Polymer Chemistry

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Lecture - 20
Chain Copolymerization (Contd.)

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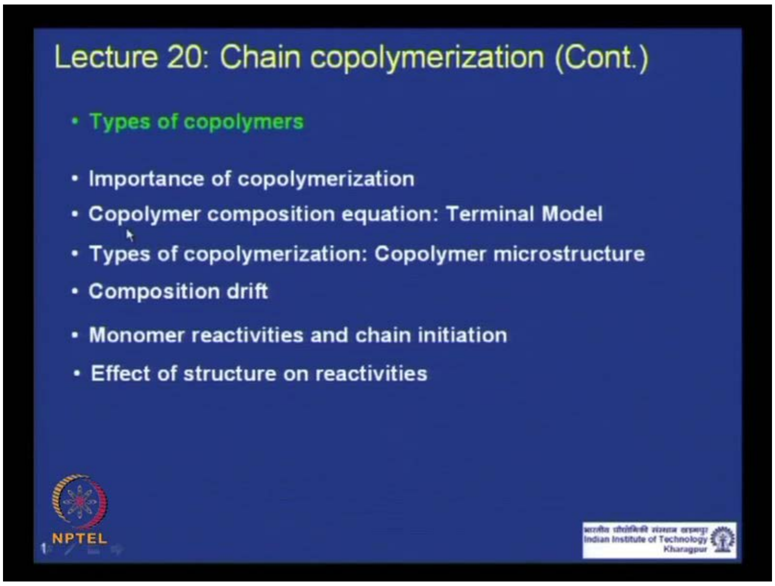

Lecture 20: Chain copolymerization (Cont.)

- Types of copolymers
- Importance of copolymerization
- Copolymer composition equation: Terminal Model
- Types of copolymerization: Copolymer microstructure
- Composition drift
- Monomer reactivities and chain initiation
- Effect of structure on reactivities

Welcome back this to this course on polymer chemistry, and this lecture we will continue our discussion on chain copolymerization, which we just studied in our last lecture. In this lecture, we will talk about the importance of copolymerization, and then copolymer composition equation, and then go into different types of copolymerization process, and resulting different microstructure of copolymer, and then talk about composition drift, and monomer reactivities, and then corresponding the effect of chain initiation reaction on monomer reactivities.

Now in last lecture, we completed our discursion on ionic chain polymerization, and we also studied our discussion on chain copolymerization, and we talked about or we discussed different types of copolymerization; namely we talked about statistical copolymer, alternate copolymers, and block copolymers, which could be different types of block co polymers, block, linear block trapped, and brass type of co polymers as well. Now just to complete the types of co copolymerization we have discussed in the last lecture.

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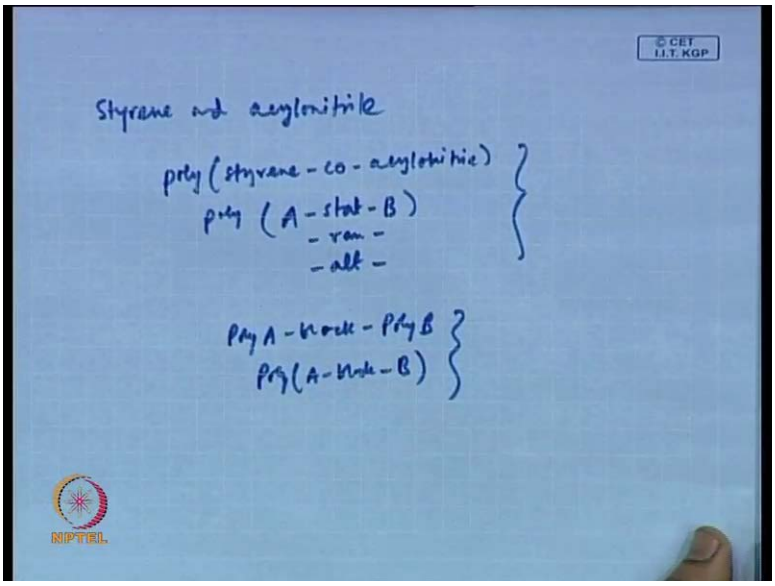

Styrene and acylonitrile

poly (styrene - co - acylonitrile)
poly (A - stat - B)
- ran -
- alt -

Poly A - block - Poly B
Poly (A - block - B)

How do you write them in terms of nomenclature, if you make say copolymer with styrene and acylonitrile. Now, if we do not want to specify the microstructure, whether it is a statistical copolymer, as alternate copolymer, block copolymer, then we can simply write poly styrene, and write co in between acylonitrile. If you now that, this is a statistical copolymer, then instead of co you can write stat in between, and if you know that this statistical copolymers is a random copolymer, which we discussed in the last lecture, then we can write ran r a n in between. If you know that this is a alternate copolymers, between any two monomers; a poly A and poly B, then we can write it is a a l t alternate, as a alternate copolymer, and if you know it is a block polymer, if you want to write block polymer, then we can write poly A block poly B or poly A block poly B, both way we can write in this case, but only write different types of copolymers like statistical random on alternate copolymer, you should follow these type of nomenclature, we just mention.

So, a alternate copolymer between styrene co-acylonitrile you can write, you should write poly, in brackets styrene, hyphen a l t, hyphen acyolnitrile.

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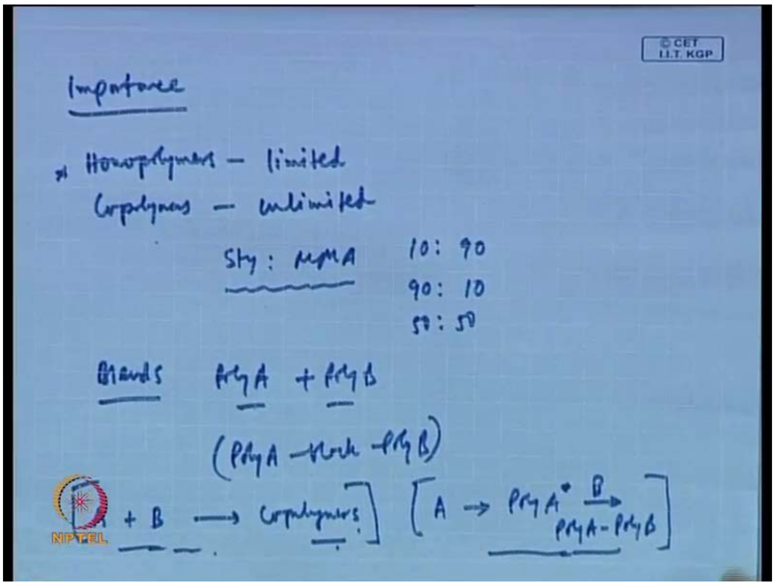

