Polymer Chemistry

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Lecture - 13
Radical Chain Polymerization (Contd.)

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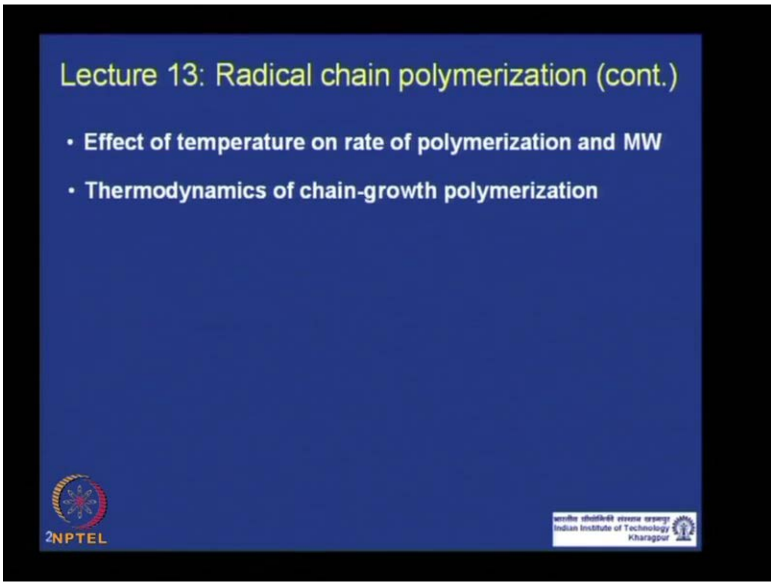

Lecture 13: Radical chain polymerization (cont.)

- Effect of temperature on rate of polymerization and MW
- Thermodynamics of chain-growth polymerization

Welcome back to this course on polymer chemistry. In this lecture thirteen, we plan to cover effect of temperature on rate of polymerization and molecular weight, and also we will start our discussion on thermodynamics of chain growth polymerization.

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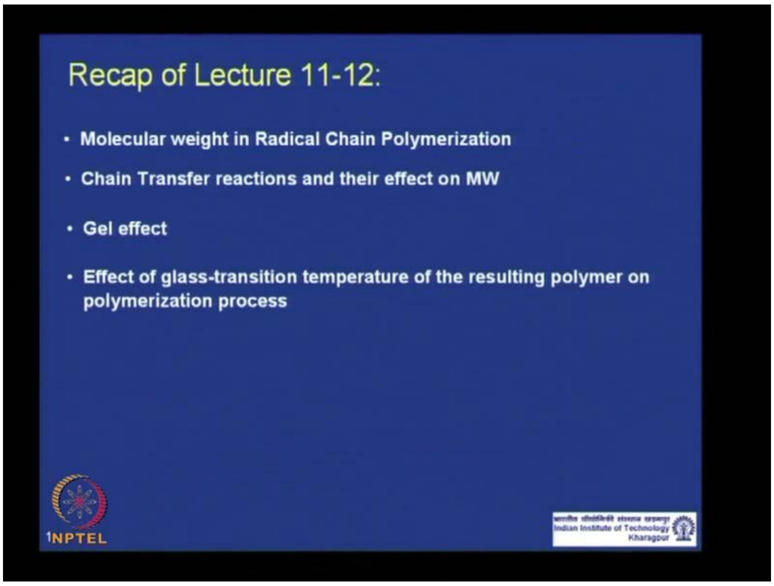

Recap of Lecture 11-12:

- Molecular weight in Radical Chain Polymerization
- Chain Transfer reactions and their effect on MW
- Gel effect
- Effect of glass-transition temperature of the resulting polymer on polymerization process

Before I start this subject, just recap the subject matter what we discussed in the last two lectures. We discussed the various types of chain transfer reactions possible in radical polymerization, and their effect; effect on molecular weight in principle, that modes are chain, more chain transfer happen, molecular weight actually gets reduced compared to if there was no chain transfer reaction. We talked about gel effect and we also talked about the effect of glass-transition temperature on the resulting polymer, effect of glass transition temperature of the resulting polymer on polymerization process.

Now, let us start what is the effect of temperature on the polymer, polymerization rate and the resulting molecular weight.

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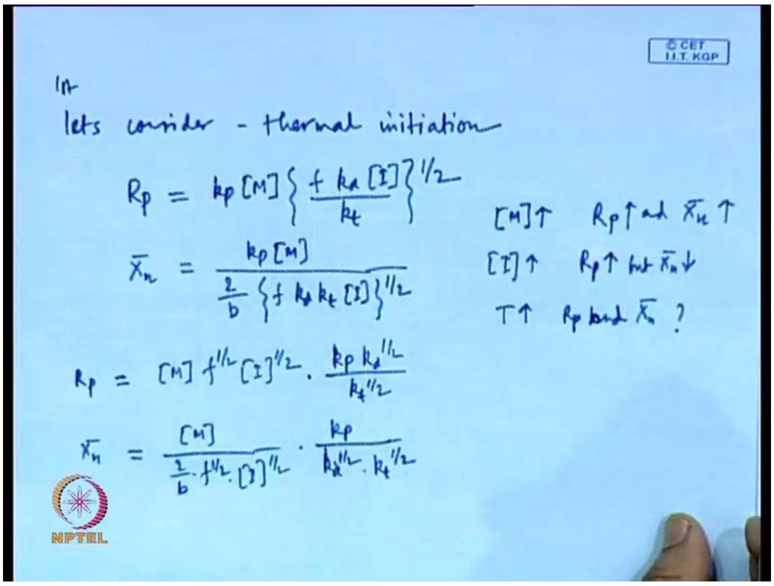

In

lets consider - thermal initiation

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

$$\bar{X}_n = \frac{k_p[M]}{\frac{2}{b}\left\{f\,k_d k_t[I]\right\}^{1/2}}$$

$[M]\uparrow$ $R_p\uparrow$ and $\bar{X}_n\uparrow$

$[I]\uparrow$ $R_p\uparrow$ but $\bar{X}_n\downarrow$

$T\uparrow$ R_p and $\bar{X}_n$?

$$R_p = [M]f^{1/2}[I]^{1/2}\cdot\frac{k_p k_d^{1/2}}{k_t^{1/2}}$$

$$\bar{X}_n = \frac{[M]}{\frac{2}{b}\cdot f^{1/2}\cdot[I]^{1/2}}\cdot\frac{k_p}{k_d^{1/2}\cdot k_t^{1/2}}$$

Now, first let us consider, consider the case of thermal initiation. We know that in case of thermal polymerization R p is given by k p M f k d I k t (( )) half. You also know that X n bar, the number average degrees of polymerization is given by expression, we have deduced this expression in earlier lectures, so you should be knowing this very well, where b is the average number of initiator residues per polymer molecules.

