Polymer Reaction Engineering
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Lecture - 42
Photochemical and Ionisation Initiation

Welcome to the next lecture of photochemical and ionisation initiation under the head of radical chain polymerization. So, let us have a brief look about the topics which we covered previously.

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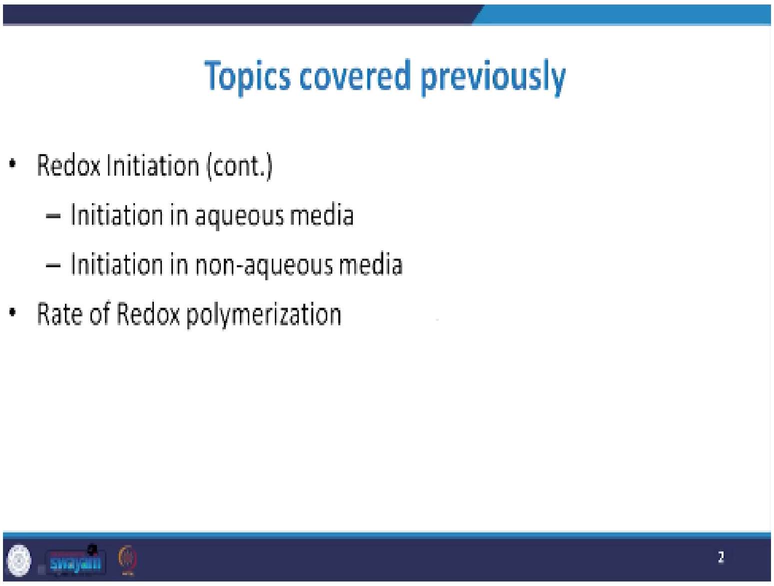

Topics covered previously

- Redox Initiation (cont.)
  - Initiation in aqueous media
  - Initiation in non-aqueous media
- Rate of Redox polymerization

We had a discussion about the Redox initiation; we discussed about the initiation process in the aqueous media as well as non-aqueous media. Then we discussed about the Redox polymerization in detail and we discussed about the mechanism of those Redox polymerization process in due course of time.

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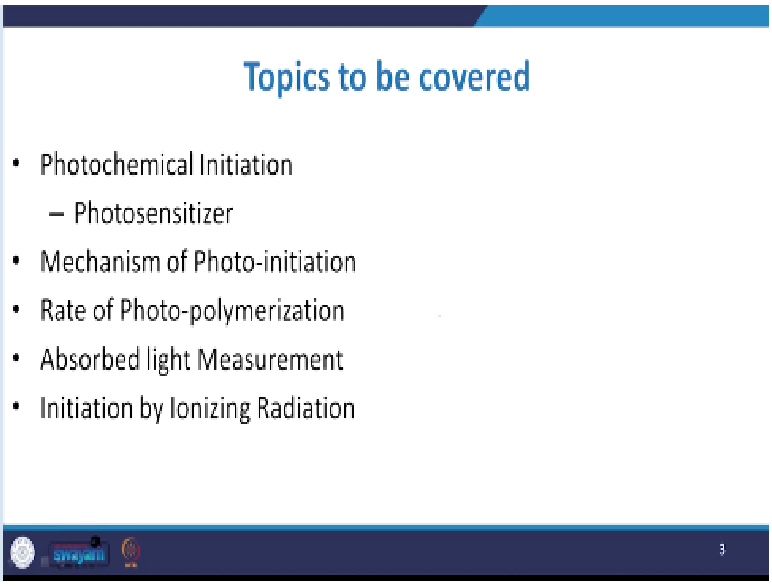

Topics to be covered

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

Now, in this particular lecture, we are going to cover the photochemical initiation with the help of a photosensitizer; then we will discuss about the mechanism of photo initiation because these photo initiation plays a very vital role in the polymerization process. We will discuss about the rate of photo-polymerization. We will have a discussion about the absorbed light measurement and the initiation of ionising radiation.

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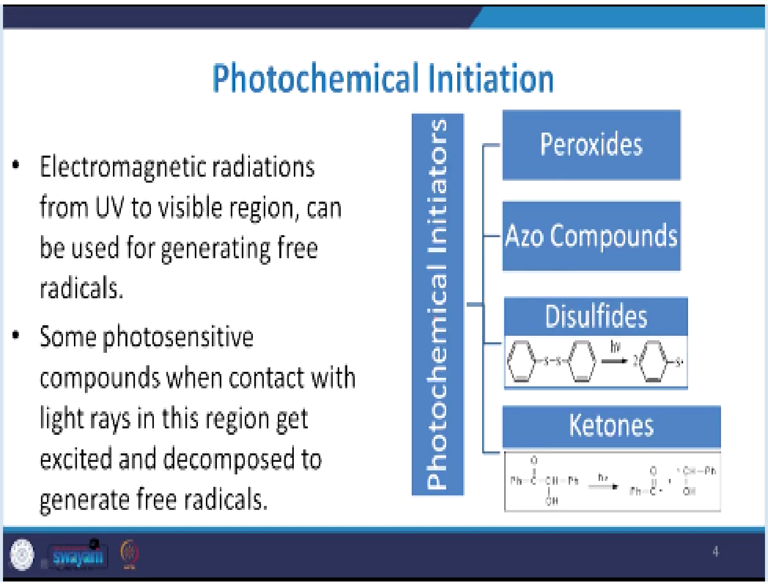


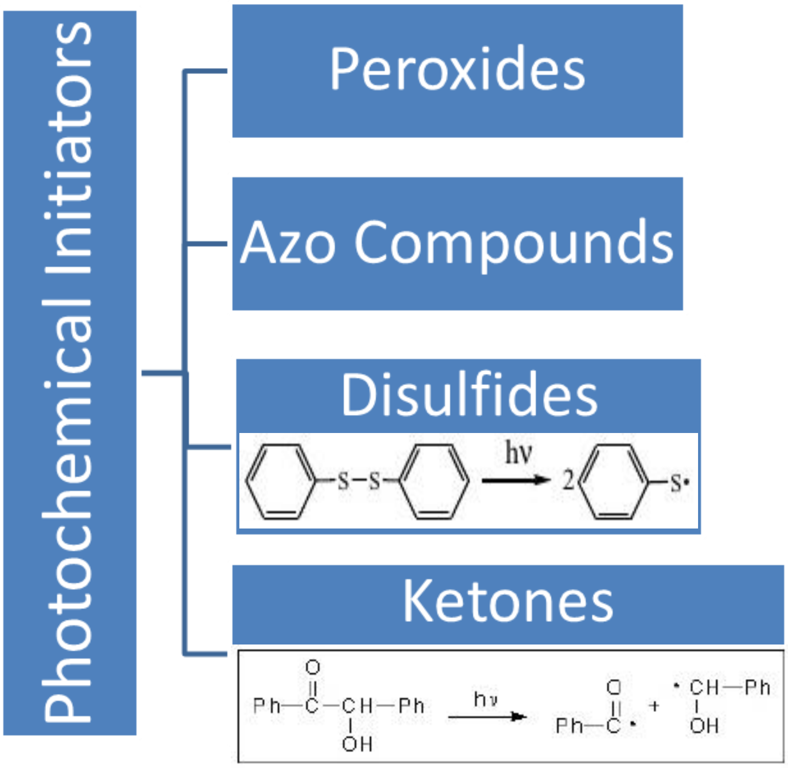
Photochemical Initiation

- Electromagnetic radiations from UV to visible region, can be used for generating free radicals.
- Some photosensitive compounds when contact with light rays in this region get excited and decomposed to generate free radicals.

Photochemical Initiators

- Peroxides
- Azo Compounds
- Disulfides
- Ketones

Let us have a look about the photochemical initiation. You see that electromagnetic radiation from UV to visible reason, this can be used for the; generating the free radicals, some of the photosensitive compounds, when they contact with the light rays in this region, they get exited and they get decomposed to generate the free radicals. Now, there are several photochemical initiators, they are enlisted like peroxide, azo compound, di-sulfides, ketones. These are the some of the photochemical initiators.



