Principles of Polymer Synthesis
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Lecture – 16
Principles of Radical Chain Polymerization (Contd.)

Hello and a very warm welcome back to this fourth week of lecture of the lecture series of NPTEL course Principles of Polymer Synthesis. Last week, we had been talking about radical chain polymerization, the main principles that govern these reactions. And today also we continue with the same topic.

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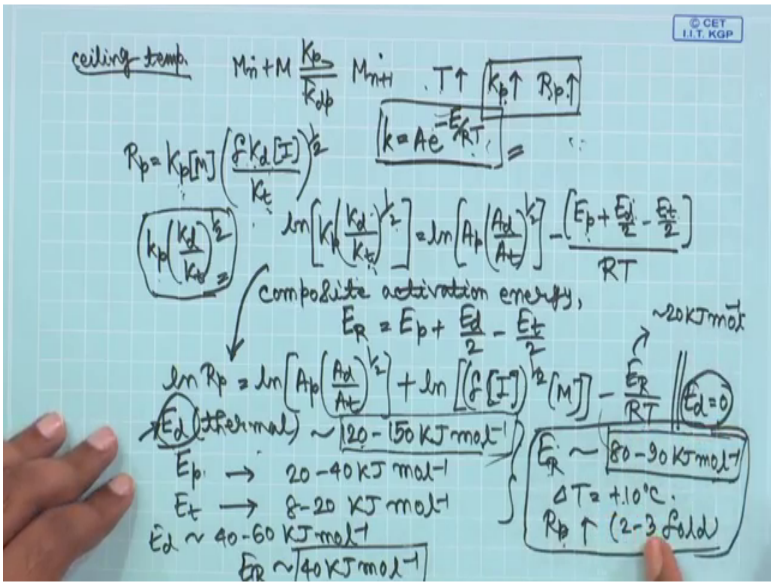

ceiling temp. $M_n^\cdot + M \underset{K_{dp}}{\overset{K_p}{\rightleftharpoons}} M_{n+1}^\cdot$ T↑ K_p↑ R_p↑

$R_p = K_p[M]\left(\frac{fK_d[I]}{K_t}\right)^{1/2}$ $k = Ae^{-E/RT}$

$k_p\left(\frac{K_d}{K_t}\right)^{1/2}$

$\ln\left[K_p\left(\frac{K_d}{K_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{\left[E_p + \frac{E_d}{2} - \frac{E_t}{2}\right]}{RT}$

composite activation energy,

$E_R = E_p + \frac{E_d}{2} - \frac{E_t}{2}$

$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[(f[I])^{1/2}[M]\right] - \frac{E_R}{RT}$ ~20 KJ mol⁻¹ $E_d = 0$

E_d (thermal) ~ 120 - 150 KJ mol⁻¹

E_p → 20 - 40 KJ mol⁻¹

E_t → 8 - 20 KJ mol⁻¹

E_d ~ 40 - 60 KJ mol⁻¹

E_R ~ 40 KJ mol⁻¹

E_R ~ 80 - 90 KJ mol⁻¹

$\Delta T = +10°C$.

R_p ↑ (2-3 fold)

If you recall from what we had discussed towards the end of the last class was the concept of ceiling temperature. And we told that for each concentration of the polymer, there is basically a corresponding ceiling temperature. Or the other way, you can also tell that for each temperature; that means, the polymerization is being done there is corresponding equilibrium concentration; corresponding to each such temperature.

So; that means, all these temperatures can be considered as ceiling temperatures for the polymerization. So, this was the polymerization, de polymerization equilibrium that we talked about. So, K p is the rate constant for propagation and K d p was the rate constant for de polymerization. And we told that at ceiling temperature, the forward reaction is equal to the backward reaction. So, that there is no net formation of the polymer and we also mentioned that if we increase the temperature to start with the rate constant for propagation goes up and the rate of polymerization also goes up.

