**Principles of Polymer Synthesis**
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**Lecture – 19**
**Principles of Chain Copolymerization (Contd.)**

Welcome back, to this NPTEL course on principles of polymer synthesis, today is lecture number19 and we continue to talk about the principles of chain copolymerization. To recap the last class, we have been talking extensively about, how to derive the composition of copolymers? Both the instantaneous copolymer composition, with respect to the comonomer composition or comonomer feed composition and also, with respect to percent conversion how the comonomer feed compostion might drift? It might drift because both the monomers do not have the same reactivity.

So, the monomer which has more reactivity it goes in more, into the copolymer it will be preferentially going into the copolymer, compared to the monomer which has less reactivity. So, then in effect what will happen is that, the comonomer feed remaining comonomer mixture that will become richer in the component which is less reactive. And so, with time then the comonomer feed composition will drift and, since the copolymer composition, it depends basically on the comonomer feed composition also because; there is this ratio of M1 and M2. If you look at this particular paper here, from the previous expression, that we had dM1 divided by dM2 equals M1 divided by M2 into r1 M1 plus M2 divided by M1 plus r2 M2; that means, M1 divided by M2 is there in this particular ratio.

So, that would also mean if your comonomer composition is drifting, correspondingly your copolymer composition also will be drifting. So, in order to have a complete understanding of the situation, you need to know how it conversion the copolymer composition changes. So, those things we have actually addressed and then finally, we also talked about the value of small r1 and small r2 the reactivity ratios. Now one thing you need to keep in mind here, that when you are talking about reactivity ratio, say we are talking about the ratio r1 which is small k11 divided by small k12.

So, k11 is basically the rate constant for the reaction of M1 star; that means, the reactive end is M1, M1 star with M1 and small k12, is the rate constant corresponding to the

reaction of M1 star with M2 now; that means, the k11 basically is the rate constant for homo polymerization. Because, at the end of M1, at the end of the chain you have M1 star and that is reacting with M1. Now you might ask this question, without going into the copolymer if you are looking at only.

So, we are talking about k11. So, you are talking about the homo polymerization of monomer M1 or monomer1. So, why not just take the monomer1, in absence of monomer2? And to a homo polymerization determine the rate constant, that you can use in this copolymerization system and take the value of k11 divided by k12, k12 you have to determined and then, this ratio is r1, but that will not work. The rate of homo polymerization of a particular monomer, if you are taking in isolation that will be something, in present of another monomer, which can copolymerize with it, then the rate of homo polymerization may change.

So, whatever rate of homo polymerization you get in normal situation, in absence of another monomer that is not the same as a rate of homo polymerization that you get in presence of the other monomer. And that is why these values of r1 r2, these values you have to determine for specific copolymer system and, you have to determine from this real system in which both the monomers are present that is the idea here. Now coming to the point, that I wanted to discuss today, it is about the microstructure of the copolymer, this is something we had given a sort of introduction of this, in the previous class.

So, we will again do the introduction here. So, it is like we are trying to find the sequence length distribution, of whatever monomer has gone in. So, if we are trying to find. So, you have monomer M1 and monomer M2 that have gone into the copolymer. So, my question then is what is the number fraction of a diad of M1? That means, M1 this unit together, flanked by M2, both sides M2 and then you have M1, in isolation M1 isolation and then, somewhere else you have only M1, M1 in isolation. Isolation means on both sides there may be M2 not M1, again somewhere else you have M1, M1 how many such M1, M1 units will be there, with respect to the total length of the polymer, that will be the number fraction distribution of that diad.

Likewise, you could look for triad say M2, M2, M2 or M1, M1, M1 so on and so forth. So, this will then, once we have discussed the microstructure, the aspect of micro structures, the analysis of micro structures that will then give us a complete picture of the

system of copolymerization. Remember we are not talking about tar polymerization for example, a copolymerization system, where we have more than 2 components those things we are not talking. We are talking about the basic principle, the simplest way we could describe this and yet, we do not simplify it too much beyond the necessity because, that will be a scene.

