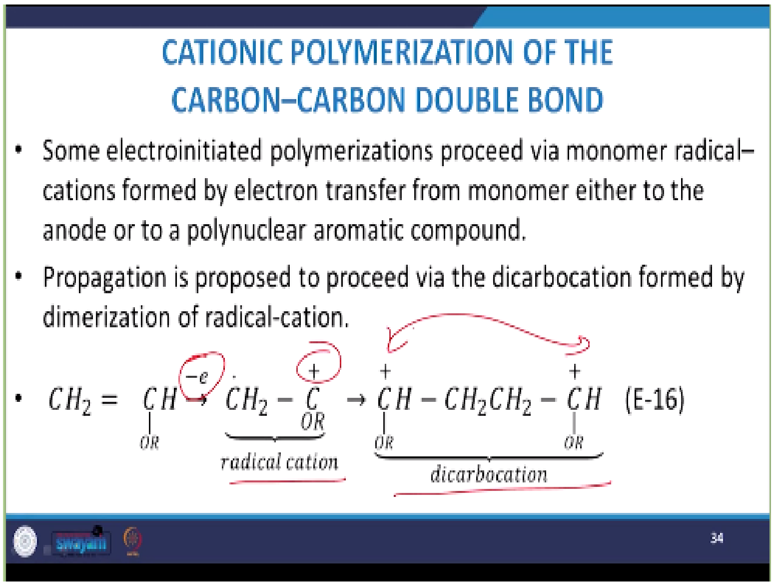

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

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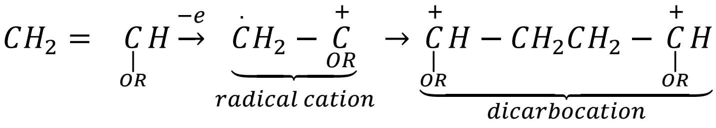
So, let us take the example



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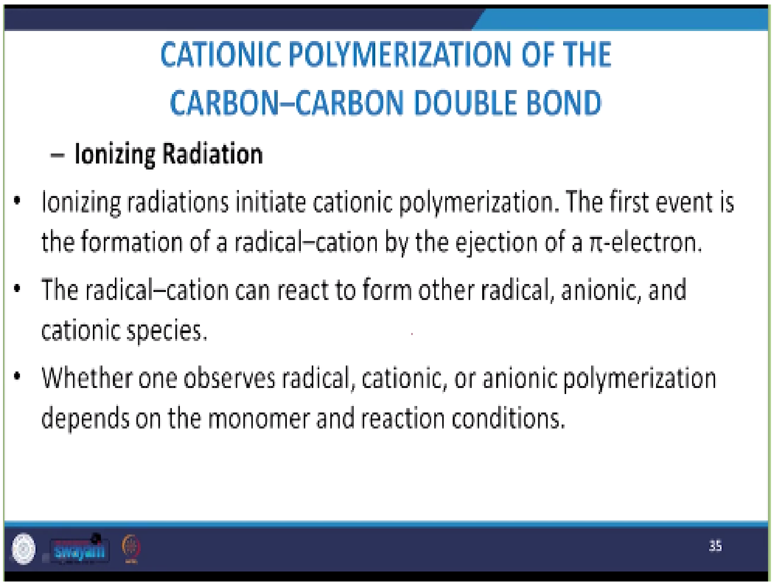

CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

– Ionizing Radiation

- Ionizing radiations initiate cationic polymerization. The first event is the formation of a radical–cation by the ejection of a π-electron.
- The radical–cation can react to form other radical, anionic, and cationic species.
- Whether one observes radical, cationic, or anionic polymerization depends on the monomer and reaction conditions.

So, this particular aspect is again very important and people are using this particular concept for carrying out various kinds of cationic polymerization for the production of specific polymers. , let us have a look about another concept that is ionising radiation. , you see that in this particular chapter, we are discussing all possible available tools for initiating for propagation under the aegis of cationic polymerization.

So, ionising radiation this usually initiate the cationic polymerization. The first event is the formation of a radical cation and by the ejection of pi electron. , basic concept is that how we can generate this radical cation. Maybe by photo photoelectric effect, maybe by some perchloric acids, maybe by the any kind of radiating species. , here you may use some pi electrons. This the the radical cation this further can react to form other radical anion and cationic species.

