Polymer Reaction Engineering
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Lecture – 60
Ionic Polymerization - V

Welcome to the lecture of ionic polymerization. And if you recall that in the previous lectures we discussed about the concept of propagation.

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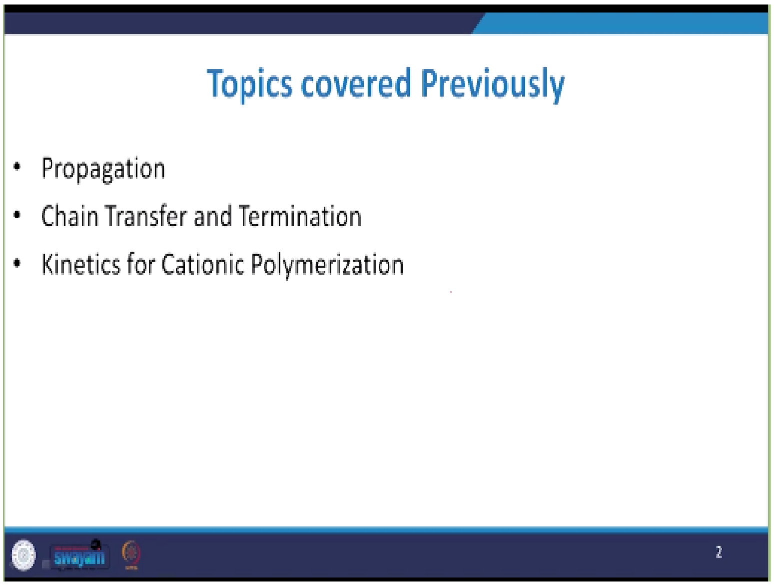

Topics covered Previously

- Propagation
- Chain Transfer and Termination
- Kinetics for Cationic Polymerization

Then we discuss about the chain transfer and termination in the second lecture of this ionic polymerization. Then we develop the various kinetic equations for this cationic polymerization.

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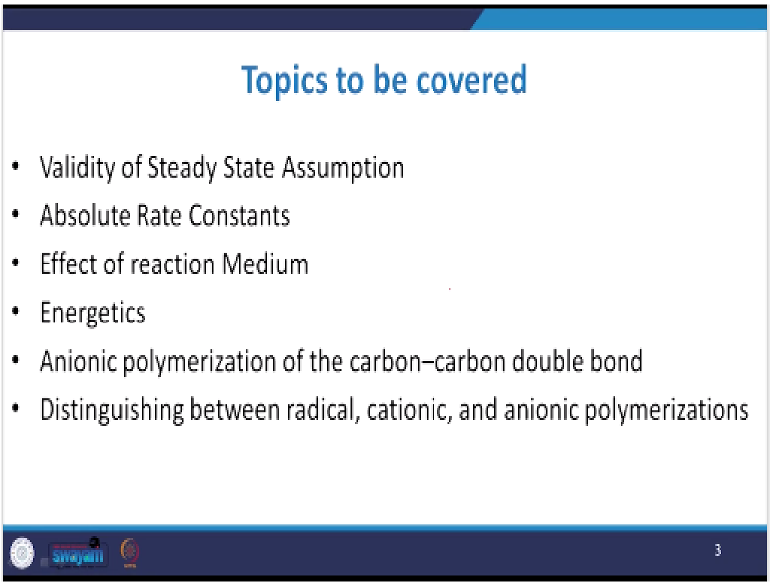

Topics to be covered

- Validity of Steady State Assumption
- Absolute Rate Constants
- Effect of reaction Medium
- Energetics
- Anionic polymerization of the carbon–carbon double bond
- Distinguishing between radical, cationic, and anionic polymerizations

And in this particular chapter or in this lecture, we will discuss about the validity of those steady state assumptions being taken care in due course of time. Then we will discuss about the absolute rate constants. We will analyse the effect of various reaction mediums we have discussed. We will discuss about the energetics and anionic polymerization of carbon carbon double bond.