Eventually of course, as we keep increasing the temperature; the rate of de polymerization keeps going up and ultimately it will catch up with this and both will become equal; the forward reaction will be equal to the backward reaction. So, we will come to this particular point and elaborate it little bit further today. So, what do we mean by this? That if we increase the temperature of course, K p; the rate constant will increase because rate constant can be expressed as A into e to the power minus E by RT; where E is the activation energy, T is the temperature of reaction and A is the collision frequency factor.

But if you look at this R p; the expression of R p basically is like this. So, you have K p as the propagation rate constant and then you have the monomer concentration and then you have f K d, I divided by K t to the power half. This we had derived before; so, you see that the R p not only depends on K p, the rate constant for propagation, but it also depends on rate constant for dissociation of the initiator and the rate constant for termination of the polymerization reaction.

So, in order to evaluate the effect of temperature on the rate; overall rate of the polymerization, what we have to do is that; we have to basically see just extract out the K values from here. So, they will be like K p into K d divided by K t to the power half. So, this particular term; this is the term that determines how the R p will change with temperature, so how this particular term is affected by temperature that is then important to study.

So, if you are considering thermal decomposition of the initiator and then if we look at the; so, the condition is that the thermal decomposition of the initiator of course, the overall expression; that I am going to write will be valid for all kinds of decompositions. But the significance of that expression will differ from whether we have thermal decomposition of the initiator or whether we have say redox initiation or whether we have photo chemical initiation. So, if we now write down this expression keeping in mind; this general expression arrhenius type equation, if we write this in terms of arrhenius frequency factor in the temperature and activation energy.

So, what you do is that take l n here; l n; K p; K d divided by K t to the power half. So, you take the l n of that; so, correspondingly this will become l n; A p, A d divided by A t to the power half; minus E by R T because you have taken l n on both sides that E will be the summation of all of them. But these two terms are on the up, this term is at the down. So, this will be negative and there is a half here; so, it will be E p plus E d divided by 2 minus E t divided by 2; this is the term here divided by R t.

So, this will be the composite activation energy that you have to look for when you are trying to see the temperature dependence of the rate of the reaction. So, composite activation energy and that is nothing, but let us say E R energy of activation of the reaction. So, that will be equal to then E p plus E d divided by 2 minus E t divided by 2; you keeping with minus E by R T; that E by R T, this E by R T summation of all these. So, this is the activation energy for propagation, activation energy for dissociation; E d and E t is activation energy for termination.

So, you put all these values and if you look at that then if you are plotting here l n; R p versus 1 by t so, basically from here; just convert that to R p value; what will happen? Because if you are putting l n; R p on this side, then l n R p equals to this and then you have is this f k d; all these expressions are there because this is K p, K d like K t to the power half only that part we have taken here.

So, you take l n R p; so that will be considering both this term as well as f and I that term. So, the expression will become something like this l n A p into A d divided by A t to the power half plus l n; f I to the power half into concentration of the monomer that comes into the picture; minus E R by R T, where E R is the overall activation energy or composite activation energy which is nothing, but this.

And if you are plotting l n; R p versus 1 by T, then you can find out say for example, this part and also this part. Because that will give you the overall activation energy as the slope because l n R p versus 1 by T will be linear, so that will be the slope of that. Now for a thermal initiation, so if you have a initiator which can be thermal decomposed and the polymerization can be initiated with that; then the activation energy for the bond dissociation and basically the activation energy for the thermal dissociation is of the order of 120 to 150 kilo joule per mole.

Now propagation activation energy is of the order of 20 to 40 kilojoules per mole and termination activation energy is of the order of 8 to 20 kilojoules per mole. So, if you take all these things into account, then for thermal initiation of the polymerization; the overall activation energy becomes in this range 80 to 90 kilojoules per mole. So, if you put this value; so, this is positive term and if you put this value here; then you can see that when you increase the temperature by say 10 degree Celsius; then the R p value will increase 2 to 3 fold.

So, everything depends on the overall value of this E R, if the E R value is close to 0, then the temperature dependence will go; it is not the case for thermal decomposition. If the E R value is close to 0 for example, if you are looking for photochemical activation; then typically you do not need to heat up your initiator.