Now, from this reaction, if you look at the equation little carefully you can find out, that if the monomer concentration increases both R p and the number average degrees of polymerization increases, which is the molecular weight. If the initiator concentration increases, then R p goes up, rate of polymerization goes up, but X n bar or the molecular weight comes down. So, what is the effect of temperature on R p and X n is we are going to discuss now.

Now, the same expression R p, I can divide into two terms, one is temperature dependent and another is temperature independent. So, if you look at the temperature independent term and put in the left hand side, I can put concentration M f to the power half and I to the power half. Now, this part is temperature independent, whereas the other term, the rate constant k p k d to the power half and k t to the power half, these are all rate constant values. So, definitely, they will depend on the temperature of the reaction you were using. Similarly, you can break down this number of degrees of polymerization, number, average degrees of polymerization into two terms, one is temperature independent, I can break into two terms, this is temperature independent and the other term, k d k t to the power half, so these are temperature dependent.

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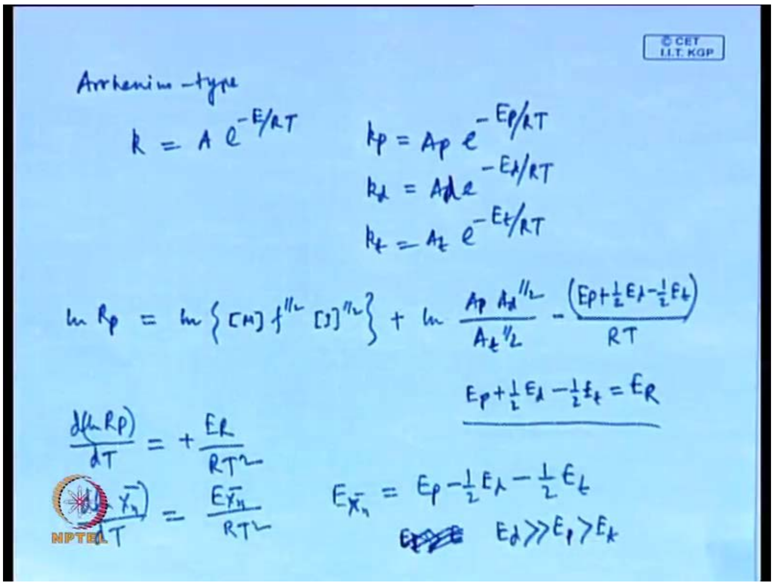

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Arrhenius-type

$$k = A e^{-E/RT}$$

$$k_p = A_p e^{-E_p/RT}$$

$$k_d = A_d e^{-E_d/RT}$$

$$k_t = A_t e^{-E_t/RT}$$

$$\ln R_p = \ln\left\{[M] f^{1/2} [I]^{1/2}\right\} + \ln \frac{A_p A_d^{1/2}}{A_t^{1/2}} - \frac{\left(E_p + \frac{1}{2}E_d - \frac{1}{2}E_t\right)}{RT}$$

$$\underline{E_p + \frac{1}{2}E_d - \frac{1}{2}E_t = E_R}$$

$$\frac{d(\ln R_p)}{dT} = + \frac{E_R}{RT^2}$$

$$\frac{d(\ln \bar{X}_n)}{dT} = \frac{E_{\bar{X}_n}}{RT^2}$$

$$E_{\bar{X}_n} = E_p - \frac{1}{2}E_d - \frac{1}{2}E_t$$

$$E_d \gg E_p > E_t$$

Now, you also know from basic physical chemistry knowledge, that rate constant can be expressed in form of Arrhenius-type equation expression where you can write rate constant is A e to the power minus E by RT, where k is rate constant, A is the frequency factor, frequency collation factor, E is the activation energy for the reaction. This is well known to you guys, so you know that.

So, we can express all the three rate constants, k p, k t and k d in terms of Arrhenius equation e to the power minus E p where E p is the activation energy for propagation. Similarly, k d is A p e to power minus E d and k t is A t e to power minus E t; E t is the activation energy for termination reaction. Now, in this, in this expression, this is the expression for rate of propagation and now we know, that the monomer is consumed both, in initiation process and in the propagation process, but because the monomer consumed in the initiation process is very insignificant compared to propagation process, rate of polymerization is equivalent to rate of propagation.

So, we are writing R p as the rate of reaction, which is same as rate of propagation, whereas k p is the rate constant for propagation and E p is the activation energy for propagation. So, I can take this expression and write this k terms in terms of the Arrhenius equation or else, we can simply write, ln R p from that earlier expression, M f to the power half I to the power half plus ln A p A d to the power, this is A d, to the power half A t to power half minus E p half E d minus half E t by RT. We can write all this from this Arrhenius-type expression and this is, this term E p plus half E d minus half E t, we are writing as the entropy of the polymerization reaction.

So, entropy of the polymerization is combination of propagation initiation, as well as, termination. So, depending upon the sign of this activation energy, the rate will depend on the temperature. We can just simply write d ln R p by dT is plus E R by RT square. If you differentiate it, (( )) you find out the rate with respect to the temperature.

Now, what is the value of E R? now, we can, before we talk about the value of E R we can similarly write from the expression of X n. If you look at these numbers here, k P k d to the power half k t to the power half, here k d is in the down. So, d ln X n, which gives you the rate of change of molecule, degrees of, average degrees of number, average degrees of polymerization as similarly E X n by RT square, where E X n is E p minus half E d minus half E t. It is coming from the expression we used in the last page. Now, what is the value of E R and E X n? Now, this will come from the individual values of E p, E d and E t.

Now, as we know the rate constant or rate of the reaction is much faster, for termination is the highest rate and then propagation and then initiation, we can simply write from or that knowledge, that E t is, should be greater than activation energy of, this must be greater than E p because this is the most, this is the fastest reaction and this is also fast reaction where the initiation is a slower reaction. So, you expect that activation energy for the initiation reaction should be higher than the other two.

