Principles of Polymer Synthesis
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Lecture – 18
Principles of Chain Copolymerization (Contd.)

Hello and welcome back, to the class number 18 on principles of polymer synthesis. We had been talking about, chain co polymerization and at present we are talking about the ideal co polymerization system, where the reactivity ratio, the multiplication is equals to 1. And we directly go back to the graph, in the slide from which we were talking in the previous class.

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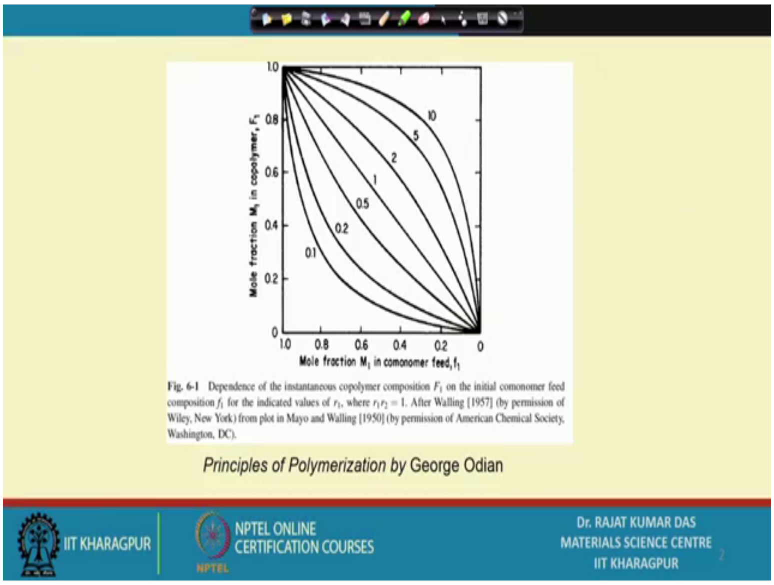

Fig. 6-1 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1, where $r_1 r_2 = 1$. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, DC).

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So, as we told that, if we have the monomer reactivity ratios very different, it becomes very difficult, to produce a polymer that, has appreciable amount of the less reactive monomer, irrespective of what is the composition of the co monomer mixture. So, if you put lot of less reactive monomers, in the co monomer mixture, still a less amount of that will go into the copolymer, because the other monomer is highly reactive. So, you can already see that this is the mole fraction of monomer 1, in the comonomer field which is quite low, but correspondingly say let us here if you look at it is. So, say 0.2, 0.2 is the mole fraction of monomer 1 in comonomer feed let us say.

So, correspondingly what will be the mole fraction of monomer 1 in the co polymer that has been produced? That will be close to 78 or 80 percent. So, it will be close to 80 mole percent, even though you have only 20 mole percent of the monomer 1 and around 80 mole percent of monomer 2 present in the starting comonomer mixture. The copolymer composition will show you, around 80 mole percent of it is only monomer 1 and rest is monomer 2.

So, this is what is given by the graph and correspondingly, if you see this particular graph, if your monomer1 r 1 value is 0.1. So, even if you have say for example, 60 percent, say 60 mole percent or 0.6 mole fractions. So, say 60 mole percent of the comonomer feed, is only monomer M 1; that means, rest of that is 40 mole percent is your monomer M 2, still less than 20 mole percent will go into the copolymer composition. So, that is the situation that we were talking about.

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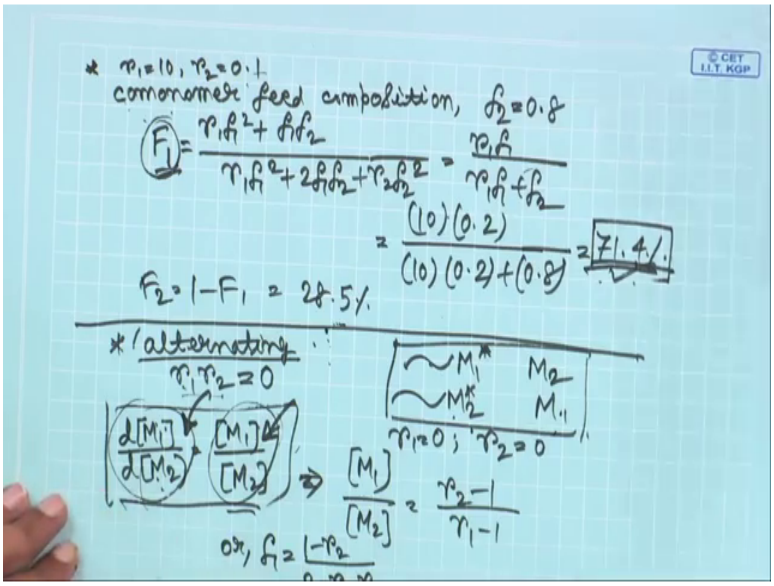