Photochemical Initiators

Peroxides

Azo Compounds

Disulfides

Ketones

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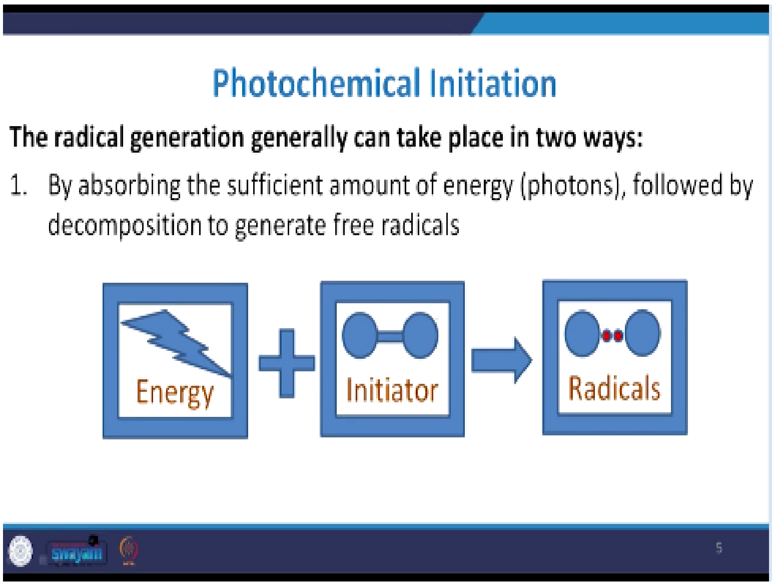

Photochemical Initiation

The radical generation generally can take place in two ways:

1. By absorbing the sufficient amount of energy (photons), followed by decomposition to generate free radicals

Now, the radical generation, generally, this can take place in 2 ways. One is that they either absorbed a sufficient amount of energy attributed to the photons and followed by the decomposition to generate the free radicals. So, like you see that they absorb certain quantum of energy and then initiator and then they produce the radicals for further polymerization process.

Now, second step is that they may absorb the desired amount of energy, then the exited compound what which absorb the energy reacts with the second compound to generate the free radicals that is called the photosensitizers. And this particular topic, we will discuss in later on. Now, this kind of a chemical substance that can either help to increase the rate of photo initiation or shift the wavelength at which the polymerization occurs.

Now, photo initiation this usually provides a variety of benefits, the polymerization can be guided spatially that is limited to the very different reasons and turn on and off by switching off and on the light source. So, you can see that this can be guided with the help of this light source under the head of different reasons. Now, the rate of initiation, it can be very fast and usually is regulated by a combination of radical source, light intensity and temperature.

Now, industrial photo-polymerization usually use some of solvent free system that provide both economic and environmental advantages. So, the major drawback of photo initiated polymerization is a poor penetration of luminous energy across a material thickness. Now, sometimes places where the penetration depth is limited like in printing, paint, coating and other surface and interfacial application, this method is well suited.

One of the approaches in this photochemical initiation is the photolithography which is one of the best example used for the production of integrated and printed circuit. Some of the other example may include like holography, stereo lithography for producing 3D structures, prototype and different parts in layer by layer fashion. It can be utilised in the medical application including curing of dental repairs, bone, cement, adhesive preparations etcetera.

Now, photo-polymerization, this can be used with the heat sensitive substrate, because even at ambient temperature, polymerization is quite simple. You can use or it can be used for the ultra fast drying of paint, varnish and other sensitive and protective coating application. So, this is having a very wide spectrum of uses. Now, let us have a brief discussion about the photosensitizers.

Now, photosensitizers, they are the molecules that absorb light energy that is photon and act as a donor by transferring the absorb energy to the acceptor molecule. The acceptor molecule usually then undergo the various reactions like isomerisation, coupling, polymerization and other similar reactions. Now, for a compound to act as photosensitizer, it should not only be a good absorber of light, but also should readily transfer it to another molecule.

Now, this compound showing such mechanism is usually known as termed as a charge transfer complex.

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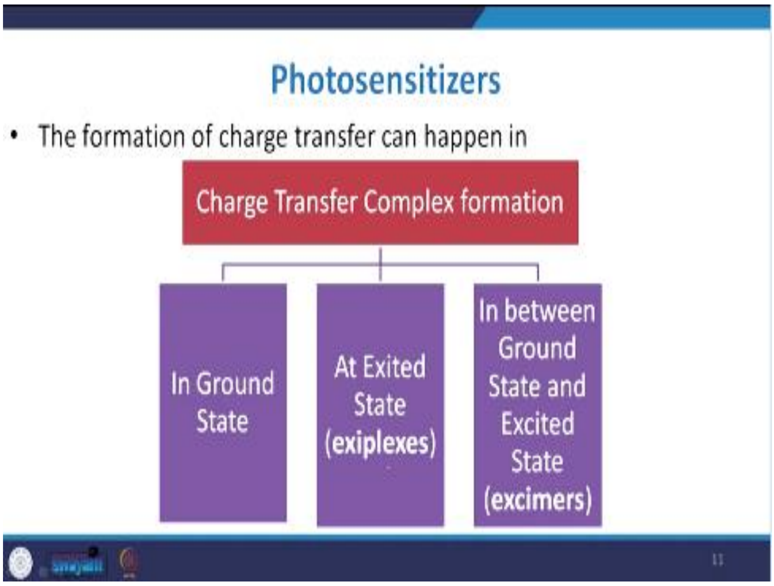


Photosensitizers

- The formation of charge transfer can happen in

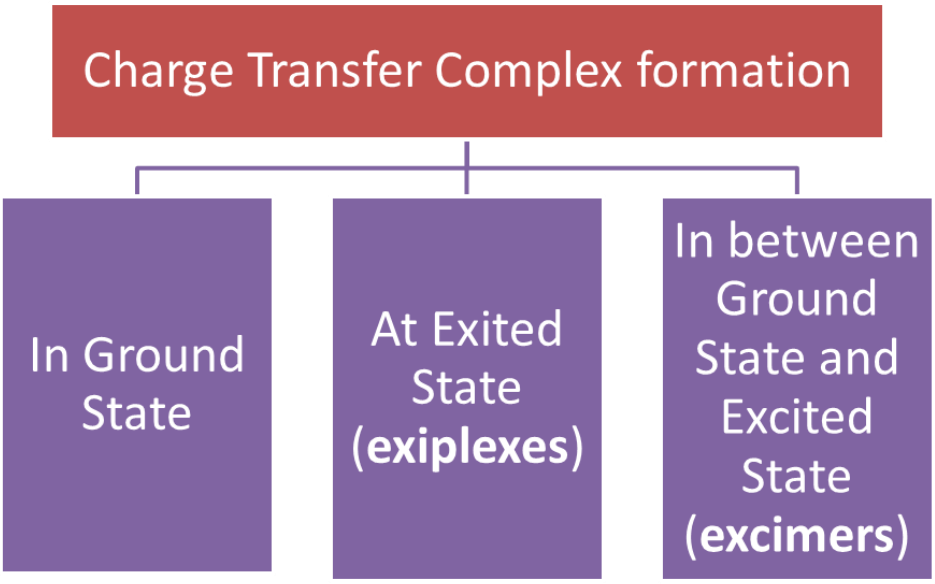
Charge Transfer Complex formation

In Ground State

At Exited State (exiplexes)

In between Ground State and Excited State (excimers)

Now, the formation of the charge transfer, it can happen that charge transfer complex formation is usually carried out either in a ground state or at an exited state that is exiplexes or in between ground state and exited states that is excimers. Now, the difference between the excimer and exiplexe is that the formal possesses binding energy in the ground state while exiplexes, they do not have any binding energy in ground state.



Charge Transfer Complex formation

In Ground State

At Exited State **(exiplexes)**

In between Ground State and Excited State **(excimers)**

So, the rate of absorption of light by any sensitizer that corresponds from the ground state say S_0 to the exited state S_1 is this one.