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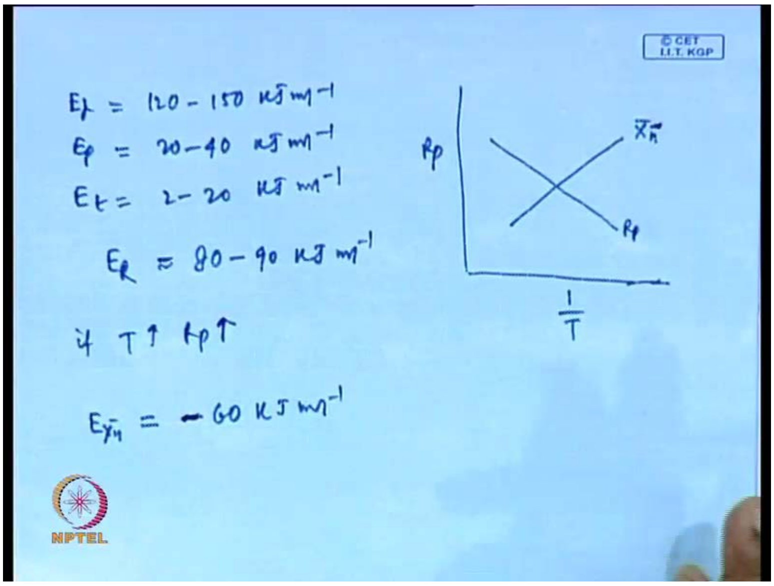

$E_d = 120 - 150\ kJ\ m^{-1}$

$E_p = 20 - 40\ kJ\ m^{-1}$

$E_t = 2 - 20\ kJ\ m^{-1}$

$E_R \approx 80 - 90\ kJ\ m^{-1}$

if $T \uparrow$ $R_p \uparrow$

$E_{\bar{X}_n} = -60\ kJ\ m^{-1}$

Now, what are the typical values of this E d and E t? Typical values of E d for thermal initiation process come about 120 to 150 kilo joule per mol, E p comes on 20 to 40 kilo joule per mol and E t is 2 to 20 kilo joule per mol, these are the experimental values. Now, that gives you the value for E R, around 80 to 90 kilo joule per mol inverse. That means that the rate will increase rate of polymerization will be, will increase with increase in temperature. If you plot the rate of polymerization, which is 1 by T, it will be coming down linearly. Now, this value indicates that for every 10 degree rise, there is around two to three fold, two to three times increase in the rate of polymerization. So, if T goes up, R p goes up and every decade, every 10 degree centigrade it will be around 2 to 3 times from the original value.

Now, if you calculate the number for E X n, you get around 60, minus 60 kilo joule per mol inverse, mol inverse, per mol, which means, that degrees of, average degrees of polymerization or the molecular rate, will, will come down as we increase the temperature. So, if you plot with 1 over T, this is the curve for R p and this will be curve for your X n, X n bar. So, this is clear to you, that from the experimental values of these activation energies you can justify, that if the temperature goes up, the rate of the polymerization will go up and similar time the molecular weight or the number average degrees of polymerization will come down.

Now, you can justify these in (( )), this way, that once you increase the temperature, the more and more radical gets generated for a given time, like more and more radical gets generated, then more and more polymer forms for a given time. When more polymer forms, rate of polymers increases, and because the radical concentration increases, increased with temperature, the termination reaction also increase. So, as the more termination is reaction is going on, the average length of the polymer chains also comes down. You can justify this drop in molecular weight with increase in temperature and increasing rate of polymerization. With increase in temperature by just thinking, that with increase you get more number of radical generated in the polymerization medium for a given time.

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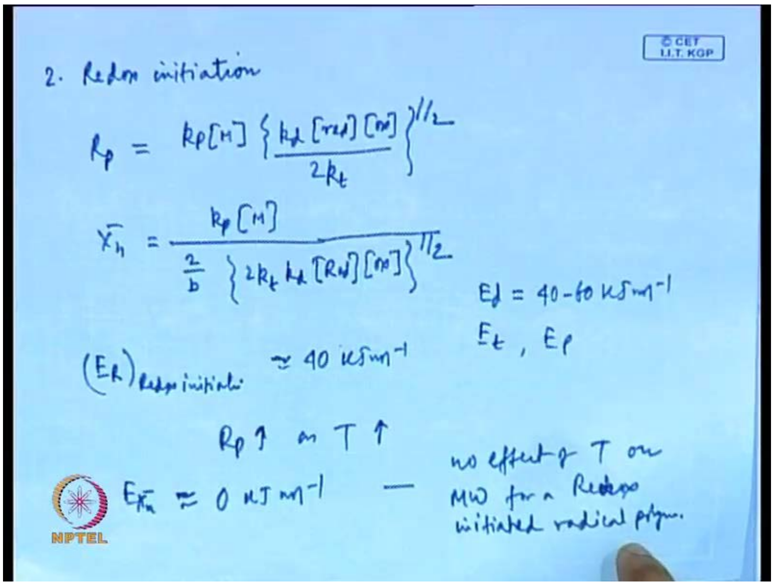

2. Redox initiation

$$R_p = k_p[M]\left\{\frac{k_d[\mathrm{red}][\mathrm{ox}]}{2k_t}\right\}^{1/2}$$

$$\bar{X}_n = \frac{k_p[M]}{\frac{2}{b}\left\{2k_t k_d[\mathrm{Red}][\mathrm{ox}]\right\}^{1/2}}$$

$E_d = 40-60\ \mathrm{kJ\,mol^{-1}}$

E_t, E_p

$(E_R)_{\text{Redox initiation}} \simeq 40\ \mathrm{kJ\,mol^{-1}}$

$R_p \uparrow$ as $T \uparrow$

$E_{\bar{X}_n} \simeq 0\ \mathrm{kJ\,mol^{-1}}$ — no effect of T on MW for a Redox initiated radical polym.

Now, if we talked about the other initiation process. This was for thermal initiation processes. Now, if we talk about the other initiation process, like redox, number two is redox initiation. Remember, the rate expression for redox reaction, it was k p M k d concentration of reductant (( )) twice k t to the power half and X n bar could give you k p to the power M k p m twice over b twice k t k d red ox to the power half. And again, you can break down this expression in the two terms, one temperature independent and another temperature dependent. Temperature dependent on terms of the rate constant k p, k d and k t and same, as you can do this and do the same exercise what we did for the thermal initiation and see what is the value of E R in this case.

E R in this case means, for redox initiation, again we will be coming around 40 kilo joule per mol. Thus, because the E d for this reaction, for this initiation process is much lower compared to a thermal initiation process, that we, while discussion in the initiation, the types of initiation process we mentioned, that redox reaction, you can do it at lower temperature, that is because the activation energy for the initiation reaction is much lower compared to thermal initiator.

