Polymer Reaction Engineering
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Lecture – 57
Ionic Polymerization - II

Welcome to the second part of this ionic polymerization. if you recall that previously we discussed about the classification scheme of various ionic species.

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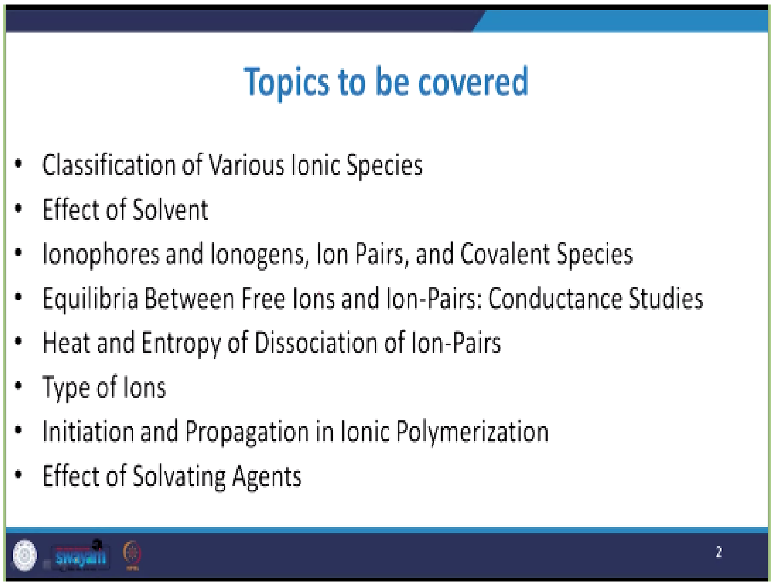

Topics to be covered

- 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

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We had a discussion about the effect of solvent in the polymerization process. We discussed about the ionophores and ionogens. Apart from this we discussed about the ionic pairs and covalent species, in the previous lecture. Thereafter, we discussed about the concept of equilibria between free ions and ionic pairs under the head of conductance studies.

Then, we had a discussion about the heat and entropy of dissociation of those ionic pairs being developed. in this particular lecture, we will discuss about the various types of ions, then, we will discuss about the initiation and propagation steps with respect to the mathematical approach under the aegis of ionic polymerization. And at last we will discuss about the effect of solvating agents.

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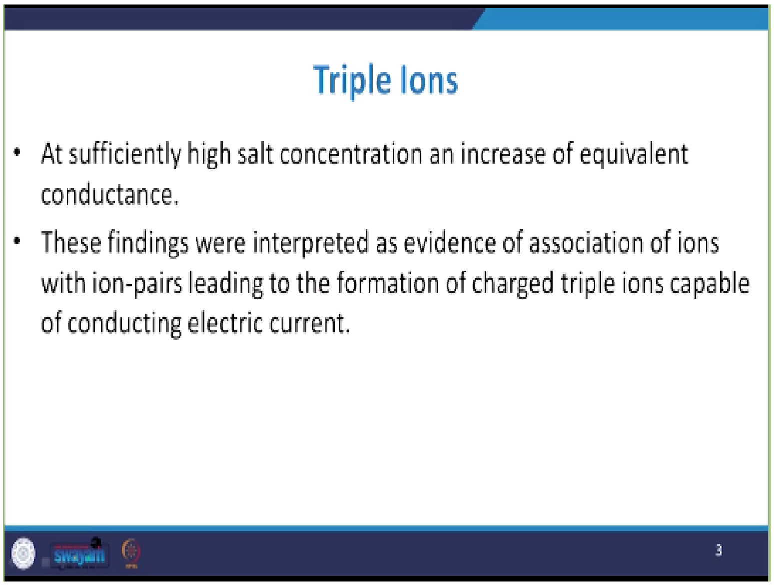

Triple Ions

- At sufficiently high salt concentration an increase of equivalent conductance.
- These findings were interpreted as evidence of association of ions with ion-pairs leading to the formation of charged triple ions capable of conducting electric current.

So, let us start with the triple ions. at sufficiently high salt concentration, there is an increase of equivalent conductance. if you recall that during the process of heat in entropic dissociation, we discussed, the conducts conductance concept. these findings they were interpreted as evidence of association of ions with ionic pairs and sometimes leading to the formation of charged triple ions, and those who are capable of conducting electric current.

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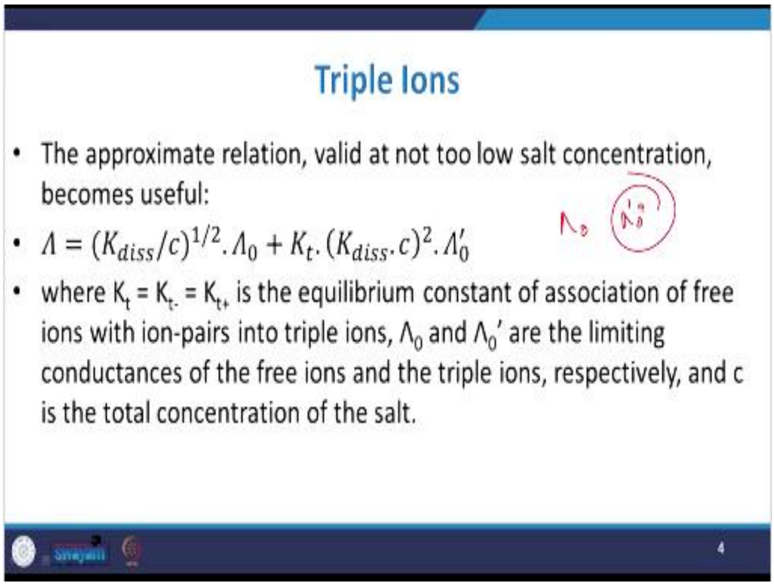

Triple Ions

- The approximate relation, valid at not too low salt concentration, becomes useful:
- $\Lambda = (K_{diss}/c)^{1/2}.\Lambda_0 + K_t.(K_{diss}.c)^2.\Lambda_0'$
- where $K_t = K_{t-} = K_{t+}$ is the equilibrium constant of association of free ions with ion-pairs into triple ions, Λ_0 and Λ_0' are the limiting conductances of the free ions and the triple ions, respectively, and c is the total concentration of the salt.

Λ_0 Λ_0'

these triple ions, sometimes they approximate relations, they possess approximate relations and these are valid at not too low salt concentration and sometimes it becomes useful.

$$\Lambda = (K_{diss}/c)^{1/2}.\ \Lambda_0 + K_t.(K_{diss}.c)^2.\ \Lambda_0'$$

where $K_t = K_{t-} = K_{t+}$ is the equilibrium constant of association of free ions with ion-pairs into triple ions, Λ_0 and Λ_0' are the limiting conductances of the free ions and the triple ions, respectively, and c is the total concentration of the salt.