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* $r_1 = 10$, $r_2 = 0.1$

comonomer feed composition, $f_2 = 0.8$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$$= \frac{(10)(0.2)}{(10)(0.2) + (0.8)} = \boxed{71.4\%}$$

$F_2 = 1 - F_1 = 28.5\%$

* alternating

$r_1 r_2 = 0$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \Rightarrow \frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1}$$

$\sim M_1^*$ M_2

$\sim M_2^*$ M_1

$r_1 = 0$; $r_2 = 0$

or, $f_1 = \underline{1 - r_2}$

Now, let us do a small problem, in order to have more understanding of this particular situation. So, let us say, your r 1 is 10, just like that graph and r 2 is 0.1. And let us say, the comonomer feed composition is given by this, f2 is 0.8 so; that means, 80 mole percent of the comonomer feed, is composed of monomer 2 which is the less reactive monomer.

So, I just want to show you that, even if you are taking a lot of monomer 2. In the comonomer mixture you will get very less amount of monomer 2, correspondingly even with this value into the copolymer, because of this discrepancy, in the reactivity ratios of the monomer1 and monomer2. So, monomer 1 will overwhelmingly go into the copolymer and, it will you know have more preference to go into the copolymer then monomer 2.

So, what is to show you in the question is, what is the instantaneous copolymer composition? This is the question. So, when your r 1 and r 2 this multiplication is 1, then the expression of F 1 which is nothing but r1 f1 square plus f1 f2 divided by, r1 f1 square plus 2 f1 f2, plus r2 f2 square, this basically reduces to a more simplified form r1 f1, divided by r1 f 1 plus f2, you can just work it out by putting r1 r2 equals to 1.

So, if you put the values here r1 is 10, f1 is 0.2 because f2 is 0.8 total is 1 mole fraction. So, this is 0.2, divided by r1 is 10, f1 is 0.2 plus f2 is 0.8. So, I have already worked it out. So, I will just write it down here. So, you will get 71.4 mole percent of monomer 1 into the copolymer and F 2 is 1 minus, F 1 it should be around 28.5 mole percent.

So, the copolymer what will be the instantaneous composition of the copolymer? 71.4 mole percent of the copolymer, in the copolymer if you take the 100 as the basis. So, 71.4 percent will be your monomer1 present in the copolymer and 28.5 percent will be monomer 2, present in the copolymer. Even though, in the comonomer feed mixture you had taken 80 mole percent of monomer 2, only 28.5 mole percent is present in the copolymer because of this overwhelming difference in the values of r 1 and, r 2. I hope this particular problem has illustrated the concept that I wanted to tell you that, I wanted to elaborate upon.

So now, we go into what we call as alternating copolymerization. Now alternating copolymerization will occur when r1 r2, this multiplication is equals to 0. Which; means M1 star, will add M2, with the overwhelming preference over M1 and M2 star will add M1, with the overwhelming preference over M2; that means, after M2 only M1 will come and, after M1 only M2 will come. So, ultimately it will be alternating M1 M2, M1 M2, M1 M2 the same way after M2 only M1 will come M2 M1, M2 M1. So, it will be alternating.

So, that kind of situation is the extreme alternating behavior and, that happens only when r1 equals to 0 and r2 equals to 0, but in other situations where r1 and r 2 both are small less than one and, the multiplication is close to 0. Then you will get what you call as you know, moderate alternating behavior, that it tends to alteration. So, the copolymer composition tends to alteration, but it is not a perfectly alternating scenario.

