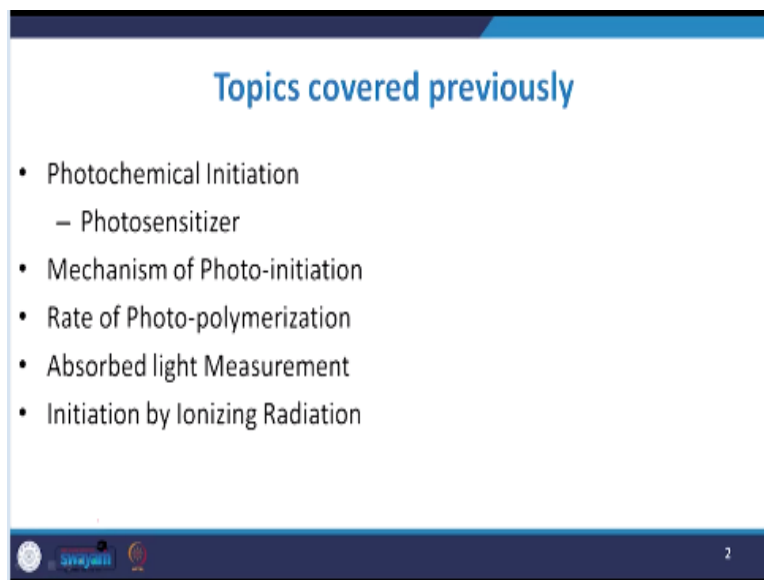


Polymer Reaction Engineering
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Lecture - 43
Other Initiation Techniques - I

Welcome to this concept of radical chain polymerization. And previously, we discussed about the photochemical initiation, in which we discussed about the photosensitizers, then mechanism of photo initiation was discussed in different chapters.

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Topics covered previously

- Photochemical Initiation
 - Photosensitizer
- Mechanism of Photo-initiation
- Rate of Photo-polymerization
- Absorbed light Measurement
- Initiation by Ionizing Radiation

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Then we had a discussion about rate of photo polymerization. And we discussed about the absorbed light measurement and had a broad discussion about the initiation process by ionising radiation.

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Topics to be covered

- Other initiation techniques
 - Electrolytic polymerization
 - Plasma polymerization
 - Sonication
- Chain Transfer
- Determination of absolute rate constant

Now, in this particular chapter, we are going to cover the other initiation techniques as the title implies and under this head, we will discuss about the electrolytic polymerization, then we will discuss about the plasma polymerization, sonication. We will describe the chain transfer concept under the head of this radical chain polymerization. And with this help, we will determine or we will derive the various mathematical equations related to the absolute rate constant.

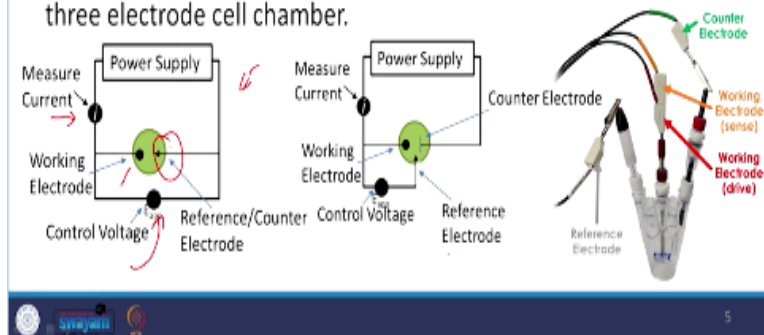
So, let us have a look about the electrolytic polymerization. Now, electrolytic or electric current is supplied in the solution containing organic solvent monomer and inorganic radical or ion providing compounds. So, by this way, the electric charge or electric current is induced in that particular solvent. So, whatever ridiculous species, they generate in this particular solution, they generate due to the electric charge provided to the solution which then initiate polymerization process.

One example can be given on the basis of electrolysis of acrylamide, tetra butyl ammonium perchlorate solution to generate ClO_4 radical formed due to the oxidation of ClO_4^- negatively charged at anode.