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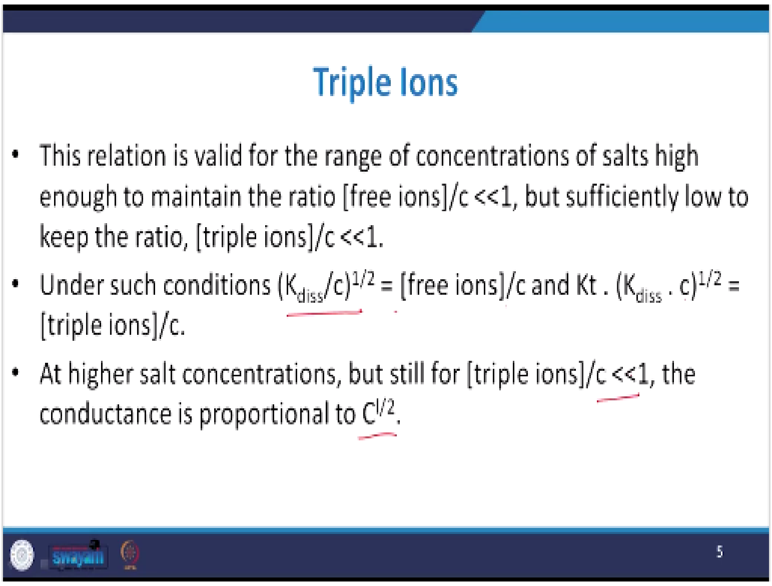

Triple Ions

- This relation is valid for the range of concentrations of salts high enough to maintain the ratio [free ions]/c <<1, but sufficiently low to keep the ratio, [triple ions]/c <<1.
- Under such conditions $(K_{diss}/c)^{1/2}$ = [free ions]/c and Kt . $(K_{diss} . c)^{1/2}$ = [triple ions]/c.
- At higher salt concentrations, but still for [triple ions]/c <<1, the conductance is proportional to $C^{l/2}$.

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Under such conditions $(K_{diss}/c)^{1/2}$ = [free ions]/c and Kt . $(K_{diss} . c)^{1/2}$ = [triple ions]/c.

At higher salt concentrations, but still for [triple ions]/c <<1, the conductance is proportional to $C^{l/2}$.

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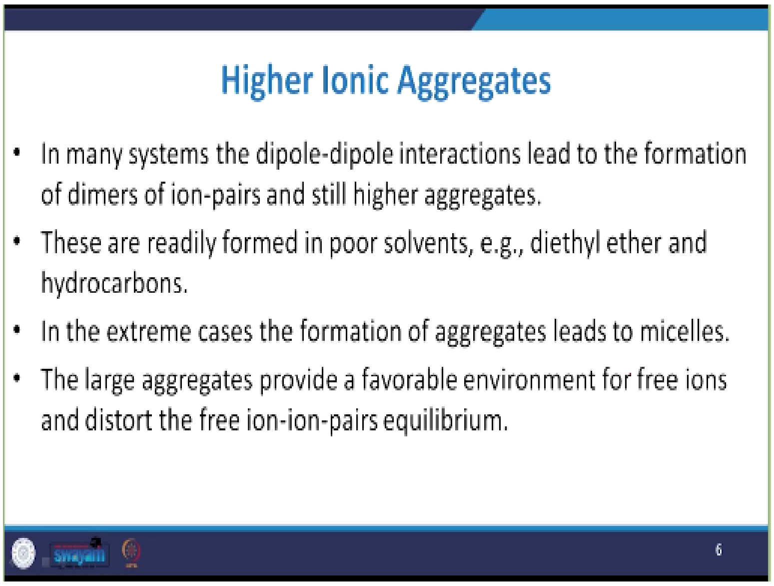

Higher Ionic Aggregates

- In many systems the dipole-dipole interactions lead to the formation of dimers of ion-pairs and still higher aggregates.
- These are readily formed in poor solvents, e.g., diethyl ether and hydrocarbons.
- In the extreme cases the formation of aggregates leads to micelles.
- The large aggregates provide a favorable environment for free ions and distort the free ion-ion-pairs equilibrium.

When we talk about the higher ionic aggregates, in several systems that dipole-dipole interactions sometimes lead to the formation of dimers of ionic pairs and still higher aggregates. So, sometimes it may create the agglomeration problem and this may lead to the higher molecular weight and higher viscosity and ultimately creates a problem to the processability of those polymer being generated.

These are the readily formed in the poor solvents that is the diethyl ether and hydrocarbons. in the extreme cases of formation of aggregate this sometimes lead to the micelles or sometimes they may create the formation of micelles. the large aggregates sometimes they provide a favourable environment for free ions and distort the free ion-ion pairs equilibrium.

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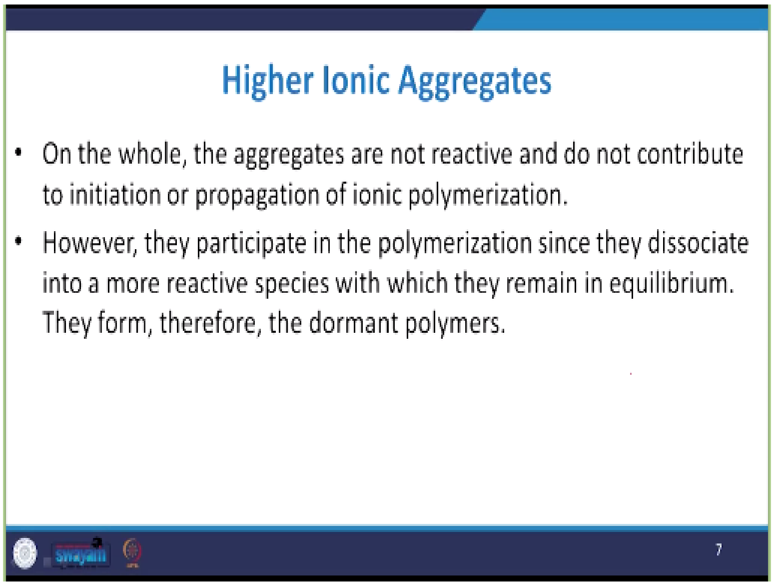

Higher Ionic Aggregates

- On the whole, the aggregates are not reactive and do not contribute to initiation or propagation of ionic polymerization.
- However, they participate in the polymerization since they dissociate into a more reactive species with which they remain in equilibrium. They form, therefore, the dormant polymers.