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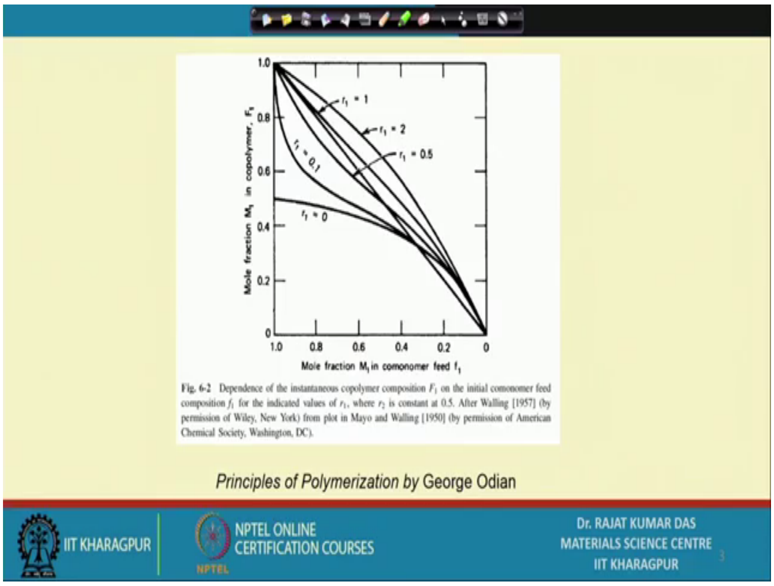

Fig. 6-2 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1, where r_2 is constant at 0.5. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, DC).

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So, let us go into the graph, in the slide to explain this further. So, again on the y axis you have mole fraction of monomer1 in the copolymer, x axis mole fraction of monomer1 in the comonomer feed. So now, this is theoretical what you can do is that your r2 value you keep constant at 0.5 and, all these graphs are for different values of r1.

So, you see r2 is 0.5, when r1 is 1, then you have kind of ideal copolymerization behavior of course, close to be. So, this is like this. So, r2 is 0.5 and this r1 is say, r1 is 2 and r2 is 0.5. So, the multiplication is actually 1.

So, this is your ideal copolymerization behavior we talked about. So, as the r1 starts to become lower, you know this graph starts to become closer to this linear curve and, when r1 goes below 1, what will happen is that, you have the curve going like this.

Now, remember when you are joining this 0 and ,1 this linear graph, that indicates capital F1 equals to small f1. So, whatever points are there, that indicates the composition of the copolymer, is equal to the composition of the comonomer. Now when your r1 has gone below 1, what is happening is that? Remember your r2 is constant at 0.5. So, if r1 keeps decreasing, then this multiplication is becoming closer and closer to 0.

So, when your r1 has gone below 1, the value of r1 then your curve goes like this. It somewhere it will always cross this straight line of capital F1 equals to small f1. So, you can see that this graph is for r1 equals to 0.5, this is crossing here, this straight line which is for capital F1 equals to small f1, which actually indicates all the points correspond to your copolymer composition is, equal to the comonomer composition.

So, in your real situation if your r1 is 0.5 and if it is going like this, if it is crossing in your capital f1 equals to small f1 curve. So, at this point, this is the point where you will have, a situation where your copolymer composition and the, comonomer feed composition are the same. So, this is the point. So, if you take a composition of the comonomer, that corresponds to this particular point. Then what will happen is that, this comonomer feed, will go into the copolymer, with the composition remaining unchanged.

So, when the copolymer is forming from the comonomer mixture, the composition remains unchanged. Whatever composition you took in the comonomer mixture, it goes directly into the copolymer formed, but when you are saying whatever composition, that composition is dictated by that particular point, when you take that composition. So, this is called as your azeotropic copolymerization. So, you know when you are talking about azeotrope, a certain ratio of the liquids, that goes into the vapor state and the vapor state composition does not change at all, that is azeotropic distillation. So, same way this is also azeotropic copolymerization.