Now, that gives, if you use the same thing you will find, that E R is coming around, whereas the values for k p and k t remains same (( )) means, the values for E t and E p remains same as the thermal initiation because they are the same reactions we are talking about. So, if you put all these numbers you will get, that e, E R coming around 40 kilo joule per mol. So, in this case also, the R p goes up as temperature goes up, but it is not as, as much increase as in the case of thermal initiation process.

Now, what is E X n 0? If you again put this number you will find, that E X n 0 is about 0 kilo joule per mol, which suggest, that there is no effect, no effect of temperature on molecular weight for a redox initiated radical polymerization, redox initiator radical polymerization. So, what for this type of initiation? We know, we found, that temperature increases, rate of polymerization also increases. Further increase is not as much as in case of thermal polymerization and because the activation energy for the molecular build up is about 0, which means, there is no effect of the temperature on the molecular weight of redox polymerization, that is why, the redox polymerization are done at room temperature or even sub-roomed temperature because temperature increase would not affect, have no effect on the radical polymerization.

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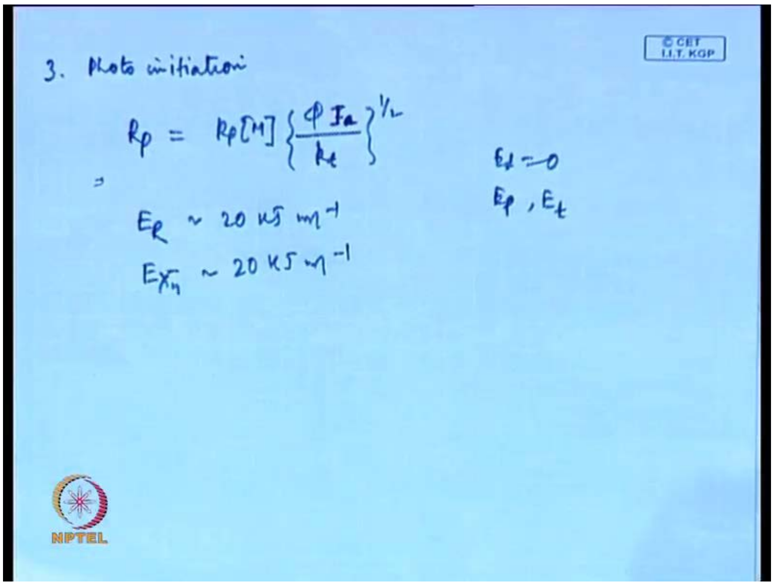

3. Photo initiation

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

$E_d = 0$

E_p, E_t

$E_R \sim 20 \text{ kJ m}^{-1}$

$E_{\bar{X}_n} \sim 20 \text{ kJ m}^{-1}$

And the, now let us talk about the third type of initiation, which is that photo initiation or photo chemical reactions, photo initiation. Now, we know again from, of (( )), it gives you phi I a k t to the power half. This is I a, I a is the intensity of light, phi is the (( )) yield. You do not see k d term because k d is for thermal initiation process, is actually E d is 0, sorry, this photo chemical reaction process E d is 0 and the other E p and E t remains same. So, if you put E d is 0 and E t, E t term (( )) values from same as earlier, you will get E r is 20 kilo joule per mol.

So, as E X n, which means, that in case of radical polymerization initiated by a photo chemical reaction, again the reaction rate, rate of polymerization increases mildly, in this case with increase in temperature and so does the molecular weight. Here also, molecular weight increases slightly with increase in the temperature. However, if you remember, that the in case of temperature effect of photo chemical reaction, which is little more complicated because the initiators, which produces radical photo chemically, they also produce radical at a higher temperature.

So, if you increase, there will be complications of the, which type of initiation is dominating and so this equation will be combination of photochemical reaction and a (( )). This will be little complicated, but for, simply we can do it at lower temperature, then that thermal decision does not come, does not play effect. Then these conclusions will be varied, will be varied, that rate of reaction or rate of polymerization slightly increases with increase in temperature and the degrees of polymerization or the molecular weight also increases with increases in the temperature slightly.

Now, remember, we, we got this expression for rate of polymerization, this and in case of thermal initiation as well, this, this expression, this expression we got assuming, that the reaction is at steady state. We, we applied the steady state approximation to, to find out the concentration of the radical, total radical present. So, these conclusions we just made the, about the effect of temperature on reaction rate and molecular weight is valid till the steady state is maintained.

Once the steady state is broken, for example, this gel effect, during the gel effect when steady state is broken, then this is not valid, this conclusions is not, are not valid anymore and you know, though the effect of temperature will remain in much more complicated than what we just discussed. So, we, we also did not consider, that there could be possibility of transfer reaction. In this case we just talked about the propagation and initiation, propagation and the termination reactions, now there could be transfer reaction, chain transfer reactions as well.

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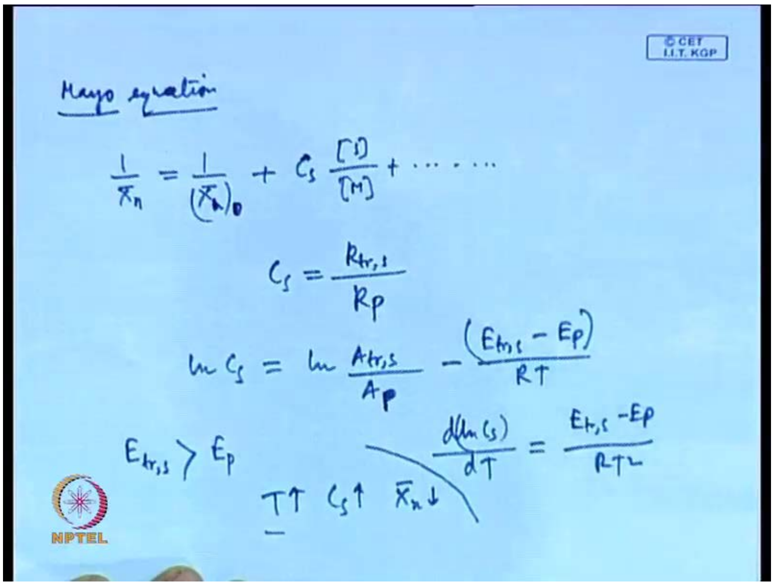

Mayo equation

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_0} + C_S \frac{[S]}{[M]} + \cdots\cdots$$

$$C_S = \frac{R_{tr,s}}{R_p}$$

$$\ln C_S = \ln \frac{A_{tr,s}}{A_p} - \frac{(E_{tr,s} - E_p)}{RT}$$

$$E_{tr,s} > E_p \qquad \frac{d(\ln C_S)}{dT} = \frac{E_{tr,s} - E_p}{RT^2}$$

$$\underline{T}\uparrow \quad C_S\uparrow \quad \bar{X}_n\downarrow$$

Now, from Mayo equation we have seen how the molecular weight varies with the chain transfer of the polymers where we can write… This is, we have in the last class or the lecture before last one, we had seen, that if there is a chain transfer, then the molecular weight actually drops as the result of chain transfer reaction and this is, this 0 is, this X n bar is the number average degrees of polymerization in absence of any chain transfer reaction.