On the whole the aggregates they are not reactive and they do not contribute to initiation or propagation of ionic polymerization. However, they participate in the polymerization since they dissociate into a more reactive species with which they remain in equilibrium and they form therefore, the dormant polymers. let us have a look about the initiation and propagation in ionic polymerization.

And we will do some mathematical approaches and discuss the mathematical approaches those who are attributed to these ionic polymerization. These propagation perpetuated by the positively charged end group or induced by a positive end have a reactive dipole. It is sometimes known as cationic or pseudo cationic polymerization. So, similarly, in anionic or pseudo anionic polymerization ensues when a negatively charged end group or negative end of dipole this constitutes the active propagating centre.

So, as a whole the initiator or its fragment remains associated in some fashion with the active end of an ionically growing macromolecule during the entire period of its growth. So, let us take the example that is the counter ion accompanying the initiating anion mentioned in the in this particular paragraph become the champion of a newly formed Polymer.

Therefore, the propagation constant and the mode of monomer addition and the other characteristics those who are featured in ionic polymerization are usually affected by the nature of initiator. And as we discussed earlier that, the initiator, nature of initiator, the concentration of initiator, then the affinity of the initiator with other monomer, this is the very vital issues which need to be addressed during any kind of polymerization, whether it is a radical polymerization or ionic polymerization.

So, in this concept or in this regard the ionic propagation, this differs from radical propagation that since, the initiator does not affect the rate constant of propagation of latter polymerization. So, let us have a look about the the mathematical approach of this initiation propagation in ionic polymerization.

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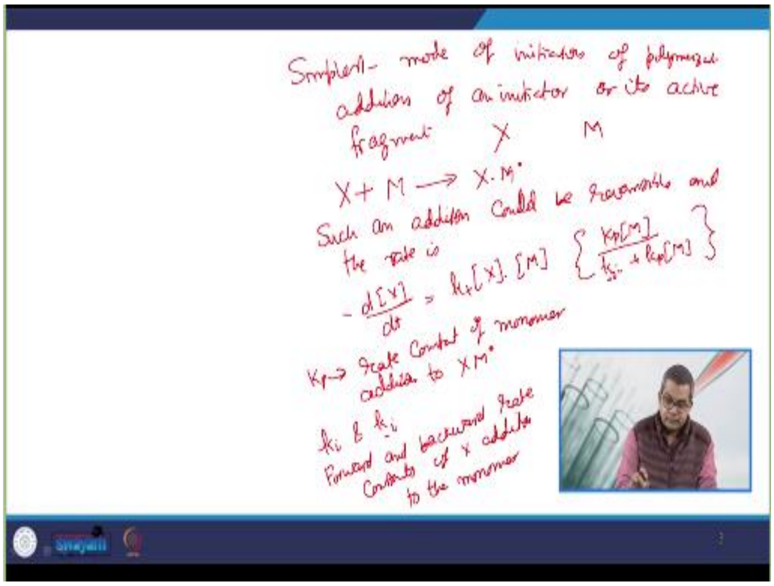

Simplest- mode of initiation of polymerization addition of an initiator or its active fragment X M

$X + M \longrightarrow X.M^*$

Such an addition could be reversible and the rate is

$-\frac{d[X]}{dt} = k_t[X].[M] \left\{ \frac{k_p[M]}{k_{-i} + k_p[M]} \right\}$

$K_p \rightarrow$ rate constant of monomer addition to XM^*

k_i & k_{-i} Forward and backward rate constants of X addition to the monomer

The simplest mode of initiation of polymerization arises upon the addition of an initiator or its active fragment, denoted by X, to a monomer M,

$$X + M \rightarrow X \cdot M^*$$

Such an addition could be reversible and then its rate is given by:

$-\frac{d[X]}{dt} = k_t[X].[M].\left\{\frac{k_p[M]}{k_{-i} + k_p[M]}\right\},$

where k_p denotes the rate constant of monomer addition to X M*, and k_i and k_{-i} are the forward and backward rate constants of the X addition to the monomer.

For $k_{-i} << k_p[M]$ this equation yields the rate of initiation, first order in X and M.

At the other extreme, for $k_{-i} >> k_p[M]$, the - d[X]/dt pertains to the rate of initiator consumption while at equilibrium with the monomer.

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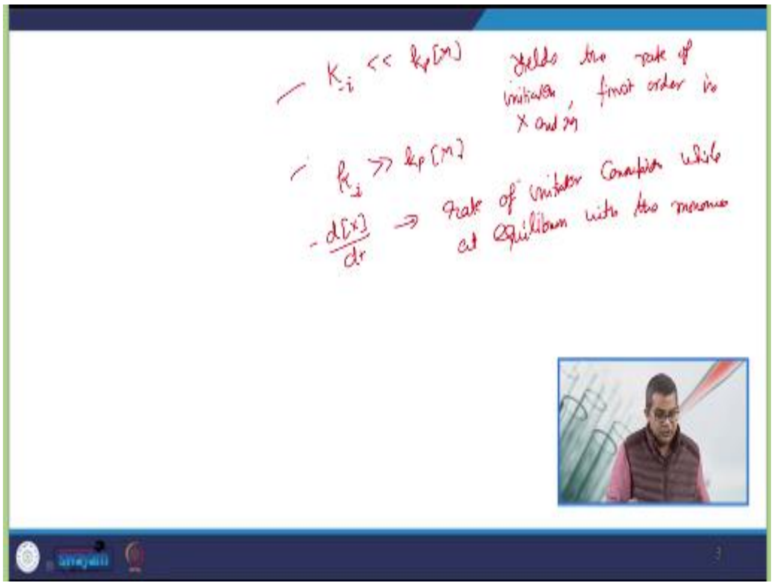

$K_{-i} << k_p[M]$ yields the rate of initiation, first order in X and M

$k_{-i} >> k_p[M]$

$-\frac{d[X]}{dt} \rightarrow$ rate of initiator Consumption while at equilibrium with the monomer

The consumption is then first order in X but second order in M, i.e.,

$$-\frac{d[X]}{dt} = k_p K_e.[X].[M]^2$$

With $K_e = k_i/k_{-i}$

The addition is always exothermic, and when its exothermicity exceeds the activation energy of the monomer addition to X·M* the polymerization speeds up on lowering the temperature and its apparent activation energy is negative.

The minus dX over dt this pertains to the rate of initiator consumption while at equilibrium with the monomer. So, by this way we we can discuss or we can have this these two extreme conditions.

