Polymer Chemistry
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Module - 1
Lecture - 12
Radical Chain Polymerization (Contd.)

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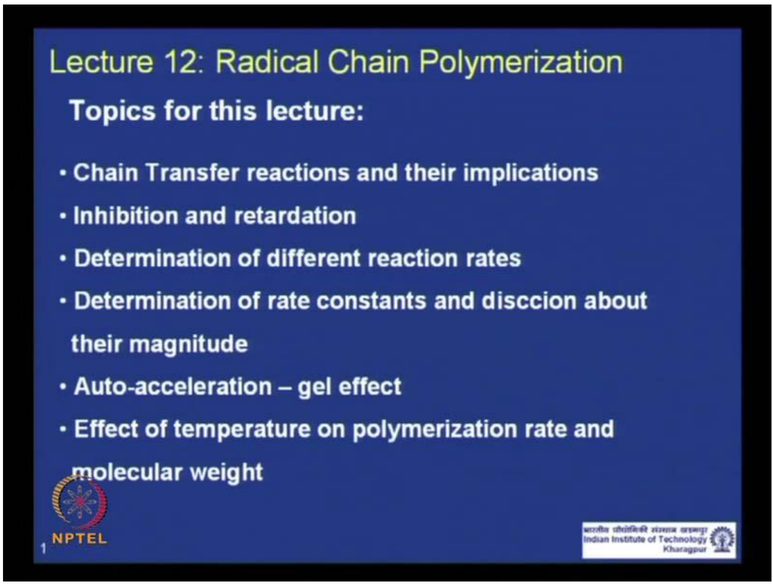

Lecture 12: Radical Chain Polymerization

Topics for this lecture:

- Chain Transfer reactions and their implications
- Inhibition and retardation
- Determination of different reaction rates
- Determination of rate constants and disccion about their magnitude
- Auto-acceleration – gel effect
- Effect of temperature on polymerization rate and molecular weight

Welcome to this 12th lecture of course in Polymer Chemistry. And in this lecture I plan to continue the discussion on chain transfer reaction and their implications. And then we talk about the inhibition and retardation reactions, we talk about how to determine or what is the procedure of determination of different reaction rates, rate of initiation, rate of termination rate of polymerization.

And we talk about and discuss now how to determine the rate constant different rate constant, and we will discuss about their magnitudes and we go next to the auto acceleration gel effect. And then finally we will talk about effect of temperature and polymerization rate and as well as effect of temperature and molecular weight of polymers.

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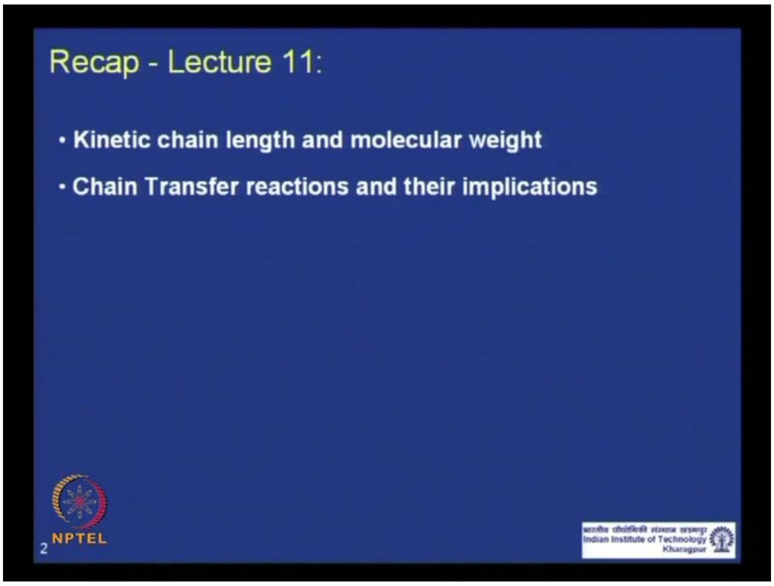

Recap - Lecture 11:

- Kinetic chain length and molecular weight
- Chain Transfer reactions and their implications

In last lecture we introduced different types of chain reactions possible and we also convince our self that if there is a chain transfer reaction, expect if the chain transfer is by the reaction with a polymer chain dead polymer chain. In all other cases the chain transfer happens then molecular weight will come down. And we also introduced the term kinetic chain length how it is related to the average number number average degrees of polymerization. And how we can determine the number of residual (( )) initiator residues per chain and how that is related to the number of degrees of polymerization.

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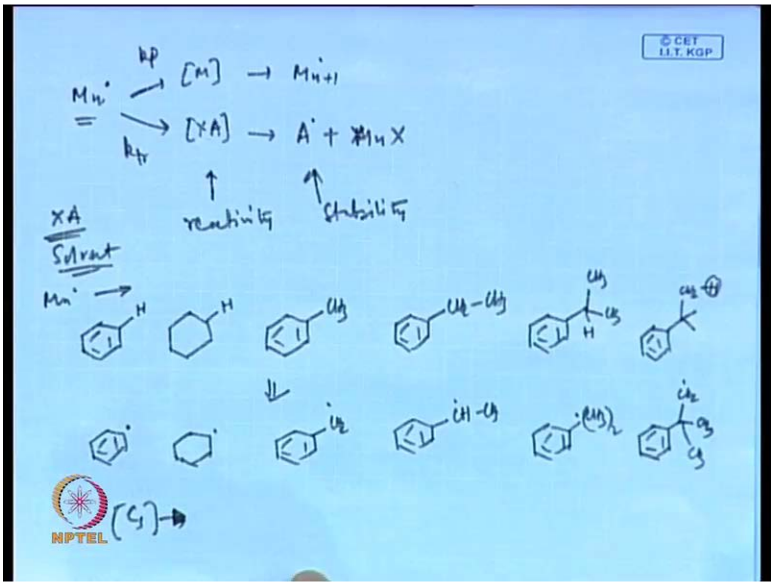

Now, let us continue the discussion having the last lecture on the chain transfer reaction. Now, we had discussed this, these molecules and their reactivity, now as we are discussing that if the more stable radical will have a tendency to react or undergo transfer reaction compared to the less stable one.