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Electrolytic polymerization

- This process usually do not require the use of oxidant
- The polymerization can be carried out in either two or three electrode cell chamber.



Now, this process usually having certain benefits that this process usually do not require any kind of oxidant which if you recall that in previous lectures, we discussed that there is no requirement of oxidant or any kind of reactive group to initiate the polymerization process. So, the polymerization in this case can be carried out in either 2 or 3 electrode cell chambers. As you can see in this particular figure, now, here this particular chamber is having one working electrode.

And by this way, you can control the voltage which you are applying to this particular segment, then there is a device to measure the current that is a metre and this is a source of power supply. Now, here this, you see that we are having one counter electrode or reference electrode. Now, if we carry out this particular thing, then again one option is that we can use this type of thing, this is the industrially available electronic polymerization tool.

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Electrolytic polymerization

- The three electrodes consist of working, counter and reference electrode.
- Two electrode system does not contain reference electrode, and the potential is directly applied between the working and counter electrode.
- In three electrode system, the potential is applied between the working and reference electrode, and the current is measured between the working and counter electrode

Now, these 3 electrodes consist of working counter and reference electrode. So, you see here, this one is the reference electrode and here this is the counter electrode. Now, 2 electrode system, it does not contain reference electrode and the potential is directly applied between the working and counter electrode. Now, however, whenever, when we use 3 electrode system, the potential is applied between the working electrode and the reference electrode, this one. And the current is measured between the working and counter electrodes.

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Electrolytic polymerization

- The operation can be carried out in two modes: In **potentiostatic synthesis** the electrode potential between the working electrode and the reference electrodes is maintained unaltered, whereas
- in **galvanostatic synthesis**, potential varies to maintain electric current unaltered.

Now, this operation, it can be carried out in 2 modes. One is the potential static synthesis, the electrode potential between the working electrode, this one is the working electrode, between the working electrode and the reference electrode is maintained unaltered whereas, when we use the galvanostatic synthesis, the potential varies to maintain the electric current unaltered.

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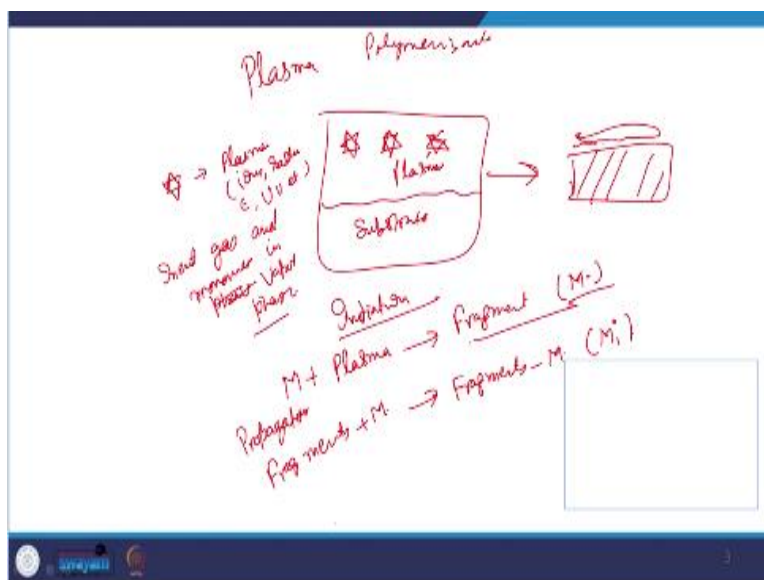
Plasma polymerization

- **Plasma polymerization** is a process where a gaseous monomer is inserted at low pressure (vacuum) in an electric discharge under conditions where a plasma is generated [Boenig, 1988; Yasuda, 1986].
- The polymeric material is formed by using either the plasma state of monomers, or reactive species created in the plasma state. The plasma source generates a gaseous ionized discharge containing sufficient energy to activate the gaseous or liquid monomer.

Now, another concept is the plasma polymerization. Now, the plasma polymerization is a process where a gaseous monomer is inserted in a low pressure vacuum in an electric discharge under the condition where the plasma is being generated. Now, the polymeric material is formed by using either the plasma state of monomer or reactive species created in the plasma state.