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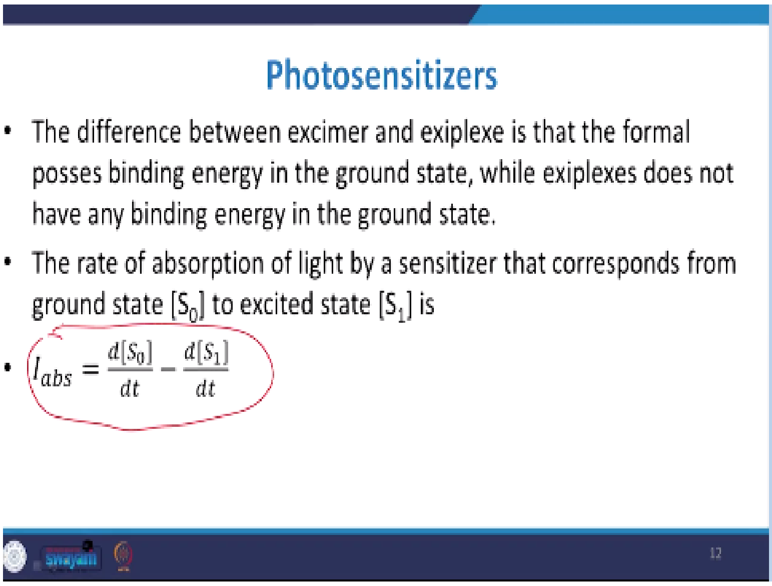

Photosensitizers

- The difference between excimer and exiplexe is that the formal posses binding energy in the ground state, while exiplexes does not have any binding energy in the ground state.
- The rate of absorption of light by a sensitizer that corresponds from ground state $[S_0]$ to excited state $[S_1]$ is
- $I_{abs} = \frac{d[S_0]}{dt} - \frac{d[S_1]}{dt}$

This can be represented like this particular equation

- $I_{abs} = \frac{d[S_0]}{dt} - \frac{d[S_1]}{dt}$

Now, the rate constant for diffusion control reaction that is k_{diff} can be defined through the Debye equation that is

- $k_{diff} = \frac{8RT}{300\eta}$

And the observed rate constant for energy transfer k_{ET} can be defined as

$$k_{ET} = \alpha k_{diff}$$

Where, α is the probability of energy transfer; R is universal gas constant; T is the temperature (K); η is the viscosity of the medium (in poise)

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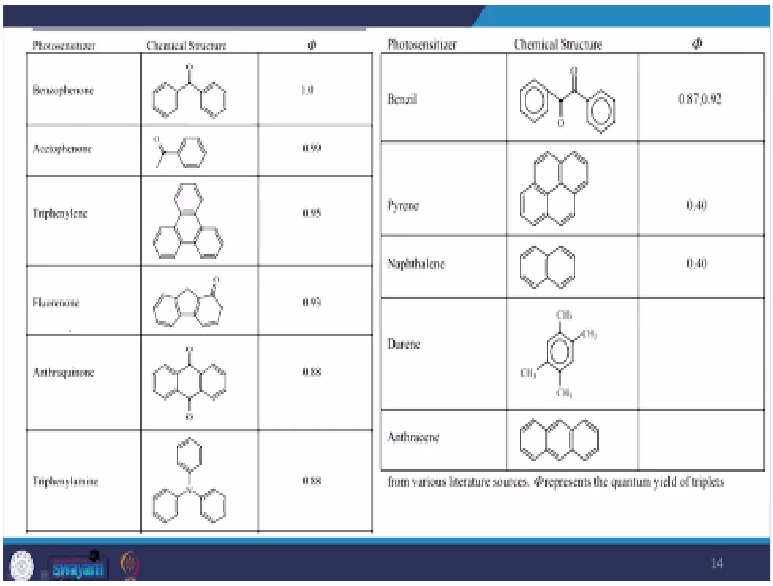


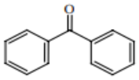
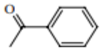
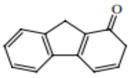
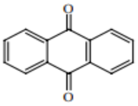
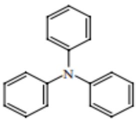
Photosensitizer	Chemical Structure	Φ
Benzophenone		1.0
Acetophenone		0.99
Triphenylene		0.95
Fluorenone		0.93
Anthraquinone		0.88
Triphenylamine		0.88

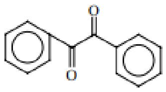
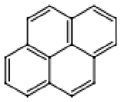
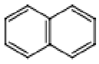
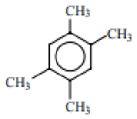
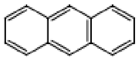
Photosensitizer	Chemical Structure	Φ
Benzil		0.87;0.92
Pyrene		0.40
Naphthalene		0.40
Durene		
Anthracene		

from various literature sources. Φ represents the quantum yield of triplets

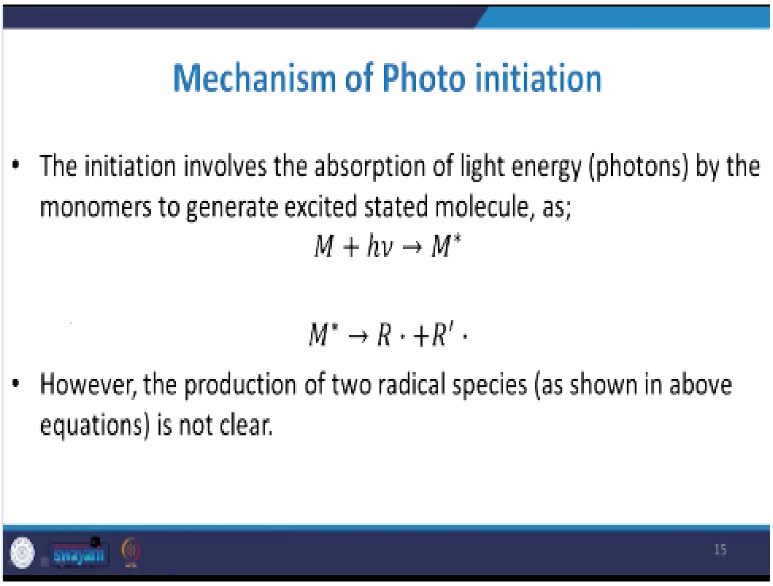
14

So, you can see there are various chemical structures attributed to the photosensitizers like benzophenone, acetophenone and benzil, pyrene etcetera. So, these are the various chemical structures, those who are listed in this particular approach.

Photosensitizer	Chemical Structure	Φ
Benzophenone		1.0
Acetophenone		0.99
Triphenylene		0.95
Fluorenone		0.93
Anthraquinone		0.88
Triphenylamine		0.88

Photosensitizer	Chemical Structure	Φ
Benzil		0.87;0.92
Pyrene		0.40
Naphthalene		0.40
Durene		
Anthracene		

from various literature sources. Φ represents the quantum yield of triplets



Mechanism of Photo initiation

- The initiation involves the absorption of light energy (photons) by the monomers to generate excited stated molecule, as;

$$M + h\nu \rightarrow M^{*}$$

$$M^{*} \rightarrow R \cdot + R' \cdot$$

- However, the production of two radical species (as shown in above equations) is not clear.

Now, let us have a discussion about the mechanism of photo initiation. Now, this initiation step involves the absorption of light energy by the monomer to get to generate exited state molecules like this

$$M + h\nu \rightarrow M^{*}$$
$$M^{*} \rightarrow R \cdot + R' \cdot$$

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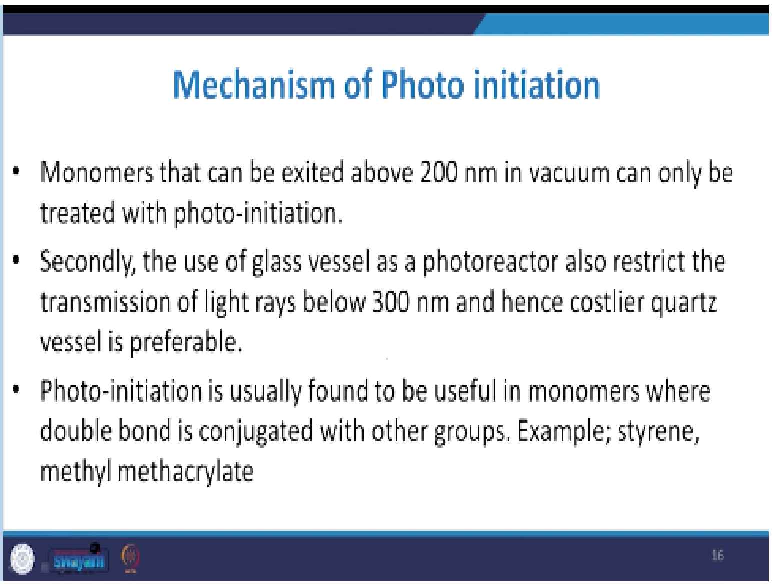

Mechanism of Photo initiation

- Monomers that can be exited above 200 nm in vacuum can only be treated with photo-initiation.
- Secondly, the use of glass vessel as a photoreactor also restrict the transmission of light rays below 300 nm and hence costlier quartz vessel is preferable.
- Photo-initiation is usually found to be useful in monomers where double bond is conjugated with other groups. Example; styrene, methyl methacrylate

Now, the monomers that can be exited about 200 nanometers in the vacuum, they can only be treated as photo initiation. Now, secondly, the use of glass vessel as a photo reactor also, they restrict the transmission of light ray below 300 nanometer and costlier quartz vessel is usually preferable to carry out this particular reaction. Photo initiation is usually found to be useful in the monomer where double bond is conjugated with the other groups like in the case of styrene, methacrylate etcetera.