The energy is promoted by the light quantum; so, then this E R is close to 0. In fact, what will happen is that it is not exactly close to 0; I apologize what I would mean here is that your E d, this dissociation energy E d will be 0 because E R is the composite activation energy of the overall reaction, so, E d is the dissociation energy.

So, for thermal it is around 120 to 150 kilojoules per mole; for photochemical it is close to 0. So, for photochemical if it is close to 0; then this E R will be approximately 20 kilojoules per mole; I mean it is not 0, but it is low value. So, it is low value so; that means, the temperature dependence will be very very less. So, this rate of polymerization we almost insensitive to temperature.

And in comparison for example; if you are looking for a redox initiation, so this is thermal and we talked about photochemical. And if you are looking for; so main change is in the dissociation energy and this is actually not dissociation energy, but this is the activation energy for dissociation; E d 120 to 150 kilojoules per mole. So, when you are talking about the dissociation energy; you are actually talking about the bond dissociation energy.

So, we already told that the initiator say peroxo bonds, thermally dissociation if you have to achieve; then basically the kind of energy that you have to provide is 120 to 150; 160 kilojoules per mole; so, that way they are basically equivalent, so this is the activation energy. Now if you are considering the E d value for a redox initiation; then that E d value is in the range of 40 to 60 kilojoules per mole.

So, you need lesser energy; so, if you now put those values here E p and E t in this range; then your E R comes means overall activation energy comes in the range of 40 kilojoules per mole. Compare that with your overall activation energy of 80 to 90 kilojoules per mole which was there for thermal initiation. Now it is 40 kilojoules per mole; so, the temperature dependence will be lower for the rate of polymerization, when you are initiating it redox process. If you are initiating with photo chemical process, then it will be almost insensitive to the increase in temperature.

So, those things you have to keep in mind; so, in general when you are increasing the temperature your rate of polymerization will increase most significantly, when you are considering thermal dissociation. But also that things are complicated for photochemical activation; by the fact that when you increase the temperature of the reaction mixture, some of the initiators that could dissociate photochemically; they could also dissociate thermally. So, then the thermal dissociation of the initiator also has to be taken into account when you increase the temperature. Then the dependence of the rate of polymerization on the temperature will be more complex.

So, those things you need to keep in mind. So, finally, one more thing I wanted to discuss here as far as the temperature dependence is concerned.

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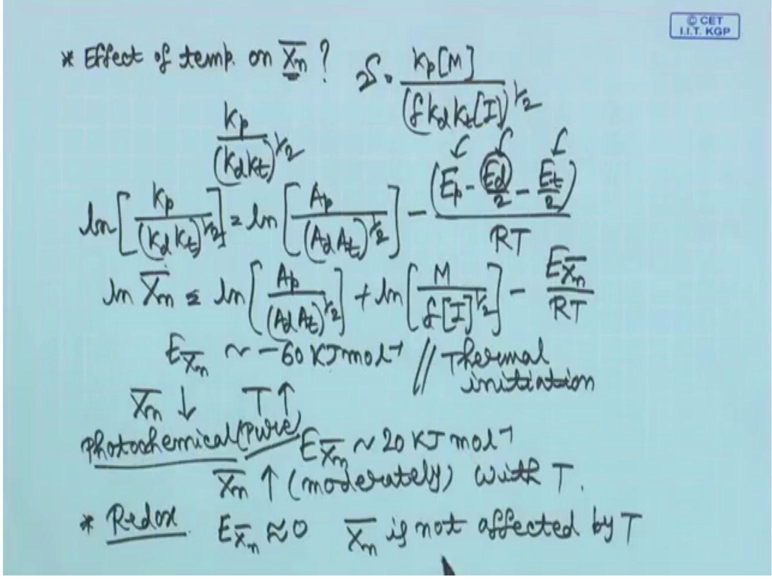

* Effect of temp. on $\overline{X}_n$? S. $\frac{k_p[M]}{(f k_d k_t[I])^{1/2}}$

$\frac{k_p}{(k_d k_t)^{1/2}}$

$\ln\left[\frac{k_p}{(k_d k_t)^{1/2}}\right] = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] - \frac{\left(E_p - \frac{\boxed{E_d}}{2} - \frac{E_t}{2}\right)}{RT}$