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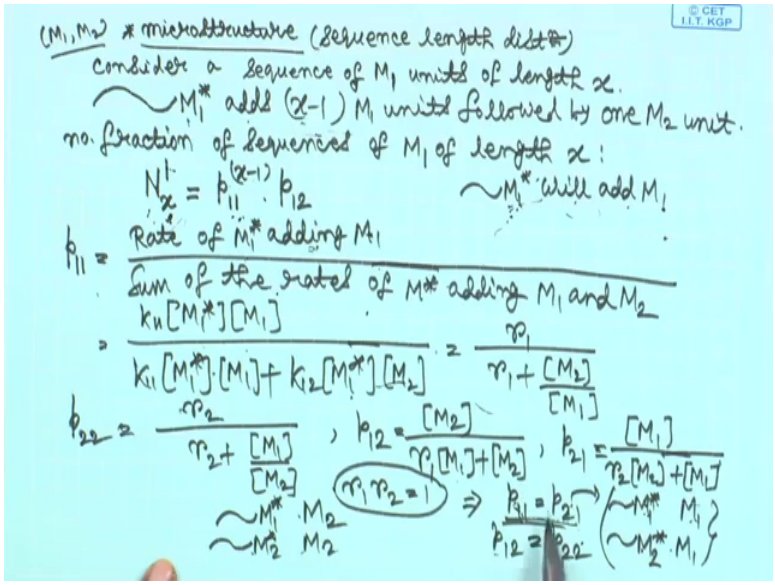


So, let us then go to the micro structure, which is the subject of today's topic. Microstructure now, consider a sequence or also sequence length distribution, I have already talked about these things and I am writing it down again because, that also gives you a little bit more time to think and, probably both are the concept. So, consider a sequence of M1 units, we are always talking about monomer system M1 and M2, that are coming together into the copolymerization M1 is monomer1 M2 is monomer2.

So, consider a sequence of M1 units of length x. So, what is the probability that you will have a sequence of M1 units of length x? So, that would mean, you start with this. So, you have an M1 unit here, now this adds x minus 1, M1 units followed by 1 M2 unit. Because, a total of M1 units of length x.

So, x number of M1 units have to be there. So, when we are looking for the probability, it is the same way that we treat, although the expressions will be slightly different. Then, when we are saying a number fraction distribution of say step polymerization, from there we have if you recall, quite some time back we talked about this number fraction

distribution and weight fraction distribution for step polymers by florys statistical approach.

And there also, we told that how many independent events are there that concern, this particular situation and of course, all those independent events up to happen together, in order for this particular situation to realize. And since, they are all independent events their probabilities will have to be multiplied, in order to get the probability of this overall situation happening, which means all the events are occurring together. So, that way then. So, what is the number fraction or probability? Number fraction both are the same in this case, number fraction of sequences of m of length x.

What is the number fraction of that? So, we will write it like this, capital Nx subscript 1 superscript. So, that will mean, this is the number fraction of a sequence of length x, for monomer1. So, superscript is for the identity of the monomer, subscript is for the length of the sequence, for which the number fraction we are trying to determine. And this full thing is a number fraction of the sequences of length x, for the monomer M1.

So, this is nothing but, p11 to the power x minus 1 into p12. Now p is basically the probability, p11 is the probability that, your M1 star will add M1 that is the probability that is why it is 11 the first number in the subscript indicates the identity of the reacting center reactive center which is this M1 star second number indicates the monomer identity.

So, p11 means the probability that M1 star will add M1. So, this probability is p11 and that has to be multiplied x minus 1 times why? Because M1 star has to add x minus 1 number of M1 units, in order for total number of M1 units to be x so, that is p11 to the power x minus 1, then that has to be multiplied by p12. Because, still the event is not complete, after M1 total of x minus 1 M1s have come. So, total number of M1s is x, but after that an M2 has to come, that event it is also important, only then you will have an in isolation and M1 total M1 units sequence length x.

So, that event also has to occur simultaneously and the probability of that event occurring is p12 because, it is the M1 star that is reacting. So, it is p1 it is reacting with M2 monomer. So, it is p12. So, both the events are occurring simultaneously and both the events are independent of each other. So, they have to be multiplied. So, Nx1 is equals to p11 to the power x minus 1 into p12, what is the probability? P11 that M1 star

will add M1, this is nothing but, rate of M1 star adding M1, divided by sum of the rates of M1 star adding M1 and M2 this is the probability.

So, rate of that particular reaction undergone by that reactive center, divided by rates of all the reactions that this reactive center could undergo. So, this is p11, what is that?