We will try to develop the distinguishment between the radical cationic and anionic polymerizations or among you can say among radical cationic and anionic polymerization.

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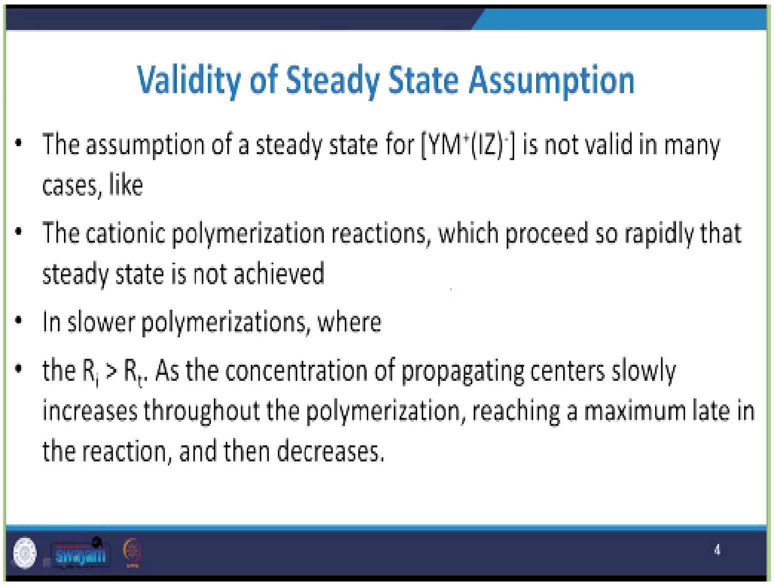

Validity of Steady State Assumption

- The assumption of a steady state for [$YM^+(IZ)^-$] is not valid in many cases, like
- The cationic polymerization reactions, which proceed so rapidly that steady state is not achieved
- In slower polymerizations, where
- the $R_i > R_t$. As the concentration of propagating centers slowly increases throughout the polymerization, reaching a maximum late in the reaction, and then decreases.

So, let us start with the first thing that is the validity of a steady state assumption. Now, during the course of the kinetic study, we need to take various assumptions to generate the various kinetic equations. Now, when we talk about those developed equation, then we need to check the validity of those assumptions being taken during the course of development of those equations.

So, in this category the equations which we had developed, we have taken the assumption of a steady state. Now, the assumption of steady state for this [$YM^+(IZ)^-$] is not valid in many cases. So, before we proceed further let us look at around that what are those cases. Now, the cationic polymerization reactions which proceeds so rapidly that sometimes these steady state is not achieved or not achievable.

And in slower polymerization, where usually when $R_i > R_t$ so as the concentration of propagating centres slowly increases throughout the polymerization reaching to a maximum late in the reaction and therefore, and then subsequently it has a tendency to decrease the existence of a steady state. This can be ascertained by measuring $[YM^+(IZ)^-]$ complex as a function of time.

Now, since, this is relatively difficult in most system, it is more convenient to observe the polymerization rate as a function of time. Now, this steady state is usually implied, if the rate of propagation is constant with conversion, except for the changes due to the decrease monomer and initiator concentration. Now, sometimes a more rapid declination in the rate of propagation with the time may be observed that indicated by the decrease in the either "M" monomer concentration or [ZY] concentration. This signifies the non-steady state condition. Now, in the absence of a steady state would also be indicated by an increase of rate of propagation with time. Now, let us have a look about the absolute rate constant, because this is again a very important concept when we talk about the kinetics.