$\ln \overline{X}_n = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] + \ln\left[\frac{M}{f[I]^{1/2}}\right] - \frac{E_{\overline{X}_n}}{RT}$

$E_{\overline{X}_n} \sim -60$ KJ mol^{-1} // Thermal initiation

$\overline{X}_n \downarrow$ $T \uparrow$

Photochemical (pure) $E_{\overline{X}_n} \sim 20$ KJ mol^{-1}

$\overline{X}_n \uparrow$ (moderately) with T.

* Redox $E_{\overline{X}_n} \approx 0$ $\overline{X}_n$ is not affected by T

So, what will be the effect of temperature on X n bar I mean this is number average molecular weight or the other way you can say that what will be the effect of temperature on molecular weight? So, let us say you have thermally initiated again, it could be other initiation also. So, your kinetic chain length was something like this K p M divided by f k d; these things we derived before, K t into I to the power half.

So, what we have to see here is this term; how it varies K p divided by K d into K t to the power half, how this varies with temperature? So, again by the same analogy; if you take that here, it will be l n; K p divided by K d into K t to the power half; equals to l n A p, this is the collision frequency factor divided by A t into at to the power half.

And then you have all these terms here E p minus E d divided by 2 minus E t divided by 2, divided by R T. And if you are considering by molecular termination and no chain transfer reaction; then your l n X n bar because an X n bar is directly related to your kinetic chain length, that will be equal to l n A p divided by A d; A t to the power half plus l n.

So, just consider that there will be another factor probably here; depending on whether it is disproportionation or coupling. But overall it is like that; I to the power half and minus this term total will be let us say it is this; you can actually term this as the overall activation energy for the degree of polymerization. So, if you put the values here and if you consider the value of E d; the dissociation energy for the thermal it was 120 to 150 kilojoules per mole; then the term E X n bar; it comes negative and it will come around minus 60 kilojoules per mole; so, that term is negative.

So, this term then becomes positive, so what happens is that X n bar, it decreases rapidly as T increases. So, this is something we mentioned the other day, but without further explanation that when you increase the temperature, your rate of polymerization will increase. Let us say you are talking about thermal decomposition; rate of polymerization will increase.

But you will have a decrease in the molecular weight. So, you will compromise the number average molecular weight, so this is the reason why that happens. And what happens if you; so, this is typically for thermal initiation. So, if you consider pure photochemical initiation; if you consider that then what happens?

For photochemical initiation, this term if you consider all these expressions that your E d is basically close to 0; for photochemical initiation and you put the other values, then this comes approximately equal to 20 kilojoules per mole. So, then this term is positive; so, what happens is that X n; it increases, but increases moderately with temperature. And finally, if you are considering redox; initiated polymerization and you take these values into account for the redox, the E d the dissociation activation energy the dissociation energy basically is 40 to 60 kilojoules per mole.

So, that will be X n bar close to 0; if you put all those value. So, there will be almost no effect is not affected by and for photochemical, we are considering pure photochemical; so no thermal initiation. So, you see the effects are more detailed; so, it required that much of detailed analysis that of course, the rate of polymerization will increase with temperature, but if it is thermal decomposition.

And if you are having photochemical decomposition then the rate almost does not show any increase. And if you have redox decomposition; redox initiation then what happens is that your effect on the rate of polymerization is less, it will still increase with temperature. And correspondingly; you can see that the degree of polymerization that will decrease significantly for thermal decomposition, thermal initiation when you are increasing the temperature; even though the rate is increasing.

So, and that will change separately I mean that that depends on the kind of initiation that you are doing. So, depending on the initiation for example, if you have a redox initiation then your degree of polymerization will not be affected at all with temperature. Even though the rate of polymerization may show some increase.

And if you are considering photochemical initiation then what will happen is that your rate of polymerization may not vary much with temperature, almost may be insignificant variation, but the degree of polymerization will increase moderately; so, those things you need to consider. So, the final thing that we want to discuss here before we draw curtains to this discussion on the radical polymerization part is the following.