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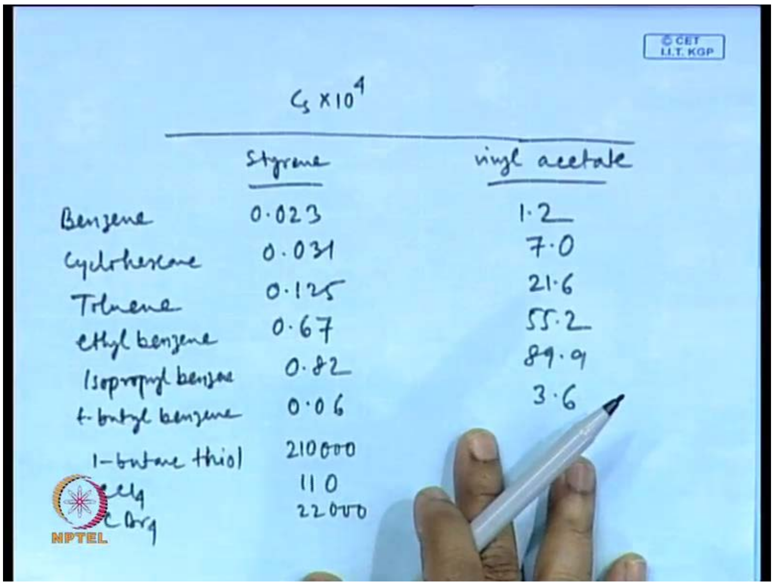

$C_s \times 10^4$

	Styrene	vinyl acetate
Benzene	0.023	1.2
Cyclohexane	0.031	7.0
Toluene	0.125	21.6
ethyl benzene	0.67	55.2
Isopropyl benzene	0.82	89.9
t-butyl benzene	0.06	3.6
1-butane thiol	210000	
CCl_4	110	
CBr_4	22000	

Now, let us look at the values of this solvents C s is the chain transfer constant for the solvent. So, the higher the value the higher is the tendency for that solvent to undergo transfer reaction. Now, we have listed here the values for two monomers, polymerization two monomers polymerization styrene and polymerization of vinyl acetate. And look at the value, you will know that this is the more stable radical then this secondary radical then this one then this and in this case because again this is a primary radical.

So, this stability would be similar to stability of this radical. So, look at the number again benzene cyclohexane toluene if you increase go toluene to ethyl benzene isopropyl benzene the tendency of transfer reaction goes up. And again we go to tarsalbutyl benzene, because again it is a primary radical, we are talking about if the tendency of transfer reaction goes down.

Now, this happens to vinyl acetate as well, but look at the comparison between vinyl acetatestyrene, vinyl acetates are the numbers for vinyl acetate are R, so higher. So, tendency of the solvents for transfer reaction for vinyl acetate is higher compared to a polymer reaction of styrene. Now, what could be reason between the difference in this tendency of the solvent towards different monomers, again as we discussed in the last lecture if this propagating radical is very reactive.

Then obviously, it will react for both the monomer as well as the solvent in this case if it is less reactive then it will choose the most feasible root. Now, between styrene radical the propagating radical from astyrene polymerization, vinyl acetate polymerization this is much more reactive compared to a styrene radical generated from styrene molecule. So, this will react much more to with the solvent molecule in this case. So, that is the reason this is this transfer constant as much higher value compared to styrene.

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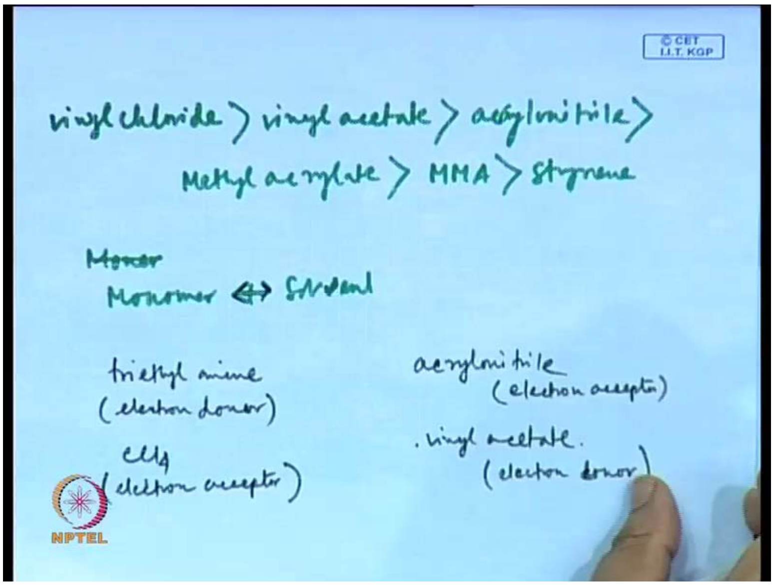

vinyl chloride > vinyl acetate > acrylonitrile >
Methyl acrylate > MMA > Styrene

~~Monor~~
Monomer ⟺ Solvent

triethyl amine
(electron donor)

acrylonitrile
(electron acceptor)

CCl_4
(electron acceptor)

vinyl acetate.
(electron donor)

So, if we want to list or rank between different monomers, the rank of the reactivity would be something like this it is vinyl chloride higher than vinyl acetate, acrylo nitrile methyl acrylate, methyl methacrylate styrene and so on. So, you can yourself from your knowledge from organic chemistry you can justify this ranking, because this is the most reactive radical generates from vinyl chloride will be much reactive compared to the other ones.

This lacks any significant stabilization mechanism either by resonance or by inductive effect, whereas, a styrene will have stabilization radical generated from styrene will have the stabilization by resonance. So, the reactivity of that radical will come down. Now, this is this ranking does not hold always there are cases where there is a specific interaction or putting a affinity between monomer molecule plus solvent, there is specific affinity between this.

If for example, if the monomer is electron donor it will have more tendency to react with a solvent which is electron acceptor, whereas if the monomer is a electron acceptor it will have a tendency to react with electron donating solvent, for let us compare between two monomer and two solvent and see whether, we can justify or we can have this verified from the experimental data.