Importance

* Homopolymers – limited

Copolymers – unlimited

Sty : MMA 10 : 90

90 : 10

50 : 50

Blends PolyA + PolyB

(PolyA –block –PolyB)

A + B ⟶ Copolymers] [$A \rightarrow PolyA^{\bullet} \xrightarrow{B} PolyA\text{-}PolyB$]

Now we were discussing about the importance of copolymerization, importance of copolymerization, why we should at all be interested in copolymers. Now we said, that when we talk about homo polymers, now we can have only limited, number of homo polymers you know ,we always using, if you have noticed same names basically coming, every time polystyrene, polyaclonoidal, polygon acetate, polymethyl like. There are limited names we actually used for all the times, and commercially also if you want to, or the homo polymers which are used in large scale, they are very limited. So, basically that limits our options to choose polymer for the particular applications. Also if sometimes happens, in the most cases it happens; that one single homopolymers do not posses, the required or the desired property we are looking for. In that case to bring, to introduce that required property, we must mix this homo polymers with another homopolymer to get the properties, good properties of both the polymers, or we need to synthesis a new copolymer. Now in terms of copolymers, that main advantage is that, the options are unlimited. You can choose any of these monomers, which were utilized to make homopolymers, and then mix them, and also you can mix them in, or make copolymers in different proportion.

You can take styrene and M M A, and get numerous amount of copolymers, if you mixed, them in different proportion styrene is to M M A use can get 10 is to 90, 90 is to 10, 50 is to 50, so you can get numerous number of copolymers, and also you can choose their different types of, the different sets of monomers. So basically that tells you, that the number of options in copolymer, if number of co polymers can be synthesis is unlimited. So if we require a definite property, or a property if you are looking for, for particular application then if that property is not available in a single homopolymer, then you can, from a prior knowledge of the properties of the homopolymers, you can actually synthesis copolymer of required proportion to get that property you want. Now you can always argue, that why not just mix, and blend the homopolymers. Take poly A, which is homopolymer, and mix poly B, which is another homopolymer. Unless you.

Here also you can actually get numerous numbers of composition, by choosing different A and B, and mixing them in different define ratio, but you know most cases, you cannot make two polymers, to homo polymers. In case of polymers to homopolymers are. In most cases they do not make miscible blends, and as a results, the property of the mixture, of polymer A and polymer B, thus not give you the required property we are looking for. Actually it gives you worst property, then the individual homopolymers, unless you have a mechanism to, comfortablize, or misapplies, or have some sort of interaction between the two homopolymers. And to do that actually you need copolymers, co polymers of. In this case if you poly A, and a block poly B, then you can actually used these copolymer, block copolymer as a comfortabalizer, between poly A and poly B, and by doing this you can actually improve the property of the blend, of poly A and poly B. So what does mean that not only, a require co polymers for improved teramid properties.

Teramid properties in a single polymer, but you can utilized this type of block polymer to comprise to homopolymer and next, and make numerous number of blend composition, but in this chain polymers, we will be discussing the chain co polymer, which where we you had mixing a monomer a, and monomer b, from beginning and making copolymers. We will not discuss this is not a part of this chain copolymerization, where you have make a monomer a, which you polymerized, by living polymerized method, poly A, and then add a second monomer to make poly A and poly B. This is the most common way making block copolymer, but we will not discuss this technique of synthesizing block copolymer in this section. We will be mainly, or exclusively discussing the copolymers, where you start with a mixture of two monomer, and then synthesis the copolymer. And in this case as we see that, most cases making block copolymer by this method is difficult, so that is why the reason why, is almost cases, this is the processes applied to make block copolymer. So we will discuss this process in coming pages.

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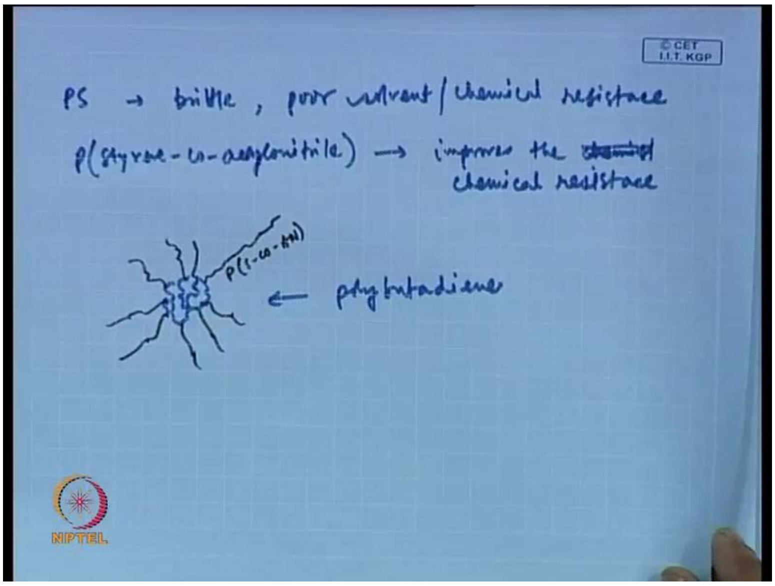

PS → brittle, poor solvent / chemical resistance

p(styrene-co-acrylonitrile) → improves the ~~chemical~~ chemical resistance

Now continuing with the importance of copolymer for example, if a polystyrene homopolymers, polystyrene homo polymerization is a brittle polymerization, brakes down easily, and also it has poor solvent or chemical resistance. So to improve of this property of polystyrene, you can actually make a copolymer of polystyrene acrylonitrile, and this actually improves the chemical resistance property of, chemical resistance of over styrene homopolymers. Now this does not improve the brittleness, of the impact properties of polystyrene too much. So, what is done industrially, you make a rubbery, rubberic code, so you make a rubberic code of poly butadiene. See by emulsion method, you make core, you make take a butadiene, and polymerize in by emulsion method to make a butadiene code, and some of the double bound which has remain unreacted. You can utilize those double bound, and make this copolymers of polystyrene and acrylonitrile, these are the copolymers of polystyrene and acylonitrile P s co A N, this is polystyrene co acylonitrile.

So, basically you can use these as such, or you add blend this two another homopolymer, and because the presents of this rubberic code, which is soft, this actually improves the impact property, because this is the soft impact, it has observe the impacts, and actually makes the polymer material, less brittle compare to either polystyrene, or a ecopolymera polystyrene, and acrynitriles, so these are my example. This the one example, where you can see that copolymerization techniques are used to improve the properties of polystyrene, by copolymerization with other copolymer ,if you have three co monomers basically we use the term third polymer, for the co polymers which are produced in this a a from this three monomers.