The plasma source generates gaseous ionised discharge containing sufficient energy to activate the gaseous or liquid monomer. Now, the activated particle whatever being generated they may be termed as the free radical monomer combined on the surface and they form a cross linked polymer using graft polymerization.

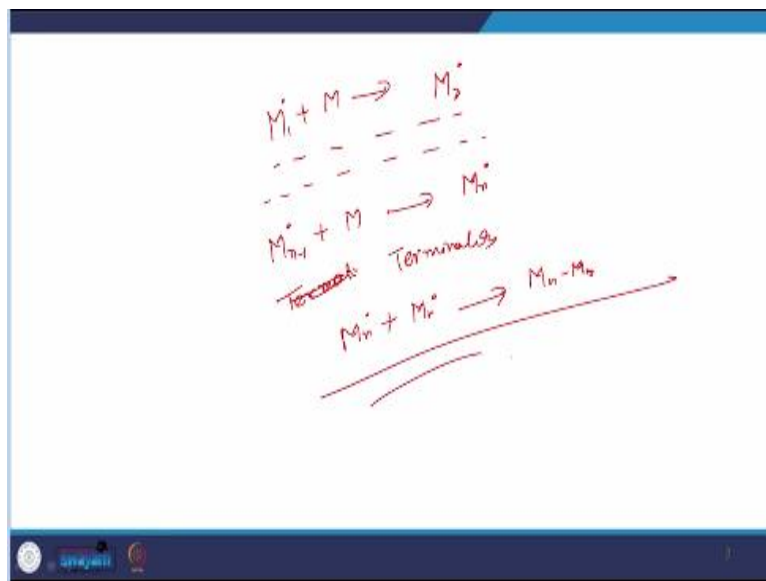
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So, we have one pictorial segment to represent this one the plasma polymerization. Here, this is the chamber where we are having the substrate and here, we are having certain segments which related to the plasma. Now, this implicates the plasma maybe ions, with the help of ions or UV radiation etcetera. Now, this inert gas and monomer, they are in the vapour phase. Now, once they synthesise, then they may create the cross linked polymeric system like this.

So, just have a brief look about the mechanism. Now, here that initiation as we recall that this is a 3 step process: initiation, propagation and termination. So, initiation, this gives you fragments. Now, this produces the radicals. Now, here see, now, if we talk about the propagation, then these fragments this one plus monomer, they may combine to gives this one and sometimes referred as this chain.

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So, this is one way to represent the propagation step. Now, if we talk about the termination one, because ultimately when you form this one, then you need to terminate the things, then this may become. So, this is your termination step.

So, by this way, you can see that whenever we talk about this plasma polymerization, it offers a very good opportunity to develop different kind of cross link polymers, sometimes using the graft polymerization. So, various advantages, they are associated with the plasma polymerization. They offer a high degree of cross linkage as compared to the other initiation process.

Sometimes, they possess a least damage to the structure because things are in the plasma form more than that we perform or in the gaseous form. Another advantage is that they have a very good thermal stability and a strong addition to the surface as you see that there is a deposition of generated polymer over the surface of substrate. other advantages associated that it is usually not dissolvable in any organic solvent, this may be attributed to the cross linking character of the polymer being generated in due course of time.

Now, compared to other initiation technique, the plasma polymerization is a single step process, whether a single monomer or copolymer is used for the chemical modification. So, these are the various advantages associated with the plasma polymerization process. It opens a broad domain for the selection of monomer. Now, as usually the volatile molecule, they can undergo polymerization, even if does not contain any vinyl or cyclic group like alkanes etcetera.

So, it opens a new horizon; it opens the new opportunity for the polymerization process. the polymer composition usually depends upon the geometry of the reaction vessel, because it is the cross link one, so, it the geometry of the reaction vessel plays a very vital role. Moreover, apart from this the operating conditions like monomer, flow rate, concentration, pressure, power discharge etcetera, they also play a very, very vital role in the determination of the polymer composition.

