Principles of Polymer Synthesis
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Lecture – 17
Principles of Chain Copolymerization

Hello and welcome back to this NPTEL course on principles of polymer synthesis. Yesterday, we have finished talking about the radical chain polymerizations, in general the radical chain polymerizations, yesterday was the concluding class and we promised we will start talking about chain copolymerization, from today now as so this is the topic of today principles of chain copolymerization and it will continue, until we have covered the principles in more or less some detail.

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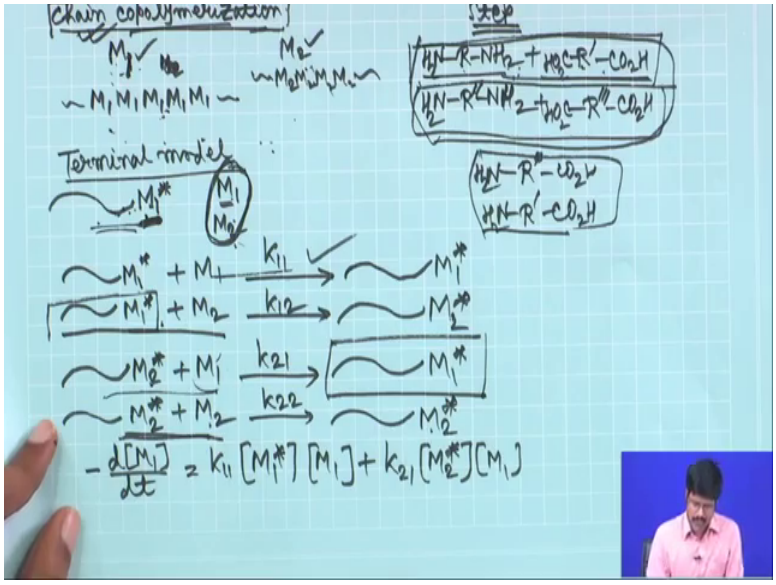

Now, copolymerization let us have a look at what do you mean by that. So, we are saying chain copolymerization so basically, this is then a type of chain polymerization only. Now this may of course, include anionic, cationic and radical copolymerization, but in general the principle that we are going to introduce will be valid for all of them. Although in general, we will mean that, we are talking about radical, because we have not talked about anionic and cationic chain polymerization at all in any detail.

Now, one question one might ask is that, what about step copolymerization and say for example, let us say you are talking about chain copolymerization and say you are talking

about radical. So, you have a monomer which enters into a radical polymerization. So, you know I am just saying monomer1 and it can create. So, it can create this kind of chain so on and so forth, you have another monomer which could also independently enter into chain polymerization. So, it can create it is own chain like this.

So, they can actually homopolymerize, now the aspect we are going to discuss for chain copolymerization is like, you put both of them together under the polymerizing condition, both of them can individually form their own chains in absence of the other. Now in presence of the other what can happen is that they are re-activities with respect to the growing radical chain, or the growing reactive chain might be different and one of them might enter more one of them might enter less; That means, in the polymer chain there will be both M 1 and M 2 present in a certain arrangement, they will be present.

Now, this is the concept of chain copolymerization that you are taking more than one monomer and doing a chain polymerization both of them are capable of doing, what you call as homopolymerizations. Now, you are going to analyze the system, where both of them are present. Some ratios whatever ratios is there, we will consider the effect of that also in the copolymer so on and so forth, if you consider say corresponding step copolymerization, you know let us say you are talking about reacting a diamine with a di acid this is a step polymerization.

Now, this step polymerization, if you are introducing the another monomer in this system, like this R double prime to differentiate these from R prime and R-NH2, NH2 and then maybe R triple, prime R, CO 2 H and CO 2 H, CO 2 H dicarboxylic acid, these particular system. So, these 2 monomers together will do polymerization, they can do now these 2 monomers can together form polymer.

Now, if you mix these things up, then what you have is a step copolymerizing system. So, just to tell you the differences here basically you have 2 monomers. When you are talking about a bi functional monomer where the both the functions are the same, but otherwise you could have a monomer which has both the functions different like an amino acid NH 2 and CO 2 H. It can actually react with itself, in that case you can take maybe R, CO 2 H, NH 2 this is a polymerizing system in itself, you can put another monomer like this, and then this is a copolymerizing system so on and so forth.