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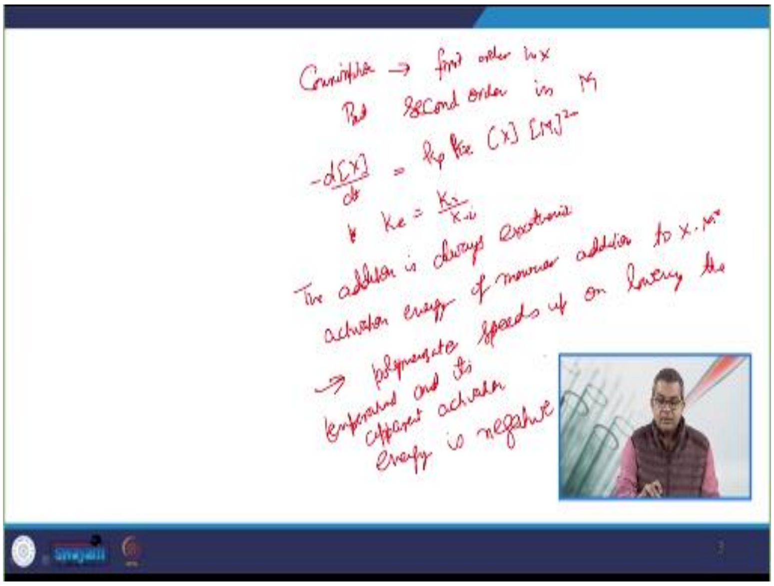

Coinitiation → first order in X

But second order in M

$$-\frac{d[X]}{dt} = k_p K_e [X][M]^2$$

& $K_e = \frac{K_1}{K_{-1}}$

The addition is always exothermic

activation energy of monomer addition to $X.M^+$

→ polymerization speeds up on lowering the temperature and its apparent activation energy is negative

It is beneficial when the rate of initiation is faster than, or at least equal to, the rate of propagation.

Under such conditions polymers of narrow molecular mass distribution could be formed, provided that the system is "living," i.e., the termination and chain-transfer are virtually avoided.

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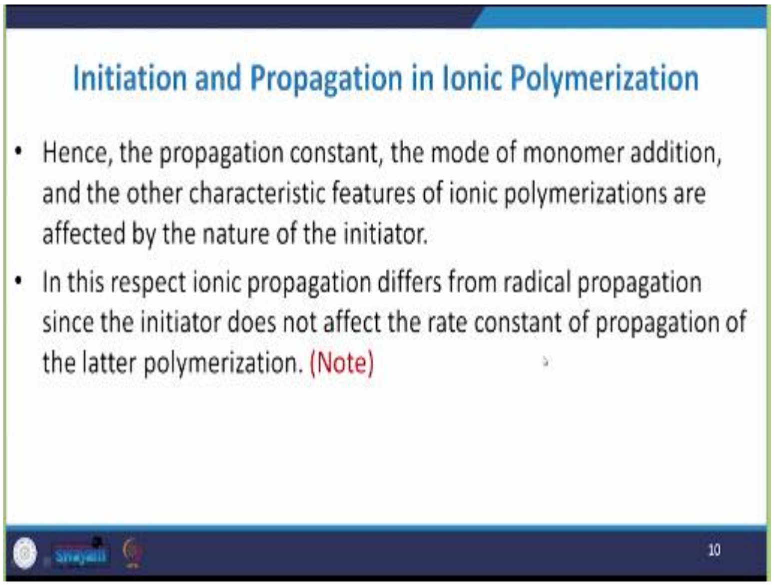

Initiation and Propagation in Ionic Polymerization

- Hence, the propagation constant, the mode of monomer addition, and the other characteristic features of ionic polymerizations are affected by the nature of the initiator.
- In this respect ionic propagation differs from radical propagation since the initiator does not affect the rate constant of propagation of the latter polymerization. (Note)

So, by this way, we can start this initiation and propagation aspect.

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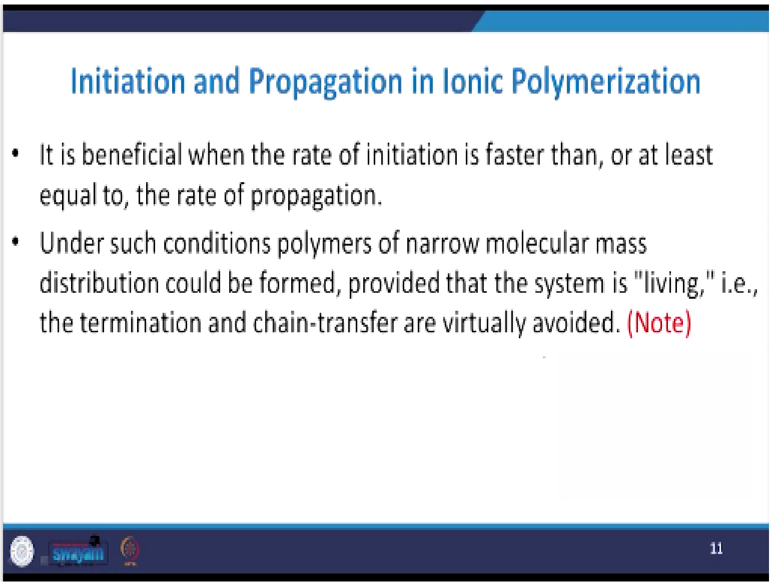

Initiation and Propagation in Ionic Polymerization

- It is beneficial when the rate of initiation is faster than, or at least equal to, the rate of propagation.
- Under such conditions polymers of narrow molecular mass distribution could be formed, provided that the system is "living," i.e., the termination and chain-transfer are virtually avoided. (Note)

it is beneficial when the rate of initiation is faster than or at least equal to the rate of propagation. So, under such condition the polymers of narrow molecule mass distribution could be formed and provided the system is living. That is the termination and chain transfer are virtually avoided or absent.