Now, I consider tri ethyl amine as a solvent now it is electron reach, so electron and c c l 4 which is electron acceptor solvent. Now, I compare between acrylonitrile and vinyl acetate, now acrylonitrile is a electron accepting monomer, where this is electron. So, obliviously this will have more tendency for react or undergoing transfer reaction with c c l 4 than trim ethylamine. And between this two monomers acrylonitrile have more tendency to undergoing transfer reaction with amine compared to vinyl acetate.

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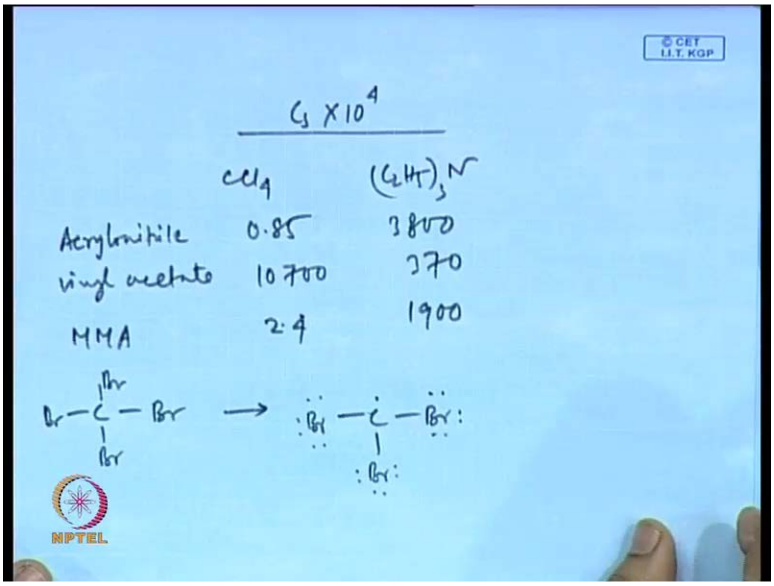

$C_S \times 10^4$

	CCl_4	$(C_2H_5)_3N$
Acrylonitrile	0.85	3800
vinyl acetate	10700	370
MMA	2.4	1900

So, if you compare the values and put a third monomer M M a methyl methacrylate which is again a electron accepting monomer and let us see whether it is more generic. So, acrylonitrile will prefer reacting with this as a transfer reaction compared to this whereas, vinyl acetate will be reacting more with this than this. So, compare vinyl acetate it has more tendency to transfer reaction with C C L 4, but the acrylonitrile has more tendencyto undergoing tri methylamine.

Now, between then comes a competition for same solvent two monomers because this is donor it will have more reacting transfer reaction tendency with acrylonitrile. So, if you look tri ethyl amine the value is higher for acrylonitrile than vinyl acetate. So, you can justify the values for methyl methacrylate, which is again a electron accepting monomer.

So, in what is the utility of transfer reaction or what is what it can help you in this learning on transfer reaction if. Say if you are your trying to polymerize a monomer and then at the end you are not able to get the H high enough molecular weight which you planned from your experiment. Then what are the possibilities it could happen if it does not build molecular weight; that means, and you know that from the monomer structure that it is it is polymerizable by say radical polymerization root.

Then it there could be transfer reactions happening it could be happening with monomer initiator or solvent or they could be impurities present in the reaction medium. Now, if you can remove you can do the reaction once again remembering all the impurities and still if you can get or you do not get the higher molecular weight, then what you need to look for is the structure for initiator and the monomers solvent. Whether they can take part in the transfer reactions and you have to rule out the possibilities, if you rule out all the possibilities have the transfer reactions by appropriate choosing the initiator and the solvent.

Then you can you can built the moleculate if it is the transfer reaction is because the monomer then then there is no other alternative we have choose different monomer al together. If there is a transfer reaction is happening with the monomer. Then they is other way you can build them monomer molecular weight, because you have use the monomers to meet the polymer. Now, if you found in the reaction they is high very high molecular weight, which you do not what then what you can do you can use this chain transfer agents which we have.

Now, what would be the chain good transfer agent which can easy participate in chain transfer reactions and those does molecules like S S N thiol, now containing S S N thiol.

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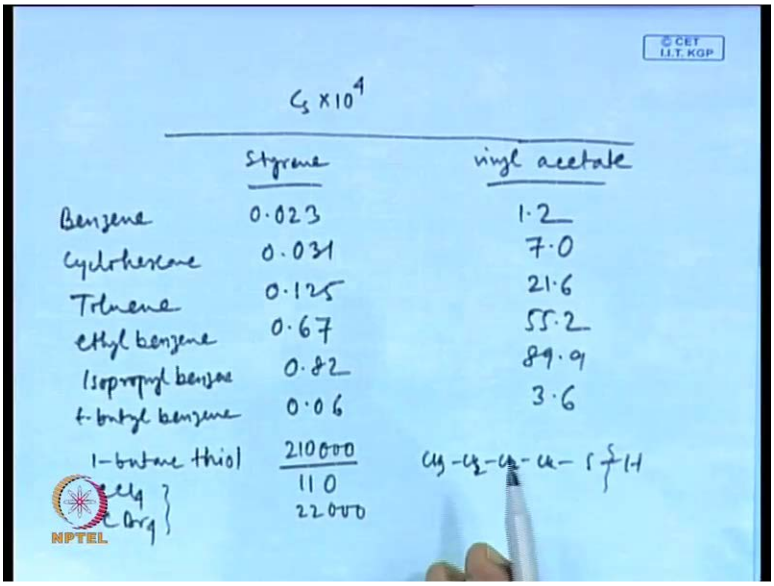

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1-butane thiol	210000	$CH_3-CH_2-CH_2-CH_2-S-H$
CCl_4	110	
CBr_4	22000	

For example, if I look the values for one butane thiol this number is very high, because in this case this is a very week bound. So, easy this hydrogen can be very easy accept by the propo vinyl acetate radicals, why using this type of chain transfer tri ethyl are butane thiol compounds the compounds you can reduce are control your molecular weight much to of your choose or if your target. Now, if you look at this solvents carbon tetra chloride and carbon tetra boride they are also have very high chain transfer constant.