Now, it is usually independent from the nature of polymer substrate and the monomer therefore, any substrate can be used like glass, organic polymers and metal etcetera. So, this advanced technique is usually used for developing of electrical insulation, sometimes you may require

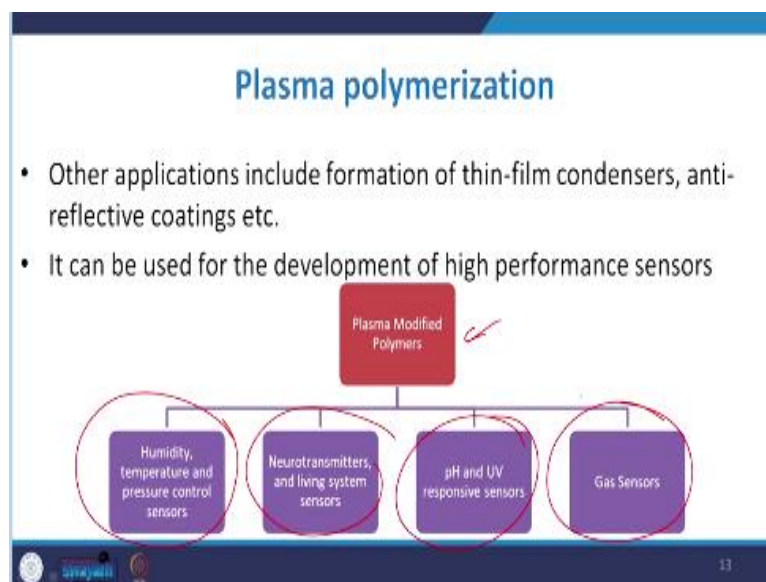
very specialised chemical protective coating to the various surfaces. So, this particular technique offers a very good opportunity for this one.

However, this technique attracts its focus towards its use in the development of advanced and durable materials like sometimes high performance membrane, which can be used in the batteries and purification and sometimes we like the membrane distillation application. So, once you are having the opportunity to develop more and more different type of polymer, then it offers the widest spectrum of application profile.

Now, sometimes people are talking about the different other applications. So, other applications this includes the formation of thin film condensers, sometimes anti-reflective coating, because again you need to deposit the polymer over the surface or over the substrate. So, it offers a very good opportunity with respect to the coating to the different substrates. So, it can be used for the development of high performance sensor.

So, in this particular diagram, we have discussed or we have described that you may have a different plasma modified polymers.

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It may be used to get the humidity temperature, controller and the pressure controller sensors. Sometimes, it can be used as neurotransmitters and the living system sensors, then pH and UV responses sensors and gas sensors. So, you see that this particular concept offers a wide spectrum of uses. So, it again gives an opportunity to develop more and more new type of polymer with the help of these type of advanced techniques for the polymerization.

Let us have a look about the other technique called sonication. Now, sonication is another technique which utilises high intensity ultrasound frequency resulting in the radical polymerization. Now, initiation usually occurs due to the cavitation effect.

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Sonication

Source: Boon Mian Teo, 2016

- **Sonication**, is another technique which utilizes high-intensity ultrasound frequencies, resulting in radical polymerization.
- Initiation occur due to the cavitation effect, in which sound waves (cycles of pressure) agitates the particles in a solution in such a manner that thousands of microscopic vacuum bubbles forms in the solution.

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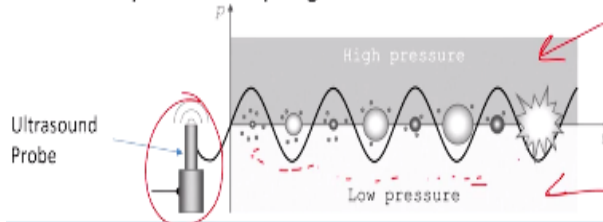
You see here, we have represented one figure. I will discuss a bit later. Now, in this cavitation, the sound waves that is a cycle of different pressure agitates the particles in a solution, such a manner that thousands of microscopic vacuum bubbles formed in the solution. Now, you see here that you are having the solution and this is the ultrasonic hall to which you are generating the ultrasonic waves.