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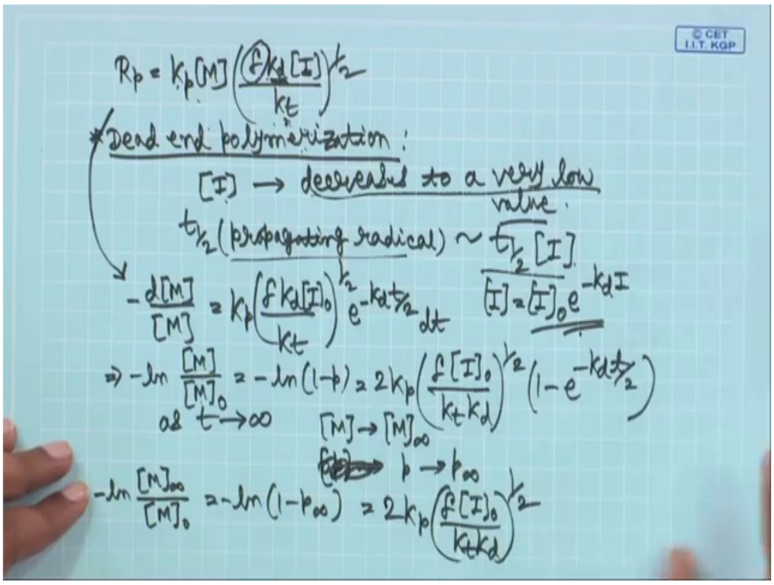

$R_p = k_p[M]\left(\frac{\boxed{f} k_d[I]}{k_t}\right)^{1/2}$

*Dead end polymerization:

$[I] \rightarrow$ decreased to a very low value.

$t_{1/2}$(propagating radical) $\sim \overline{t_{1/2}[I]}$

$-\frac{d[M]}{[M]} = k_p\left(\frac{f k_d[I]_0}{k_t}\right)^{1/2} e^{-k_d t/2}\, dt$ $[I] = [I]_0 e^{-k_d I}$

$\Rightarrow -\ln\frac{[M]}{[M]_0} = -\ln(1-p) = 2k_p\left(\frac{f[I]_0}{k_t k_d}\right)^{1/2}\left(1 - e^{-k_d t/2}\right)$

as $t \rightarrow \infty$ $[M] \rightarrow [M]_\infty$

$p \rightarrow p_\infty$

$-\ln\frac{[M]_\infty}{[M]_0} = -\ln(1-p_\infty) = 2k_p\left(\frac{f[I]_0}{k_t k_d}\right)^{1/2}$

See if you look at the particular expression of R p that is K p into n f K d; I divided by K t to the power half. So, this is the expression that we had derived before and we also had talked about that expression today. And I had actually promised to that we will talk about this initiator efficiency little bit more; so, that is what I am going to talk about now.

So, this is the expression here; so, how do you find out initiator efficiency? There are many different ways. So, one of the ways that I am going to tell you is that if you can find out if you know the value of K p divided by K t to the power half; this you can know from your mio equation, if you remember; that when you are trying to determine the monomer transfer constant this K p by K t to the power half could be found out from the graph itself. And you know the value of I and M; so, you need to know the value of K d and then you can find out the value of f for the particular initiator.

So, one particular process through which you can find out the value of K d is through dead end polymerization. So, these are the kind of polymerizations where your initiator concentration; we assumed the initiator concentration is constant for the reaction which is not always true; most of the cases ten twenty percent decrease of initiator concentration will be there and that is the reason why all those constants that we derived chain transfer constants for mio equation, we derived at a low conversion.

So, this initiative concentration during the course of the polymerization; if it decreases to a very low value decreases to a very low value; that you can actually control how? By controlling the choice of initiator because initiator will have different half life values depending on what initiator you are choosing.

So, for this experiment to determine the value of K d, you choose an initiator the concentration of which decreases to a very low value as the polymerization progresses. So, once this kind of situation is achieved; the half life of the propagating radical half life of the propagating radical which is already quite low; radicals are transient species the life of the radicals are seconds or less than.