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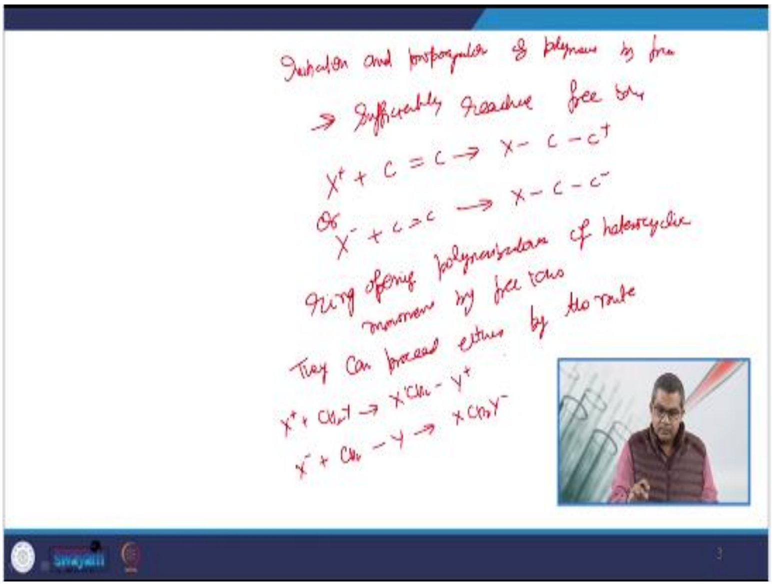

Initiation and propagation of polymers by free

→ Sufficiently reactive free ions

$X^+ + C=C \rightarrow X-C-C^+$

or $X^- + C=C \rightarrow X-C-C^-$

Ring opening polymerization of heterocyclic monomers by free ions

They can proceed either by the route

$X^+ + CH_2-Y \rightarrow X'CH_2-Y^+$

$X^- + CH_2-Y \rightarrow XCH_2Y^-$

Initiation and Propagation of Polymerization by Free Ions

Ionic polymerization may be induced by a sufficiently reactive free ion, as exemplified by the following idealized schemes:

$x^+ + C = C \rightarrow X - C - C^+$,

or

$X^- + C = C \rightarrow X - C - C^-$

Slightly modified schemes describe the initiation of ring opening polymerizations of heterocyclic monomers by free ions.

They proceed either by the route:

- $X^+ + CH_2Y \rightarrow XCH_2 - Y^+$ and
- $X^- + CH_2 - Y \rightarrow XCH_2Y^-$

or

- $X^+ + Y - CH_2 \rightarrow XY^+ - CH_2$ and
- $X^- + Y - CH_2 \rightarrow XY^- - CH_2$

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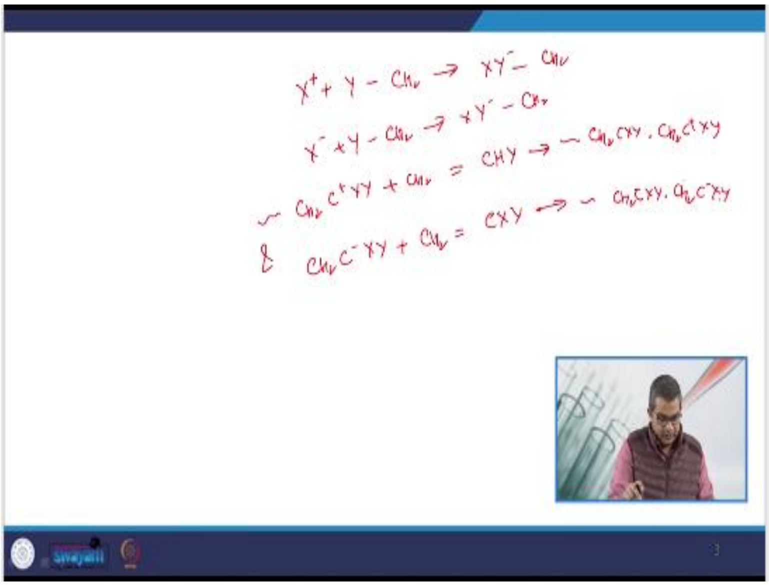

$X^+ + Y - CH_2 \rightarrow XY^- - CH_2$

$X^- + Y - CH_2 \rightarrow XY^- - CH_2$

$\sim CH_2C^+XY + CH_2 = CHY \rightarrow \sim CH_2CXY \cdot CH_2C^+XY$

$\& \; CH_2C^-XY + CH_2 = CXY \rightarrow \sim CH_2CXY \cdot CH_2C^-XY$

- These initiations resemble the respective propagations induced by the free ions of growing polymers, e.g.,
- $\sim CH_2C^+XY + CH_2 = CXY \rightarrow \sim CH_2CXY \cdot CH_2C^+XY$

and

- $\sim CH_2C^-XY + CH_2 = CXY \rightarrow \sim CH_2CXY \cdot CH_2C^-XY$

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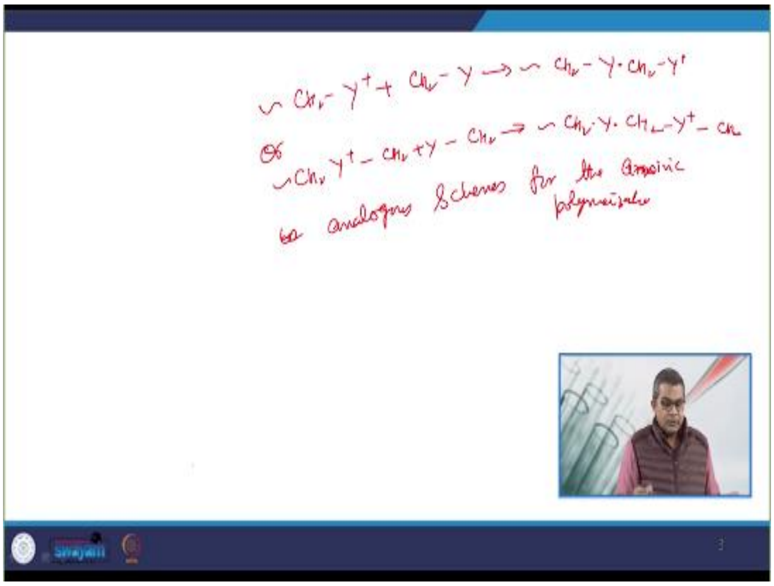

$\sim CH_2 - Y^+ + CH_2 - Y \rightarrow \sim CH_2 - Y \cdot CH_2 - Y^+$

Or

$\sim CH_2 Y^+ - CH_2 + Y - CH_2 \rightarrow \sim CH_2 \cdot Y \cdot CH_2 - Y^+ - CH_2$

wa analogous Schemes for the anionic polymerization

whereas in the ring opening polymerization they proceed according to the schemes:

$$\sim CH_2 - Y^+ + CH_2 - Y \rightarrow \sim CH_2 - Y \cdot CH_2 - Y^+$$

Or

$$\sim CH_2Y^+ - CH_2 + Y - CH_2 \rightarrow \sim CH_2 \cdot Y \cdot CH_2 - Y^+ - CH_2$$

with analogous schemes for the anionic polymerization.