And you see here, there are droplets of monomer and with monomer and here this is, you see the cavitation bubble so, that you can create the radicals over there. Then you perform the polymerization sometimes to alter the surface effect, you may require the certain surfactant to carry for the ease of this sonication process.

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Sonication

- These bubbles when collapse cause extreme effects locally, such as generation of liquid jets of up to 1000 km/hrs, localized pressure of up to 2000 atm, and temperature rise of up to 5000 K, near the boundary of the collapsing bubbles.



Now, these bubbles which we generated over here, these bubbles when collapsed, they cause to the extreme effect locally such as the generation of liquid jets up to you can say, the 1000 kilometres per hour, localised pressure up to say, 2000 atmosphere and sometimes temperature may rise up to say, 5000 Kelvin near the boundary of collapsing bubbles. So, you see that here you are having the 2 pressure zone.

One is the high pressure and other one is the low pressure zone and here you are creating the ultra sound and the sonicator, then there is a formation of bubbles and ultimately when they enlarge their size, then they collapse and create such kind of effect which we discussed in this particular slide.

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Sonication

- These extreme localized conditions lead to the formation of thousands of radicals at time. However, the conversion efficiency is found to be very low (<15%) and the formed high viscosity polymers also obstructs the cavitation process.

Now, these extreme localised conditions like here which we described, these extreme localised conditions, they lead to the formation of thousands of radicals at a time. So, you can anticipate the efficiency of this sonicator. Now, the conversion efficiency is usually found to be very low, sometimes it is less than 15%. So, the formed high viscosity polymer, they also obstruct the cavitation process.

So, these are the some of the hindrance being observed in the sonication process. Now, let us have a look about this chain transfer, sometimes you may experience the premature termination of propagating polymer may create to the decrease in molecular weight of the final product as compared to that theoretical determined value.

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The slide is titled "Chain Transfer" in blue text. In the top right corner, there are three handwritten chemical equations in red: $P_1 + R \rightarrow R_2$, $R_1 + R_2 \rightarrow R_3 \rightarrow n$, and $R_2 + R_1 \rightarrow$. The main content consists of a bulleted list. The first bullet point states that premature termination of a propagating polymer leads to a decrease in molecular weight. The second bullet point lists the reasons for this: transfer of hydrogen or other atoms from the same monomer, an initiator, or a solvent. At the bottom of the slide, there are logos for "Swayam" and "MOOC" on the left, and the number "17" on the right.

Theoretically you can anticipate that what should be the molecular weight distribution pattern in your formed polymer, but because of certain operational difficulty attributed to the either experiment or industrial scale, you may experience the premature termination of any kind of propagating polymer.

So, thereby, when there is a premature termination, then if you are anticipating say, this is the P_n , you may have say n number of chains, you may have $n - m$ number of chains that is why your molecular weight distribution pattern may disturb and that is why because molecular weight distribution plays a vital role in deciding the property of the polymer. In that case, it may create a problem for future processability of your polymer.

So, therefore, this thing needs to be addressed. So, when we talk about this particular concept, the reason for the premature termination, this can be attributed to the transfer of hydrogen, other atoms to the propagating polymer maybe from either same polymer, same monomer or maybe from the initiator or maybe from the solvent. So, these 3, 4 different aspects which you need to address to see the concept of a premature termination.

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Chain Transfer

- These reactions are called as chain-transfer reactions, and can be expressed as

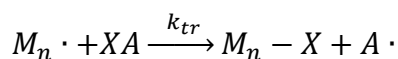
$$M_n \cdot + XA \xrightarrow{k_{tr}} M_n - X + A \cdot$$

- Where XA represents the compound from which transfer is occurring and X indicates the transferring atom or species.
- The rate of reaction for chain-transfer can be expressed as;

$$R_{tr} = k_{tr}[M \cdot][XA] \rightarrow$$

- Here, k_{tr} is the rate constant for chain transfer

- These reactions are called as chain-transfer reactions, and can be expressed as



- $M_n \cdot$ is the radical and XA represents the compound from which transfer is occurring and X indicates the transferring atom or species.
- The rate of reaction for chain-transfer can be expressed as;