Now, other different thermal and Redox initiation initiator species, it can also be used in the photo initiation utilising similar initiation step as we earlier discussed. It can also be used into too high temperature polymerization due to its wide selectivity of photo initiation. So, at higher temperatures, several bonds break and different radical and ionic species, they do form to initiate the polymerization process. Sometimes aliphatic, aromatic, ketones are the example of high temperature initiator species.

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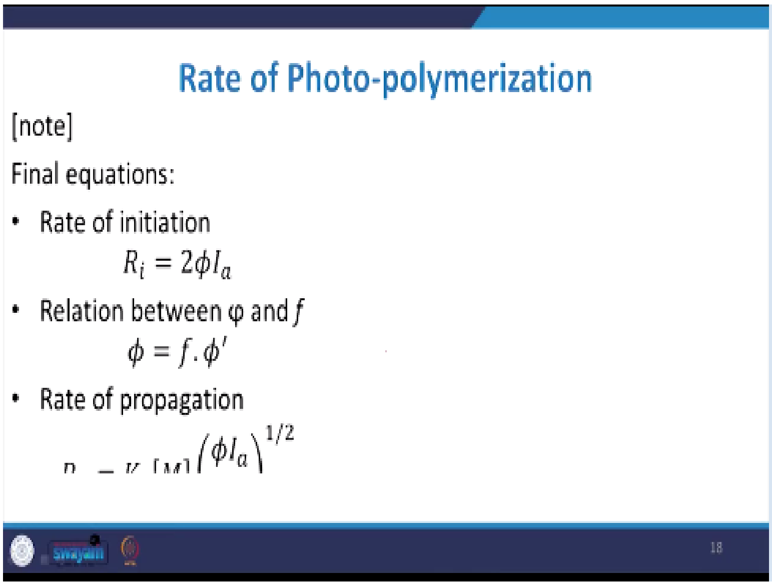

Rate of Photo-polymerization

[note]

Final equations:

- Rate of initiation

$$R_i = 2\phi I_a$$

- Relation between φ and f

$$\phi = f.\phi'$$

- Rate of propagation

$$R = K[M]\left(\phi I_a\right)^{1/2}$$

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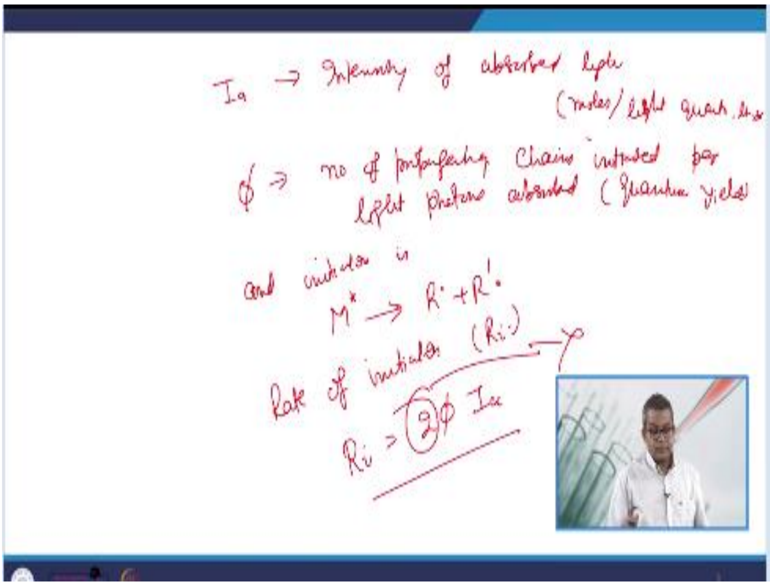

I_a → Intensity of absorbed light
(moles/light quanta

ϕ → no of propagating chains initiated per light photons absorbed (quantum yield

and initiation is

$M^* \rightarrow R^\cdot + R'^\cdot$

Rate of initiation (R_i) → f

$R_i = \boxed{2}\phi I_a$

Final equations:

- Rate of initiation

$$R_i = 2\phi I_a$$

- Relation between ϕ and *f*

$$\phi = f.\phi'$$

- Rate of propagation

$$R_p = K_p[M]\left(\frac{\phi I_a}{K_t}\right)^{1/2}$$

I_a → Intensity of absorbed light
(moles/light quanta . lt.s

ϕ → no of propagating chains initiated per light photons absorbed (quantum yield)

and initiation is

$$M^* \longrightarrow R^\cdot + R'^\cdot$$

Rate of initiation (R_i)

$$R_i = \boxed{2}\phi I_a$$

Now, when we talk about the rate of photo-polymerization, so, let us have a discussion about the mathematical representation of this one. So, let us say that if I is the intensity of absorbed light usually represented in terms of moles of light in one litre second and phi is that number of propagating chains initiated per light photons absorbed that is quantum yield and initiation is considered under the following equation. Now, let us see that this reaction generates the 2 radicals.

Now, the rate of initiation R i; now, this factor 2 indicates that 2 radicals are produced during the initiation reaction per molecule. So, if one radical is produced, then this factor can be omitted, so, you can eliminate this factor.

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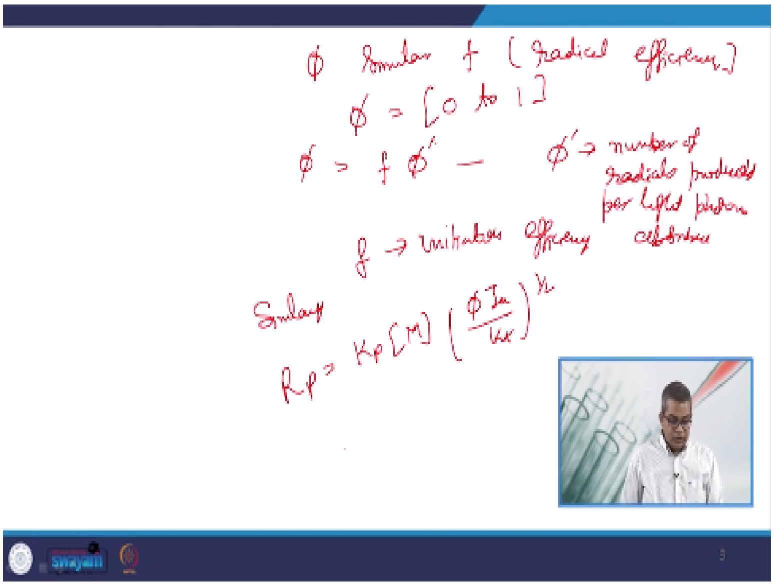


ϕ similar f (radical efficiency)

$\phi = [0 \text{ to } 1]$

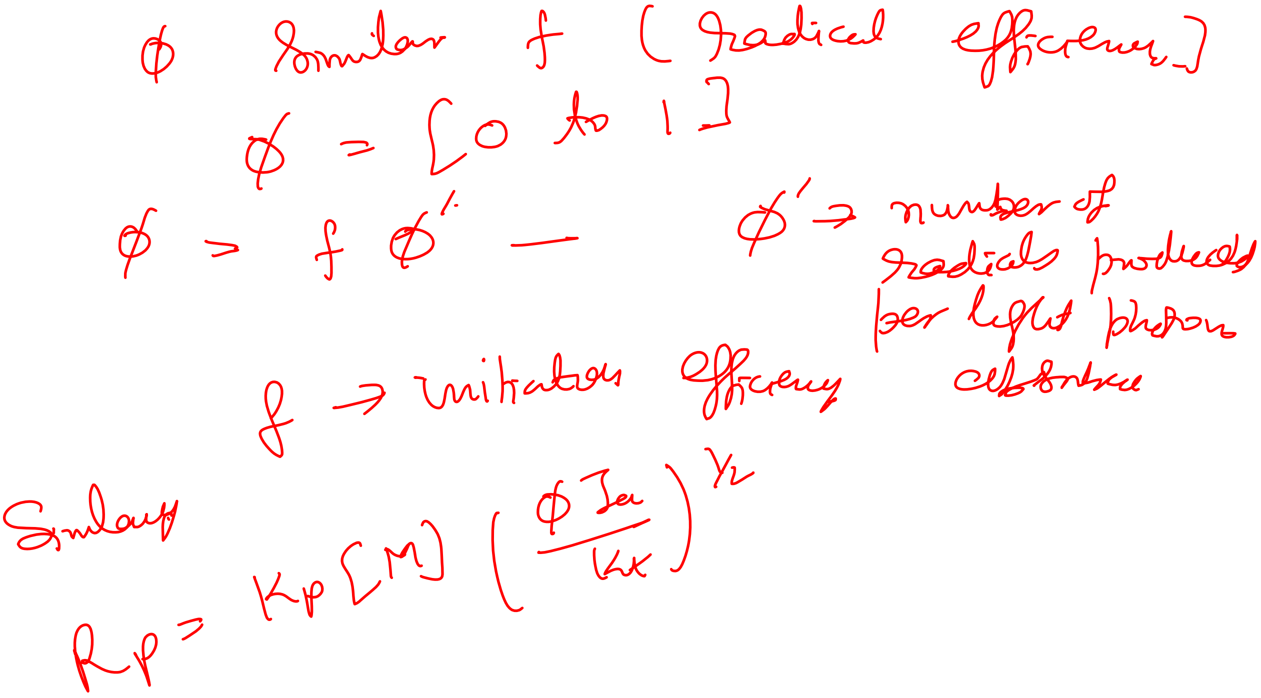
$\phi = f\phi'$ — $\phi' \rightarrow$ number of radicals produced per light photon absorbance