So, if there is any chain transfer reaction, the actual value of X n bar will come down and C s and other C s, it could be A s, could be a monomer a solvent or a molecule, which are added from outside by deliberately or by, it present as impurities. And this is, this is, this R stand for transfer constant and are given by the rate constant for the transfer and rate constant for the propagation. So, we can again write same another equation and write ln C s as similar to the earlier cases.

Now, generally, E (( )), activation energy for transfer is higher than the (( )) activation energy for the propagation, which means, with, with increase in temperature C s goes up, the value of C s goes up. From this expression you can see, you can write the other, similar to other expressions as well, which gives you E transfer s minus E p by RT square from this expression. You can clearly see, that with increase in temperature, here temperature goes up, this values of transfer coefficient, transfer constant goes up and if this transfer constant goes up, that means, what will happen? Molecular weight, molecular weight will further come down.

So, we have, we have seen how you can get quantitatively the average number, average degrees of polymerization in presence of chain transfer reaction and from this expression we have seen, that if we increase the concentration of chain transfer agents the molecular weight goes down. And if the chain transfer or transfer constant goes up, then also the molecular weight comes down compared to the case where there is no transfer. Now, C s value, as we seen from the activation energy for transfer reaction and the propagation reaction, that if temperature goes up, C s goes up, which means, X n come down.

So, increase in temperature has to affect increase in temperature by itself even if there was no transfer reaction. It was decreasing the molecular weight and in places of transfer reaction is further reducing. So, if you have a transfer reaction going on, then the increase in temperature will affect more, it will decrease the molecular weight more in comparison where there is no transfer reaction going on. Both the cases, the molecular weight drop, with, with increase in temperature, but if there are transfer reaction going on, then the drop will be much more compared to situation where is, when there is no transfer reaction.

Now, that basically says, now what the effect of temperature on rate of polymerization and, and molecular weight for different radical processes means, different radical processes is initiated by different initiation reaction as and also, in case of the radical reaction where you have chain transfer reactions.

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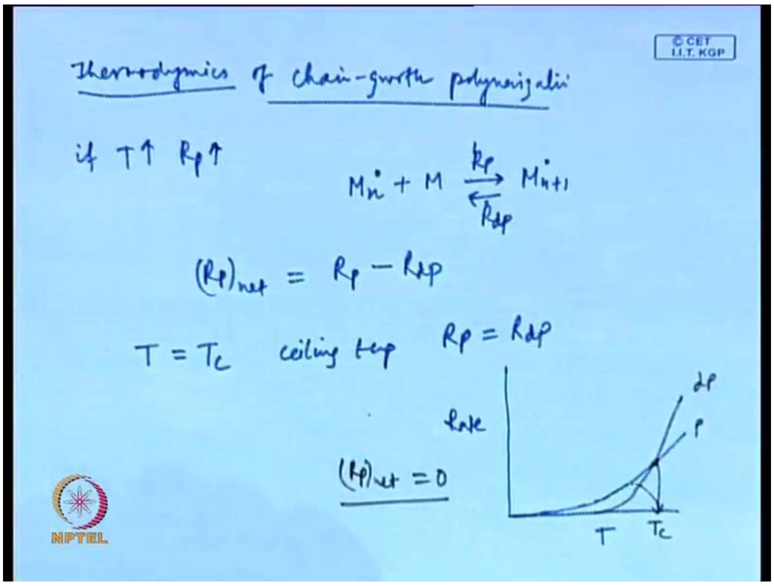

Thermodynamics of chain-growth polymerization

if T↑ R_p↑

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftarrows}} M_{n+1}^\bullet$$

$$(R_p)_{net} = R_p - R_{dp}$$

$T = T_c$ ceiling temp $R_p = R_{dp}$

$(R_p)_{net} = 0$

Now, let us talk about thermodynamics of, of radical polymerization. In fact, this is true for any chain growth polymerizations, so we can generalize this chain growth polymerization. Now, we have just concluded, that if T goes up, R p goes up, we just concluded in our discussion few minutes back. It does not mean, that if you increase, keep on increasing the temperature, rate always will go up. The answer is no because in this case, we have only considered the forward reaction, we are talking about propagation reaction, whereas there could be backward reaction, depropagation reaction as well.

This is k p and this is k dp, depropagation reaction. Now, we do not consider normally the reverse reaction because the temperature, we do for most of the monomers, the reverse reaction is almost nil, that is why, we always talk about rate of forward reactions. So, actually the rate of, so net rate of polymerization would be rate of, polymers, propagation minus rate of depropagation. Now, as I said, that in normal case, whatever temperature we use for most of the polymers, this is 0. We consider rate of polymerization as the rate of propagation altogether.

But if you think, to increase the temperature at some temperature the rate of depolymerization will also be insignificant, in those cases we have to consider the rate of depolymerization also. And if we increase the temperature further, rate of depolymerization also increases, so as rate of polymerization, as we discussed just now.

So, at some temperature, some temperature T, which we call T c, ceiling temperature, ceiling temperature, this R p becomes R dp. So, basically this propagation and depropagation reaction, they reach in equilibrium. So, rate of polymerization reaction, propagation reaction is same as rate of depropagation reaction, if I want to show this in, in a figure, what we can, so if this is your rate. And if this temperature, rate of polymerization or rate of propagation increases with temperature.

Now, at some point of time, some point temperature, rate of depropagation also, this is dp and this is p, is a propagation and this is depropagation also increases. Now, that point, so net, so net reaction, net polymerization reaction, which is R p net, how it will act, it will look like? It will be something like this because below this temperature the rate of polymerization is higher and then the depolymerization becomes significant and at this temperature, which is, t's, T c, the net polymerization is 0. That means, if you do not see any change in the concentration of monomer, which means, that no polymerization is taking place. If you comeback after some time and take the, these are the concentration of the monomer and you see, that the monomer concentration is same as before, which means, that monomer is not, monomer is not participating in further polymerization reaction. So, that is the time when the quick decision is reached.