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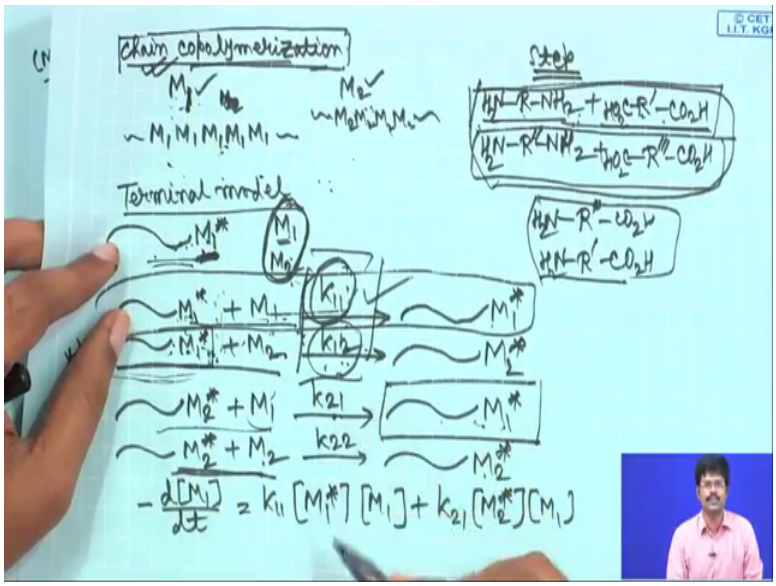


If you recall our analysis from the previous class in the chain copolymerization, we had all these sequence of reactions that were present. So, what is the rate of M1 star adding M1? There is K11 into M1 star plus in M1. What is the rate at which K1 so, M1 star adds M2? That is K12 into M1 star into M2.

So, in the denominator these 2 rates have to be summed up, because that is a complete description of, what can happen to your M1 star, it can either react with M1 or it can react with M2. So, that will be in the denominator and in the numerator only the rate of reaction of M1 star with M1. So, that will be then K11 into M1 star into M1 divided by K11 into M1 star into M1 plus K12 into M1 star into M2.

Now, if you remember that K11 divided by K12 is r1 and, if you put those values here and M1 star actually is going out from here, and you divide by K12 on both sides up and down. So, you can write this expression in terms of reactivity ratio and the monomer concentrations and, it becomes something like this M2 by M1. And there is a certain symmetry in these expressions in that, if you want to calculate p22, again that is the

probability that M2 star adds M2. If you want to calculate p22 that is having a symmetry with respect to this that will be r2 divided by r2 plus M1 divided by M2. Actually, I would not remember recommend in these expressions, if you have a problem just work it out working out is easier than remembering these expressions, then you can make a mistake.

If your concept is clear, you can actually determine this very easily. So, this is p22 similar way p12 can be shown to be equal to M2 divided by r1 M1, plus M2 and correspondingly p21 has the same certain symmetry, you see M2. So, it becomes M1 here instead of r1 M1, you have r2 M2 plus M1. Now let us try to understand what we mean by ideal copolymerization we say the propensity of M1 star and M2 star to add to M1 is the same. So, that is something like this.

In these expressions, you say it r1 r2 equals to 1, which is your ideal copolymerizing so, called ideal co polymerization. If you put that, it turns out that your p11 is equals to p21 and p12 is equals to p22. What does that mean p11 equals to p21? The probability that M1 star will add M1 and, the probability that M2 star will add M1 are the same; that means, whether M1 will add at the end of that chain or not does not depend on whether at the end of the chain it finds M1 star or M2 star same way, this p12 equals to p22; that means, your the probability of adding M1 star, probability of M1 star reacting with M2 and the probability of M2 star reacting with M2 are the same. That does not mean that all 4 probabilities have to be the same.

If all 4 probabilities became same, you will have a perfectly random distribution which means r1 equals to r2 equals to one, but in this case, you do not have a perfectly random distribution. Remember that these 2 are equal; these probability may be 5 times this probability that is also possible. So, if this probability is 5 times this probability that would mean, basically that M1 will add. So, you have a more M1 in the system, but that does not change the fact that probability of addition is the same. So, the reactivity and the probability that way they are different things.

So, in that case also you have a random situation, but not a perfectly random situation. You have more M1 less M2 and then, they will be in the random management. So, that is the situation then. Now let us try to work out some problems related to this say for

example, you have r1 equals to 5, r2 equals to 0.2; obviously, these problems are worked out, because I want to illustrate the principle I do not want to derive it sitting here.