$f \rightarrow$ initiation efficiency

Similarly

$$R_p = K_p[M]\left(\frac{\phi I_a}{k_t}\right)^{1/2}$$

Now, as compared to thermal and Redox initiation that term phi is similar to f that is radical efficiency. So, phi may be in the range of 0 to 1. So, if we try to replace the phi, this can be replaced as phi is equal to f phi dash; here, this phi dash is the number of radicals produced per light photon absorbed and f is quite obvious that is that initiation efficiency. So, similarly, one can write that rate of propagation can be expressed as R_p is equal to K_p concentration of monomer phi.



ϕ similar f (radical efficiency)

$\phi = [0 \text{ to } 1]$

$\phi = f\phi'$ — $\phi' \rightarrow$ number of radicals produced per light photon absorbance

$f \rightarrow$ initiation efficiency

Similarly

$$R_p = K_p[M]\left(\frac{\phi I_a}{k_t}\right)^{1/2}$$

Now, keeping in mind the factor that the photo initiation is dependent upon the depth of light as at a particular distance.

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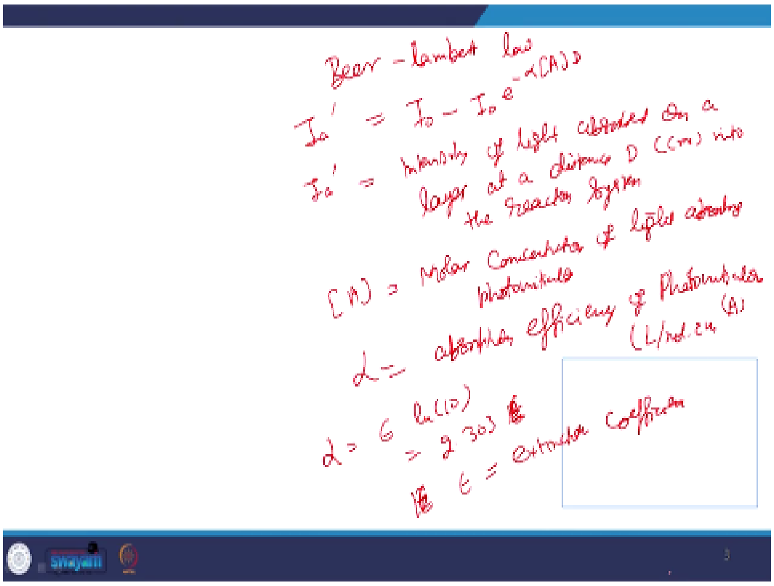

Now, if we use the Beer-Lambert law, because, it is quite important in this head.

Beer-lambert law

$I_a' = I_0 - I_0 e^{-\alpha[A]D}$

I_a' = intensity of light absorbed on a layer at a distance D (cm) into the reaction system

[A] = Molar concentration of light absorbing photoinitiator

α = absorption efficiency of photoinitiator (A) (L/mol.cm)

$\alpha = \epsilon \ln(10)$

$= 2.303\ \epsilon$

ϵ = extinction coefficient

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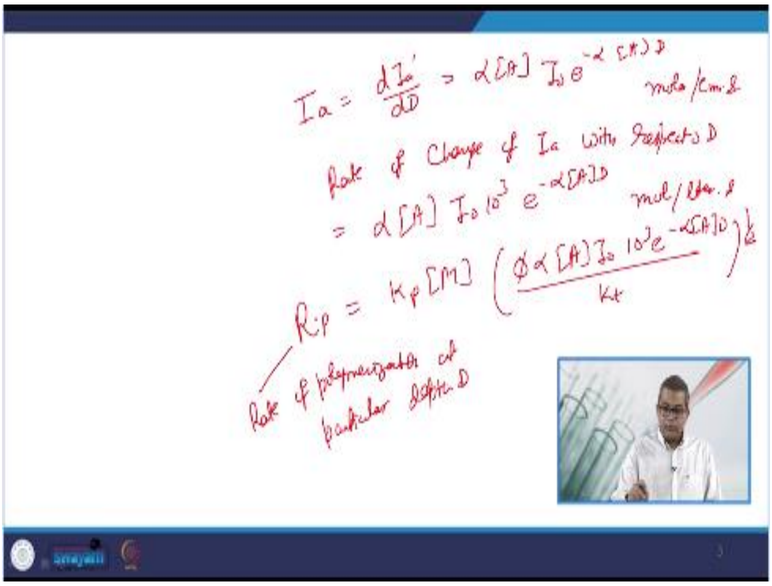

$$I_a = \frac{dI_a'}{dD} = \alpha[A] I_0 e^{-\alpha[A]D}$$ mole/cm·s

Rate of change of Ia with respect to D

$$= \alpha[A] I_0 10^3 e^{-\alpha[A]D}$$ mol/liter·s

$$R_p = k_p[M]\left(\frac{\phi\alpha[A]I_0 10^3 e^{-\alpha[A]D}}{k_t}\right)^{1/2}$$

Rate of polymerization at particular depth D

Now, rate of change of I a with respect to D, this can be calculated as

$$I_a = \frac{dI_a'}{dD} = \alpha[A] I_0 e^{-\alpha[A]D}$$ mole/cm·s

Rate of change of Ia with respect to D

$$= \alpha[A] I_0 10^3 e^{-\alpha[A]D}$$ mol/liter·s

$$R_p = k_p[M]\left(\frac{\phi\alpha[A]I_0 10^3 e^{-\alpha[A]D}}{k_t}\right)^{1/2}$$

Rate of polymerization at particular depth D

This is the rate of polymerization at particular depth D.

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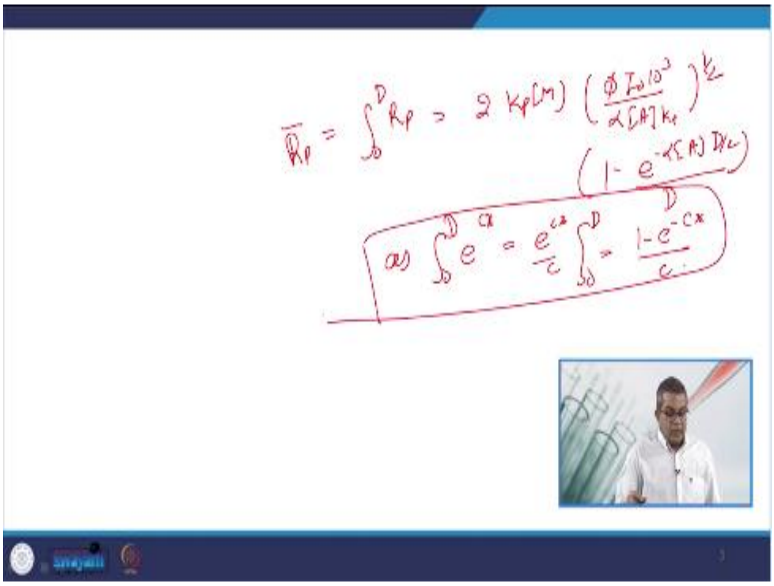

$$\bar{R}_p = \int_0^D R_p = 2K_p[M]\left(\frac{\phi I_0 10^3}{\alpha[A]k_t}\right)^{1/2}\left(1-e^{-\alpha[A]D/2}\right)$$

$$\boxed{\text{as } \int_0^D e^{cx} = \frac{e^{cx}}{c}\int_0^D = \frac{1-e^{-cx}}{c}}$$

Now, if we integrate this equation and gives the value of layer average polymerization, so, that is this is the layer average polymerization rate; this may be represented as like this.