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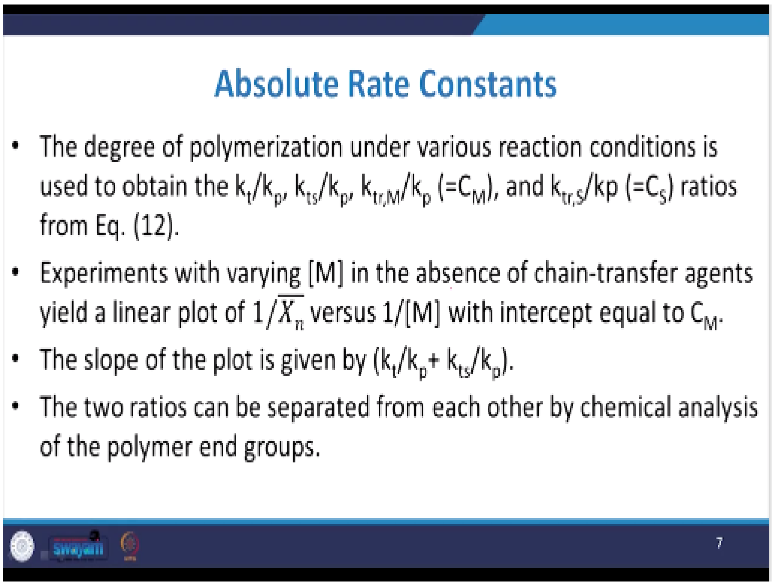

Absolute Rate Constants

- The degree of polymerization under various reaction conditions is used to obtain the k_t/k_p, k_{ts}/k_p, $k_{tr,M}/k_p$ $(=C_M)$, and $k_{tr,S}/kp$ $(=C_S)$ ratios from Eq. (12).
- Experiments with varying [M] in the absence of chain-transfer agents yield a linear plot of $1/\overline{X}_n$ versus 1/[M] with intercept equal to C_M.
- The slope of the plot is given by $(k_t/k_p + k_{ts}/k_p)$.
- The two ratios can be separated from each other by chemical analysis of the polymer end groups.

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So, there are various tools available as on date through which you can perform those analyses to assess what kind of polymer and groups what is the concentration of those polymer groups are present in the reaction mass.

Now, the spontaneous termination and the chain transfer to monomer both yield the polymers with unsaturated end groups. So, while combination with the counter ion yields polymer and groups they derived from the counter ion. The end-group analysis combined with the calculated values of C_M and (k_t/k_p+ k_{ts}/k_p) allow the separation of the latter two ratios.

The value of C_s is usually obtained by carrying out experiments with varying amount of chain transfer agents. So, you cannot nullify the importance of those experiments, which are essential part of these polymerization process.

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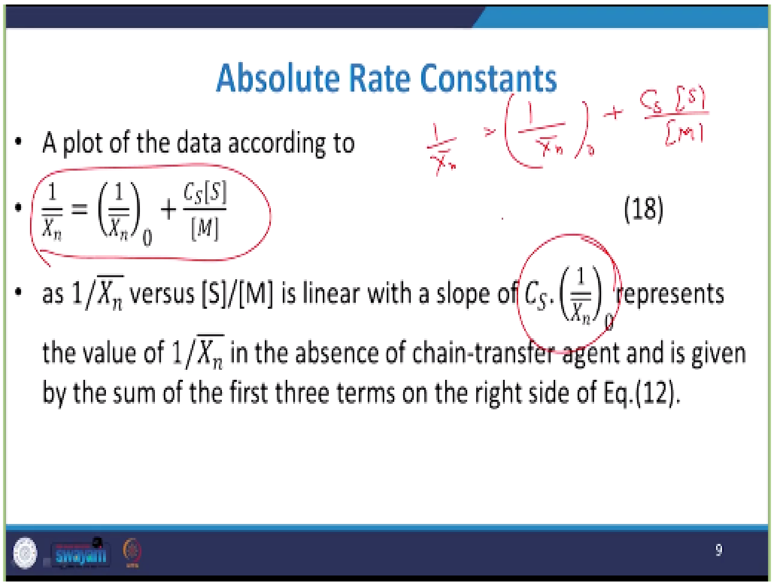

Absolute Rate Constants

$\frac{1}{\overline{X}_n} = \left(\frac{1}{\overline{X}_n}\right)_0 + \frac{C_S[S]}{[M]}$

- A plot of the data according to
- $\frac{1}{\overline{X}_n} = \left(\frac{1}{\overline{X}_n}\right)_0 + \frac{C_S[S]}{[M]}$ (18)
- as $1/\overline{X}_n$ versus [S]/[M] is linear with a slope of C_S. $\left(\frac{1}{\overline{X}_n}\right)_0$ represents the value of $1/\overline{X}_n$ in the absence of chain-transfer agent and is given by the sum of the first three terms on the right side of Eq.(12).