So, first thing is that you need to initiate this thing with the help of a pilot trawl and then the thus form the radical cation and they can further react with the other radicals, sometimes other anionic species or cationic species. So, whether one observes radical or cationic or anionic polymerization, it depends on the monomer and the reaction conditions.

Reaction conditions sometimes may prevail about the intensity of those pi electron, sometimes the radiation level of the media and then the concentration and other things related to the the reaction media. , one of the best example which will we would like to discuss is that is styrene. This styrene can undergo polymerization, but all 3 mechanisms which we discussed.

For super dry reaction system sometimes carried out at 25 degrees Celsius, the overwhelming mechanism of polymerization is cationic with about 2.5% anionic and sometimes the negligible react radical reaction. So, the radical polymerization becomes the dominant process with increasing the reaction temperature. The sometimes the presence of water or you may say the other protogens they decreases, decrease the extent of ionic polymerization relatively to radical polymerization.

One of the best example of such category is isobutylene. , it shows the negligible tendency to undergo any polymerization except cationic and that occurs only at you can say the lower temperature, usually, you need to carry out such type of thing below zero degrees Celsius. So, considerably below zero degrees Celsius is important in this particular polymerization process.

If you see the higher temperature see people have attempted to carry out this ionising aspect at a higher temperature, but at higher temperature no polymerization occurs. Since, the cationic reaction is usually not favoured under higher temperature and sometimes people may ask that what is the higher temperature So, always above zero degrees Celsius is referred as the higher temperature.

So, the actual species those who are responsible for the cationic polymerization they initiated by ionising radiation is usually not established as on date. The most frequently described mechanism it postulates the reaction between the radical cation and monomer to form the separate cationic and radical species. Subsequently, the cationic species propagates rapidly, while the radical species propagate very slowly.

So, this is the difference between the cationic species and the radical species. The former it propagates very rapidly or fastly, the radical species or latter one propagates small is very slow or you can say infinitely small aspects. , the proposed mechanism for isobutylene because once we established the polymerization process or development of this cationic polymerization.

, as far as the examples are in question, the best example as we discussed that is the isobutylene. So, isobutylene the proposed mechanism of isobutylene involves the transfer of a hydrogen radical from monomer to the radical cation to form the tertiary butyl carbo cation and unreactive alkyl, allyl type of radicals.

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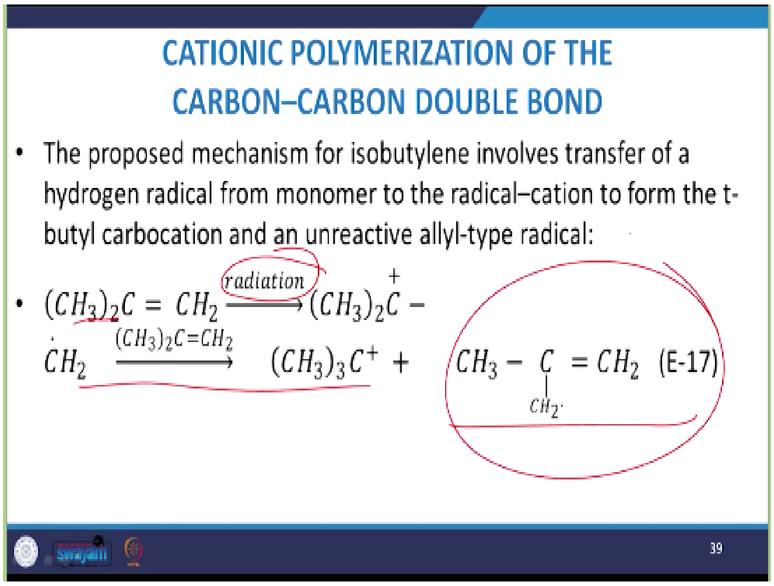
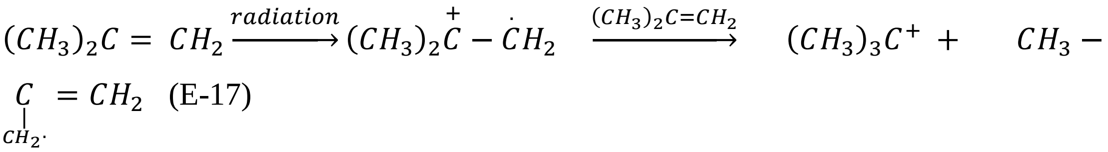