$$\bar{R}_p = \int_0^D R_p = 2K_p[M]\left(\frac{\phi I_0 10^3}{\alpha[A]k_t}\right)^{1/2}\left(1-e^{-\alpha[A]D/2}\right)$$

$$\boxed{\text{as } \int_0^D e^{cx} = \frac{e^{cx}}{c}\int_0^D = \frac{1-e^{-cx}}{c}}$$

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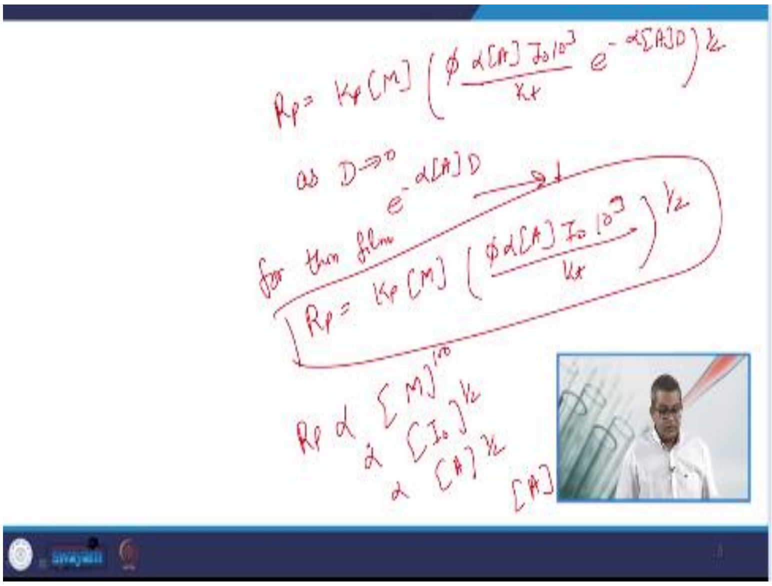

Now, for the thin film, if D is very thin and therefore, it can be written as

$$R_p = K_p[M]\left(\frac{\phi\,\alpha[A]\,I_0 10^3}{K_t}\,e^{-\alpha[A]D}\right)^{1/2}$$

as $D \to 0$

$e^{-\alpha[A]D} \to 1$

for thin film

$$\boxed{R_p = K_p[M]\left(\frac{\phi\,\alpha[A]\,I_0 10^3}{K_t}\right)^{1/2}}$$

$R_p \propto [M]^{1.0}$

$\propto [I_0]^{1/2}$

$\propto [A]^{1/2}$

$[A] = [M]$

For photo excited monomers, this concentration of A is equal to concentration of M.

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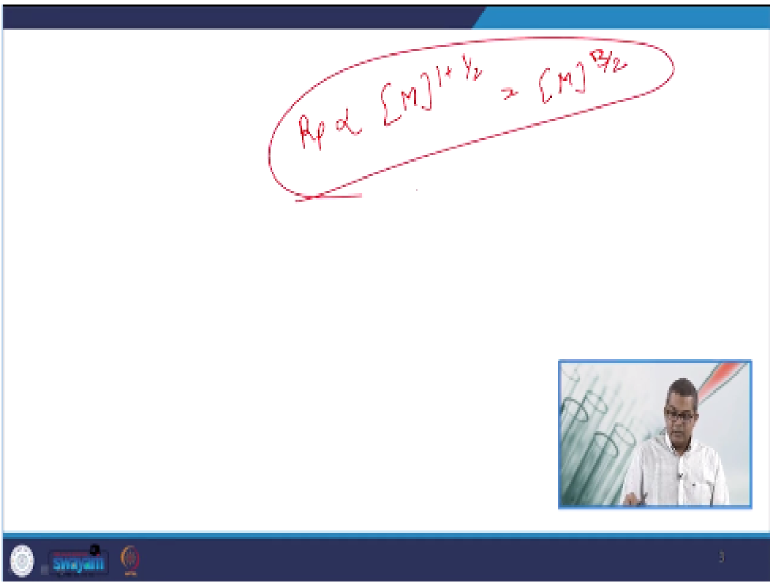

$R_p \propto [M]^{1+1/2} = [M]^{3/2}$

In that case, this R p is proportional to 3/2.

- Rate of polymerization at a particular depth D;

$$R_p = K_p[M]\left(\frac{\phi\alpha[A]I_o10^3e^{-\alpha[A]D}}{K_t}\right)^{\frac{1}{2}}$$

- Layer-averaged polymerization rate $\overline{R}_p$;

$$\overline{R_p} = 2K_p[M]\left(\frac{\phi I_o10^3}{\alpha[A]K_t}\right)^{\frac{1}{2}}\left(\frac{1-e^{-\frac{\alpha[A]D}{2}}}{D}\right)$$

- For thin films rate of polymerization;

$$R_p = K_p[M]\left(\frac{\phi\alpha[A]I_o10^3}{K_t}\right)^{\frac{1}{2}}$$

So, this is the entire equation of rate of polymerization. So, if we try to write the final equation, which can be represented in this slides that is R i is equal to 2 phi I a and the relationship between the phi and f, we have already discussed and we have already discussed this thing for the thin film and other.

Now, intensity of light is usually provided in the energy units such as the kilo joule per second. So, if we convert it into the mole per litre second, we can use this Einstein equation, which is

$\boldsymbol{E = R_N hv = R_N hc/\lambda}$ **…… mol/L.s**

Where,

h is the plank's constant (6.626×10^{-34} m^2kg/s); R_N is the Avogadro's number (6.023×10^{23} mol^{-1}); c is the speed of light (3×10^8 m/s)

In SI system of unit; $\mathbf{E = 0.12/\lambda}$ **mol/L.s**

Now, let us have a look about the absorbed light measurement.

- Actinometry is the concept used of calculating the intensity of light in photopolymerization.
- Three types of actinometers are used viz; Chemical, thermal and electrical actinometers.
- Thermal and electrical actinometers work on the principle of converting photon energy into either electrical or thermal energy. E.g. photomultipliers, semiconductor photodetectors and thermocouples.
- For example, potassium ferrioxalate $K_3Fe(C_2O_4)_3$ is commonly used chemical actinometer.
- In presence of irradiation, the ferric ions start reducing to ferrous ions. The concentration of the ferrous ions (which turns into red color when 1,10-phenanthroline is added to the solution) is measured through UV spectrophotometer.
- Apart from UV-Visible rays, other electromagnetic rays such as γ and x-rays are also used for initiation of radical chain polymerization. Particulate radiations which include electrons, neutrons, and alpha particles also found application in this field.
- Compared to UV-Visible rays having photon energy in the range of 1-6eV, ionizing radiation have very high photon energy in the range of 10keV-100MeV.

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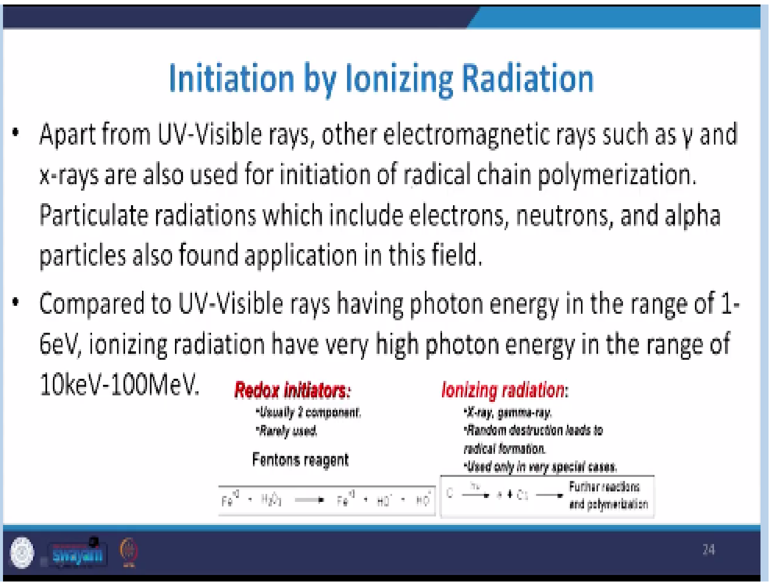

Initiation by Ionizing Radiation

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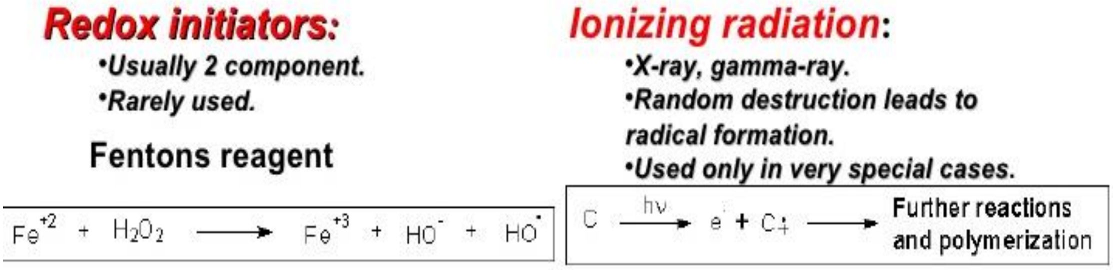
- Compared to UV-Visible rays having photon energy in the range of 1-6eV, ionizing radiation have very high photon energy in the range of 10keV-100MeV.