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Experimental Determination

Now, let us have a look because when we talk about the validity, then again these validity concept is usually supplemented by the experimental determination. So, the experimental determination when we talk about this experimental determination, this one involves the short stopping of polymerization system by addition of a high efficient terminating agent.

Now, also all propagating centres are sometimes quickly terminated with incorporation into the polymer of an end group derived from the terminating agent. Now, those end group in the polymer they are analysed after separation of the polymer from the other components in the reaction system and that is quite obvious, because there are usual experimental methods through which you can you can analyse and you can analyse the concentration.

You can find it out that what kind of different polymers are being formed during the course of the reaction within the reaction system. Now, this particular method is limited by the general difficulty of end group analysis since the concentration of end groups can be quite low and by the need to assume the terminating agent terminates all kind of propagating centres.

Now, second aspect in this particular approach is that is attributed for the determining the propagating sign species concentration. This involves a direct UV visible spectroscopic analysis of propagating species during the polymerization. Now, the high extinction coefficient of some aromatic carbocations propagating the species they are coupled with the availability of higher accurate spectrophotometers.

They are resulted in the extensive use of that particular method and it is very common technique for analysis or for experimental determination. Now, the measurement of UV absorbance of a polymerizing system as a function of time this allows one to determine that k_i that is the rate constant for initiator then R_i that is a rate of initiation step, the concentration of propagating species and the rate constant of the propagating reaction.

Now, the UV method this is also being used to study very fast polymerization. Now, sometimes in a **stop the flow or a rapidscan spectroscopies** are also feasible. Now, this separate monomer and initiator solution with the help of a rapid force through a mixing chamber where the instantaneous mixing usually occurs and then it is subjected to a capillary tube located in the spectrophotometer then the flow is stopped and the progress of reaction being followed by measuring the change in the absorbance with time.

Another new method is referred as the **diffusion clock method**. This offers an alternate approach to obtain the propagation rate constant. Now, usually this involves the polymerization in the presence of a highly active terminating agent. Now, these are specifically known to have a high rate constant for reaction with the carbocation set the diffusion control reaction limit.

And sometimes these limits are in the range of $k \approx 3 \text{ X } 10^{9}$ L mol^{-1} s^{-1}. Now, the ratio of the rate constant for the propagation to that for termination is obtained from the measurement of the amounts of monomer and that terminating agent whatever it being consumed because of a reaction system. Now, these ratios are this ratio multiplied by the diffusion controlled reaction rate constant k yields the propagation rate constant.

Now, sometimes you need to incorporate the various corrections in calculating the rate constant. Now, these corrections are attributed to the kinetic expressions those who are written in terms of only one type of propagating species and usually shown as ionic pair. Now, usually this is incorrect since both ionic pairs and free ions are simultaneously present in most polymerization system and sometimes they are in the equilibrium with each other.

Therefore, the correct expression for the rate of any step initiation, propagation, termination, transfer. So, the rate of any step in the polymerization should include the separate terms for respective contributions of the two type of a propagating species.