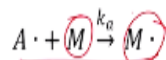
$$R_{tr} = k_{tr}[M \cdot][XA]$$

- Here, k_{tr} is the rate constant for chain transfer

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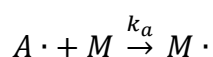
Chain Transfer

- The new radical A· generated during this reaction can reinitiates the polymerization reaction by;



- There can be four kind of scenarios as described in the following table:

So, now, if we see that the new radical A dot, which is formed in this particular reaction, this new radical A is generated during this reaction and can be re-initiates the polymerization reaction by this particular reaction, where you can see that A this combined with the monomer to give you that monomer radicals. So, this gives you another opportunity to understand the chain transfer.



- There can be four kind of scenarios as described in the following table:

Rate constants	Effect on Chain	Rate of polymerization (R_p)	Number average degree of polymerization (\bar{X}_n)
$k_{tr} \ll k_p; k_a \cong k_p$	kinetic chain length remains unchanged	Unchanged	Decrease
$k_{tr} \gg k_p; k_a \cong k_p$	Telomerization (generation of very small size particles)	Unchanged	Greatly decrease

$k_{tr} \ll k_p; k_a < k_p$ (Reinitiation is slow)	Retardation	Decrease	Decrease
$k_{tr} \gg k_p; k_a < k_p$ (Reinitiation is slow)	Degradative Chain Transfer	Greatly Decreases	Greatly decrease

There are various cases which we are going to discuss in this particular segment, sometimes you may have k_{tr} is less than with the rate of propagation.

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Chain Transfer			
Rate constants	Effect on Chain	Rate of polymerization (R_p)	Number average degree of polymerization (\bar{X}_n)
$k_{tr} \ll k_p; k_a < k_p$ (Reinitiation is slow)	Retardation	Decrease	Decrease
$k_{tr} \gg k_p; k_a < k_p$ (Reinitiation is slow)	Degradative Chain Transfer	Greatly Decreases	Greatly decrease

And then the kinetic chain length, it remains unchanged and the rate of polymerization which we talked about this remains unchanged. However, the number average degree of polymerization which is referred to as \bar{X}_n is decreased. Now, if we say that the rate constant for the transfer of reaction is greater than, greater than the rate constant of propagation, then in

that case, the telomerization that is the generation of a very small sized particle sometimes you cannot even notice all kinds of these small sized particles.

So, the effect on chain can be attributed to the telomerization and the rate of polymerization usually unchanged and number average degree of polymerization is greatly decreased. Similarly, if we talk about the; say, that rate of transfer is less than less than K_p , then the effect on change will be the retardation and the rate of polymerization decreases. Simultaneously, the number average degree of polymerization will also decrease.

And sometimes, when you see that rate constant transfer of chain is increased or is greater than, greater than the rate constant of propagation, then you may experience the degradative chain transfer and in this case, the re-initiation step is slow. So, in that case, the rate of polymerization usually decreases substantially and number average degree of polymerization also greatly decreases or sometimes it is more significant compared to the other cases.

Now, let us discuss these things with respect to the different cases. Now, there are various cases under this head. Now, first case that if rate constant that is purely based on this particular table. **(Refer Slide Time: 23:32)**

Chain Transfer

Case 1: If the rate constant for transfer reaction is very less than that of propagation, and the rate of reinitiation is comparable with the original propagating radical, then there will be no effect on the rate of propagation and chain length will remain unchanged.

Case 2: In this case when the rate constant for transfer reaction is very large than that of propagation, while the rate of reinitiation is comparable with the original propagating radical, then there will be no effect on the rate of propagation but the chain length will change drastically and several very small size polymer will form. This phenomenon is called as telomerization.

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Case 1: If the rate constant for transfer reaction is very less than that of propagation, and the rate of reinitiation is comparable with the original propagating radical, then there will be no effect on the rate of propagation and chain length will remain unchanged.