Redox initiators:
•Usually 2 component.
•Rarely used.

Fentons reagent

Ionizing radiation:
•X-ray, gamma-ray.
•Random destruction leads to radical formation.
•Used only in very special cases.



Redox initiators:

- Usually 2 component.
- Rarely used.

Fentons reagent

$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + HO^- + HO^\cdot$

Ionizing radiation:

- X-ray, gamma-ray.
- Random destruction leads to radical formation.
- Used only in very special cases.

$C \xrightarrow{h\nu} e^- + C^{+\cdot} \longrightarrow$ Further reactions and polymerization

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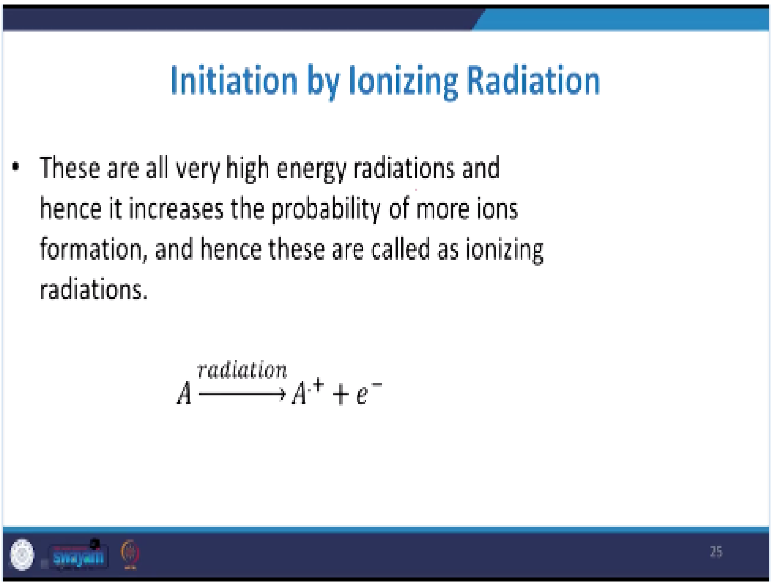

Initiation by Ionizing Radiation

- These are all very high energy radiations and hence it increases the probability of more ions formation, and hence these are called as ionizing radiations.

$$A \xrightarrow{radiation} A^{\cdot +} + e^-$$

Now, these are all very high energy radiations and it increases the probability of more iron formation. Therefore, they are called the ionising radiations. So, let us this particular equation give you a brief outline about this particular concept

$$A \xrightarrow{radiation} A^{\cdot +} + e^-$$

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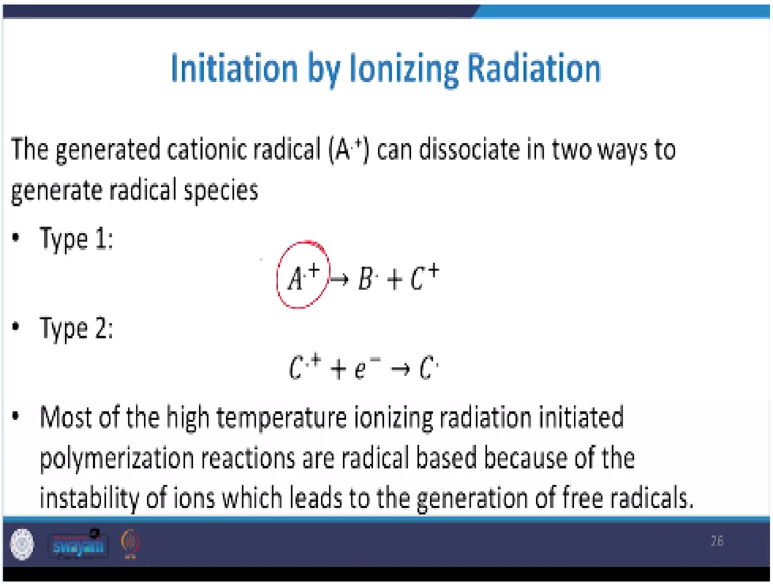

Initiation by Ionizing Radiation

The generated cationic radical ($A^{\cdot +}$) can dissociate in two ways to generate radical species

- Type 1:

$$A^{\cdot +} \rightarrow B^{\cdot} + C^{+}$$

- Type 2:

$$C^{\cdot +} + e^{-} \rightarrow C^{\cdot}$$

- Most of the high temperature ionizing radiation initiated polymerization reactions are radical based because of the instability of ions which leads to the generation of free radicals.

Another generated cationic radical which we generated in the previous slide, this can dissociate in 2 ways. One is that this form like this and other one is that they can go like this. So, most of the high temperature ionising radiation, they initiated polymerization reactions, they are radical in nature.

The generated cationic radical ($A^{\cdot +}$) can dissociate in two ways to generate radical species

- Type 1:

$$A^{\cdot +} \rightarrow B^{\cdot} + C^{+}$$

- Type 2:

$$C^{\cdot +} + e^{-} \rightarrow C^{\cdot}$$

- Most of the high temperature ionizing radiation initiated polymerization reactions are radical based because of the instability of ions which leads to the generation of free radicals.

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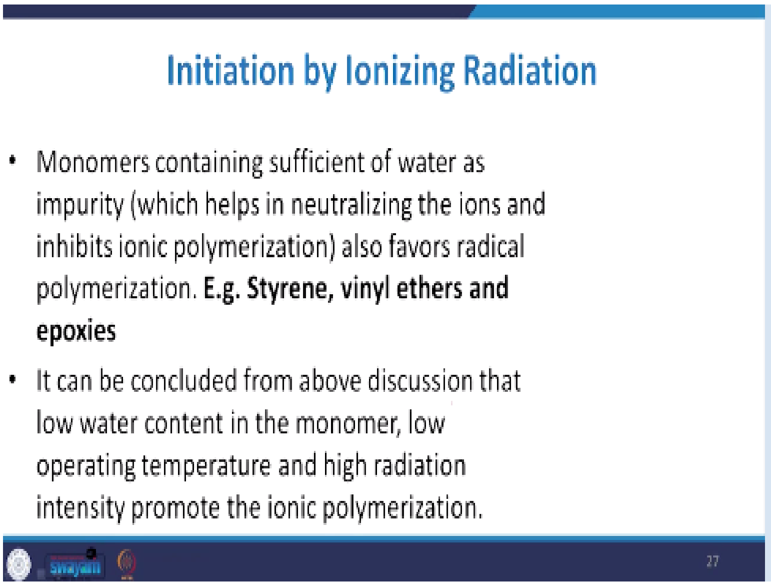

Initiation by Ionizing Radiation

- Monomers containing sufficient of water as impurity (which helps in neutralizing the ions and inhibits ionic polymerization) also favors radical polymerization. **E.g. Styrene, vinyl ethers and epoxies**
- It can be concluded from above discussion that low water content in the monomer, low operating temperature and high radiation intensity promote the ionic polymerization.

Now, monomer containing sufficient of water as impurity sometimes it is quite common phenomena, which helps in neutralising the ions and inhibits the ionic polymerization, they also favours the radical polymerization.

Sometimes, styrene, vinyl ethers and epoxies etcetera. So, it can be concluded from this discussion that low water content in the monomer low operating temperature and high radiation intensity, sometimes, more ionic polymerization.

Electron beam technology is again one of the example of ionising radical polymerization. But due to the high operating cost and adverse effect to health and safety issues and moreover, the compact reaction mechanism, this technology is not much popular as compared to the UV visible radiation techniques.

- We can now look about the kinetic chain length concept. Kinetic chain length (ϑ) defines the number of monomer units reacted with an active center (radical) during initiation to termination step.
- Kinetically this can be defined as the ratio of the polymerization rate to the initiation/termination rate

$$\vartheta = monomer\ added\,\frac{per\ unit\ time}{Number\ of\ Chains\ formed} = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

Now, kinetically, this can be defined as the ratio of polymerization rate to the initiation or termination rate.