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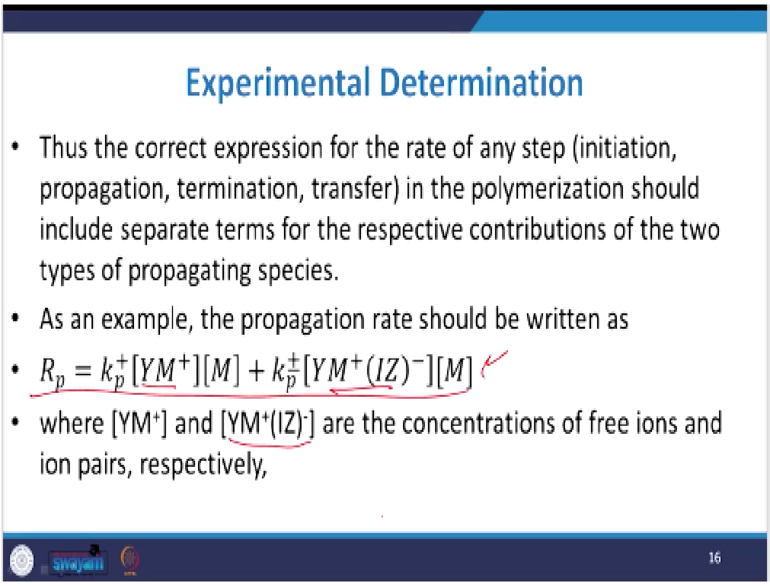

Experimental Determination

- Thus the correct expression for the rate of any step (initiation, propagation, termination, transfer) in the polymerization should include separate terms for the respective contributions of the two types of propagating species.
- As an example, the propagation rate should be written as
- $R_p = k_p^{+}[YM^{+}][M] + k_p^{\pm}[YM^{+}(IZ)^{-}][M]$
- where $[YM^{+}]$ and $[YM^{+}(IZ)^{-}]$ are the concentrations of free ions and ion pairs, respectively,

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where $[YM^+]$ and $[YM^+(IZ)^-]$ are the concentrations of free ions and ion pairs, respectively, and k_p^+ and $k_p^\pm$ are the corresponding propagation rate constants.

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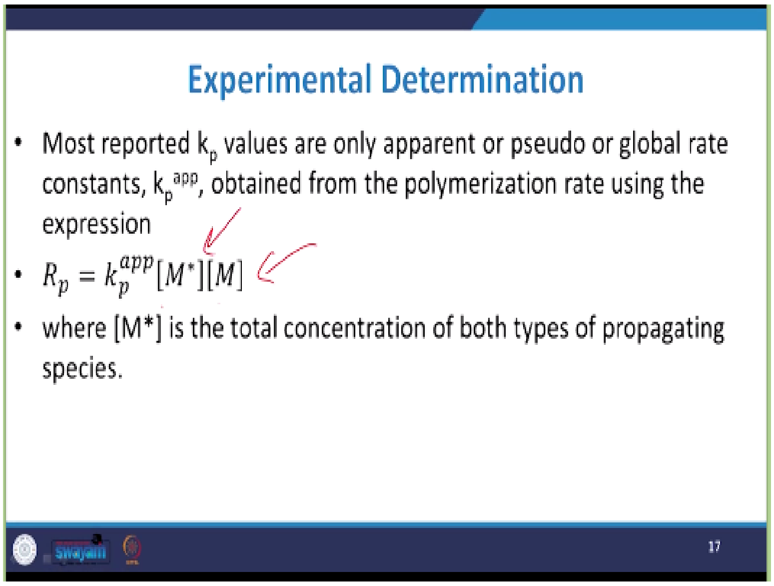

Experimental Determination

- Most reported k_p values are only apparent or pseudo or global rate constants, k_p^{app}, obtained from the polymerization rate using the expression
- $R_p = k_p^{app}[M^*][M]$
- where [M*] is the total concentration of both types of propagating species.