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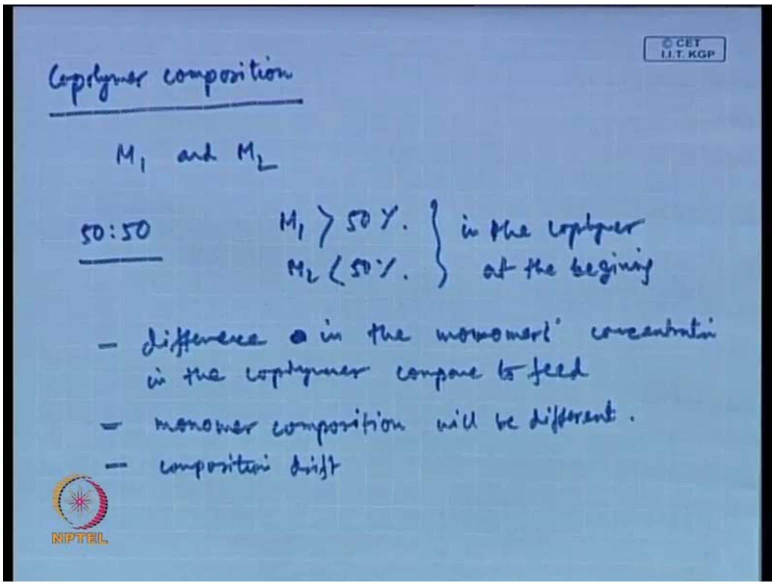

Copolymer composition

M_1 and M_2

50:50 $M_1 > 50\%$ } in the copolymer
$M_2 < 50\%$ } at the begining

- difference in the monomers' concentration in the copolymer compare to feed
- monomer composition will be different.
- composition drift

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Now, will talk about copolymer form position, now in most cases what happened, because we are mixing M 1 and M 2, and you are copolymerizing form there. Most cases this M 1 and M 2 m will have difference in reactivity, and results what happened one of the monomers get incorporated in the growing copolymer, much faster rate compared to the other. For example M 1 is more reactive compare to the M 2, then in the propagating copolymer chain M 1 will get incorporated, faster rate, in faster rate than in two polymers. So, as a result what will have if you start each side 50 50 ratio of M 1 and M 2, you will get eco polymer at the beginning. At the beginning you will get a copolymer, which will have M 1 greater than 50 percent, and M 2 less than 50 percent, this is in the copolymer, at the beginning.

So, because M 1 is more reactivity, you will get in the chain much faster, so you will get eco polymer, which reach in M 1 compare to M 2. So you will have a difference in, the monomers concentration in the copolymer, compared to feed. Now as reaction goes with more and more M 1 is getting incorporated, now first a rate then M 2. Soon the reaction medium will have less M 1, because most M 1 monomer then M 2, because most of the M 1 has get you know, as incorporate, got incorporated in the copolymer chain, so feed monomer concentrations, of M 1 will lower than beginning. As a result the monomer composition in the medium, in the reaction medium, will be different than the beginning. So, now the copolymers which will forms at the later part of your polymerization copolymerization, because the monomer composition in this case, the ratio of M 1 M 2 or different from beginning numbers.

The copolymers which will form, which will have different monomer content, then the copolymers which form in the beginning or at the beginning. So what we will have, we will have a composition drift, which means the copolymers which form at the beginning they will have different composition, than the copolymers which are forming at the later part of the copolymerization reaction, so is have so you can understand that the monomer content in the copolymers will be different, then the feed ratio at the beginning, and with time the monomer composition will be different, from the beginning, and there will be composition drift. So these things will be offering during your copolymerization reaction. To predict the monomer or the composition of the copolymer, you can look at the polymerization rate of the individual homopolymers, likes for example if you.

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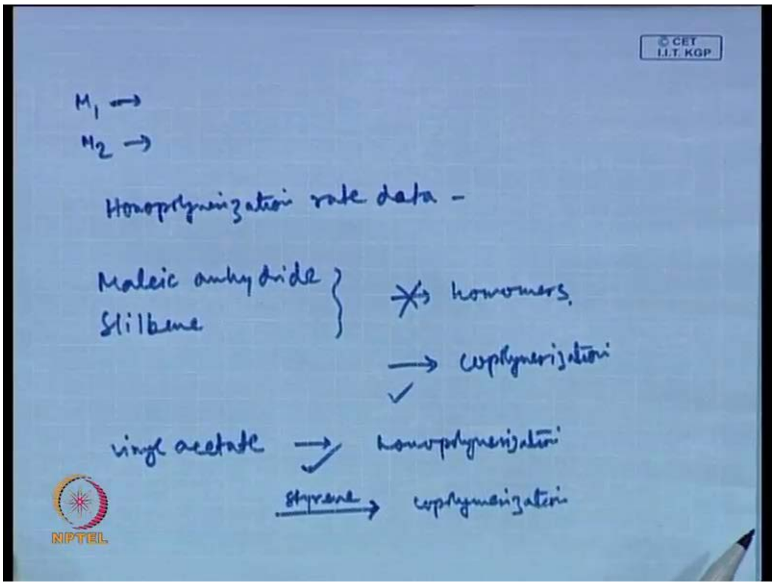

$M_1 \rightarrow$
$M_2 \rightarrow$

Homopolymerization rate data –

Maleic anhydride } $\nrightarrow$ homomers.
Stilbene } $\rightarrow$ copolymerization
✓

vinyl acetate $\rightarrow$ ✓ homopolymerization
$\xrightarrow{\text{styrene}}$ copolymerization

You can look at the homopolymerization rate of M 1 and M 2, and from that you can have idea about the homopolymerization, but the homopolymerization data, homopolymerization rate data, actually has very little significance or resiblance with the rate of consumption, or rate of reaction of a monomer during a copolymerization reaction, which means that, if a monomer, the rate at which a monomer; say M 1 undergo homopolymerization , that could be quite different, when you have M 2 in the reaction medium. For example, if I take say consider maleic anhydride, we talked about that maleic anhydride or say stilbene. We talked about in these molecules during our discussion on radical polymerization. Now these monomers, actually do not undergo homopolymerization by itself, we discussed about that, and the reason for that, but they can undergo copolymerization, in fissile by, with other monomers like styrene ethynemethyne and… So, if you have the data, reaction rate data from the homopolymers; that is not useful when you predict the composition or the reaction rate, when this monomers are reacting with the second co monomers to form a copolymerization. Take another example where if you consider as a vinyl acetate.