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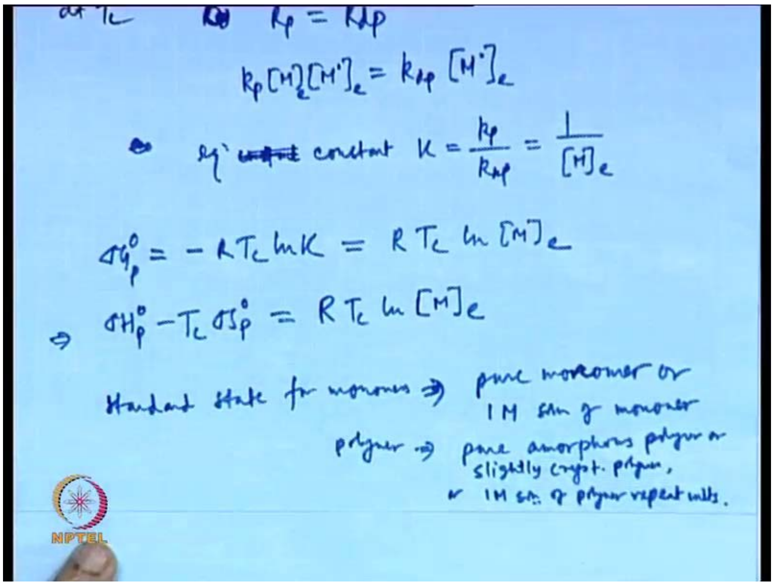

at T_c $R_p = R_{dp}$

$$k_p [M]_e [M^\cdot]_e = k_{dp} [M^\cdot]_e$$

eq^n constant $K = \frac{k_p}{k_{dp}} = \frac{1}{[M]_e}$

$$\Delta G_p^0 = -RT_c \ln K = RT_c \ln [M]_e$$

$$\Rightarrow \Delta H_p^0 - T_c \Delta S_p^0 = RT_c \ln [M]_e$$

Standard state for monomer ⇒ pure monomer or 1 M soln of monomer

polymer ⇒ pure amorphous polymer or slightly cryst. polymer, or 1M soln of polymer repeat units.

Now, let us prove this phenomenal little more. At T c you have R, R p is same as R d p now r p you know k p M and M dot and this will be M dot. So, what is the equilibrium constant? Equilibrium constant k is k p by k dp is 1 by M at equilibrium now at i write e because this is an equilibrium. So, I write, substitute e for these all this concentration. So, at, equilibrium constant is related to the concentration of the monomer in this case only. Now, this is a special case where you do not see the concentration of product is appearing in your equilibrium constant, it is only the reactants. In this case, the monomer, which is appearing in the, your equilibrium constant value.

Now, I can write few thermodynamic expressions. We know del G 0 standard gives energy change for polymerization R T c ln k, where k is the equilibrium constant. We can write from this R T c ln M e and we can write, del G 0 p as del H 0 p minus T c del S 0 p this side; right side R T c ln M e. This as you know, this, this is the standard enthalpy of polymerization reaction and this is standard entropy of the polymerization and this is standard state for monomer is considered. Standards state for monomers is either pure monomer, pure monomer or 1 molar solution of monomer, whereas for polymer, it is pure amorphous polymer, pure amorphous polymer or slightly crystalline polymer, or, or 1 molar solution of polymer repeat units.

So, what does del H and del S 0 means? That you take a pure monomer and convert to pure polymer associated enthalpy, chain, change will give you delta S 0 or you take one molar solution of the monomer and convert it completely into polymer. Now, the associated enthalpy chains will give you del H 0 and the entropy change will give you the del S 0 of the polymer.

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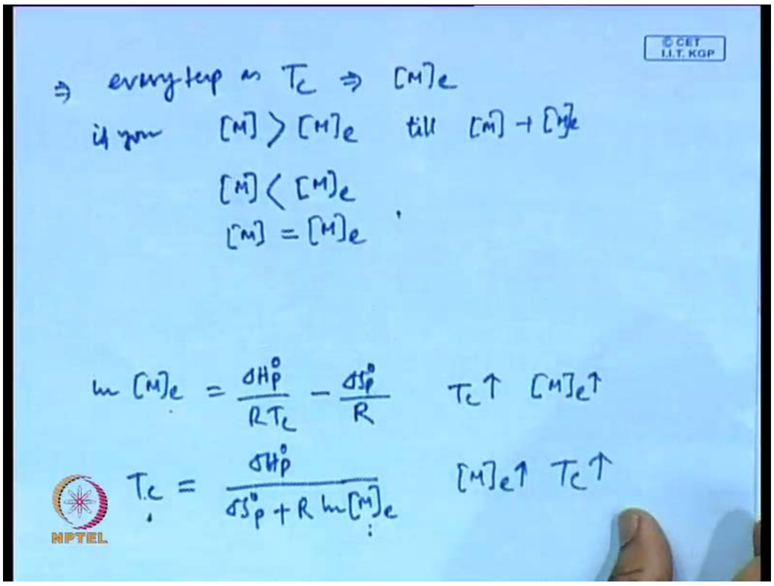

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⇒ every temp as T_c ⇒ $[M]_e$

if you $[M] > [M]_e$ till $[M] \rightarrow [M]_e$

$[M] < [M]_e$

$[M] = [M]_e$

$$\ln [M]_e = \frac{\Delta H_p^0}{RT_c} - \frac{\Delta S_p^0}{R} \qquad T_c\uparrow \ [M]_e\uparrow$$

$$T_c = \frac{\Delta H_p^0}{\Delta S_p^0 + R \ln [M]_e} \qquad [M]_e\uparrow \ T_c\uparrow$$

Now, relook at this expression and we can, this expression and let us write from this expression, thus ln M e is del H 0 p by R T c minus del S 0 p by R. Similarly, we can write, T c is del H 0 p by del S 0 p plus R ln M e. Now, what does these two expressions says, that T c and M e are related, they are not independent to each other. If you change T c, if you increase T c, the equilibrium constant, concentration of the free monomer increases and so as the other thing, M e increases, equilibrium constant, concentration of the monomer increases, then T c also increases.

This is a very important thing, that T c is not a single temperature, it, it depends on the composition of your polymerization reaction. It is not that every polymer has or every monomer has a single ceiling temperature. This and this often is understood, that T c is the single number, it actually depends on the monomer concentration as well.