That means, this solvents are very poor solvents if you want to build higher molecular weight in the radical polymerization. The reason for this monomers are the solvents to participate in chain transfer reaction is because of there stability of stabilization of the resulting irons. So, if I have for example, I talk about one participating transfer reaction it produce this radical.

Now, this is can be easy stabilized by all this roaming molecular, which can participation the reguise instructed. So, this that is the reason that this type of solvent carbon tetra chloride and in specially carbon tetra boride participation the chain transfer reaction very much high extent. So, always avoid in this type of solvent for alginated only in that sense because alginated solvent will always breezily it can be easily acceptable. Now, always its try to avoid these acrylonitrile solvent specially for this carbon tetra chloride and carbon tetra boride type solvents.

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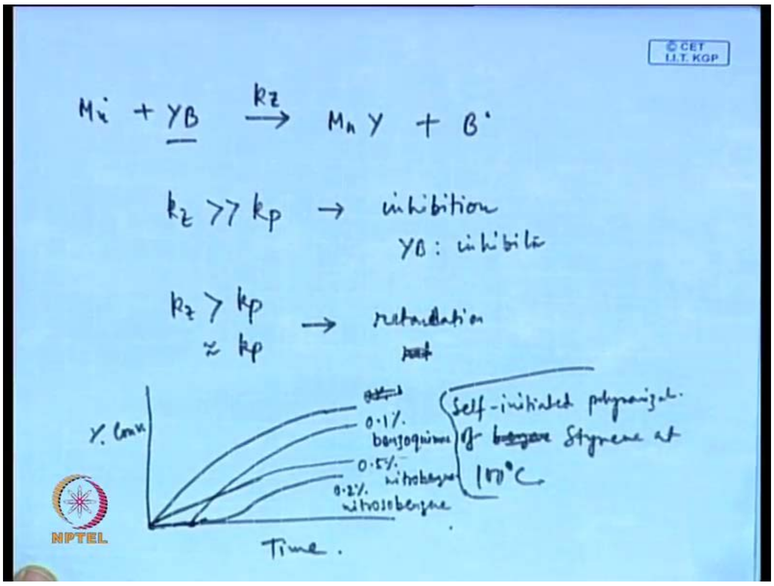

$$M_n^{\cdot} + \underline{YB} \xrightarrow{k_z} M_nY + B^{\cdot}$$

$k_z >> k_p$ → inhibition

YB : inhibitor

$k_z > k_p$ → retardation

$\approx k_p$

Self-initiated polymerization of ~~benzene~~ Styrene at 100°C

Now, if I look at that transfer reaction one more time, so if I take a mu, so YB inter x a am writing YB and now it is producing M n Y plus B dot, k z is the red constant for reaction. Now, if this b dot which is this radical is very stable that it is does not take part in further reaction, further chain in reaction, it might degrade or it may react with itself forming non radical sphere.

But, it does not react with the monomers to initiate he chain molecules a new chain or if it is at all reactive with monomer the rate is very, very small which means practically in this reaction transfer reaction you are producing a death chain. Even if you are producing an radical which is as good as death death chain, because it is not talking part in initiation of a mu chain.

In this case what happen if k z is much higher then k p which means that this reactions this happening at much higher extent compare to the normal propagation reaction then you will not have a polymer at all, because as soon as this chain initiate it will react with this and form a death chain. So, we will not have at all any polymers, so polymer is get inhibited. So, it is a inhibition reaction and this YB is a inhibitor if k z is little higher or may be comparable with k p, then are even part of the M n is under going this reaction and part of the M n is undergoing normal propagation reaction.

So, what happen your rate of polymerization it become slower, so this is retardation and the molecule called retardence. For example, if I talk about a self initiated thermal polymerization, polymerization of benzene styrene a 100 degree centigrade this is percentage of conversation and this is time, is normally have reaction rate of reaction like this by time more propagation happenings. So, more monomer is undergoing polymerization reaction, so higher is the conversation.

If I had this is 0 percent any external molecule there is no external molecule in this case, if it is 0 percent 0.1 percent benzoquinone, benzoquinone this is benzoquinone. So, what happen for some time there is no polymerization reaction at all the monomers is not consuming at all, which means as soon as radical is form it is reacting with your benzoquinone present. So, there is no polymer no monomer is converting in to polymer once this benzoquinone is over then the polymerization reaction start normally.

Now, this is a typical example how this common monomers are shift or store, because most monomers when there are shift from between different countries are locally there are stabilized with small amount of this inviters. For example, hydroquinone or benzoquinone, because there should not self polymerizes either by little bit of heat oil from the binateor or by self initiation reaction. So, when you do reaction base to s to disallowed that benzoquinone hydroquinone stabilizer or inviter or you can add little excess initiator compensating the inviter molecule.

So, that we do the reaction till all the benzoquinone and hydroquinone gets consume after that normal reaction happens. There is a third possibility is like this 0.5 percent nitrobenzene nitro benzene in this case reactions starts from beginning, but with the much smaller rate. So, it is a example of a retardation there would be four possible, which is a combination of inhibition and retardation something like this a starts at a sometimes as well as the reaction is slower, this happens if we add 0.2 percent nitro benzene.

So, this as a the reaction possible with different types of this is the typical or happen if your inhibitor or retardation or a combination of both of that and examples of inhibitors again this is when this radicals is very stable.