So, we would not discuss any further about step copolymerization, now we will concentrate solely on chain copolymerization. Now, as I was telling that more than one monomer is present in the system and they will enter simultaneously into the chain, and what we are interested in is the instantaneous copolymer composition, what does that mean is that you start with certain composition of the monomers, which is called comonomer feed composition. Comonomer, because you have more than one monomer present in your starting system and feed means you are starting with that so it is a feed.

So, comonomer feed composition means, at the start your M 1 and M 2 there at a certain molar ratio and then what you are doing, you are forming a copolymer let us say, from that starting composition of the comonomer you are doing less than 5 percent of the conversion, and then when the copolymer is forming the composition of that copolymer you are analyzing.

So, that is what you call as instantaneous copolymer composition that, actually can vary if you are further doing a copolymerization, but that is not are the subject of our discussion at the moment, we are talking about instantaneous copolymer composition; that means, a very small percent conversion from the starting comonomer feed composition, this terms are very important comonomer feed composition you are going into, so your whatever you are starting M 1 and M 2 say, M 1 is 80 mole percent M 2 is 20 mole percent.

So, then this information that one is 80 mole percent, automatically the other1 is 20 mole percent, this information constitutes the full information about the comonomer feed composition. The question, then I am going to ask you is at a less than 5 percent conversion instantaneously, what is the composition of the copolymer that you are going to get from there. So, what are the facts at governing those things.

So, in order to determine that, what we call is a terminal model so which means, suppose you have a growing chain and at the end of it, you have say M1, I am talking about 2 monomers M 1 and M 2 only. So, 2 monomers we are talking about not tar polymerization, we are not talking about 3 monomers to be that 2 monomers.

So, at the end of the chain you have M 1 and then I am putting star star means, some reactive center not telling radical or anion or cation. Now the second species could be another monomer, the same monomer M 1 that could add to the growing chain, or

another monomer M 2 could add to the growing chain, now these monomers the propensity of these monomers to add to this growing chain will only depend on the identity of the last unit, not the unit that was there previously that is the terminal model, that we are going to use to simplify the matters to analyze the process.

So, at the growing chain end whatever unit is there that will determine whether M 1 will at or M 2 will at not the preceding unit. The preceding unit is M 2 the result will be the same, whatever be the result here, if the preceding unit is M 1 you will have the exactly same result with respect to this, that will depend on the reactivities so on and so forth, now let us now start the analysis.

So, you have 2 growing chains M 1 star at the end of it, you might have M 1 or you might have M2, now this can suffer2 fates it can either react with M 1 or it can react with M2, because 2 monomers are present same way your M 2 star can react either with M 1 or it could react with M2. So, that is a the rate constant for this reaction is K11, the first term indicates the identity of this unit, second term second subscript indicates the identity of this unit that is, how we are going to determine this.

So, then what will be the species that will be forming again M 1 star only, because after that M 1 is added so this will be M 1 star like this. This is K12 rate constant species will be M 2 star, because M 2 has added. So, only identifying the last unit here, this will be K 12 correspondingly, it will be M 1 star and this will be K22 and this will be M 2 star.

So, what is the rate of dM 1 dt from this. So, there are rate of dM 1 dt is this reaction has to be considered K 11 into M 1 star and just abbreviating the concentration here into M 1 plus this reaction, where M 1 is being consumed. So, it will be K 21 into M 2 star into M 1.

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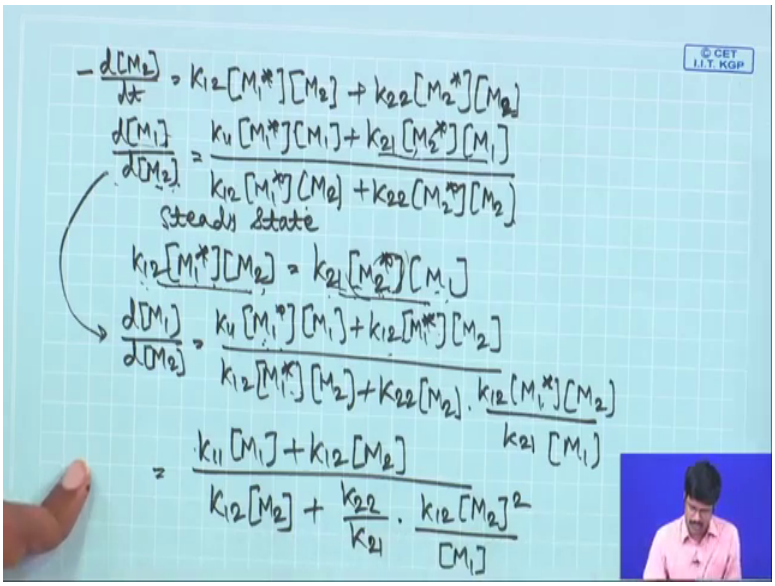

Similarly, minus dM2 dt will be equal to K12 into M 1 star into M 2 plus K22 into M 2 star into M2, because you are considering this reaction, where M 2 is be consumed and this reaction. So, if you take a ratio of the 2 dM1 divided by dM 2, you can immediately see this ratio will tell you the composition of the copolymer. So, these much amount of M 1 has gone into the copolymer, these much amount instantaneous has gone into the copolymer.