So, if you look at the condition for azeotropic copolymerization, it is like this say, you are taking this particular equation for instantaneous copolymerization. So, dM1 divided by dM2 that will be equal to M1 by M2, because this is the ratio at which, you are taking your comonomer feed, the same composition will be maintained in the co polymer. So, this ratio, will then become equal to this, this is the condition for azeotropic polymerization and, if you elaborate this particular thing, it will become equal to, you know you have this expression of, dM1 divided by dM2 somewhere here, that I had drawn that will be this this expression. So, you equate this expression equals to M1 divided by M2.

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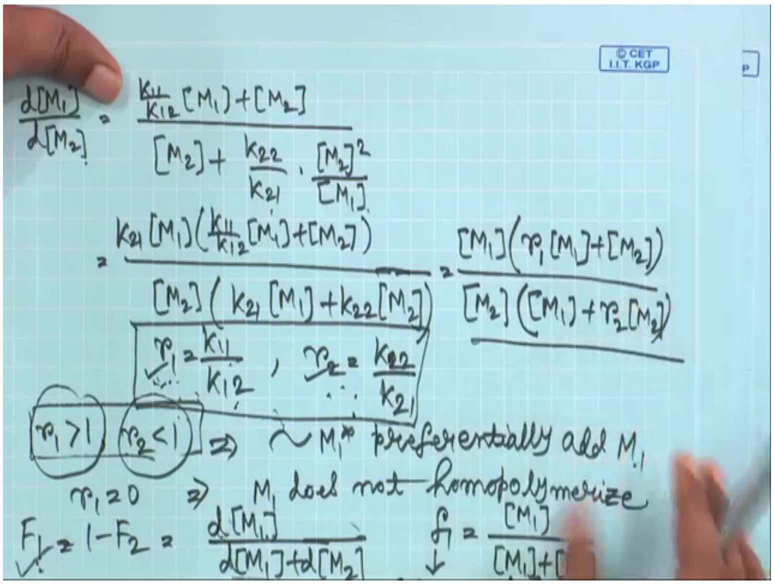

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}}{k_{12}}[M_1]+[M_2]}{[M_2]+\frac{k_{22}}{k_{21}}\cdot\frac{[M_2]^2}{[M_1]}}$$

$$= \frac{k_{21}[M_1]\left(\frac{k_{11}}{k_{12}}[M_1]+[M_2]\right)}{[M_2]\left(k_{21}[M_1]+k_{22}[M_2]\right)} = \frac{[M_1]\left(r_1[M_1]+[M_2]\right)}{[M_2]\left([M_1]+r_2[M_2]\right)}$$

$$\boxed{r_1 = \frac{k_{11}}{k_{12}},\quad r_2 = \frac{k_{22}}{k_{21}}}$$

$\boxed{r_1 > 1 \quad r_2 < 1} \Rightarrow \sim M_1^*$ preferentially add M_1

$r_1 = 0 \Rightarrow M_1$ does not homopolymerize

$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1]+d[M_2]} \qquad f_1 = \frac{[M_1]}{[M_1]+[}$

So, if you equate this expression with that. Then what you will get is M1 divided by M2 equals to r 2 minus 1, divided by r 1 minus 1 or f1 equals to 1 minus r2 divided by 2 minus r1, minus r2 this you can derive separately.

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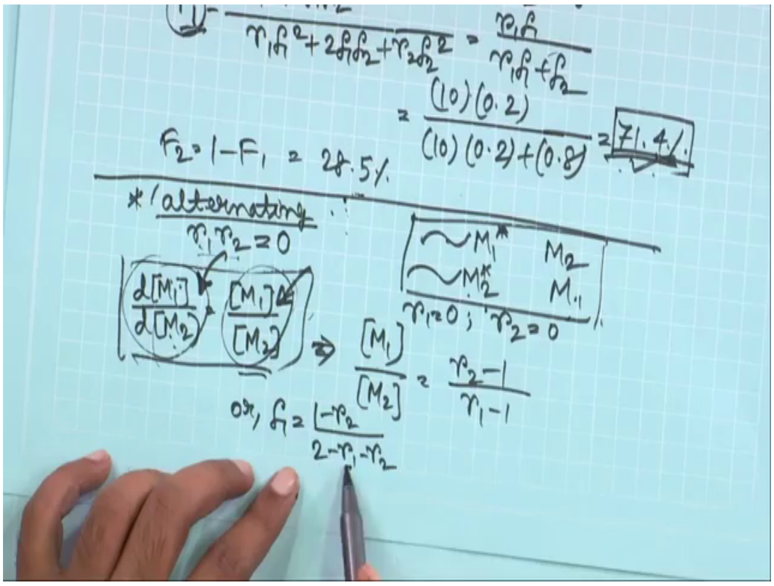