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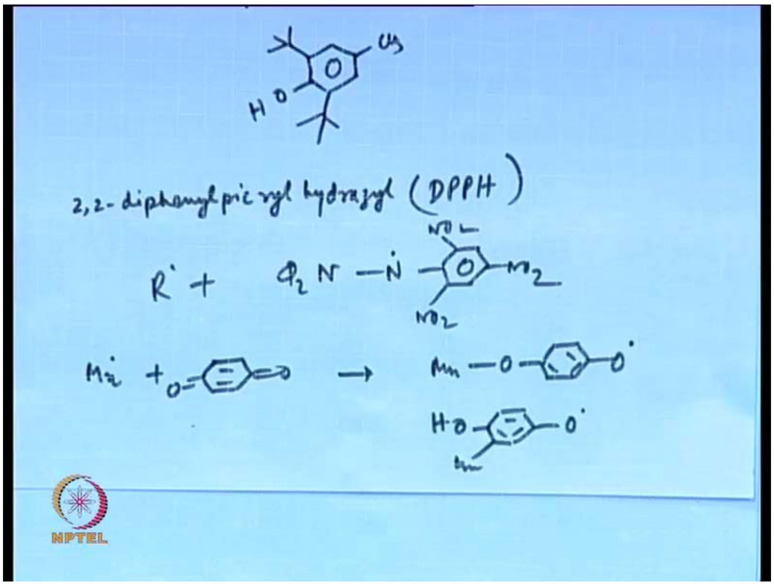

For example, if I have a butyl butylated hydroxy toluene, when this forms a radical where from a hydrogen you can am not writing you can imagine that the dot will come here. And which is extremely stable radical which does not participate in the nutrition reaction it might degrade or react with self, but it does not participate example of a inhibitor. The other example is like 2 2 Di Phanyl Picryl Hydrazyl DPPH, when it reacts with this this is extremely it does not react with any monomer it reacts with the only radicals and form a non radical specious this benzo hydroquinone can react with a propagating radical.

And from either this or this radical both of the, which her resitable radical. So, that is a reason there act as a inhibitor molecule. Another very common inhibitor which we come across at always is oxygen.

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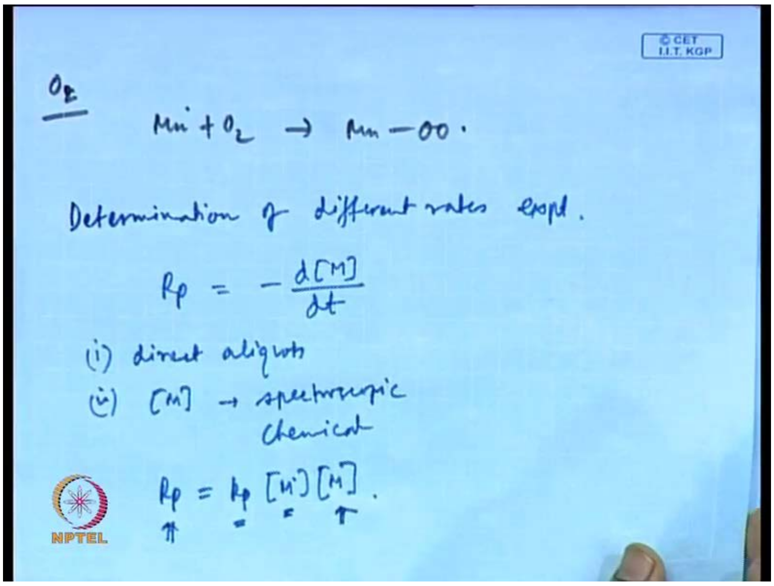

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O_2

$M_n^{\cdot} + O_2 \rightarrow M_n{-}OO^{\cdot}$

Determination of different rates expt.

$$R_p = -\frac{d[M]}{dt}$$

(i) direct aliquots

(ii) $[M] \rightarrow$ spectroscopic
chemical

$$\underset{\Uparrow}{R_p} = \underset{=}{k_p}\,\underset{=}{[M^{\cdot}]}\,\underset{\uparrow}{[M]}.$$

NPTEL

This can react with this self form non radical specious and this can form with other M n dot and can form a non radical specious. So, that is the reason, that the transfer coefficient or or the transfer constant is very high for the reaction that is the tendency of oxygen molecule to undergo this reaction is very extremely high.

So, which means that when you do reactions chain polymerization reaction, radical chain polymerization reaction is must remove the oxygen molecule from the reaction medium as much as possible. To avoid this killing of the radical propagating radical by which it will stop the reaction and also reduce the molecular weight. So, we have now learnt transfer reaction and inhibitor inhibition relation and retardation reaction as well; now let us talk about how one determine this different rates experimentally by experiment.

Now, R p which is the disappears of the monomer or reaction of monomer from the reaction medium, you can directly determined the monomers consideration by talking a alicot from the reaction medium. And precipitating the polymer and then waying the polymer to find out the healed, which means waste is the monomer, so by which you can know what is the monomer present or how much monomer is reacted directly do at from a solution. So, direct aligcot can be taken at different time M and the polymer can be fastigiated out from the reaction; second you can directly measure the concentration either by spectroscopic technique or any chemical techniques.

Now, it can be applied not only for radical polymerization these experiments can be done for step polymerization as well. Where you can stop the reaction in between and find out the functional group, in case of step polymerization by in case of these is the conservation monomer molecule, so from this you can get the value of R p. Now, we get it once s more time this the expression for k p is just for your reminder that this is this.

So, we know this now from the experiment and we can find out the concentration of aim as well, so this k p and M dot are the two unknown quantities. Now, this M dot in in theory or in principle can be found out directly from a sides measurements which get the total initiator concentration specially at that stage, this stage. For because the life time or the life time of this radicals are very small is normal user technique is not very accurate to find out the concentration or M M dot the valve of M dot. So, a sides does not give a very accurate results of the M dot value.