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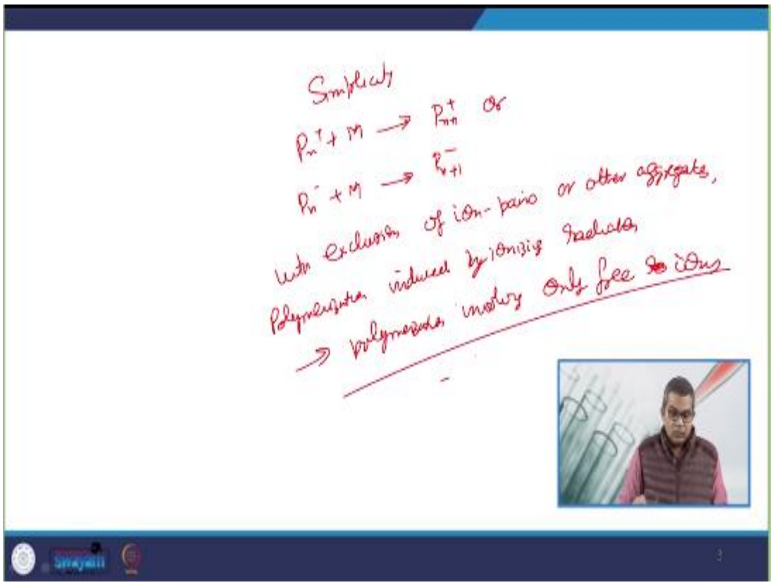

Simplicity

$P_n^+ + M \rightarrow P_{n+1}^+$ Or

$P_n^- + M \rightarrow P_{n+1}^-$

with exclusion of ion-pairs or other aggregate,

Polymerization induced by ionizing radiation

→ polymerization involving only free ions

For simplicity this can be noted as

$P_n^+ + M \rightarrow P_{n+1}^+$ or $P_n^- + M \rightarrow P_{n+1}^-$

It should be stressed, however, that systems involving free ions, with exclusion of ion-pairs or other aggregates, are hardly known; polymerization induced by ionizing radiation is an example of polymerization involving only free ions.

This is an example of polymerization involving only free radicals free sorry free ions. So, by this way, we can give a small description of initiation and propagation usually induced by salt. This is another way.

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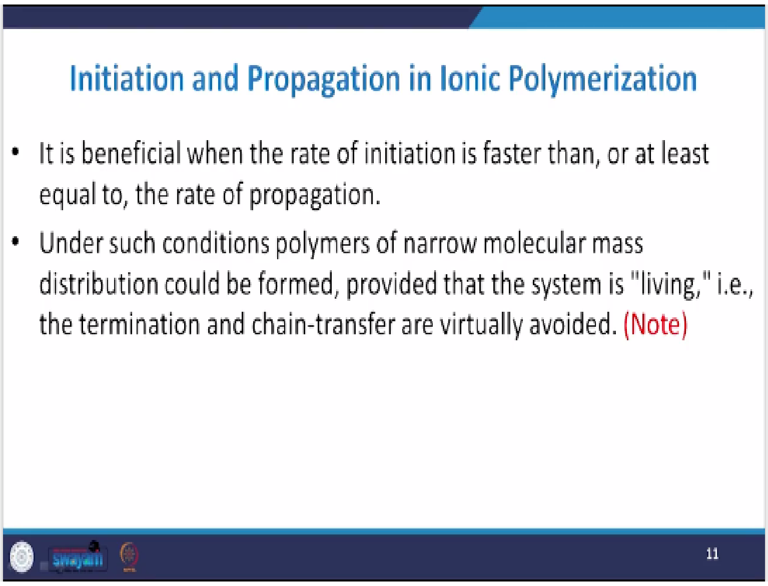

Initiation and Propagation in Ionic Polymerization

- It is beneficial when the rate of initiation is faster than, or at least equal to, the rate of propagation.
- Under such conditions polymers of narrow molecular mass distribution could be formed, provided that the system is "living," i.e., the termination and chain-transfer are virtually avoided. (Note)

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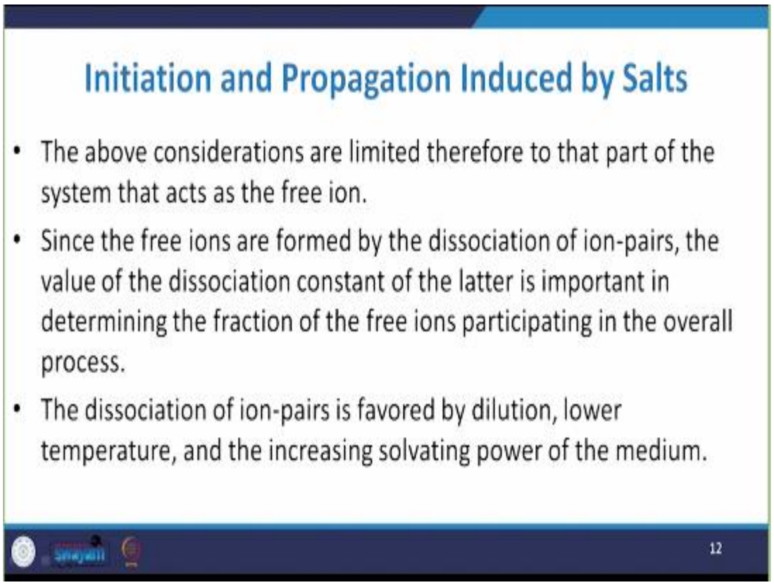

Initiation and Propagation Induced by Salts

- The above considerations are limited therefore to that part of the system that acts as the free ion.
- Since the free ions are formed by the dissociation of ion-pairs, the value of the dissociation constant of the latter is important in determining the fraction of the free ions participating in the overall process.
- The dissociation of ion-pairs is favored by dilution, lower temperature, and the increasing solvating power of the medium.

this consideration are limited therefore that part of system that acts as a free ion. since, free ions are usually formed by the dissociation of ionic pairs, the value of dissociation constant of the latter is important in determining the fraction of free ion participating in the overall process. So, the dissociation of ion pair is usually favoured by dilution, sometimes lower temperature and the increasing solvating power of the medium.

let us have a look about the initiation and propagation induced by the salts that the degree of dissociation of the salt sometime initiating anionic polymerization. They may vary widely depending on their nature and the nature of the solvent. So, the solvation of free ion increases the degree of dissociation of their ion pair. But sometimes it reduces the reactivity of free ion, because at least 1 molecule of the solvent has to be removed from their solvation shell to allow to contact with the monomers.

these free ions sometimes, they are often most reactive initiating species and they initiate the polymerization by direct attack on a monomer, electrophilic and cationic nucleophilic and anionic processes. The intrinsic reactivity of an initiating or propagating ion usually, this depends on the charge density on that of its atom which ultimately becomes sometimes linked with the covalent bond or with other bonds to the polymerized monomer.