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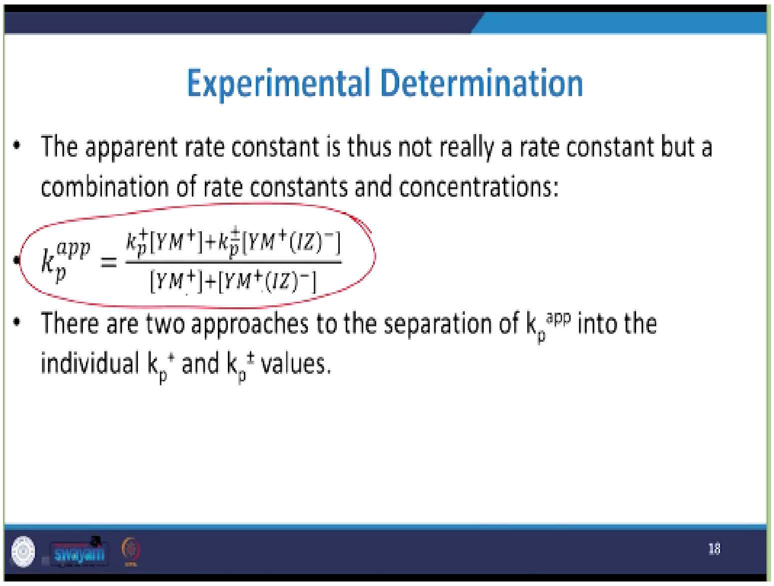

Experimental Determination

- The apparent rate constant is thus not really a rate constant but a combination of rate constants and concentrations:
- $k_p^{app} = \frac{k_p^+[YM^+]+k_p^\pm[YM^+(IZ)^-]}{[YM^+]+[YM^+(IZ)^-]}$
- There are two approaches to the separation of k_p^{app} into the individual k_p^+ and $k_p^\pm$ values.

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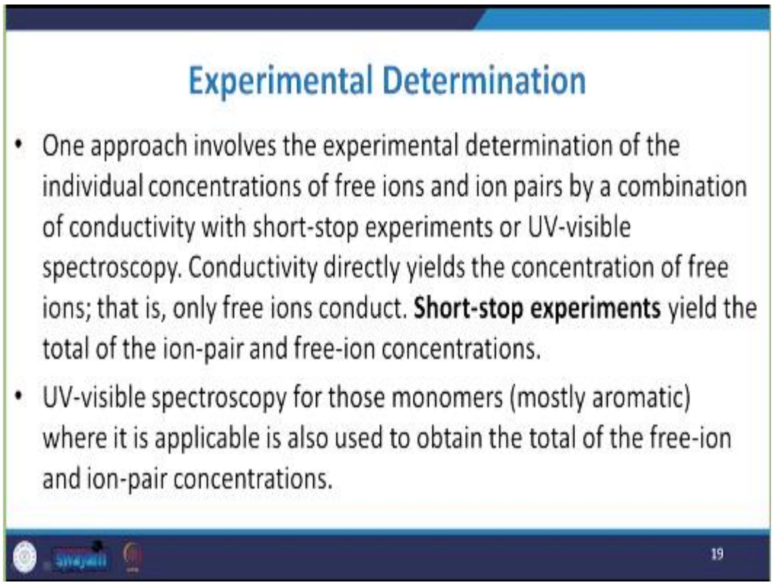

Experimental Determination

- One approach involves the experimental determination of the individual concentrations of free ions and ion pairs by a combination of conductivity with short-stop experiments or UV-visible spectroscopy. Conductivity directly yields the concentration of free ions; that is, only free ions conduct. **Short-stop experiments** yield the total of the ion-pair and free-ion concentrations.
- UV-visible spectroscopy for those monomers (mostly aromatic) where it is applicable is also used to obtain the total of the free-ion and ion-pair concentrations.

Now, one approach involves the experimental determination of the individual concentration of free ions and ion pair by a combination of conductivity with the **short stop experiment or the UV visible spectroscopy**. Now, conductivity directly yields the concentration of free ions That is only free ion conduct short stop experiment. Now these this short stop experiment yield that total of ion pair and free ion concentrations. So, it may have the combination of both.

Now UV visible spectroscopy for those monomer sometimes these monomers are aromatic in nature. So, these where it is applicable this also used to obtain the total of free ion and ion pair concentrations. Now, it usually assumed that ion pair they show the same UV visible absorption as free ion, since the ion pair in cationic systems are looser ion pair that is attributed to the largest size of negative counter ions.