$$\frac{}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$$= \frac{(10)(0.2)}{(10)(0.2)+(0.8)} = \boxed{71.4\%}$$

$F_2 = 1 - F_1 = 28.5\%$

*/ alternating

$r_1 r_2 = 0$

$\sim M_1^* \quad M_2$

$\sim M_2^* \quad M_1$

$r_1 = 0;\ r_2 = 0$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \Rightarrow \frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1}$$

$$\text{or, } f_1 = \frac{1-r_2}{2-r_1-r_2}$$

So; that means, if both r1 and r2 value are less than 1, then there is a condition for azeotropic polymerization. And that condition will only be satisfied when you take, the mole fraction of monomer1 equal to this value, dictated by this value if you take the mole fraction of monomer1 as this, rest of the thing is your monomer2 1 minus f1 is your f2.

So, if you take this value, this mole fraction for monomer1, then that particular composition of the comonomer feet when you are copolymerizing, your copolymer composition will remain exactly, the same as the co monomer composition. So, this is your azeotropic copolymerization remember both r1 and r 2 value is the 2 less than 1.

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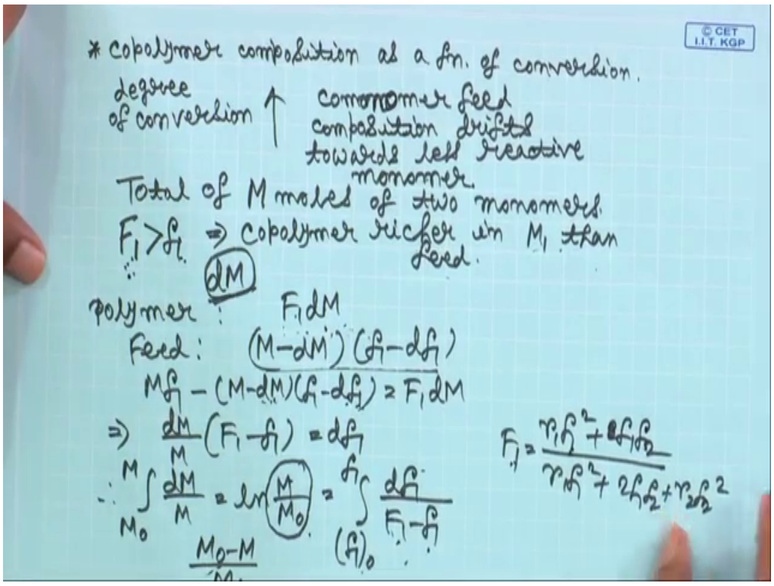

* copolymer composition as a fn. of conversion.

degree of conversion ↑ comonomer feed composition drifts towards less reactive monomer.

Total of M moles of two monomers.

$F_1 > f_1 \Rightarrow$ copolymer richer in M_1 than feed.

$\boxed{dM}$

polymer : $F_1 dM$

Feed: $(M - dM)(f_1 - df_1)$

$$Mf_1 - (M-dM)(f_1 - df_1) = F_1 dM$$

$$\Rightarrow \frac{dM}{M}(F_1 - f_1) = df_1$$

$$\therefore \int_{M_0}^{M} \frac{dM}{M} = \ln\boxed{\frac{M}{M_0}} = \int_{(f_1)_0}^{f_1} \frac{df_1}{F_1 - f_1}$$

$M_0 - M$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

Otherwise, that curve of the composition that, we had capital F1 versus small f1 that curve will never cross. That capital F1 equals to small f1 straight line which indicates that, line whatever point is there on that line, indicates composition of the copolymer is equal to the composition of the comonomer mixture.