So, the rate of free ion addition to a series of monomer, this may vary with their nature. In cationic polymerization the rate increases with increasing monomer's nucleophilicity, e.g., it decreases in the order:
$N - vinylcarbazole > vinylethers > p - methoxystyrene > p -$
$methylstyrene > cyclopentadiene > a - methylstyrene > styrene > indene.$
The reverse order governs the rates in anionic polymerization.

Sometimes a substitution of alpha hydrogen of a monomer by a methyl group accelerates the cationic initiation or propagation, but it retards the anionic one. So, as on the whole the initiation is often efficient when the initiating ion is less stable than the one formed in the process. The position of attack by an ion is uniquely determined in the initiation of vinyl or vinyl diene monomer, but unsymmetrical dienes to alternative sites of attack are possible.So, the preference being determined by the difference of electron densities.

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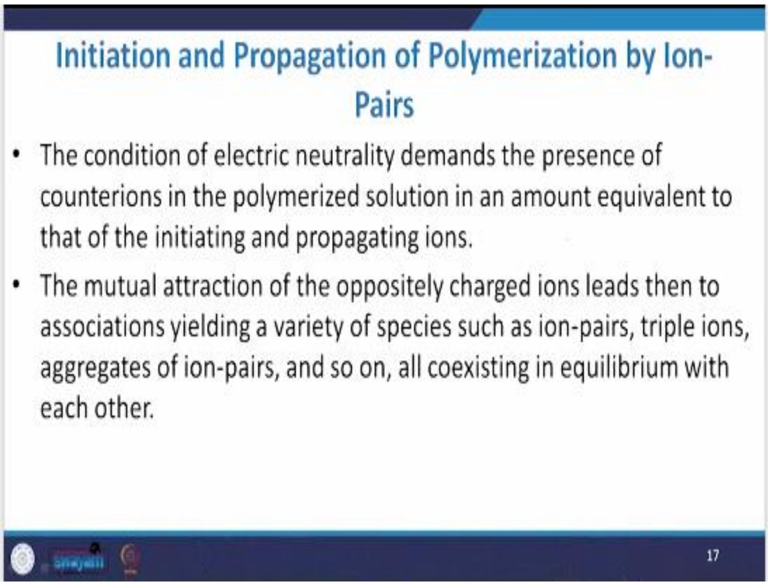

Initiation and Propagation of Polymerization by Ion-Pairs

- The condition of electric neutrality demands the presence of counterions in the polymerized solution in an amount equivalent to that of the initiating and propagating ions.
- The mutual attraction of the oppositely charged ions leads then to associations yielding a variety of species such as ion-pairs, triple ions, aggregates of ion-pairs, and so on, all coexisting in equilibrium with each other.

Sometimes, we may look into the other concepts like the condition of electric neutrality depend upon the presence of counter ions in the polymerized solution in an amount equivalent to that of the initiating and propagating ions. The mutual attraction of oppositely charged ion, this sometimes lead then to association yielding a variety of species such as ion pair, triple ion, aggregates of ion pairs and so on, so, all coexisting in equilibrium with each other.

Some of these associates act as initiators in their own right and contribute to the rate of initiation proportionally to their mole fraction f_i weighted by their characteristic initiation rate constant $k_{in,i}$

The apparent Initiation and Propagation of initiation rate constant, $k_{in,ap}$, derived from the experimental data is given, therefore, by the relation:

$k_{in,ap} = \sum f_i . k_{in,i}$

A similar relation provides the apparent rate constant of propagation of ionic polymerization since the propagating polymers may form also a mixture of distinct species, i.

Hence, the experimentally derived overall propagation rate constant, $k_{p,ap}$, is given by the relation:

$k_{p,ap} = \sum g_i . k_{p,i}$

where g_i denotes the mole fraction of a respective kind of the growing polymers i's, and $k_{p,i}$ their propagation rate constant.

Anionic Systems

At least two kinds of ion-pairs participate in the reactions ensuing in many anionic systems: the highly reactive loose ion-pairs and the relatively unreactive tight contact pairs.

The reactivity of loose ion-pairs depends on the nature of the species solvating the cations, although variation of the solvating agent rarely affects their reactivity by a factor greater than 10.

The most extensive data reveals the behaviour of ion and ionic pair in an ionic system. It is it was obtained through studies of an ionic polymerization of styrene in ethernal solvents or ethereal solvents. in the absence of impurities, oxygen, moisture etcetera, these reactions are proceed free of termination and chain transfer.

That is the pertinent polymers, they are termed as the living polymers. let us talk about the dependency of propagation rate constant on cation size. the propagation rate constant is affected by the nature of counterions.

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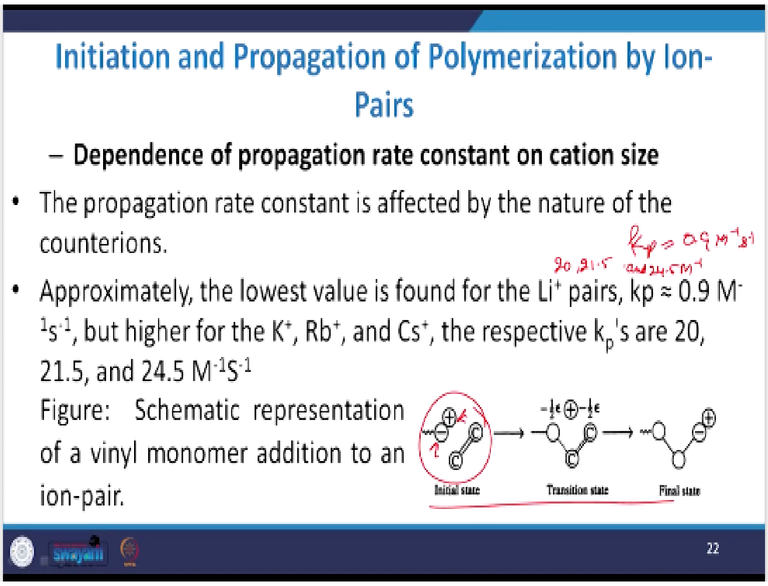


Initiation and Propagation of Polymerization by Ion-Pairs

– **Dependence of propagation rate constant on cation size**

- The propagation rate constant is affected by the nature of the counterions.
- Approximately, the lowest value is found for the Li^+ pairs, kp ≈ 0.9 $M^{-1}s^{-1}$, but higher for the K^+, Rb^+, and Cs^+, the respective k_p's are 20, 21.5, and 24.5 $M^{-1}S^{-1}$

$k_p \approx 0.9\ M^{-1}s^{-1}$

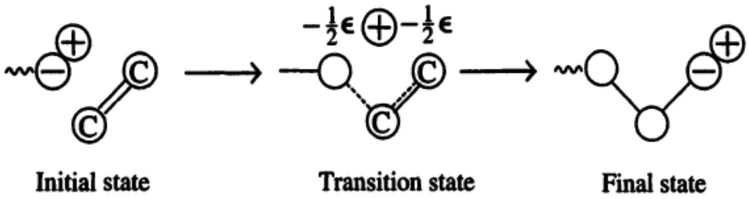
20, 21.5 and 24.5 M^{-1}

Figure: Schematic representation of a vinyl monomer addition to an ion-pair.