Now, this approach is limited by assumptions and or sometimes our experimental difficulties inherent in that various measurements. Now, there are several experimental difficulties may be attributed to the irreversibilities associated with those experimental procedures. So, it is quite obvious. Now, the conductivity measurements on systems those containing the low concentration of ion are difficult to perform and impurities can easily lead to the error in the results.

Now, the short stop experiment does not distinguish between ion pairs and free ions. The assumption of the equivalence of free ions and ionic pairs in the spectroscopic method is usually all you can say not firmly established. So, the second approach this involves the determination of polymerization rate at various concentrations of coinitiator and initiator or in both, the presence or absence of an added common ion salt.

So, we discussed various salts in due course of time. Now, this latter containing the counter ion of the propagating carbocation, this actuates the propagation by ion pairs by depressing their ionisation to free ions. Now, let us talk about the about the effect of reaction media because the reaction media again play a very vital role in deciding the fate of these polymerization process.

So, the change in the rate of polymerization sometimes can occur when the solvent or counter ions are changed, because both of them are act as a reaction media. So, it can affect as the equilibrium between the free ion and ionic pairs that may be shifted towards the free ions by high polarity solvent, this usually result in the increased polymerization rate. Now, the largest solvent effects they can be seen for the system in which the counter ion has a significant tendency to form a covalent bond to the carbocation.

Now, sometimes, low polarity solvent plays a vital role. Now, these low polarity solvent they drive the reaction system towards the covalent species I which does not propagate or at most propagates much more slowly then does the free ion or ionic pair. Then, let us talk about some energetics within this particular polymerization scheme. Now, the cationic polymerization they are usually exothermic in nature since, the reaction involves that conversion of p-bonds to s-bonds. The heat of polymerization for any particular that we need to look into now, the monomer is essentially the same irrespective of the mode of initiation.

Energetics

The composite activation energies E_R and $E_{\bar{X}_n}$ for the rate and degree of polymerization, are obtained as

$$E_R = E_i + E_p - E_t$$

$$E_{\bar{X}_n} = E_p - E_t$$

where E_i, E_p, and E_t are the activation energies for the initiation, propagation, and chain termination steps, respectively.

For the activation energy for X_n, E_t will be replaced by an E_{tr} term or terms when transfer occurs.

anionic polymerization of the carbon- carbon double bond

Now, let us talk about the anionic polymerization of the carbon carbon double bond. Now, because previously we discussed about the cationic polymerization of carbon carbon bond now, let in the same line, we will discuss about this carbon - carbon double bond concept under the aegis of anionic polymerization.

The propagating species are anionic ion pairs and free ions with a relative concentration that depend on the reaction media as we discussed in the cationic polymerization. Now, in an unlike cationic polymerization, there is a large difference between the reactivities of ionic pair and free ions in anionic polymerization. Although anionic polymerization generally proceeds rapidly at a very low temperature.

So, they are they are seldom as temperature sensitive as cationic polymerization. So, you will see that we are differentiating between these anionic polymerization and cationic polymerization under the aegis of carbon carbon double bond. So, there are having a very minute or you can say not much difference between these 2 polymerization schemes. Now, most anionic polymerization possesses positive E R values and proceed well at you can say or somehow somewhat above ambient temperatures.

And many anionic polymerizations are easier to understand. Since, the identities of initiating a species and counter ion are much better established in this case. The range of solvents useful for the anionic polymerization is usually limited to aliphatic and aromatic hydrocarbons and ethers. Sometimes, people may consider the halogenated solvents, so, halogenated solvents they are suitable for cationic polymerization cannot be used for anionic polymerization.

Because they emphasise nucleophilic substitution reaction with the carbon ions. So, other polar solvents such as esters, ketones, they are also excluded in anionic polymerization as a result or as an because of their affinity under the reaction with carbon ions. Termination usually occurs by a transfer of positive fragments, usually a proton from the solvent or from some other transfer agent both deliberately added.