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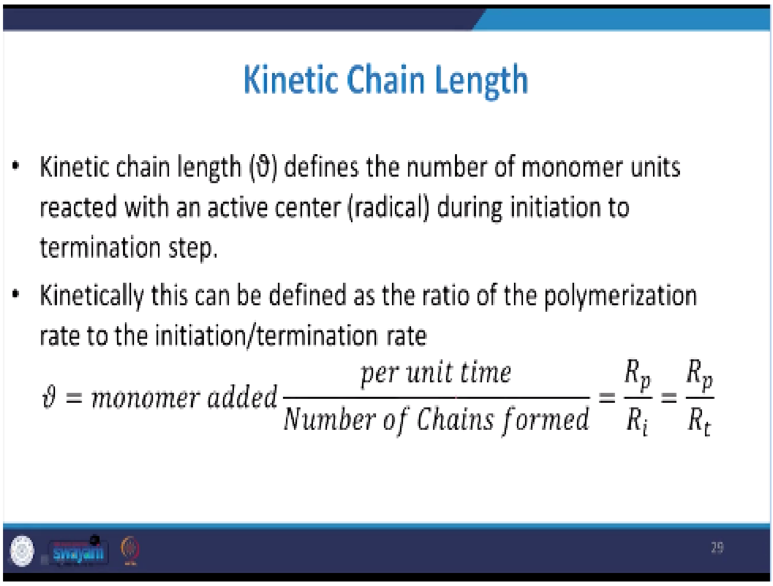

Kinetic Chain Length

- Kinetic chain length (ϑ) defines the number of monomer units reacted with an active center (radical) during initiation to termination step.
- Kinetically this can be defined as the ratio of the polymerization rate to the initiation/termination rate

$$\vartheta = monomer\ added \frac{per\ unit\ time}{Number\ of\ Chains\ formed} = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

Now, this is related to the monomer added per unit time number of chains form. So, it can mathematically, it can be represented as R p upon R i or this is equal to R p upon R t.

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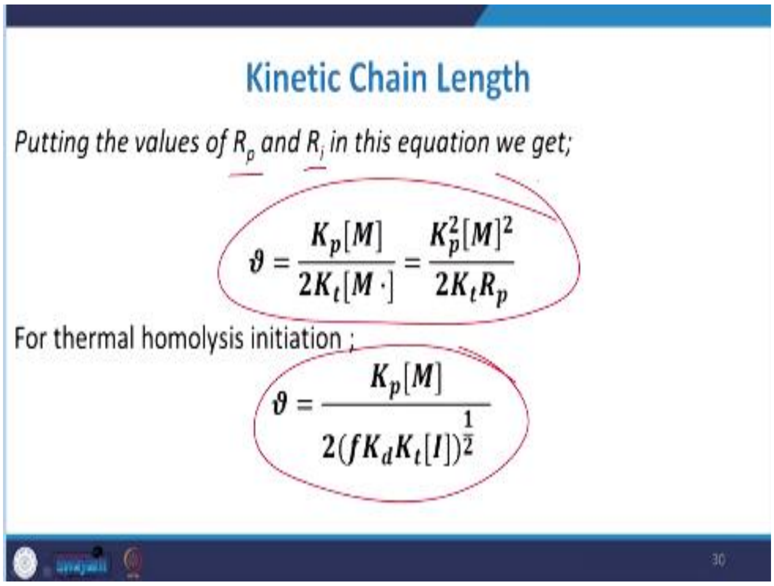

Kinetic Chain Length

Putting the values of R_p and R_i in this equation we get;

$$\vartheta = \frac{K_p[M]}{2K_t[M\cdot]} = \frac{K_p^2[M]^2}{2K_tR_p}$$

For thermal homolysis initiation ;

$$\vartheta = \frac{K_p[M]}{2(fK_dK_t[I])^{\frac{1}{2}}}$$

Putting the values of R_p and R_i in this equation we get;

$$\boldsymbol{\vartheta = \frac{K_p[M]}{2K_t[M\cdot]} = \frac{K_p^2[M]^2}{2K_tR_p}}$$

For thermal homolysis initiation ;

$$\boldsymbol{\vartheta = \frac{K_p[M]}{2(fK_dK_t[I])^{\frac{1}{2}}}}$$

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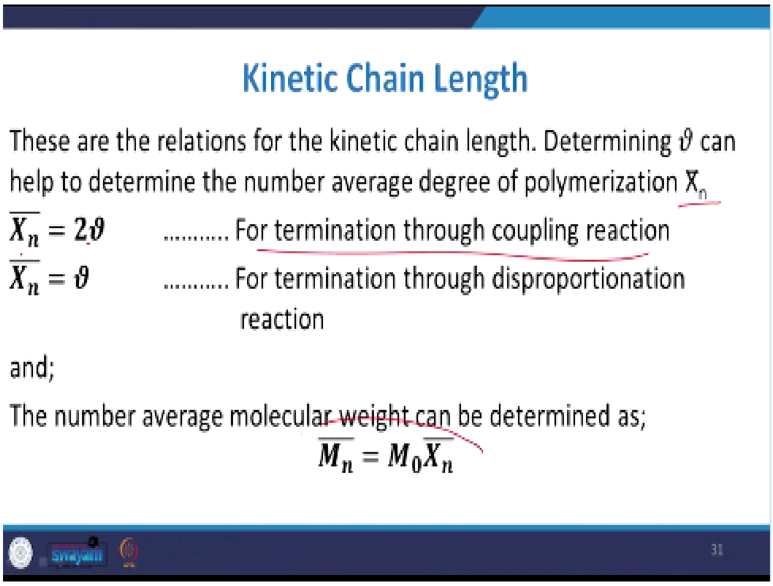

Kinetic Chain Length

These are the relations for the kinetic chain length. Determining ϑ can help to determine the number average degree of polymerization $\overline{X}_n$

$\overline{X_n} = 2\vartheta$ ……….. For termination through coupling reaction

$\overline{X_n} = \vartheta$ ……….. For termination through disproportionation reaction

and;

The number average molecular weight can be determined as;

$$\overline{M_n} = M_0\overline{X_n}$$

These are the relations for the kinetic chain length. Determining ϑ can help to determine the number average degree of polymerization $\overline{X}_n$

$\boldsymbol{\overline{X_n} = 2\vartheta}$ ……….. For termination through coupling reaction

$\boldsymbol{\overline{X_n} = \vartheta}$……….. For termination through disproportionation

reaction

and;

The number average molecular weight can be determined as;

$$\boldsymbol{\overline{M_n} = M_0\overline{X_n}}$$

And the number average molecular weight by this way, you can determine by the multiplication of this degree of polymerization into initial monomer. So, this gives you the number average molecular weight.

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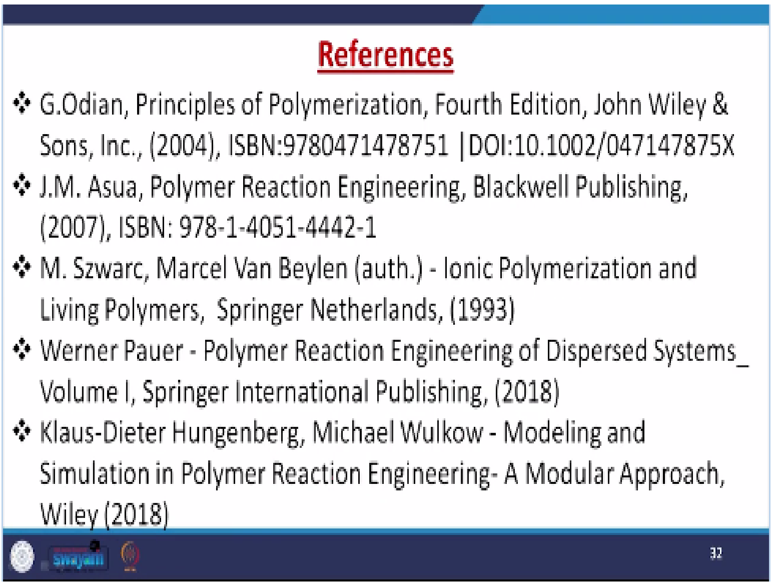

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Now, in this particular lecture, we have discussed about the different concepts of Redox reaction, their mechanism etcetera. Now, if you wish to have a further reading attributed to this particular chapter, we have listed several references for your convenience, we can go through. Thank you very much.