Now, how to, how to sort of read these equations? Let us understand, every, if you can, you can consider every temperature, you can consider every temperature as, you can consider whatever reaction you are doing as a ceiling temperature. Now, there is always an associated equilibrium value of the monomer. If you start a reaction, if you start or if at any point of time in a reaction, if M concentration is or the monomer is higher than equilibrium value, then the reaction will proceed till M becomes M e, then reaction will not take place further; that means, rate of propagation will be same as depropagation. So, every temperature, there is associated, for every temperature there is a ceiling temperature, there is associated equilibrium monomer concentration.

So, if you start or anytime during your reaction, if your free monomer concentration is higher than the equilibrium monomer concentration corresponding to tact temperature, your reaction temperature, then what will happen? The reaction will continue, propagation will continue till your free monomer concentration becomes as the equilibrium free monomer concentration. At any point, I say, you start a reaction with your free monomer concentration less than M e, then will what will happen?

You fix a temperature for your reaction and you start with a monomer concentration, which is lower than your equilibrium monomer concentration, which means, the reaction will not go. Rather, if the polymer chain can be initiated, polymer chains can be broken at some, some place and you get a radical or some active center, the polymers will depropagate, unzip to form monomers, so that the free monomer concentration goes up and gives you the equilibrium monomer concentration. And if your, at any point of time if your monomer concentration is equivalent to your equilibrium monomer concentrate, then the reaction will stop, that means, that there will be no appreciable or there is no change in the concentration of the free monomers. So, apparently, there is no reaction going on. Actually, there is a rate of propagation is same as rate of depropagation.

So, again, one more time let me emphasize, that if you, every temperature, every, your reaction, you can choose any temperature of your reaction and consider that as a ceiling temperature. Now, that temperature corresponds to an equilibrium value of the free monomer determined by the values of del H 0 and del S 0. Depending upon this value you get the relation between T c and M e. So, for every temperature there is a M e value and if your, at any point of term your reaction concentration, the free, free monomer or the concentration of your free monomer is higher than the equilibrium monomer concentration, reaction will proceed till the reaction, the mono, free monomer concentration is same as the equilibrium monomer concentration.

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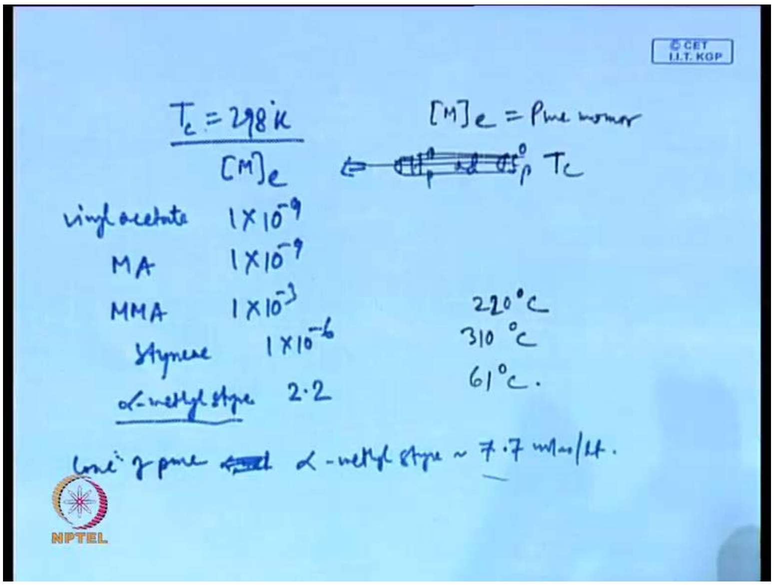

$T_c = 298\,K$ $[M]_e$ = Pure monomer

$[M]_e$ $\Leftarrow$ ~~ΔH_p and ΔS^0_p~~ T_c

	$[M]_e$	
vinyl acetate	1×10^{-9}	
MA	1×10^{-9}	
MMA	1×10^{-3}	220°C
Styrene	1×10^{-6}	310 °C
α-methyl styrene	2.2	61°C.

Conc of pure α-methyl styrene ~ 7.7 moles/lt.

Let us take an example. Now, for temperature 298 K or 25 degree centigrade, what is the M e for different monomers? Now, M e you can get, again T is given, T c is given, so that is your temperature reaction. You can get it from the values of del 0 p and del S p. If you know these, this R you know and your reaction temperature you know, then you will get this value of the free monomer concentration at equilibrium. So, that is, let us, vinyl acetate, 1 into 10 to power minus 9 moles per liter; methyl acrylate, moles per liter; methyl metacrylate; styrene, moles per liter and alpha methyl styrene, 2.2 moles per liter.

So, if you can carry out a polymerization reaction of these monomers at 25 degree centigrade, the reaction will stop or in accurate sense, reaction will be equilibrium till your monomer concentrations comes down to this level. See, if you start with the pure methyl meta acrylate and do the reactions at 298 degree centigrade, 298 K, at 25 degree centigrade and reaction will proceed, polymerization will proceed till the free concentration or the concentration of the free monomer becomes 10 to the power minus 3 moles per liter, which also means, that you can never complete a reaction, you can never complete 100 percent, entire methyl meta acrylate to the polymer stage because before that there will be stage where equilibrium, where for any temperature where the propagation step and depropagation step are same.

Now, look at the values of alpha methyl styrene, that is, 2.2 moles per liter. Now, the pure, the concentration of pure alpha methyl styrene comes about 7.7 moles per liter. So, these monomers will polymerize at 25 degree centigrade. If you can, of course, 25 degree cannot polymerize because you have to generate, that is very difficult, you have to increase the temperature for the reasons you know. If you can start a polymer or you can polymerize alpha methyl styrene at 25 degree centigrade, then the polymerization will take place till the concentration becomes 2.2 moles per liter. Once it reaches this value, it will not proceed.

Now, it will be interesting to see what is the value for T c when you start with the pure monomer. That is interesting because if you start with the pure monomer and if your T c is your reaction temperature, then the equilibrium value of your free monomer is same as the pure monomer. That means, reaction will not at all proceed. Now, let us put this number for the same, same monomers, the t c values. Let me cut this and put this, this is value for equilibrium concentration of the free monomer, at, which is pure monomer.

So, what will be the T c? For styrene it is 310 degree centigrade, for alpha methane styrene is 61 degree centigrade, for styrene is (( )) 220 degree centigrade, what does it mean? If you start a reaction of alpha methyl styrene from pure monomer at 61 degree centigrade, what will happen? These are already reached, pure monomer is equilibrium (( )). So, that means, it has already reached the equilibrium, then it will be never polymerized further.