Although other modes of termination can also be occurring during this anionic polymerization step. Now, many anionic polymerizations are living polymerization, when the reaction components are appropriately chosen. So, now at the last when we discussed about because we have discussed the radical polymerization, we discussed the cationic polymerization, we discussed anionic polymerization in brief.

Distinguishing between the radical cationic among radical, cationic and anionic polymerization

There is a common question that as to whether a particular initiator or initiator system initiates polymerization by radical, cationic or anionic means? Such a question can easily arise for various example. For example, in polymerization initiated by ionising radiation.

The mode of initiation of a particular initiator can be distinguished by a consideration of its characteristics compared to those known radical, cationic, anionic initiators. So, we have been listed a couple of things related to this distinguishing factor, the ionic polymerization usually proceeds at a lower temperature than the radical polymerization. Although the ionic reaction temperature are usually below zero degrees Celsius, there are numerous ionic polymerization that proceeds at higher temperature.

But, their rate is a bit lower compared to the those who are happening at below zero degree Celsius. Radical polymerization on the other hand almost or you can say always proceeds at a temperature appreciably above approximately 50 degrees Celsius. Further the ionic polymerization invariably has lower activation energy, than the radical counterparts. In some cases, there may be actually possess negative activation energy.

So, that is the point to be addressed and that is very important point. Another part is that the ionic polymerization is distinguished by their marked sensitivity towards the change in the polarity and the solvating ability of the reaction media and counter ion effects. Usually radical polymerization, they do not show such kind of effects. The next part is that the addition of known radical scavengers like dpph radical in the polymerizing system with the hard polymerization, if it is a radical reaction.

Now, ionic polymerizations will be unaffected by such kind of additions. One thing very important that one must be very careful or we are not to use the radical is scavengers that also affects the ionic polymerization. Therefore, the benzo benzo quinone would be a poor choice as a radical scavenger, since it can also act as an inhibitor to ionic polymerization.

So, the feasibility of these type of compounds need to be addressed prior to using any kind of polymerization system. Another part that is the chain transfer constant for an additive or solvent in the polymerization it can be determined. Now, this value can be compared with the the transfer of constants for the same substance and the polymerization of the same monomer by known radical, cationic or anionic initiators.

So, in this particular chapter, we discussed the remaining part of anionic polymerization. Then, we discussed about the various aspects of the cationic polymerization steps, then we discussed the distinguishment bit among the radical, cationic and anionic polymerization.

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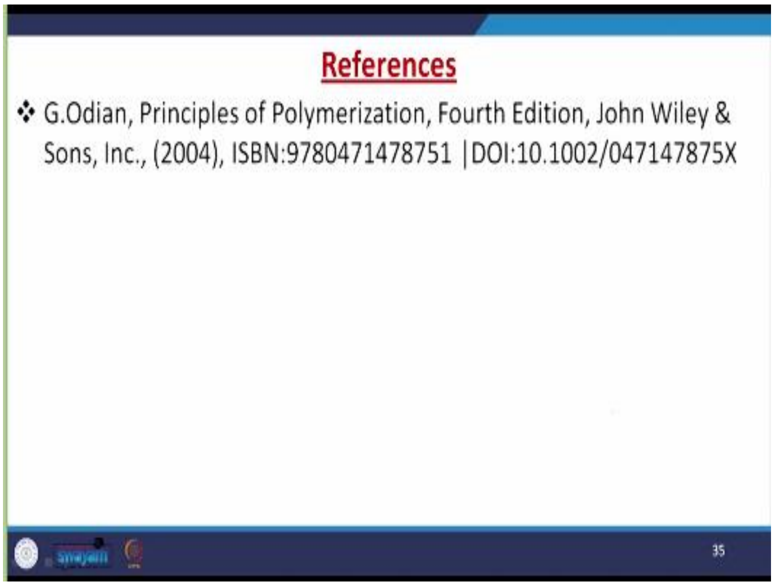

References

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Again we took the reference from this particular source and for further studies usually promoted if you are interested and you can seek the help of these references which are enlisted in this particular slide. Thank you very much.