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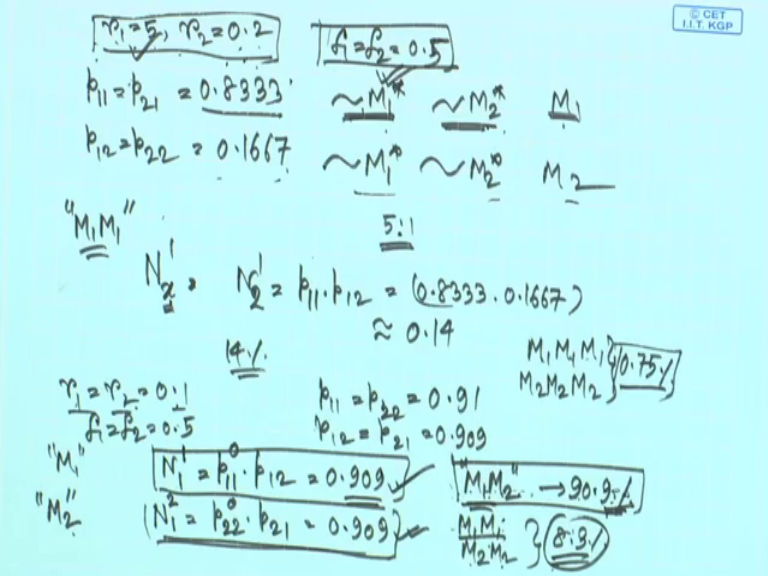


So, r1 equals to 5 and r2 equals to 0.2 let us say this situation. So, this is the ideal polymerization situation, ideal copolymerization situation r1 equals to r2 equals to 1.

But r1 is higher r2 equals to r2 is lower. So, how does that translate into probabilities? So, you probabilities let us say small f1 equals to small f2 equals to 0.5. You take both of them in equal proportion both the monomers in equal proportion. So, this defines your comonomer feed composition, now if you derive the expressions. Your p11 is equals to p21 and p12 is equals to p22, you can actually derive those expressions, because you know, you have your p11 is r1 divided by r1 plus M2 by M1, M2 by M1 you know in this case it is f2 by f1.

So, this is equal proportion. So, it is 1 r1 values you know. So, corresponding you can find out p11, same way you can find out p22. All are in terms of your comonomer feed composition and your r1 and r2 all these things are known. So, you can find out these values. So, if you find those values you see indeed p11 equals to p21 and p12 equals to p22 and look at these values here, it is 0.8333 and this is 0.1667, this is what I wanted to tell you, that the propensity. So, you see both M1 star and M2 star they will add M1 and M2.

So, both M1 star and M1, M1 star and M2 star will add M1 with the same probability of course, and they will add to M2 with the same probability. But these probability is 5 times this probability so; that means, both M1 star and M2 star will add to M1, with a 5 is to 1 tendency, or let me make a statement little bit in a different way. So, both M1 star and M2 star have a 5 is to 1 tendency, to add M1 over M2, 5 is to 1 tendency. So, even though these probabilities are equal, there were 5 is to 1 tendency, because your M1 is more reactive.

So, 5 is to 1 tendency means; obviously, more of M1 will go into the system. Now let us say, you are trying to find out, what is the number fraction of this diad M1 M1? So, the number fraction of this diode is N, you say Nx1. So, x is basically 2 because this is diad. So, here you are talking about N21 and your expression was basically, this p11 to the power x minus 1. So, this will be p11 to the power 2 minus 1 into p12. So, that will be equal to p11 to the power 2 minus 1 So, p11 into p12 and these values if you put here. So, this is 0.8333 into 0.1667. So, that becomes 0.14.

So, basically you have 14 percent diad in the system. Now if you are considering something else, let us say you are talking about an alternating polymerization copolymerization, r1 equals to r2 equals to 0.1 both of them are low, but they are not 0 so; that means, there is no perfect alteration. If there is a perfectly alternating system then, both the monomers will go in equal proportion to the copolymer and is a perfectly non-random fashion; means M1 M2, M1 M2, M1 M2 this is non-random perfectly non-random fashion. And regardless of what is the feed composition of the comonomer? You will have 1 is to 1, both the monomers going into the copolymer.