Now, if you take this ratio it will be K11 into M 1 star into M 1 plus K21 into M 2 star into M 1 M 2 divided by K12 into M 1 star into M 2 plus K22 into M 2 star into M2. Now, let us consider a situation steady state situation. So, that steady state situation will mean that, the rate at which this M 1 star is being consumed has to be equal to the rate at which this M 1 star is being produced same way the rate at which, this M 2 star is being consumed has to be equal to the rate at which the M 2 star is being is being produced.

So, because that is the steady state condition for you. So, that the total concentration of the radical remains the constant. So, if you are considering this particular situation in the steady state situation. So, what will be the equation that you want to write down here. It will be K12 into M 1 star into M 2 equal to K21 into M 2 star into M1. So, you see these expressions here K12 into M 1 star into M2.

So, we are considering this reaction. So, this tells you the rate at which the M 1 star is disappearing, and what about this one K21 into M 2 star into M 1 that is this expression

here. So, this tells you the rate at which the M 1 star is appearing. So, the rate of disappearance of the M 1 star has to be equal to the rate of appearance of M 1 star otherwise, the steady state cannot be maintained. So, this is the assumption then that we will make.

Now, once we have made this particular assumption, if you are telling taking this particular expression here. So, dM1 divided by dM2 that will be equal to your K11 into M 1 star into M1. So, on the top this K21 into M 2 star into M 1 this you replace by this term. So, that will be K12 into M 1 star into M 2 divided by K12 into M 1 star into M 2 plus K22 into M 2 and then this M 2 star you replace by this expression. So, M 2 star from this equation you replace by other terms.

So, the M 2 star will be nothing, but K12 into M 1 star from this expression into M 2 divided by K21 into M1. So, this then reduces to your M 1 star will be going from both sides. So, it will become K11 into M 1 plus K12 into M 2 divided by K12 into M 2 K12 into M 2 plus K22 by K21 into K12 into square divided by M1.

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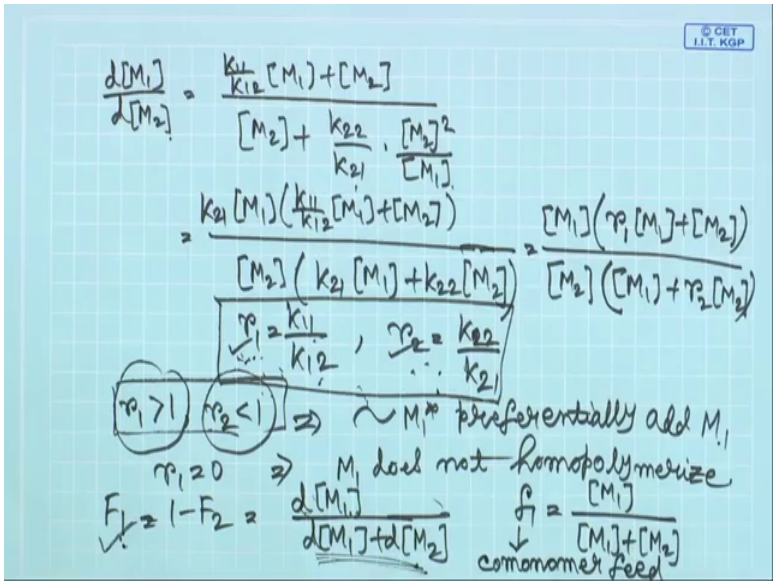

So, now K11 divided by K12. So, what you can do is that you can divide throughout by K12 and what you will get is the following dM1 divided by dM2 will be equal to K11 divided by K12 into M 1 plus M 2 divided by K12 has is gone here M 2 plus K22 divided by K21 into M 2 square divided by M1. So, from here this K21 comes up here.

So, that will be K21 into M 1 comes here K11 divided by K12 into M 1 plus M 2 divided by M 2 into K21 M 1 plus K22 M2.