Dependence of propagation rate constant on cation size

The propagation rate constant is affected by the nature of the counterions.

Approximately, the lowest value is found for the Li^+ pairs, kp ≈ 0.9 $M^{-1}s^{-1}$, but higher for the K^+, Rb^+, and Cs^+, the respective k_p's are 20, 21.5, and 24.5 $M^{-1}S^{-1}$



This is the schematic representation of a vinyl monomial addition to the ionic pair. you see that here we are having the initial one with these 2 charges and then this is the transition state or sometimes you may refer as the intermediate state and this one is the final one.

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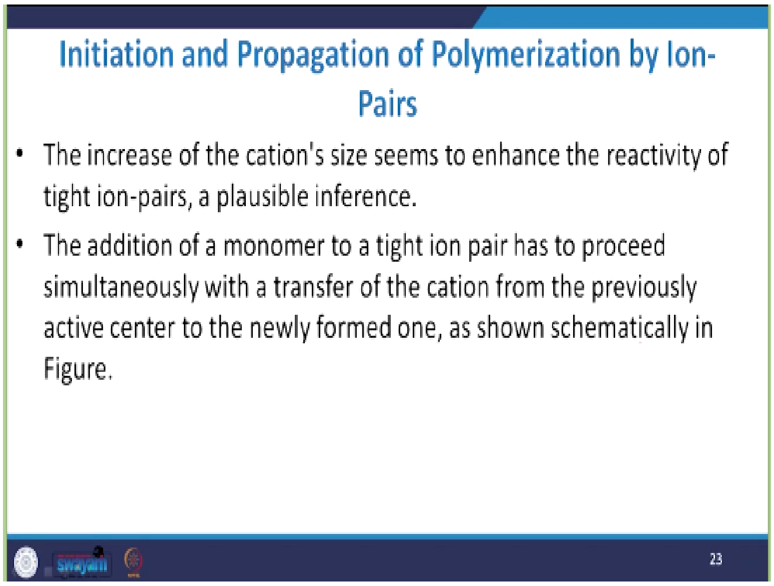

Initiation and Propagation of Polymerization by Ion-Pairs

- The increase of the cation's size seems to enhance the reactivity of tight ion-pairs, a plausible inference.
- The addition of a monomer to a tight ion pair has to proceed simultaneously with a transfer of the cation from the previously active center to the newly formed one, as shown schematically in Figure.

So, the increase in the cation size seems to enhance the reactivity of tight ion pair and it is a plausible inference, the addition of a monomer to a tight ion pair, this has to proceed simultaneously with a transfer of cation from previously active centre to the newly formed one. this we have already represented in this particular figure. such a transfer is usually opposed by the columbic attraction between the ion of the pair.

the attraction decreases with the bulkiness of Cation. And it is a very common phenomena. So, while their complete solvation is hindered by the cloudiness in the transition state, so, if there are more and more particles being formed in the transition state, then it is usually hindered. So, the change in the electrostatic interaction sometimes might the cause of observed enhancement of propagation.

So, for a sufficiently large but sometimes not referred as too large cations that transfer may take place without separation of ions. at last we discuss about the effect of solvating agent. So, although the suppression of concentration of loose ion pairs sometimes co exist in equilibrium with the the tight one is not feasible, the increase in their proportion is readily accomplished by the addition of solvating or coordinating agent to their solution.

Thus, they may produce the loose pair separated by the added agent. Large enhancement of the rate of initiation or propagation is sometimes achieved under this phenomenon.

Effect of push-pull mechanism

Let us discuss about the push and pull type of mechanism, the cooperative action of anion and cation, so, when jointly interacting with the monomer. This is another important factor that affects the rate of addition.

Sometimes this is known as the push and pull mechanism like this one, one is pushing and thereby this is adding. But its accelerating effect, this means the separation of those ions. Therefore, its contribution to the reaction is large than the separation of ion retards the monomer addition. Apparently, the coordination of cryptate that is a coordination complex in which metal cation is bound within a 3 dimensional interior cavity of a cryptand.

This cryptate with the cation that may separate the ions of a pair reduces the beneficial effect of cation and the resulting loss is greater than the gain arising from the reduced electrostatic work required for the partial ion separation. So, this is again a very important thing which we need to address. we have gone through about the solvation ability, solvating agent, we discussed about the initiation propagation induced by varying agents in this particular chapter.

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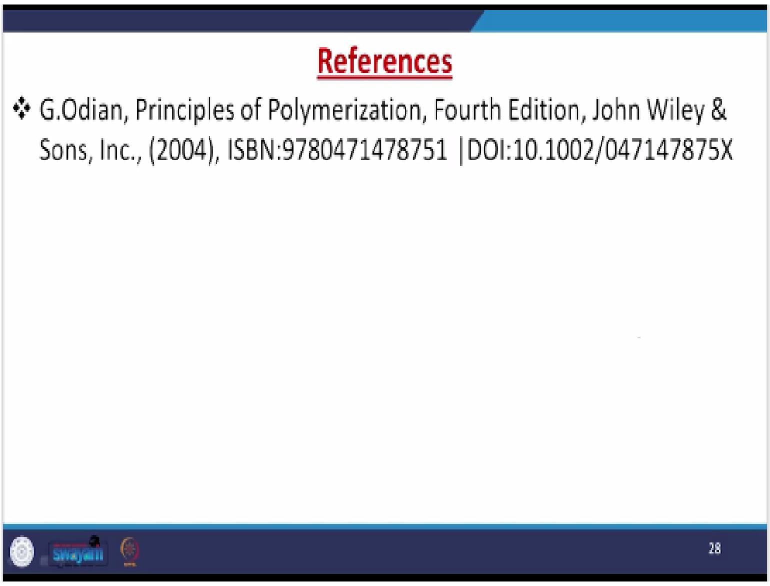

References

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

And we took the help of this particular reference for conceptualising this particular lecture and if you wish to have further studies, then you may go through this particular reference. Thank you very much.