CATIONIC POLYMERIZATION OF THE CARBON–CARBON DOUBLE BOND

- The proposed mechanism for isobutylene involves transfer of a hydrogen radical from monomer to the radical–cation to form the t-butyl carbocation and an unreactive allyl-type radical:
- $(CH_3)_2C = CH_2 \xrightarrow{radiation} (CH_3)_2\overset{+}{C} - \dot{C}H_2 \xrightarrow{(CH_3)_2C=CH_2} (CH_3)_3C^+ + CH_3 - \underset{\substack{| \\ CH_2\cdot}}{C} = CH_2$ (E-17)

So, you can see over here that this is with the help of a radiation and you see that these are the the polymeric reaction product which we are discussing that this particular allyl type of things practically inactive.



$$(CH_3)_2C = CH_2 \xrightarrow{radiation} (CH_3)_2\overset{+}{C} - \dot{C}H_2 \xrightarrow{(CH_3)_2C=CH_2} (CH_3)_3C^+ + CH_3 - \underset{\substack{| \\ CH_2\cdot}}{C} = CH_2 \quad \text{(E-17)}$$

So, at last when we discuss about the mechanism of this isobutylene the evidence for this mechanism is based on mass spectroscopy of gas phase radiolysis of isobutylene which may not be applicable to the typical liquid phase polymerization system. , initiation in some times we may refer to have a condensed system. So, initiation in condensed system may follow or sometimes follow the same course as electro initiation coupling of radical cations to form the dicarbocations.

Cationic polymerization, when we say that, it is initiated by ionising radiation, usually markedly different from other cationic polymerization in that the propagating species is a free ion remote from a counter ion. So, this is the difference with the comparative note between the ionising radiation induced cationic polymerization with other cationic polymerization. So, this is the basic difference between these two protocols.

Sometimes, overall electrical neutrality is maintained by electron trapped by the monomer. So, at last in this particular chapter, or in this particular lecture, we discussed the cationic polymerization of carbon carbon double bond with the help of several examples, specific specifically we discussed the common example. And since this cationic polymerization is extremely important in the development of various industrial oriented polymers.

So, that is why and we discussed all kind of initiation tools available as on date maybe by the radiation initiator, maybe by the photoelectric radiations, maybe with the help of Lewis acids etcetera.

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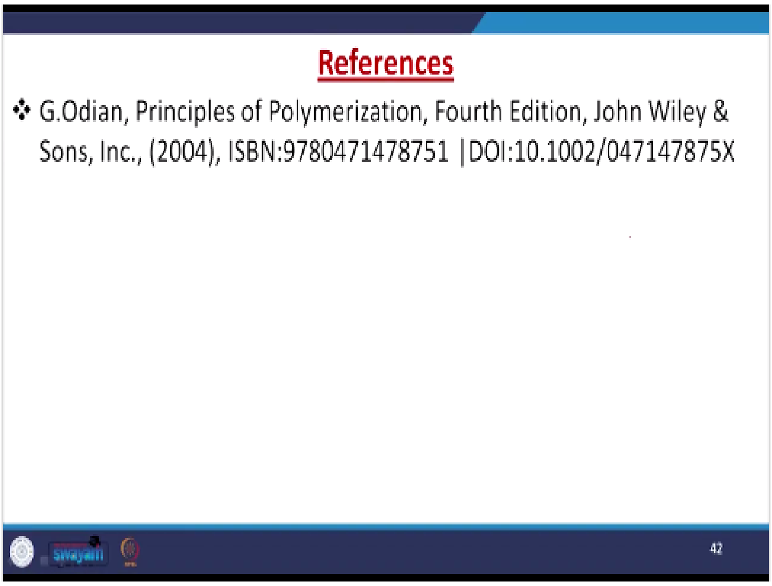

References

- G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 |DOI:10.1002/047147875X

So in case if you wish to have further study we have listed on example for reference for your for the reading. By this way we are summing up this particular lecture. Thank you very much.