Now vinyl acetate, obviously undergo very fissile homopolymerization, but when you have a styrene as a second monomer. What happened, homopolymerization become very low, as long as styrene is present, because the copolymerization rate of vinyl acetate with styrene, it is much faster than the homopolymerization. So as long as styrene is present, vinyl acetate will only form copolymer, and after styrene is over, consume from the reaction medium, then only it actually form homopolymerization. So from here, also if you look at the homopolymer data of vinyl acetate, and then try to utilize these data to have a idea about the copolymer composition, and the reaction rate between the vinyl acetate and the styrene, that we will be of, very little significance for these copolymerization. So, basically these homopolymer data rate for this. These individual monomers are not very useful, when we discuss or copolymerization reaction. So we need to predict, in order to predict the copolymerization composition, what we need to do, we need to construct a kinetic model and the simplest is the terminal model.

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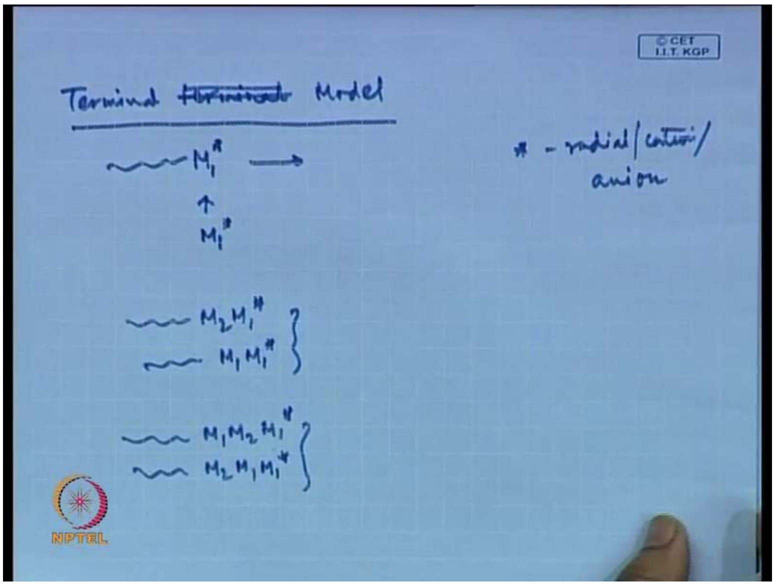

We will talk about the simplest model, which is known as terminal model. Now what it says, it says that, the reactivity of a propagating species, only depend on the monomer with unit which is present at the growing chain end. The chemical re reactivity of the propagating chain in a copolymerization, only depends on the monomer unit present at the end of the growing chain, which means that the chemical reactivity of these propagating chain, will only depend upon the reactivity of the M 1 group. Now star could be radical, cations or anion, so this is valid, this terminal model is valid for any initiation process. To elaborate this if we have say, this two or this two, because in all this cases the terminal group, or the monomer unit which is present at the growing in a same, all these will have same chemical reactivity for propagation reaction, so this is the assumption we are making in the terminal model. So what are the four possible propagation reactions possible in, during this copolymerization, lets around right those.

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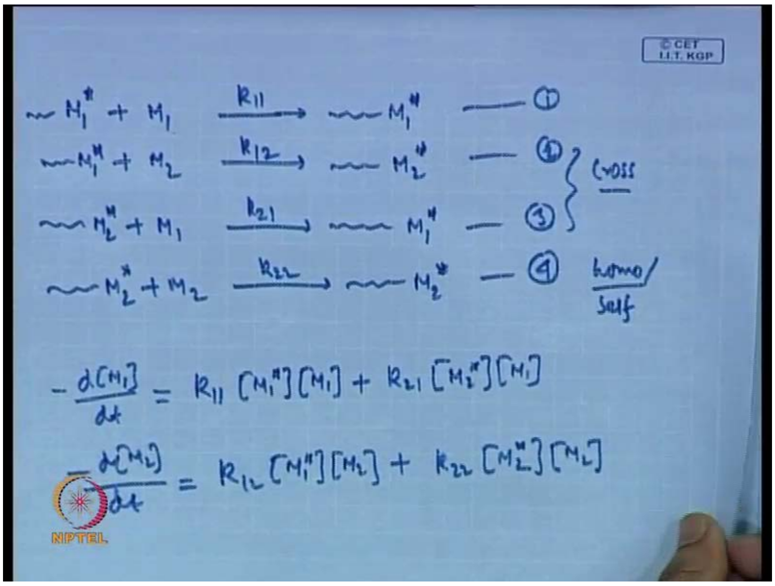

$$\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^* \quad — ①$$

$$\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_2^* \quad — ②$$

$$\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^* \quad — ③$$

$$\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2^* \quad — ④$$

②, ③ cross

④ homo/self

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]$$

So M 1, star can react with M 1, M 1 and M 2 are two monomers, produced M 1, M 1 star can react with M 2, M 2 to star can react with, M 1 react with. Now this reactions in one and four, where M 1 is reacting with M 1, and M 2 is reacting with M 2 from the same, see same propagating species, these are called homo propagation or self propagation, and these two, where M 1 in which is reacting with M 2 forming M 2, these are cross propagation reaction these are, these two are cross propagation, and one and four are homo or self propagation reaction. Now what is the rate of reaction, or rate at which M 1 is getting incorporated in the copolymer chain. This step one and step three are where M 1 is getting consumed, and getting incorporated in the chain; see we will write K 1 1 M 1 star M 1 plus K 2 1 M 2 star M 1, and 1 2 plus K 2 2 into star into. Now how do. Look at these rate constants, basically the first number represents the radical, sorry the propagating species, where the radical cation or anion it does not matter, so this is first one is from the propagating reacting species, and the second one is for the monomer. So one in the second means M 1, two is the second means M 2 and so on. Now at any instance, the rate at which M 1 and M 2 is getting incorporated, in the copolymer chain, which will be given by the rate at which, this M 1 and M 2 is getting consumed.