That that will become comparable to the half life of the initiator and then what will happen is that, as you go to infinite time, as you consider the polymerization going to infinite time; what will happen is that the conversion of the monomer to polymer will be limited, even if you are keeping the polymerization on for as long time as possible.

So, if you look at this expression here and if you just recognize that rate of polymerization is nothing, but minus d of M; d t where change of concentration of monomer with time and that d t you take here. Then you will have this expression minus d M by M equal K p into f K d by K t to the power half. Now I the concentration of the initiator will decrease like this, so this is the initiator concentration to start with this is the final concentration of the time T; that will be e to the power minus K d into I; where K d is the dissociation rate constant for the initiator.

So, if you look at this and if you are replacing; I with this value, then what you will get is this. So, this will be I is 0 to the power half and this comes out and there is to the power half. So, it will be e to the power minus K d t divided by 2; d t; the d t has come on this side minus d n; d t; d t has come on this side.

Now if you do the integration, what you will get is minus l n; M by M 0 equals to minus; so minus; So, M by M 0 is nothing, but 1 minus p; p is the extent of conversion, this we had shown before because p is M 0 minus M by M 0. So, this is this and you are doing the integration; so, it will come out; you can actually work that out f I 0 divided by Kt, K p to the power half into 1 minus e to the power minus K d t divided by 2.

Now, as T tends to infinity; what will happen is that the monomer concentration will tend to M infinity all of them will delete some limiting concentration. Even if we does not mean that infinite concentration of monomer, it means the concentration of monomer at in finite time. So, it will be like that and concentration of your; so your conversion will go to p infinity; p infinity means conversion at infinite time.

So, if you now replace these values at that point of time, it will be minus l n M infinity divided by M naught equal to minus l n; 1 minus p infinity equal to 2 K p into f I 0 divided by K t; K d to the power half. Now, if you if you take the ratio of this and if you rearrange and then take a natural logarithm on both sides what will happen is the following.

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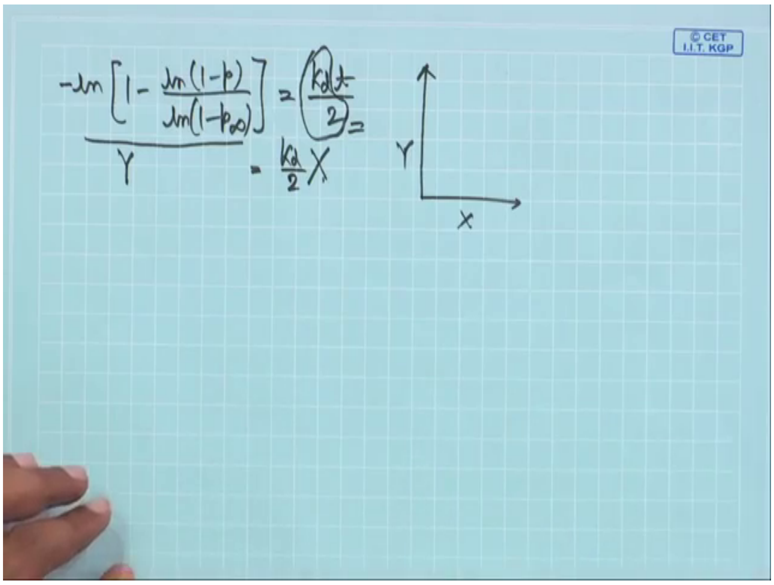

$$\underbrace{-\ln\left[1-\frac{\ln(1-p)}{\ln(1-p_\infty)}\right]}_{Y} = \boxed{\frac{k_d t}{2}} = \frac{k_d}{2}X$$

I am just writing down the final expression here; minus l n one minus l n; 1 minus p divided by l n 1 minus p infinity; and that will be equal to K d t divided by 2. So, you can see that these two expressions, these expression and this expression. So, you are taking a ratio rearranging and then taking an l n of that again.