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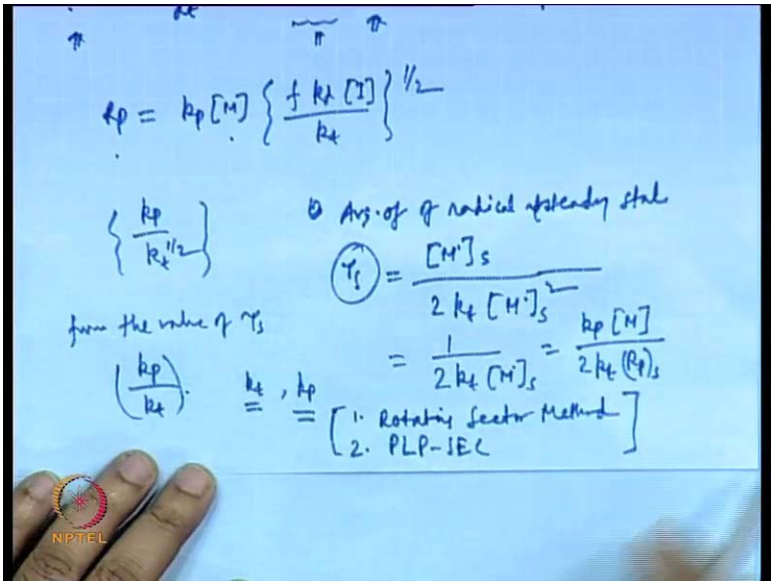

$$R_p = k_p [M] \left\{ \frac{f k_d [I]}{k_t} \right\}^{1/2}$$

$$\left\{ \frac{k_p}{k_t^{1/2}} \right\}$$

① Avg. of radical at steady state

$$\tau_s = \frac{[M^{\cdot}]_s}{2 k_t [M^{\cdot}]_s^2} = \frac{1}{2 k_t [M^{\cdot}]_s} = \frac{k_p [M]}{2 k_t (R_p)_s}$$

from the value of τ_s

$$\left(\frac{k_p}{k_t}\right) \quad \underline{\underline{k_t, k_p}} = \begin{bmatrix} \text{1. Rotating Sector Method} \\ \text{2. PLP-SEC} \end{bmatrix}$$

Now, we know R I is minus d I by d t. So, we can find out the I initiator molecule concentration of time, so we know we know the value of R I. So, we know value of R I we also can find out the value of I. So, we know the value of f k d this known now this is known this is known, so you know this is for thermal thermal polymerization. So, you we can write the expression one more time for the rate of polymerization for thermal polymerization is k d I by k t to the power half.

Now, in this expression e e know this, we know this we know this, we know this, we know this, this is all known. So, what is unknown is k p by k t by half, so this is unknown quality, rest of the things we know from experiment. Now, how do we get this, to get this we found the average life time we defined average life time of a radical at steady state at steady state tau s is the concentration of total radical species as steady state by the rate of termination square or 1 by 2 k t.

So, now, this can be we can put this value of R p here, so we can get k p M by twice k t R p at steady state, so if you know tau s we know k p by R p. So, from the value of tau s we know k p by k t this is known this is known, so this by this as to be unknown this is unknown. So, we know this, so we know this we know this if we both are known then obviously k t is known and k t is known k p is also known, so this is the logic. Now, how do you determine this there two establish method, one is rotating sector method and second is PLPSEC, which is Pals Laser Polymerization Size Exclusion Comotography plases lesere polymerization size exsultion conmoetrgraphi.

Now, am not going in to detain about this method how there how there use to determine the value of tau s, but because this is not the scope of the courses, but if for your knowledge that this are the method are applied to get the value of tau s. And now once you know the value of tau s we know this and we know from this expression this, so we know k p k t.

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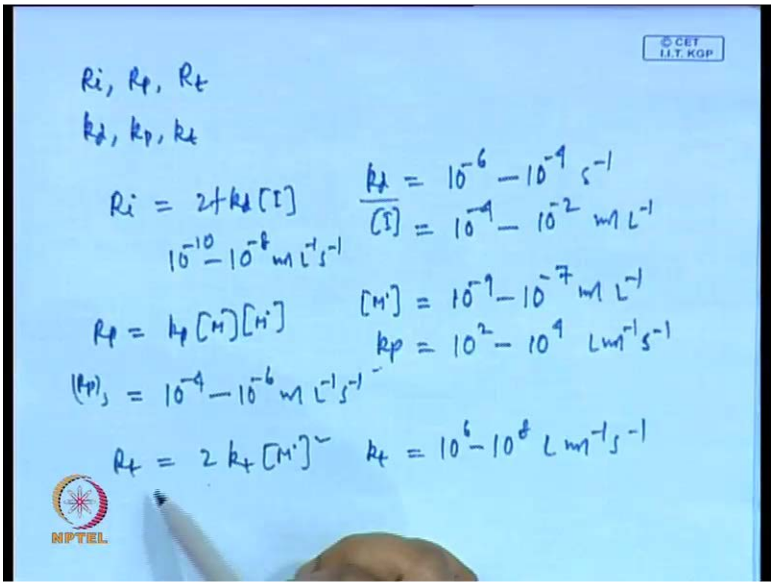

R_i, R_p, R_t

k_d, k_p, k_t

$R_i = 2fk_d[I]$ $\quad k_d = 10^{-6} - 10^{-4}\ s^{-1}$

$10^{-10} - 10^{-8}\ m\ L^{-1} s^{-1}$ $\quad [I] = 10^{-4} - 10^{-2}\ m\ L^{-1}$

$R_p = k_p[M][M^\cdot]$ $\quad [M^\cdot] = 10^{-9} - 10^{-7}\ m\ L^{-1}$

$k_p = 10^{2} - 10^{4}\ L\ m^{-1} s^{-1}$

$(R_p)_s = 10^{-4} - 10^{-6}\ m\ L^{-1} s^{-1}$

$R_t = 2k_t[M^\cdot]^2$ $\quad k_t = 10^{6} - 10^{8}\ L\ m^{-1} s^{-1}$

So, now we know that by experimentally we can know the rates the individual rates we know R I, we know R p, we know R t and we also know k d, k p, k t we know all this from experiments. Now, what is the typical values of this what are the typical values for radical polymerization R I is twice f k d I k d is 10 to the power minus 6 10 to the power 4 second (( )) typically used.

So, R t comes around similarly r P M M dot M dot value typically is between 10 to the power minus 9 to the 10 to the power minus 7 hole square liter, k p is 10 to the power 2 10 to the power 4 liter mole inverse second inverse so R p value is (()) R p value is minus 4 by minus 6 mole detain inverse. And R t is twice k t M dot square M dot value is listed here, k t his 10 to the power 6 10 to the power 8 liter whole inverse second inverse.