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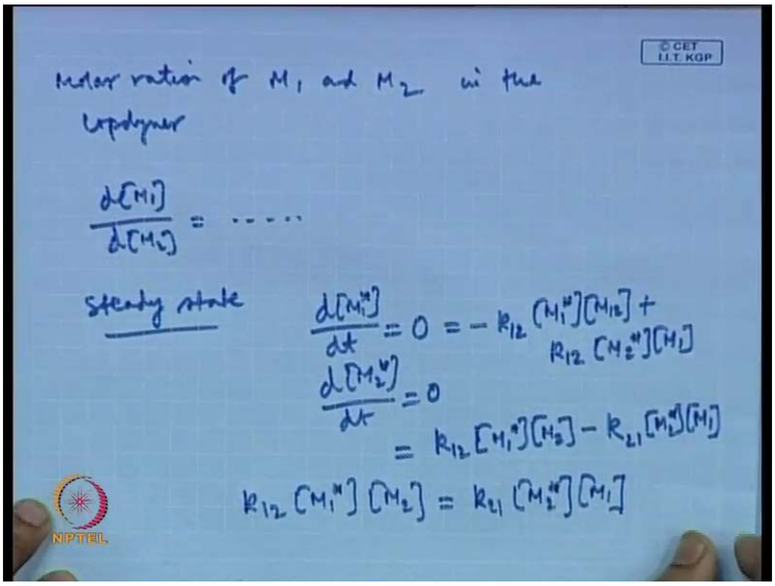

Molar ratio of M_1 and M_2 in the copolymer

$$\frac{d[M_1]}{d[M_2]} = \cdots\cdots$$

steady state

$$\frac{d[M_1^*]}{dt} = 0 = -k_{12}[M_1^*][M_{12}] + k_{12}[M_2^*][M_1]$$

$$\frac{d[M_2^*]}{dt} = 0$$

$$= k_{12}[M_1^*][M_2] - k_{21}[M_2^*][M_1]$$

$$k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1]$$

So the molar ratio of M 1 and M 2, in the copolymer at any instance, is given by d M 1, because this is the rate at which, they are getting consumed, during the reaction. So you can write the rest of the things from the two expressions, we got in the last one. Now we can apply the study state, where the rate of change of M 1 star is zero; like we discussed in the case of our chain polymerization, at the steady state the concentration of M 1 and M 2 star remains constant, so rate of change is actually zero at steady state. Now the steps which M 1 is, M 1 star is getting consumed, for in the reaction one, where 1 M 1 star is consuming, getting consumed, and 1 M 1 star is forming, so they are not changing the concentration on M 1 star. In the fourth reaction 1 into star is getting consumed, and 1 into star is getting produced, so they also do not change, this reaction also do not change the concentration of M 2 star.

So these are the two reaction where in this case; M 1 is getting M 1 star is getting consumed in M 2 star forming, and in this case M 2 star is getting consumed, and M 1 star is forming. So we can write down the expressions for M 1 star and M 2 star, is minus K 1 2, you can do from the expression in the last page, plus K 1 2, and in case of M 2 this is a step; step two where M 2 is getting into ties getting produced, and in the step three, where M 2 star is getting consumed. These are basically two same reactions, so from here we can write K 1 2 M 1 star M 1.

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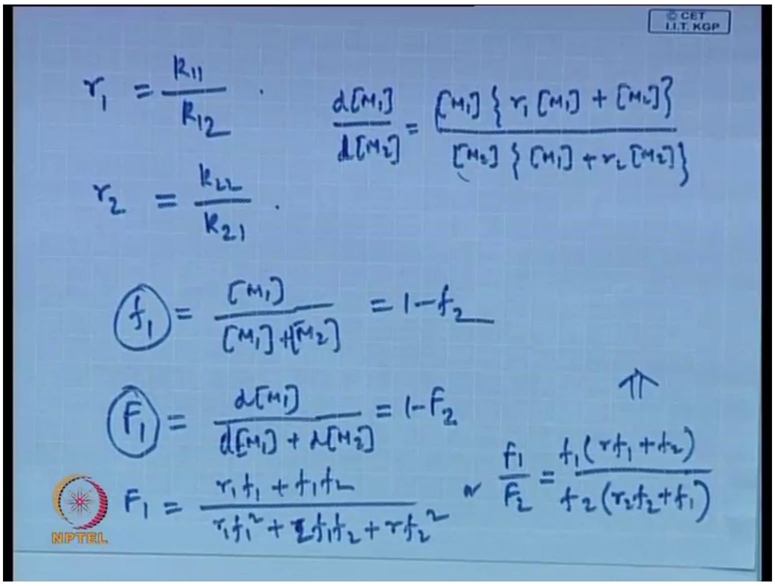

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$$r_1 = \frac{k_{11}}{k_{12}} \qquad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]\{r_1[M_1]+[M_2]\}}{[M_2]\{[M_1]+r_2[M_2]\}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

$$\bigcirc\!\!\!\!\!\!\;\; f_1 = \frac{[M_1]}{[M_1]+[M_2]} = 1-f_2$$

$$\Uparrow$$

$$\bigcirc\!\!\!\!\!\!\;\; F_1 = \frac{d[M_1]}{d[M_1]+d[M_2]} = 1-F_2$$

$$F_1 = \frac{r_1 f_1 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r f_2^2} \quad \sim \quad \frac{F_1}{F_2} = \frac{f_1(r f_1 + f_2)}{f_2(r_2 f_2 + f_1)}$$

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Now, here defining two more term R 1, which is K 1 1 by K 1 2, and R 2 K 2 2 by K 2 1, and if we apply these conditions, steady state condition and use this two expression, then we can write the composition of the two monomers, in the copolymer as this. Now this expression, which gives the molar ratio of M 1 and M 2 in the copolymer form that any instance, when the monomer concentration in the reaction medium, is M 1 for M 1, and M 2 for M 2 monomer. So this is the molar ratio of monomer M 1 and M 2, in the copolymer, any instance where the corresponding concentration of free monomer, in the reaction medium, given by this M 1 and this M 2. Now it is easy to express the concentrations in terms of molar ratio, where F 1 is the molar ratio of pre monomer in the reaction medium, so we can write, this as M 1 M 1 plus M 2. And if we write F 1, is the molar ratio, or mole fraction.

This is the mole fraction of M 1 in 3 M 1 in the reaction medium, and this is the mole fraction of M 1 in the copolymer, so we can write the d M 1 plus the d M 2, 1 minus F 2. So, you can simply write F 1 is R 1 F 1, plus F 1 F 2 or F 1 by F 2 is. One more time F 1 is the mole fraction of the pre monomer in the reaction medium, and F 1, capital f of upper case, is the mole fraction of M 1, in the copolymer. Now this expression has been verified for innumerable copolymer systems, and they are, this expression is equally applicable to cationic and anionic and radical copolymerization. And it is not dependent on the reaction initiation system you are following. Now, these fellow R 1 and R 2, they are almost independent of the reaction medium, or reaction conditions for radical polymerization, but the values of R 1 and R 2 could be quite different, when you talk about different initiation system, and we will talk about giving a specific example in few minutes.