So, this is the expression that you get finally, now if you are plotting the left side as a function of t. So, this left side is Y equals to K d divided by 2 into X; X is your t. So, as a function of time if you are plotting this term; Y versus X; then the slope will give you the value of K d kd divided by 2 to be exact; so the slope will give you the value of K d,

Now once you know the value of K d, the dissociation rate constant you can put it here; you know the initiator concentration, you know the value of K p divided by K t to the power half from your other experiments, other experiments means I told you that from mio equation when you are trying to determine the different constants.

So, 1 divided by X n bar when you are plotting against rate of polymerization; they are actually the initial plot was linear and that slope will give you the value of K p divided by kt to the power half.

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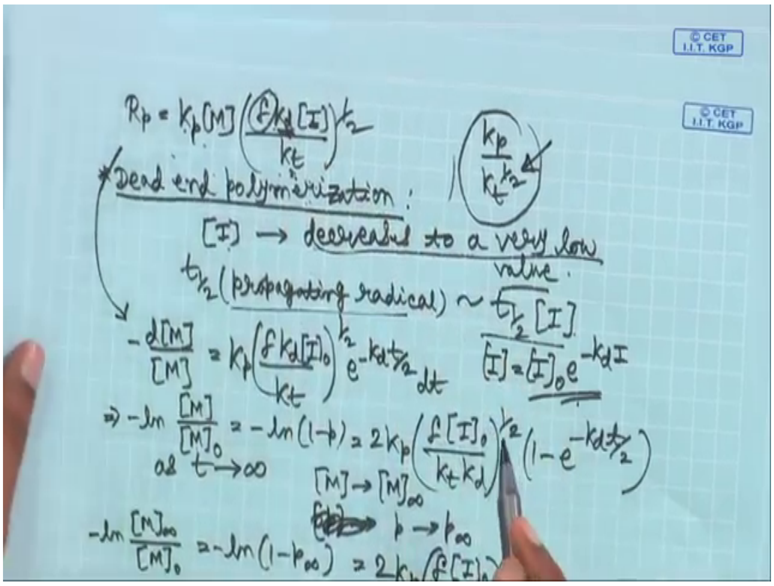

$R_p = k_p[M]\left(\frac{f k_d[I]}{k_t}\right)^{1/2}$ $\frac{k_p}{k_t^{1/2}}$

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$t_{1/2}$ (propagating radical) ~ $t_{1/2}[I]$

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$\Rightarrow -\ln\frac{[M]}{[M]_0} = -\ln(1-p) = 2k_p\left(\frac{f[I]_0}{k_t k_d}\right)^{1/2}\left(1 - e^{-k_d t/2}\right)$

as $t \to \infty$ $[M] \to [M]_\infty$

$p \to p_\infty$

$-\ln\frac{[M]_\infty}{[M]_0} = -\ln(1-p_\infty) = 2k_p(f[I]_0$

And I also told you that this term K p divided by K t to the power half is very important because it is appearing in almost everywhere. So, independently then you can find out this value and K d also you can find out from this technique called dead end polymerization, where you have chosen the initiator. So, that the half life it considering the half life of the initiator, it will decrease the very low value; the concentration of it after a certain period of time the polymerization.

So, that after the long time also there will be a limiting conversion that will be reached for the polymerization. And under that condition, this expression is valid and when you are plotting these two as a function of time, then you can find out the value of K d and put the value in R p and you can find out the value of f.

So, with this we will conclude our discussion on the general radical polymerizations. What we will do in the next class is; we will start to talk about chain copolymerization reactions; means copolymerization means two of the monomers which could independently enter into the chain polymerization. When you are putting both of them together, how the composition of the polymer will vary? How much of one of the monomers will go into the polymer with respect to the other; those things we will start discussing in the next class.

And finally, we will come back to the radical polymerization in a way that whatever we have discussed till now; are normal radical polymerizations, normal radical chain polymerizations. Now we will talk about what we call as living radical polymerizations; where we can control the molecular weight more precisely; that is towards the end. But we will stop the discussion of that until we finish the discussion on chain copolymerization which is the subject of the next class until then.

Thank you and goodbye.