Case 2: In this case when the rate constant for transfer reaction is very large than that of propagation, while the rate of reinitiation is comparable with the original propagating radical,

then there will be no effect on the rate of propagation but the chain length will change drastically and several very small size polymer will form. This phenomenon is called as telomerization.

So, if the rate constant for transfer reaction is very less like in this case, we have discussed, then that of the propagation, you see here that this is very less, then the rate of any re-initiation is comparable with the original propagating radical, you see that we have already enlisted that rate of re-initiation of the step and this is compatible with the original propagating radical, then there will be no effect on the rate of propagation and the chain length will remain unchanged.

Another case which we described over here that the rate constant for the transfer reaction is very large, then that of propagation so, while the rate of re-initiation is comparable, you see here, the rate of re-initiation is comparable, in this case with the original propagating radical, then there will be no effect either on the rate of propagation, but the chain length will change drastically, you see here the chain length is changing drastically.

So, this is again, this phenomena is usually which we refer as the telomerization and under this head, you may experience the formation of a very small sized polymer. So, this may adversely alter your molecular weight distribution pattern. Another case which we discussed with the help of that particular table that if the rate constant for the transfer reaction is very less, here you see.

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Chain Transfer

Case 3: If the rate constant for transfer reaction is very less than that of propagation, and the rate of reinitiation is less than the original propagating radical, then there will be a decrease in the rate of propagation and \bar{X}_n , while the reaction will slow down.

Case 4: In this case when the rate constant for transfer reaction is very large than that of propagation, while the rate of reinitiation is less than the original propagating radical, then the rate of propagation and \bar{X}_n will greatly effect and degradative chain transfer reaction will proceed.

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And the rate of re-initiation is less than the original propagating radical, then there will be a decrease in the propagation, you see over here and when we talk about the number average degree of polymerization, the reaction will slow down. last case is that when the rate constant for transfer reaction is very large, here you see and we described that re-initiation would be very slow.

So, in that case, the rate of re-initiation is less than the original propagating radical and then the rate of propagation and degree of polymerization will greatly affect and the degradative chain transfer reaction will proceed. So, when the polymerization is initiated by the thermal hemolysis and termination, whenever it occurs through the combination of coupling and sometimes disproportionation and chain transfer to monomer initiator and compound sometimes as this is referred as the chain transfer agent, the number average degree of polymerization will take place.

$$\bar{X}_n = \frac{R_p}{(2 - a) \left(\frac{R_t}{2} \right) + k_{tr,M}[M \cdot][M] + k_{tr,S}[M \cdot][S] + k_{tr,I}[M \cdot][I]}$$

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Chain Transfer

If polymerization is initiated by the thermal homolysis and termination occur through combination of coupling and disproportionation and chain transfer to monomer, initiator, and the compound S (referred to as a chain-transfer agent), the number average degree of polymerization follows

$$\bar{X}_n = \frac{R_p}{(2 - a) \left(\frac{R_t}{2} \right) + k_{tr,M}[M \cdot][M] + k_{tr,S}[M \cdot][S] + k_{tr,I}[M \cdot][I]}$$

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$$\bar{X}_n = \frac{R_p}{(2\alpha)\left(\frac{k_t}{k_p}\right) + k_{tr,M}[M] + k_{tr,S}[M] + k_{tr,I}[I]}$$

$$= \frac{R_p}{k_{tr,S}[M] + k_{tr,I}[I]}$$

The first term in the denominator denotes the termination sometimes it may be the first term in the denominator, this denotes the termination by a combination of coupling and disproportionation.

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Chain Transfer

- The first term in the denominator denotes termination by a combination of coupling and disproportionation, and the other terms denote chain transfer by monomer, chain-transfer agent, and initiator, respectively. Consider now the simpler case when disproportionation does not occur.
- A chain-transfer constant C for a substance is defined as the ratio of the rate constant k_{tr} for the chain transfer of a propagating radical with that substance to the rate constant k_p for propagation of the radical. The chain-transfer constants for monomer, chain-transfer agent, and initiator are then given by

$$C_M = \frac{k_{tr,M}}{k_p} \quad C_S = \frac{k_{tr,S}}{k_p} \quad C_I = \frac{k_{tr,I}}{k_p}$$


And other terms denote the chain transfer of by monomer chain transfer agent and initiator respectively. So, consider now, we can have simpler cases when disproportionation does not occur. So, a chain transfer constant C is introduced over here.