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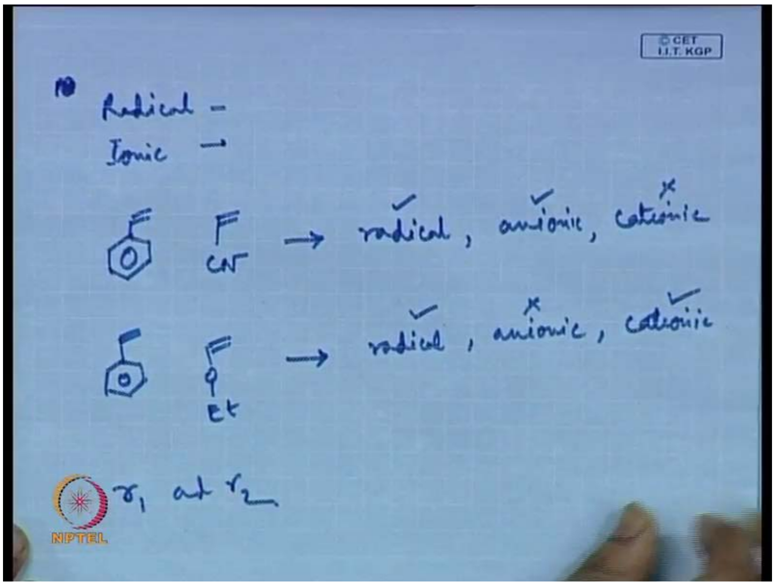

Now, let us talk about this monomer. In case of radical it has said that at several combination of monomer possible, because we know that most of the monomers we have seen during our discussion, initial discussion in chain polymerization that, most of the vinyl monomers, they do undergo radical polymerization. So hence lot of monomers can be utilized or, can be make utilized to copolymer by radical mechanism. Whereas ionic polymers; in case of anionic polymers mono monomers selective, it is not every state of two monomers can be utilized for, making ionic copolymerization. They are very selective; for example if I take a specific example of styrene and acrylonitride.

Now this can be copolymerized by radical, it can be copolymerized by anionic, but it cannot be copolymerized by cationic. Whereas if I takes styrene and vinylether, again it can be polymerized by radical, but it cannot be polymerized, because this is, cannot be polymerized by anionic, in this case, it is cannot be polymerized by cationic, but it can be polymerized by cationic polymerization. So it is said that, you can basically choose any two co monomers, which in most cases can polymerized radically, but if you want to use any of this cationic or anionic technique then the number of pairs of co monomers you can choose are limited, as we discussed in during our chain polymerization discussion.

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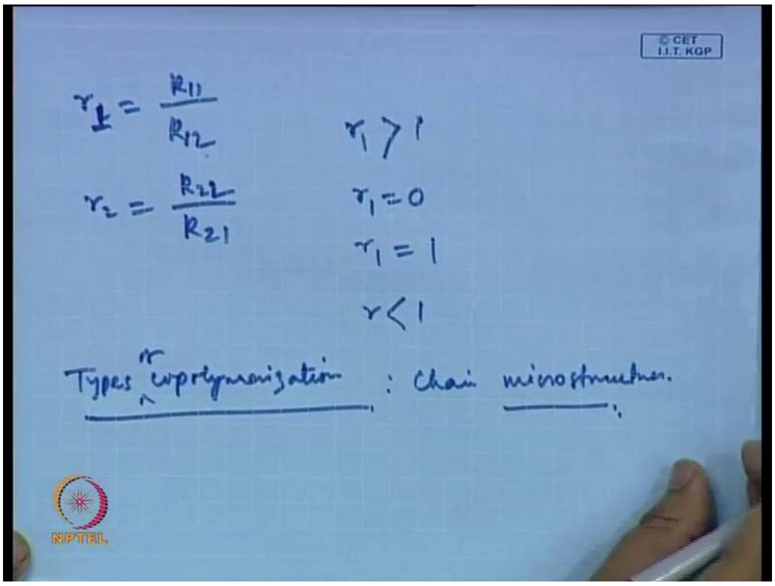

$r_1 = \frac{R_{11}}{R_{12}}$

$r_2 = \frac{R_{22}}{R_{21}}$

$r_1 > 1$

$r_1 = 0$

$r_1 = 1$

$r < 1$

Types of copolymerization : Chain microstructure.

Now, lets us discuss more about R 1 and R 2; as we define R 1 given by K 1 1 by K 1 2, and R 2 is given by K 2 2 and K 2 1. Now this is basically the rate at which, this is R 1, this is the ratio of homo propagation and cross prosperous. This is the homo propagation and this is a cross propagation, and this is also a, this is homo propagation and this is pros propagation. So basically R 1 and R 2, this is reactivity, monomer reactivity ratio, are the ratios of corresponding homo propagation and cross propagation. Now R 1 is greater than 1, then the tendency for homo propagation is more compared to pros propagation, which means that tendency for homopolymer is more than formation of copolymerization, if R 1 is zero, which means there is no tendency of homopolymerization, it is only, it can only undergo copolymerization.

If R 1 is 1, then both are equal; that means there is no preference were homo propagation and copolymerization, so it completely random copolymer is formed, and if R is less than 1 then the tendency to the co-polymerise, is more than the tendency to homopolymerized. Now in the expression of R 1 and R 2, we do not have any rate constant for the termination and initiation reactions, which means that if we talk about that expression. If we talk about this expression, here we do not have any rate constant coming or appearing from initiation reaction, termination reaction and so forth the from the chain transfer reaction as well the, which mean that the rate of initiation or termination or say invation or chain terminate transfer reactions, do not have any significant on contribution, do not affect the two copolymer composition at all. So basically if you talk about different radical mechanism; for example if you talk about, radical initiation by thermal initiation, or a photochemical initiation, or say redox reaction in initiation.

In all those cases as long as your M 1 and M 2 are same, the composition in the copolymer would be same, irrespective of the initiation mechanizing you have applied, and also it does not depends upon whether there is presence or absence of chain transfer reactions in the medium or not, but as I said that if the mode of initiation, like whether its anionic cationic or radical, that change, then obviously the composition of the two monomers in the co polymers will change. And as you can understand that the, polarity of the solvent in which you are doing the reaction, and that will effect more when you have a ionic chain co polymerization, compare to when you have a radical chain co polymerization. Now let us talk about different types of co polymerization, and corresponding chain micro structures; types of co polymerization and corresponding chain micro structure.