See, if you compare the values typical this are the typical values now the values would be different for different monomers and solvent choices. And also it would vary on depend it would vary on various methods, we have utilized to determine this values. So, depends on the method depends on the monomers and the choice of solvent, but this are the typical values of the different rate constant and rates. Now, look at this number k d is very small where k p is much higher compare to k d.

So, the destination are the initiation reaction is very slow k p is first. So, the propagation reaction is fast and termination reaction is much faster. But, it does mean the rate all rate of termination is faster because the concentration of M dot his very low rate constant is very high the intrinsic the reaction his intrinsic very fast but because the concentration of the radically specious is very low the rate of termination is also low and that actually enables is to reach a steady state.

So, again just for one more time that the initiation rate constant his much lower compare to a propagation chain propagation which is much faster reaction very termaist much faster even faster reaction. But, at this state there rate of rate of inhibition and rate of termination becomes 12 because the concentration of M dot is much lower it is about 10 to the power minus 8 moles per liter.

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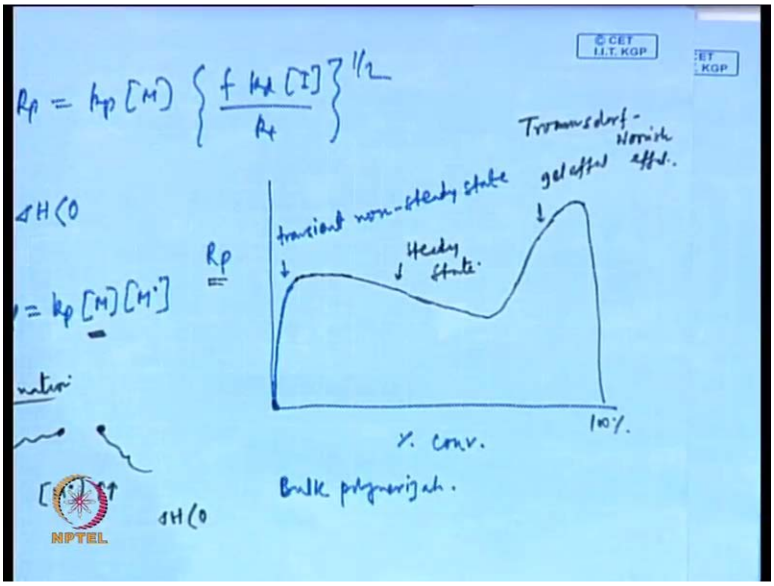

$$R_p = k_p [M] \left\{ \frac{f k_d [I]}{k_t} \right\}^{1/2}$$

$\Delta H < 0$

$= k_p [M][M^{\cdot}]$

Now, what are the assumption if did use this expression R p his k p a M, what are the assumption we made one was that initiation was slow, propagation his fast and termination was even faster. We had convinced our self now with the values of individual rate constant that our assumption was not, not in accurate assumption was accurate. We also assume that the individual rate constant for the propagation steps where equal.

That means, the reactivity of a propagating radical towards a monomer does not depend among the length of the polymer chain at the end of which the radical is present. And we have found that to be true as well what we did not, which we did not consider is that giving polymer reaction, we know that is a H O thermic reaction. Now, once the H O thermic reaction happen, if we do not have arrangements to take out that heat which his evolve chain the reaction, then there will be change in temperature.

If we cannot take out that heat which his generated by the exothermic reaction giving the polymerization process why effectively, then the temperature is raise and once the temperature we raise all this red constant will also vary. So, the rate of polymerization is also vary, if we cannot take out this the heat which is generated due to polymerization reaction that we did not consider did using at this steady state kinetics. Now, if I consider this then how this rate will look like.

So let us plot R p verses conversation for a bulk polymerization; that means, 100 percent polymerization again, remember R p is k p M M dot. Now, initially before the steady state happened M dot increase slowly before it steady state happen. So, with very low conversation to take little time to, so that his the transient non steady state, before the steady state happen. This transient happen this is the transient is is transient it does in take much longer time, does not take too much conversation to achieve that.

Now, once this steady state reached R t will be all most constant, but with time what happen to concentration aim, monomer consideration decreases steady state means the concentration of M dot is fixed the time. So, no change in the concentration of M dot this is constant and steady state, but with more and more reaction happening, more and more conversion is happening. M n M should put down concentration monomer should go down, so R p go down slowly, so it go down slowly.

Now, if at this movement the the medium viscosity is quite high what happened if the if the medium viscosity as become very high, so that the chains are not diffusing at the same rate when the viscosity was lower. Now, we know to termination to happen termination is a by molecular reaction between say to to propagate radical, we know termination would be by add a coupling or by this propagation reaction.

Now, if this two cannot defuse fasten off to find each other and react then obviously the termination rate will come down, it will become diffusion control; that means, the intrinsic is very fast. But, the rate at which this two radical his finding each other is determined the diffusivity of the this molecules. So, the termination reaction becomes diffusion control the higher is the diffusion higher is the termination reaction, but because the medium viscosity is quit high, so diffusion rate is low.

So, the termination reaction his low now once the termination reaction his low steady state is lost. So, more and more radicals are not terminated now because here the termination his come down, so the concentration of M dot increase. Because, the viscosity is very high if the reaction the termination reaction his become diffusion control it is difficult that the propagating radical finding difficult to by other propagating propagating radicals to undergo a by molecular termination reaction.

So, the reaction the concentration of the radical the propagating radical goes up. Now, once this concentration goes up what happen to the rate if this goes up rates goes up rates goes up now we know del H is negative exothermic reaction, once rate goes up goes up more and more heat involved and more heat involved means will know in a minute that of if we increase the temperature the medium rate of polymerization even goes up.

So, whatever if there auto acceleration is happening because rates goes up rate of polymerization goes up more heat is generated more heat is generated we cannot take out effectively that because the medium is high. So, temperature goes up as a temperature goes up rate of polymerization again goes up, as a rate of polymerization goes up more and more heat is generated. So, basically there is auto acceleration the rates zooms the rate of polymerization becomes to much accelerated as a results you get a gel at the end.