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C Ratio of rate constant k_{tr} for the chain transfer of a propagating radical with that substance to rate constant k_p for propagation of radical.

$$C_M = \frac{k_{tr,M}}{k_p}$$

$$C_S = \frac{k_{tr,S}}{k_p}$$

$$C_I = \frac{k_{tr,I}}{k_p}$$


So, the chain transfer constant C for substance is usually defined as the ratio of the rate constant that is the ratio of rate constant k_{tr} for the chain transfer of a propagating radical with that substance to the rate constant k_p for propagation of the radical. Now, the chain transfer constant for monomer chain transfer agent and initiator, then thereby given by

$$C_M = \frac{k_{tr,M}}{k_p} C_S = \frac{k_{tr,S}}{k_p} C_I = \frac{k_{tr,I}}{k_p}$$

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$R_p = R_t$ yields

$$\frac{1}{\bar{X}_n} = \frac{R_i}{2R_p} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]}$$

OR

$$\frac{1}{\bar{X}_n} = \frac{k_t k_p}{k_p^2 [M]^2} + C_M + \frac{C_S [S]}{[M]} + C_I \frac{k_t k_p [I]}{k_p^2 [M]^2}$$

Qualitative effect of various transfer reactions on number-average degree of polymerization



- Combining Eqs. with $R_i = R_t$ yields

$$\frac{1}{\bar{X}_M} = \frac{R_i}{2R_p} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]}$$

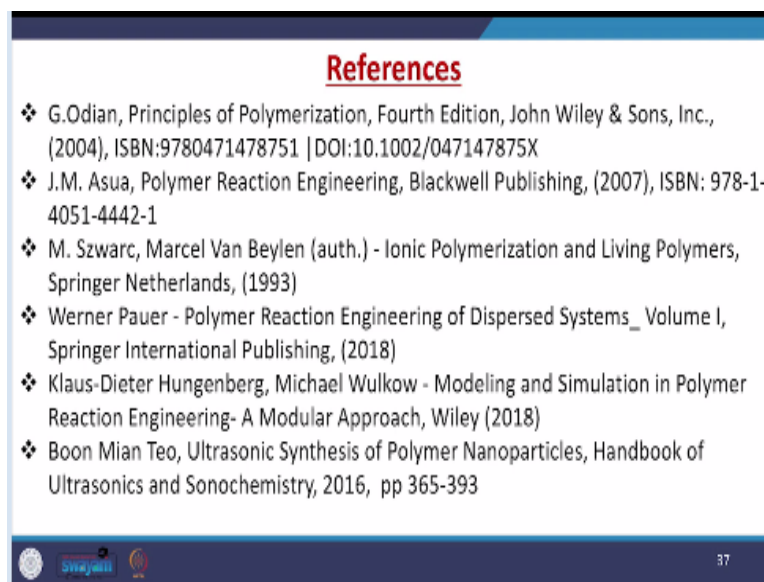
Or

$$\frac{1}{\bar{X}_M} = \frac{k_t R_p}{k_p^2 [M]^2} + C_M + \frac{C_S [S]}{[M]} + C_I \frac{k_t R_p^2}{k_p^2 f k_d [M]^3}$$

which show the quantitative effect of the various transfer reactions on the number-average degree of polymerization.

Now, this shows the quantitative effect; this quantitative effect of various transfer reactions which we discussed in the things on number average degree of polymerization. So, this is the very important concept especially attributed to this chain transfer concept. Now, let us have a look about the determination of absolute rate constant which we discussed.

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Up to now, we have discussed about the concept of a chain transfer and we discussed about the various techniques or tools available for this particular concept and we discussed the development of various equations attributed to the chain transfer. We discussed various cases related to chain transfer concept. Now, we will continue with this particular approach attributed to the determination of absolute rate constant in the subsequent lecture. Thank you very much.