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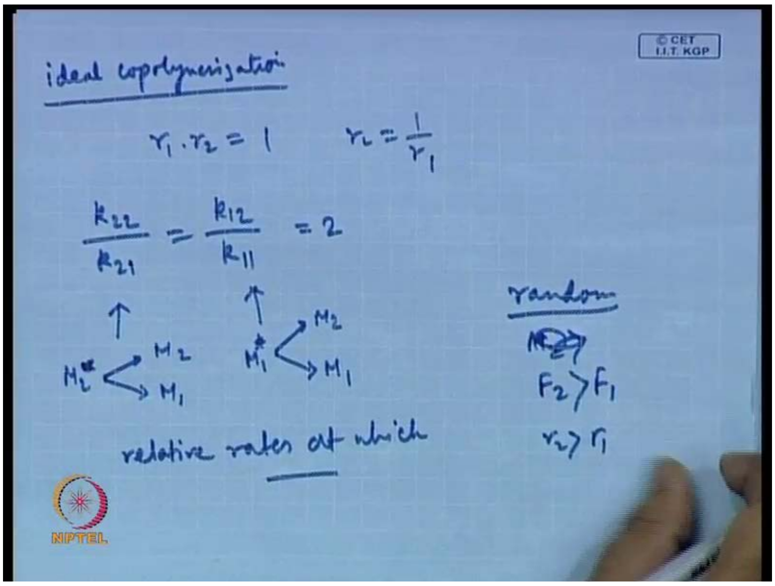

ideal copolymerization

$r_1 \cdot r_2 = 1 \qquad r_2 = \frac{1}{r_1}$

$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} = 2$

$M_2^* \to M_2, \; M_1 \qquad M_1^* \to M_2, \; M_1$

relative rates at which

random

~~[illegible]~~

$F_2 > F_1$

$r_2 > r_1$

Now, let us talk about the first case, where we talked about ideal co polymerization. In this case, R 1 multiplied by R 2 is 1 or R 2 is 1 by R 1, we can write k 2 2 by K 2 1 K 1 2 K 1 1. Now, this gives you the reaction with, the ratio, or the relative reaction of M 2 dot M 2 star, with M 1, M 2 and M 1, and this keeps M 1. Now, if i consider this value as two, let us consider this value, which means that M 2 star will react twice as faster with M 2, compare to M 1, so does M 1 star, M 1 star also will react with M 2, twice as fast at it reacts with M 1. So, respective of which propagating species you have in the reaction medium, it is always the reaction with M 2 will be faster, and M 2 will more reactive than M 1. Or other sense, M 2, if you talk about reverse way, M 2 will be more reactive, towards both m star and M 1 star, which means that the rate, relative rates at which, two monomers incorporative in the co polymer chains, are the same, irrespective of the identity, of the unit, which is present at the end of propagating species.

So, relative rates at which M 2 and M 1 is getting incorporated in the chain, copolymer chain is independent of which is present at the end, and the addition of, or incorporation M 2 in the copolymer chain is unbiased; that means, whether M 2 will get added next M 2 star, or M 1 star, are statistically same. So, they will, the sequence distribution of this case of the repeat unit in this copolymers is random, so you will get. You will make this the copolymer at the beginning, you will get more numbers M 2 is getting incorporated in the polymer copolymer chain, but the M 2, addition of M 2 M 1 will be complete random. There will be no biasness of M 1 sitting next to M 2, or M 1 seating next to M 1. So, which we have random distribution of, or sequence of the copolymer, and also M 2; this is a, M 2 is, or F 2 in this case, F 2 is higher than F 1, if R 2 is higher than R 1.

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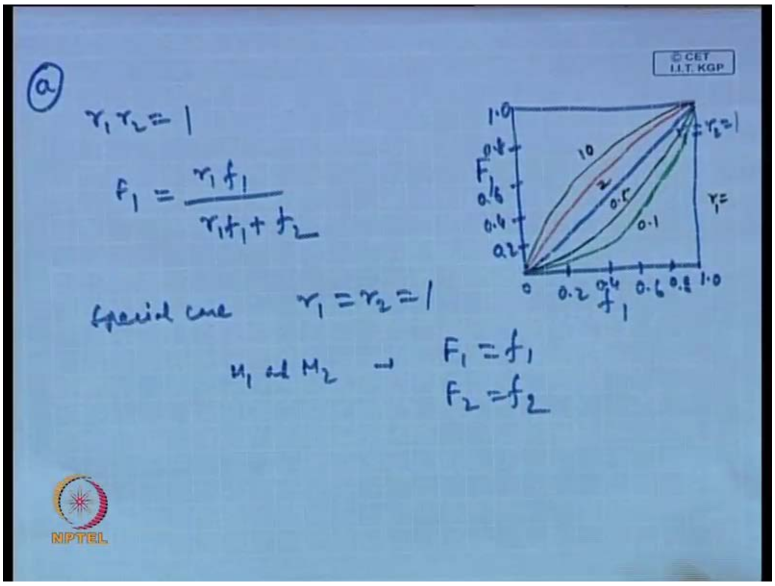
ⓐ

$r_1 r_2 = 1$

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

Special case $r_1 = r_2 = 1$

M_1 and M_2 → $F_1 = f_1$

$F_2 = f_2$

Now, we can simply write R 1, and R 2 is 1, and used as (( )) in this expression, this expression, and we can right F 1 R 1 F 1 and R 1 F 1 plus F 2. Now a special case, where R 1 and R 2 is 1, what happen again. In this case as we discussed earlier that, tendency to homo propagate, and tendency to cross propagate is same, so what happen. Again M 1 and M 2 will get in incorporated randomly in the copolymer chain, and F 1 would be same as F 1, and F 2 would be same as F 2, because the reactivities, the monomer reactive ratio of this two are same, and they are one. So, obviously, the rate at which M 1 and M 2 getting incorporated in a co polymer chain, are same as their ratio in the monomer field. So, if I want to plot; say F 1 versus F 1; that is the, 0.2 0.4 0.6 0.8 1, this is correspondence to the 20 percent composition of monomer aim in the, free monomer in the reactions mixture.

Whereas this correspondence to, the 80 percent of free monomer M 1 in the reaction mixture, while this is correspondence to 80 percent of the monomer aim in the co polymer. Now when R 1 and R 2 is R 1 is R 2 is 1. Now, whatever the composition in the feed; that is also in the copolymer you have; this is a the 0.1, this a 0.5, this is a 2, and this is 10, r is 0.1, R is 0.2 and 10 R 1. So, in this case, because the reactivity of monomer m is lower , they get incorporated much lower rate, than monomer m 2, where if the higher rate, reaction reactivity of M 1 is higher compare to reactivity of m 2, that M 1 and incorporated in much faster rate compared to in m 2. Now this cross a similar to the vapor liquid equilibrium of ideal liquid mixtures, so that is why, that is from where this name of ideal (( )) has come.