If you do it at lower temperature, then M e value will come down and reaction will proceed till that equilibrium value of the monomer concentration. If you do above 61 degree, the M e value is even higher than the pure monomer, which means, again there is no polymerization possible. I hope you got this concept of this ceiling temperature and how does it influence you polymerization process. So, again, every temperature you can consider as ceiling temperature.

Normally, you do reaction little at a higher temperature for, say, at 80 degree or 100. Now, if you do at 80 degree, then you can only reach polymerization. You can carry out the polymerization till the free monomer concentration reaches the equilibrium value of the temperature and because these numbers are low, 10 to power minus 9, 10 to power minus 6 and minus 3, which is considered, say, 25 five degree centigrade. Now, if we increase, say, around this 25 degree centigrade, say 50 degree or say 100 degree, it will come down little bit, go up little bit even though the numbers will be very low, which means, if you do it at 100 centigrade, you almost quantitatively convert the monomers. But there will be always some free monomer remaining, which is equal to the free monomer concentration at equilibrium for that particular temperature.

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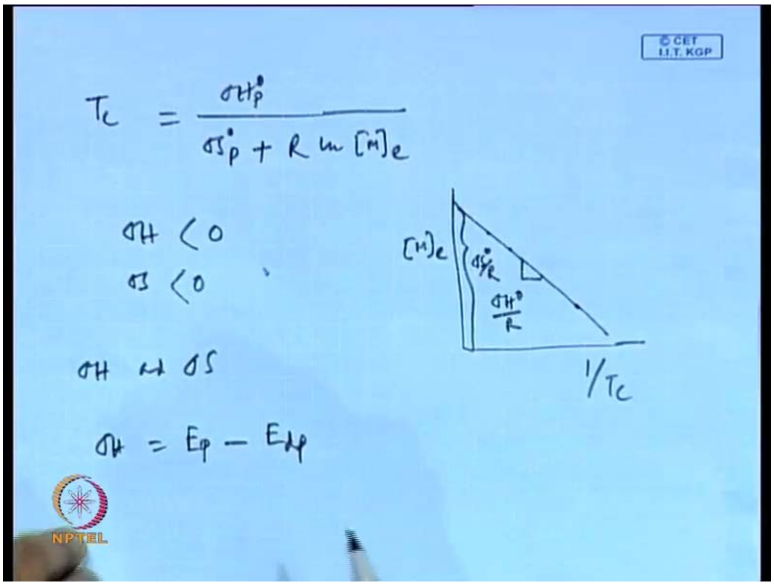

$$T_c = \frac{\Delta H_p^\circ}{\Delta S_p^\circ + R \ln [M]_e}$$

$\Delta H < 0$

$\Delta S < 0$

ΔH and ΔS

$\Delta H = E_p - E_{dp}$

Now, how do you get the values of T c? Now, we know that again from that expression. We just talked about plus R ln M e, how do you get the relations between T c and M e? If we know the reaction, the values of delta H p and delta S p, now what is delta S p sign? Del H is negative because it is an exothermic reaction, pi bond is converting to a sigma bond and del S is also less than 0 because the monomers is getting tied up into a more ordered state compared to a disorder state.

So, if we, we can plot M versus e versus 1 over T c and from the slope we can, if you know this, by experimental process we can get this values from the slope and interest rate is, so if we know these values we can get the value for del S and del H. And reverse history, if we know the values of del S and del H, we can find out the relation between the M e and T c. Now, each point, each point in this represents a particular T c and corresponding M e value, which means, that T c is not a singular number, it varies along with your free monomer concentration.

Now, how does these numbers, del H and del S, vary with different monomer? Now, del S is, del H we know is basically the difference in the activation for the propagation reaction and the depropagation reaction.

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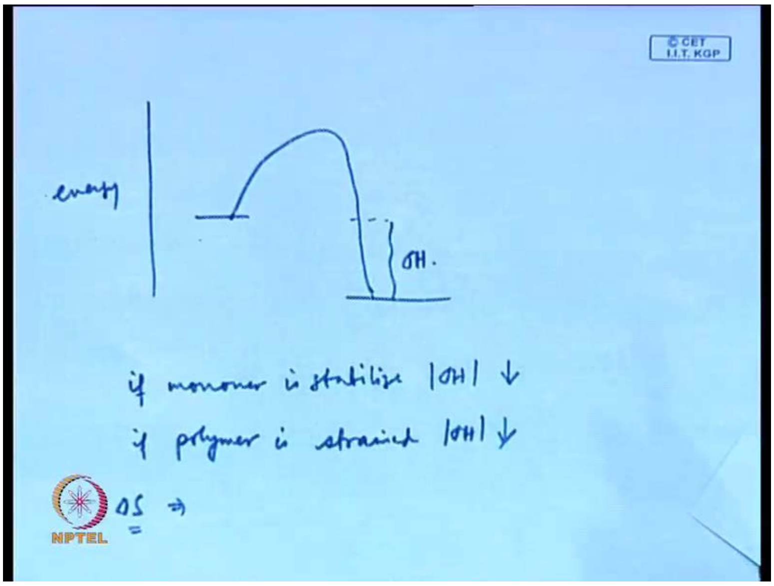

if monomer is stabilize $|\Delta H| \downarrow$

if polymer is strained $|\Delta H| \downarrow$

$\Delta S \Rightarrow$

So, if I plot, say, energy and this, your monomer and this is your polymer, so this difference is your del H. So, anything, anything, which stabilizes this energy, the monomer energy will decrease the difference and over anything, which actually increases the energy of the polymer, the produce or resulting polymer, it also will reduce your magnitude of del H.

Now, so anything, if monomer is stabilized, then del H, magnitude of del H will come down. Now, this stabilization could be due to resonance in the active effect or hyper conjugation or even by inter-monomer association or inter-polymer association and if the polymer is strained, then also this goes up, del H comes down. So, that will depend on the structure of the monomers and we will talk about that more in next lecture.

Now, what about del S? Del S is basically difference between your translational, rotational and vibrational entropy of monomer and polymer. Now, whatever vibrational, rotational entropy is lost by the monomers is actually gained by the polymer. So, it is basically the entropy, the delay value is basically the entropy of change in, entropy of the translational, entropy of the monomers resulting in a polymer. Now, this translational entropy does not depend too much on the monomers structure. So, we will find that the delays values are more or less independent or every monomer in this chain polymerization.

So, we will start next lecture from this, this page and talk about more on the values of del H and del S and how a monomer structure actually determine or influence the value of del H, and which in turn determine the thermodynamic feasibility of polymerization of a monomer. So, we will start from this page in the next lecture.