So, you get a gel is very high viscous material, so it is a gel effect this called gel effect, this is gel effect or is called (( )) effect, this is steady state. Now, for a bulk polymerization this rates comes down rustically at the end will come and discuss why in a minute from now. So, this is in a actual case if the rate of polymerization depends on the conversation, now obviously this gel effect whether it will exists or if exists at what conversion that will depend upon the viscosity of the medium.

If you are doing reaction in the solution then if you are concentration in the monomer in the solution is slower, then viscosity does in go up that much and because the polymers are forming in a solution the heat management is very good. So, there is not heat acumination as a low increase in temperature, so the gel effect does not happen.

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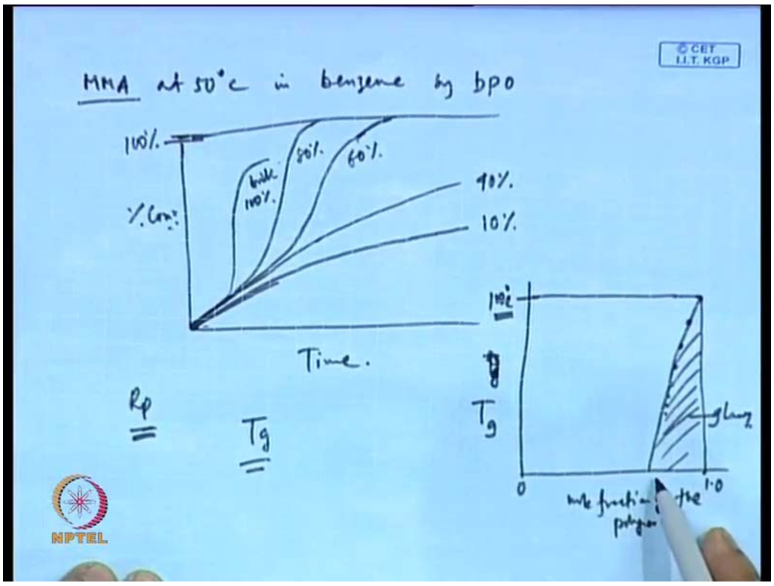

So, we plot a methyl methylacrylate polymerization at 50 degree centigrade in benzene by benzoquinone polyoxide initiator it is look like this time percentage conversion. It is basically gives the rate of the polymerization times verses conversion gives you rate of polymerization. When the 10 percent monomer in the solution the reaction you are doing in a dilute condition the heat management is very good, viscosity is not high, so no gel effect happen.

If you do it in a little higher say about 40 percent you get like this if you say 60 percent is the 60 percent monomer in the solution, you gel effect 80 percent you get even before the this 100, 100 percent conversion, this is bulk. This conversion verses time gives you rate of polymerization if you do it at a 10 percent concentration then the rate goes down slowly, but no gel effect happen if does in happen for 40 percent as well. What if the concentration of the monomer is very high 60 percent, then there is a gel effect.

If it is even higher the viscosity for the medium becomes very high even at low conversion at lower time. At 80 percent at gel effect initiates as much lower conversation at lower time or even for bulk which is 100 percent monomer it happens even before that. So, you are now convinced or you understand this understood this concept. Now, one thing you might have noticed that for 100 percent bulk whether 80 or 60 percent it as reached a 100 percent conversion of the monomer where for the bulk polymerization 100 percent of the monomer as not reacted and make polymers, it as not polymerized 100 percent.

All the monomers present in the medium there have not polymerized, now what would be the reason now we know glass transition temperature I have not discussed in this till now will discussed in later. But, time being glass transition is a temperature at which a polymer becomes soft below which polymer become glassy. So, the mobility of the polymer chains becomes very low below the glass transition temperature the mobility of the polymer segments is very low and they have no translation emotion there is no translation movement of the polymer molecules.

Now if you do the reaction at the temperature which is below T g now T g for polymethyl methyl acrylate is little excess then 100 is close to 100. So, if you do a reaction say at 50 degree centigrade or 60 degree centigrade that his below the T g glass transition temperature. Now, T g of the polymer also becomes slower in presences of solvent in this case M M a as a monomer, which is called plasticization which is basically the reduction of T g in presences of any solvent in this case solvent is the monomer itself.

So, it is Tg is drops down as long as reaction temperature is below above T g of the polymer in that condition the chains or mobility. So, the kinetic chains have mobility. So, there can react with the monomer and participate in a polymerization reaction the movement the reaction temperature becomes below of the T g of the polymers in that medium the polymers lose all the mobility. So, reaction stops the polymers becomes classy, so no low reactions can happen.

And this reduction of T g from original 100 degree for polymethyl methyl acryculate we be lower reduction means the T g value will becoming down more and more if you have more and more monomer in the medium. So, if you increase the conversation that may be more and more polymer forming less and less monomer present in the medium then means the T g of the polymer present is becoming higher and higher because you are reducing the amount of monomer present in the media.

So, if I this is temperature and this is 100 degree centigrade is your T g for t n M a in this case this is mole friction of the polymer, if this monomer mole fraction of the polymer is one then the T g would be 100 degree centigrade for the pure polymer. If you have little amount of monomer then T g will come down plasticization will happen more monomer more plasticization. So, you if you draw T g with mole fraction you are going to get like this, so this your glassy part. So, you have to carry out reaction the temperature below above glass transition temperature and you the glass transition temperature come down with more and more monomer present in the system of the polymerization medium.

So, in the bulk polymerization as this is the point where the T g as become lower T g of that polymer present in this case as become higher then the reaction temperature if the reaction temperature is 60 degree in this case 50 degree. So, reaction m is 50 degree for T g this polymers as become higher than 50 degree, so no more conversation can happen; at this conversation T g of this polymer present T g of the polymethyl methyl acrylate present here at become higher then 50 degree which is the reaction medium.

So, once the polymer become glassy then the polymer chain the kinetic chain are not participate for the reaction and cannot take the cannot make new polymers. So, in this glassy region the polymer cannot the temperature is below the glass transition it cannot make any more further any more it can take up participate in further polymerization. So, what we going to do in the next lecture is we what to find out the effect of temperature in the polymerization rate.

And also the effect of temperature on the molecular weight of the resulting polymer and will talk about thermodynamics of the chain radical chain polymerization in the next lecture.