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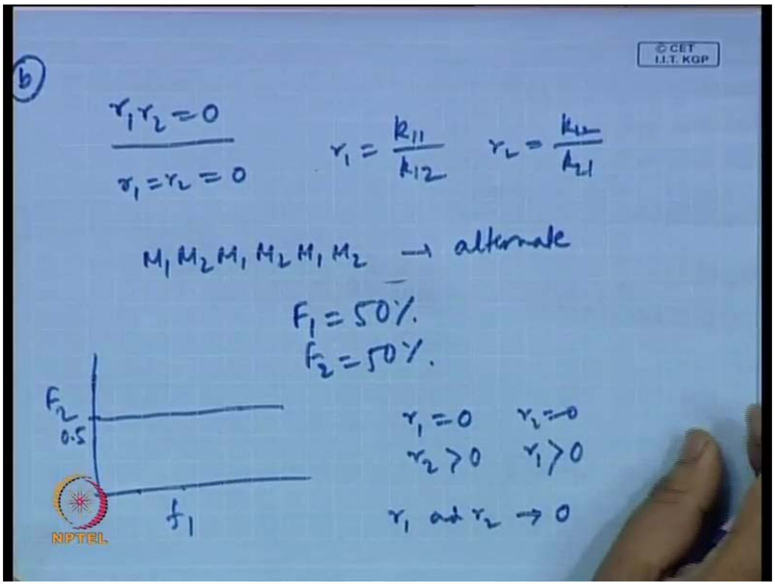

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$r_1 r_2 = 0$

$r_1 = r_2 = 0$ $\quad r_1 = \frac{k_{11}}{k_{12}}$ $\quad r_2 = \frac{k_{12}}{k_{21}}$

$M_1 M_2 M_1 M_2 M_1 M_2 \rightarrow$ alternate

$F_1 = 50\%$
$F_2 = 50\%$

$r_1 = 0 \quad r_2 = 0$
$r_2 > 0 \quad r_1 > 0$

r_1 and $r_2 \rightarrow 0$

Now next we will talk about, the second case. This was we discussed case number a, and next talk about case number b, where we have R 1 and R 2 is 0, so either we can R 1 and R 2 is both are zero. In this case, you can, R 1 is as we said K 1 by K 2 by, and R 2 is K 2 2 by k 2

1, obviously in both the monomer M 1 M 2, there is no tendency to homopolimerise, so they there will only form copolymer. So, M 1 will only react with M 2 star, and M 2 only react with M 1 star, only the cross propagation happen, which means you have copolymer of this type. M 1 star will only react with M 2, and m 2 star will only react with M 1 and so on, so you have a perfectively alternate copolymer, just alternate arrangement of the monomers, and F 1 and F 2 both will be fifty percent in this case.

So, as long as there is 1 monomer is left in the reaction continue, and once 1 of the monomer get consumed, the reaction will stopped there, because the second monomer even if that is present in the reaction medium, that cannot participate in the homopolymerisation, so reaction is not proceed further. So, if you plot F 1 verses F 2, no matter what is the concentration of F 1, you always get fifty percent incorporation in the copolymerstion, this can be achieved, also if 1 of the monomer is, R 1 is zero, reactivity is zero, it could be rather way on, R 2 is, 1 is 0. If R 1, or it could be R 1 and R 2 both are near to zero.

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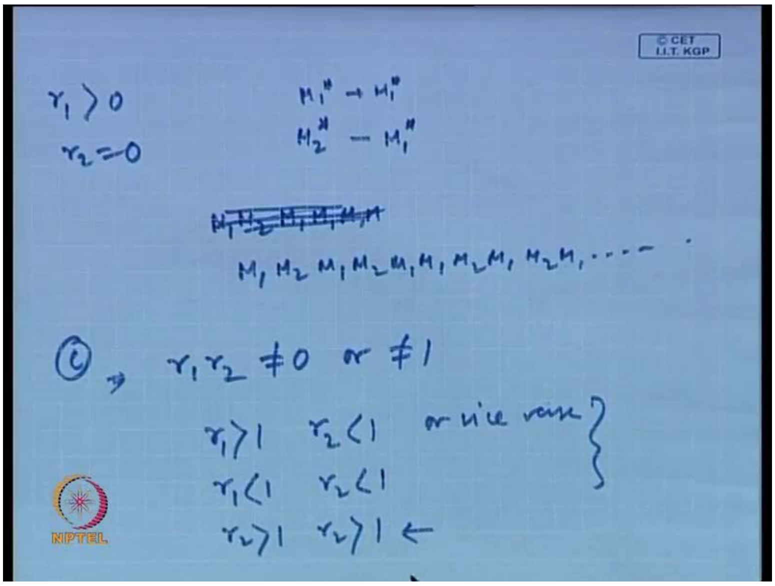

So in this case what happened it do not get a perfect alternate, if for example if I take the case of R 1, greater than zero and R 2 zero, then M 2 star only can react with M 1 star. Whereas M 1 star can react with M 1 star in some extent, so what will happen, you will get a something like this. In most cases, it will be alternating, but there will be some cases, there will be two M 1 and three M 1 sitting next to next each other. So, it is essentially alternate copolymer with some random incorporation of, or statistically incorporation of M 1, because in that case, where some tendency to homo polymer, M 1, because R 1 is higher than zero; that is not exclusively participate in cross propagation, this sometime can participating homopolymers, homopropogation, so you will get essentially a alternate copolymer, but some cases will, some incorporation of M 1. Now there is a third case, where R 1 and R 2 not equal to zero or not equals to 1.

Now, you can have situations like R 1 greater than 1, R 2 less than 1 or vice versa, or R 1 less than 1 or closer than 1, R 1 greater than 1, R 2 greater than 1. These are three possibilities, this is not happened very practically, but these two are very common in practice. So, what will they do in next lecture, we will start form this case, and talk about types of copolymer it forms, and the microstructure of that resulting copolymers, and also talk about composition drift in this copolymerstion medium and copolymerstion reaction, and also talk about the reactivity. No, how the value of the R 1 and R 2 which is sincerely the monomer reactivity ratios, how they vary with the reaction parameters, and the monomer structure, what is the structure of monomer structure in the reactivity of the monomer reactivity ratios. To with this, we just stop into this lecture, so we will come back, and continue this discussion on chain copolymerization in next lecture.