So, this is the expression that you get here, now if you divide throughout by K21 then what you will get finally, is this particular expression M 1 into small r1 M 1 plus M 2 divided by M 2 into M 1 plus r2 M2. So, where your small r1 is K11 divided by K12 and small r2 is K12. So, this is small r2 is sorry K22 divided by K21.

So, these are called monomer reactivity ratios r1 is the reactivity ratio of monomer1 r2 is the reactivity ratio of monomer2. So, the reactivity ratio is then the ratio of the rate constant of the reaction with the same species divided by the rate constant of the reaction with the different species. So, basically this ratio K11 divided by K12. So, this is the monomer reactivity ratio. So, the rate constant for this reaction, where M 1 star is reacting with M 1 and rate constant for this reaction, where M 1 star is reacting with M2. So, these 2 rate constants the ratio will be the reactivity ratio of monomer1 because the identity at the end of the growing chain is M1. So, that is what we are considering.

Similarly, M 2 star the rate constant for the reaction in which M 2 star acts the same species which is M 2 divided by the rate constant of the reaction in which M 2 star adds the other species which is M 1 that ratio is the reactivity ratio of monomer2. Now these are very important terms and you have to keep in mind that when you are talking about r1 and r2.

So, this r1 and r2 are valid for this pair only. So, if you are taking monomer1 and monomer2 and in this particular pair of co monomers you are determining the value of r1 and r2 then these values will be different, when you are taking another monomer with respect to say your M 1 is the same if you take the other monomer that is monomer2 if you change then this K12 will change, because K12 is corresponding to the rate constant of M 1 star reacting with M2. So, if you change the identity of M 2 then K12 will change. So, correspondingly the reactivity ratio will change.

So, the reactivity ratio that is specific for a specific monomer pair that is very important to keep in mind. So, if you are saying for example, your r1 is greater than 1 and r2 is less than 1, that would actually mean that your M 1 star this thing the growing chain at the end of which M 1 is there that will preferentially add monomer1, that is what it means

that will prefer to add monomer1 then monomer2. So, the react because the reactivity ratio of monomer1 is higher than the reactivity ratio of monomer2.

Now, if r1 is 0 for example, reactivity ratio of monomer1 is 0. So, that would mean this K11 divided by K12 is 0. So, this particular reaction homopolymerization M 1 star reacting with M1. So, this particular reaction will not occur at all. So, which means r1 equals to 0 implies that M 1 does not homopolymerize same thing can be said about r2. So, that is the concept of reactivity ratio. So, if r1 is greater than 1 and that would mean that your M 1 star, when I say M 1 star that is; that means, M 1 is there at the end of the reacting chain that adds preferentially to M 1 if r1 is 0 then M 1 does not homopolymerize if r1 is less than one then M 1 star adds preferentially to the other monomer which is M2.

Now, we also will define these terms for example, capital F1 this is the mole this is basically the mole fraction of monomer1 in the copolymer; that means, this is the mole fraction of the monomer1 in the copolymer which actually, indicates that the corresponding amount of monomer has gone into the copolymer. So, this F1 capital F1 is nothing but 1 minus F2, F2 is the mole fraction of monomer2 in the copolymer, this is equal to dM1 divided by dM1 plus dM2. Because, this much of monomer has gone into the copolymer you are talking about instantaneous copolymerization. So, d small amount of monomer has gone in monomer1 and this is the total amount F2 monomers that has gone in. So, this ratio gives you capital F1, which is your mole fraction of monomer1 in copolymer correspondingly small F1 is the mole fraction of monomer1 in the comonomer feed, which is nothing but M 1 divided by M 1 plus M2. So, this is the mole fraction of monomer1 in the comonomer feed.

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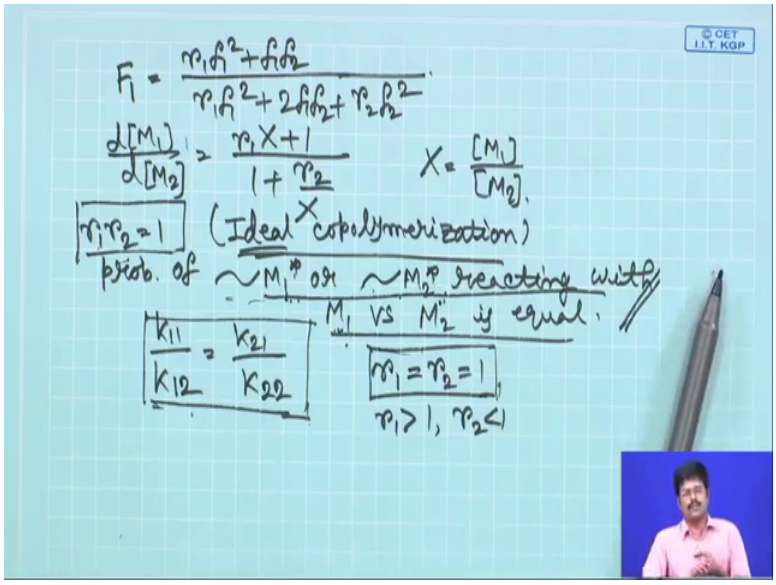