So, whether you take a 80 mole percent M1, 20 mole percent M2 or whether you take 80 mole percent M2 and 20 mole percent M1 will not matter. If both r1 and r2 are 0, both of them will go in 1 is to 1 proportion into the copolymer and they, will go like M1 M2, M1 M2, M1 M2 that is the thing. Now let us say r1 and r2 both are low, but not equals to 0 then what happens? This is close to an alternating situation but not close enough, not perfectly alternating. So, you might reasonably ask what is the proportion of a system where you have only M1. It will be 100 percent if it is perfectly alternating because M1 M2, M1 M2 there is no diad, like M1 M1 there is no triad like M1 M1 M1.

If r1 equals to r2 equals to 0, but in this case, you will have diads you will have triads. Nevertheless, the proportion will be very low because, it is close to being perfectly alternating, but it is not perfectly alternative because, r1 and r2 are very low. So, let us find out, from these kinds of microstructure analysis, you can have the answer to all these questions. So, r1 equals to r2 equals to 0.1. Let us say, this then your p11, if you are putting that thing here. So, p11 equals to p22. This comes as 0.91 and p12 equals p21 that comes as 0.909 and let us say, you have taken f1 equals to f2 equals to 0.5.

So, then the question is, what is the sequence length distribution for a single M1 unit? So, M1 unit, that will be N1 1. So, single unit and this is the identity of the monomer. So, this is N1 1. So, that is nothing but p11 to the power x minus 1. So, this is 0 x is 1 in this case, because single unit into p12. So, that will be nothing but 0.909 now. So, this is the this much percent of single M1 sequence, what is the situation of a let us say M2 unit? M2 unit, which has a single unit present; that means, only M2 and flanked by M1s so, that will be N1 2 because, this is the second monomer1 is the sequence length.

So, that will be p22 to the power 0 into p 21 that will be also equal to 0.909. So, the propensity to have only one M1 unit isolated is 0.909, only one empty unit isolated 0.909. So, basically you will have M1 M2 unit's propensity to have M1 M2 unit's 90.9 percent, something like that not 100 percent because this is not perfectly alternating situation. So, if you are looking for a diad for example, M1 M1 or M2 M2, you can actually work it out, it will be 8.3 percent. And if you are looking at say for example, a triad M1 M1 M1 and M2 M2 M2 I mean, here it is a special scenario where r1 equal to r2 equals to 0.1, that is why these are equal, then these may not be equal, depending on these values.

But I am trying to illustrate an important point here; you see that they are tending towards alteration. M1 M2 units the number fraction distribution is around 91 percent, if it was perfect the alternative, it will be 100 percent. But it is not perfectly alternative, because this marked is r1 equals to r2 equals to 0.1, this value is not 0, if it was 0 then the probability of having M1 M2 sequence will be 100 percent, but here it is not 0. So, it is tending towards alteration. So, 90 around 91 percent you have and what about the rest of the things, say M1 M1 you will be surprised, but M1 M1 or M2 M2 say diads you can find 8.3 percent.

So, out of the total sequence distribution, the total number of M1s that are present in this particular length of the polymer, on an average out of that 2 of them are together, like M1 M1 again M1 M1 again M1 M1. Out of the total number of M1s the percent distribution, the number fraction distribution it keeps you 8.3. So, what is the number fraction distribution? It is a total number of those sequences say, M1 M1. How many M1 M1 sequences are there divided by total number of M1 units? Something like that.

So, that is a number fraction distribution, total number of this is there total number of M1 say 100 is there. So, how many of them are distributed like M1 M1 units that is your number fraction distribution, that is what we are talking about all through. So, you see that 8.3 percent of M1 will be distributed as M1 M1. So, this is not perfectly alternative and when you go to M1 M1 M1 it is only 0.75. So, when you go to tetrad still certain percent will be present, but that amount will be very, very low because it is going towards close to the alternating, but not close enough 90 percent not 100 percent ok.

So, finally, we will finish this, with another problem which I hope will strengthen the concept, if at all certain questions are remaining.