So, if you put the expressions, if you compare these 2 expressions you can actually derive some useful things like, capital F1 is equal to small r1 F1 square plus F1 F2 divided by r1 F1 square plus 2 F1 F2 plus r2 F2 square this is a useful expression and also this dM1 divided by dM2 I mean all these terms are very similar with respect to say this expression here, you can simplify also like this r1 X plus 1 divided by 1 plus r2 divided by X, where X is nothing but M 1 divided by M2.

Now, let us consider a case where this multiplication r1 r2 is equal to 1, this is the situation which is called ideal copolymerization, the term ideal does not have anything to do it the most desirable or not, I will tell you what the term ideal means, in a little while. So, r1 r2 equals to 1 this is ideal copolymerization in this kind of situation the probability of M 1 star or M 2 star reacting with M 1 versus M 2 is equal, which means that the propensity of M 1 to add to the growing chain will not depend on whether you have M 1 star at the end or M 2 star at the end, which actually will transpire to this kind of relation K11 divided by K12 equals to K21 divided by K22, because r1 r2 equals to 1.

So, you can directly come to this particular expression here. This particular thing will become more clear when you talk about the probability and all what does this actually mean; that means, the probability of addition of this M 1 star to M 1 will be equal to the probability of addition of M 2 star to M 1 nothing else these does not tell you about the relative reactivities of M 1 and M 2 that we will come to after. So, this is the relationship that will be that will hold under this kind of situation.

Now, r1 r2 equals to 1 this particular term r1 r2 equals to 1 this particular condition can be satisfied by many different scenarios for example, you can have r1 equal to r2 equal to 1 or you can have r1 greater than 1 r2 less than 1 or the opposite and still the multiplication may be equals to 1, but here one thing is important to mention that this term here this means, that basically you have a random copolymerization.

So, the monomer1 and monomer2 will be placed randomly, whether they will be in perfect random placement or imperfect random placement in the copolymer that will depend on the relative values of r1 and r2, if r1 and r2 both are equal to 1 that will mean they a perfectly random copolymerization will result, if r1 is greater than 1 and r2 is less than 1, that will be the monomer1 which corresponds to r1 is more reactive then monomer2 which corresponds to r2. So, there will be a larger proportion of the more reactive monomer which is the monomer1, that will be now placed in the copolymer in a random placement.

So, steel monomer1 and monomer2 will be placed in a random placement, because the probability that M 1 star will add to M 1 and the probability that M 2 star will add to M 1 both are equal. So, correspondingly then it will be a random placement and the other probabilities are also equal we will talk about that in detail after. So, it will be a random copolymer that will be produced, but whether it is perfectly random or not depends on the values if r1 equals to r2 equals to 1 that will be a perfect random placement, if r1 is greater than 1 there will be more proportion r1 is greater than 1 and r2 is less than 1, because the multiplication is equals to 1 there will be more proportion of the more reactive monomer that goes into the copolymer less proportion of the less reactive monomer2 that goes in, but when they go in they will still be placed in a random placement. So, that is the idea here.

So, if your r1 is more than 1 as I told you more proportion of that goes, in now what happens if you keep changing these values and what happens if one of the values is much greater than one of the values is much less than one means, r1 and r2 values are very different. So, for that let us go into this particular slide here in the power point presentation.

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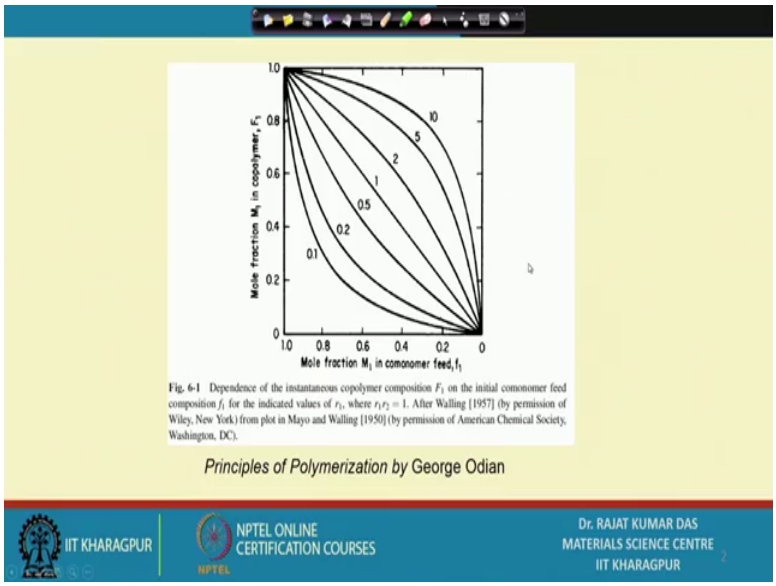

So, here you will see dependence of the instantaneous copolymer composition y axis is the mole fraction y axis is the mole fraction here of the monomer in the copolymer.

So, monomer1 in copolymer it is capital F1 is the mole fraction of monomer1 in the copolymer X axis is the mole fraction of monomer1 is the comonomer feed that is small f1. So, if you see this particular graph here. So, for all these graphs r1 r2 equals to 1 and all these values that you are getting are the values that you set the value of r12; that means, if you set the value of r1 equals to 1 then the value of r2 is automatically equals to 1 and then you get this kind of linear graph.

So, what will happen. So, for example, if you are looking at say 0.5 mole fraction 0.5 mole fraction here on the X axis; that means, 0.5 is the mole fraction of monomer1 and then 0.5 is the mole fraction of monomer2 in the comonomer feed the copolymer will be produced with the exactly the same composition. So, copolymer also will have 0.5 mole fraction of monomer1 which will be indicated by this point if you go draw a horizontal line here and 0.5 mole fraction of monomer2.

Now, what happens if the value of r1 becomes higher and higher than 1 of course, r1 and r2 multiplication is 1; that means, r2 is going down suppose the value of r1. So, the curves will become like this, now this is the reason why this is called an ideal copolymerization system, because these curves are very similar in resemblance to your ideal liquid mixture vapor liquid equilibrium curves, they also look like this and that is

the reason why you call this as ideal copolymerization nothing else nothing like what you desire or not.

And here for example, if you are looking at say the value of 10. So, this keeps increasingly becoming bent like this as you keep increasing the value of r1. So, correspondingly the value of r2 is decreasing. So, let us say the value of 10; that means, for this curve your r1 is 10 and r2 is 0.1. So, the monomer reactivity ratios the ratios are very, very different monomer reactivity ratio of monomer1 is 10, monomer2 is 0.1 that will mean an overwhelming proportion of monomer1.

Now goes into the copolymer irrespective of what the monomer feed composition is in the comonomer mixture; that means, if your r1 value is 10 and r2 value is 0.1 no matter what you do, if you want to put substantial amount of monomer2 into the copolymer you might think that your comonomer feed to start with 2 monomers you are taking right you might take a large amount of monomer2, because it is reactivity is lower very low large amount of monomer2 very small amount of monomer1.

So, you expect maybe a lot of monomer2 will go into the copolymer, that will not happen if your r1 is much greater than 1, I mean if your r1 and r2 are very different and the multiplication is 1 then it is very difficult to have any appreciable amount of monomer2 into the copolymer irrespective of whatever is the composition of the comonomer mixture.

So, you can see from this graph. So, here for example, if you look at the power point slide here for example, you see the mole fraction of monomer1 is close to 0 this point somewhere here, but so; that means, the mole fraction of monomer2 is that much higher. So, say 0.9 close to 0.90 mole percent many monomer2, but what is the composition of the copolymer that is given by say for example, this point if you go by a vertical line it will be this point. So, you will see that the composition of the monomer2 is something like this, here it is close to say 0.55 or 0.58, I do not from the value say 0.58.

So, they at least then 58 mole percent will be monomer M 1 and rest will be monomer M2. So, you will see that even at very low amount of monomer1 present in the comonomer mixture a large amount of monomer1 actually has gone into the copolymer, because of the high difference in the reactivity ratio. So, it becomes very difficult to produce a copolymer with substantial amount of monomer2 no matter, how much of

monomer2 you take in the starting monomer mixture, because the reactivity ratios are very different. So, we will stop here today and in the next class we will elaborate on this further.

Thank you for your attention and see you then in the next class.