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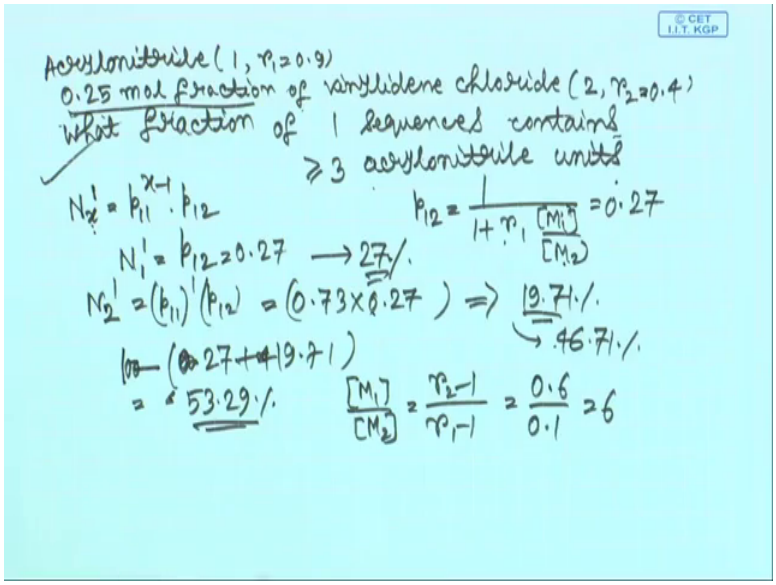


So, let us say acrylonitrile, the structure in this case is not important. You are doing a copolymerization of acrylonitrile say, you are saying this is monomer 1 and r1 is 0.9. You are copolymerizing this with 0.25 mole fraction of vinylidene chloride; this is monomer2 r2 equals to 0.4. Now which one of them you take monomer1 and monomer2 does not

matter, corresponding the calculation will change, as long as your concept is clear you can work it out and structure in this case does not matter ok.

So, this is a copolymer system your comonomer feed composition is given. So, you have 25 mole percent of monomer2 and, rest of that is 75 mole percent of monomer1 that is present and, correspondingly these are r1 and r2 values. So now, the question is what fraction of monomer1 sequence or acrylonitrile sequences contains more than equal to 3 acrylonitrile units? So; that means, you have to find out what fraction contains one unit? What fraction contains 2 units? And then you have to subtract that from the total. Then you can find out what fraction contains at least 3 number of monomer1 or acrylonitrile units?

In this case so, then if you go ahead so, that will be Nx 1 general term for monomer1, x number of sequences, it will be p11 to the power x minus 1 into p12 so, in this case your x let us say you take N1 1. So, that will be equals to p12, you can calculate these things say for example, p12 I will just calculate one of them and leave the rest for you, 1 plus r1 into M1 by M2 and you can find this from this ratio. So, you know the ratio because 0.25 mole fraction is there. So, the 0.25 divided by 0.75 r1 value is there. So, p12 will be according to what I have calculated here 0.27.

So, you can put that value here there will be 0.27. So, 27 percent. So, 27 percent of total monomer1 is present as only unit single unit. What about 2 units together? That will be p11 to the power1 into p12 and you can actually calculate this, but I will not show you here, take it as homework. This into 0.27 this comes as 19.71 percent. So, you just do a total of this I think it will come something around 46.71 percent.

So, then how much fraction contains greater than equals to 3 acrylonitrile units, that will be 1 minus summation of these 2. So, you are taking 1 you could take 100 also. So, if you take 100 then you have to take 27. If you take one that will be taking 0.27 plus 40, so, plus 19.71 so, 100 minus that so, it will be 53.29 percent. So, that will be your answer. And then if you are asked the next question, the final question if I am asking what is the feed composition such that the copolymer composition does not vary with conversion? Or what is the feed composition such that during copolymerization the composition does not change, that is azeotropic copolymerization? Excuse me that will be valid here, because r1 and r2 both are less thaN1.

So, you can use the formula or you can derive the formula also, if you do not remember M1 by M2 equals to r2 minus 1 divided by r1 minus 1, put the values r2 and r1 and you will get 0.6 divided by 0.1. So, 6. So, if you take 6 is to1 mole ratio of acrylonitrile vinylidene chloride, you will get a copolymer with exactly the same composition that is 6 is to 1. Acrylonitrile vinylidene chloride will be present in the copolymer because, that is the azeotropic composition of the comonomer mixture.

So, with this we come to the end of this particular class and as far as I am concerned I have discussed satisfactorily, whatever principles I wanted to I hope you will agree with me about the copolymerizations of a 2 monomer units, chain copolymerization did not talk about step called copolymerization and the status will remain. So, in this particular course. So, what we are going to talk about in the next class is living chain polymerization and I am going to talk about why it is living? And why it is important? In terms of the kind of compositions of the polymer that you want to get in terms of the molecular weight of the polymer that, you want to get and in terms of the molecular weight distribution of the polymer, that you want to get and the industrial ramifications of that; that could emerge out of that and that is why these kind of living chain polymerizations are important till then.

Thank you and goodbye.