Now, next what we want to talk about is, copolymer composition as a function of conversion. Now we are basically talking about all this instantaneous copolymer composition, that we are saying is at a very low conversion,

I have already talked about that. So, the comonomer feed composition remains relatively, unchanged under this situation, but what happens in real scenario? You keep on doing the copolymerization conversion to seats.

Now, if 1 of the monomers is more reactive, it is continuously going more into the copolymer. As I told you, if you have an ideal copolymerization, your r1 r2 equals to 1.

Suppose r1 is 10, r2 is 0.1 then more and more of monomer 1is going into the copolymer, we were already now until now we were satisfied with the instantaneous copolymer composition; that means, a very small percent conversion from your comonomer mixture that is all.

Now, the question is, what happens as the conversion goes on? This is a valid question because, if more and more monomer1 is going into the copolymer, then your comonomer mixture, which had a certain mole ratio of monomer1 and monomer2 to start with. This becomes you know, poorer in content of monomer1, because monomer1 is going into the copolymer. So, it becomes richer in content with respect to monomer2 so; that means, your comonomer composition is drifting with conversion.

So, if the comonomer composition drifts with conversion, correspondingly then your copolymer composition will also drift with conversion. So, you need then to understand, how the copolymer composition changes with conversion, you need some expressions for that which is not provided by your instantaneous copolymer composition equation, which we have been discussing until now. I hope this concept is clear with this.

Now, let us try to do an analysis as far as that is concerned. So, let me write it down like this. So, as the degree of conversion, goes up as it proceeds high towards higher degree of conversion, your comonomer feed composition, drifts towards less reactive monomer. We have already explained this.

So, let us say you have a total of, m moles of 2 monomers. You are starting with total of m moles of 2 monomers M1 and M2 and, your capital F1 is the mole fraction of the monomer1, that has gone into the copolymer, we are talking about instantaneous copolymer composition.

And, let us say your monomer1 is more reactive, then your capital F1 will be greater than small f1, because more and more monomer1 is now present, in the copolymer with respect to what is there in the monomer.

So, your copolymer actually richer in monomer1, than your monomer feed. So; this means copolymer richer in M1, then feed. This is the composition your copolymer is richer in M1 then feed. So, your mole fraction of monomer1 in copolymer is higher than, mole fraction of monomer1 in the comonomer feed.

So, let us say dM, is a number of moles of monomer that has been copolymerized. Total number of moles of monomers, of both the monomers have been copolymerized. So, dM is the total number of moles of monomer. So, the polymer. So, what is the number of moles of monomer1 present in polymer? Now it is f1dM because, total of dM moles have been converted. And f1 is the mole fraction, of the monomer1 in the copolymer. So, capital F on dM is the number of moles of monomer1 in polymer.

So, what is the number of moles of monomer1 in the comonomer feed? Now that will be m minus dM into small f1 minus small d f1, this is the number of moles of monomer1 in the comonomer feet. So, if you do a material balance then, Mf1 was the number of moles to start with, for the monomer1 in the comonomer feed and now, you have this many number of moles present, in the comonomer feet. So, this subtraction will be equal to the number of moles of the monomer present in the copolymer.

So, if you do the. So, you know you have, if you just elaborate this thing your dM df1 that will be cancelled because, these are 2 small terms and then ultimately if you rearrange, you will get something like this. Now if you integrate some the initial value of M0 to the final value of M, this is the number of moles not the concentration. So, dM by M will be equal to ln M by M0, that will be equal to integral, small f1 0 to small f1; that means, small f1 0 is the initial value of f1 and, the final value of f1. So, this will be df1 divided by capital F 1 minus small f1.

Now capital F1, already we know that capital F1 is nothing but, r1 f1 square plus 2 plus f1 f2, by r1 f1 square plus 2 f1 f2 plus r 2 f2 square. So, basically capital F1 can be calculated as a, function of f1 small f1 because, small f2 is equals to 1 minus f1. So, this capital F1 can be replaced here and this M by M0 is related to conversion because, conversion is nothing but M0 minus M by M0.

So, then as a function of conversion, we can actually find out from this particular equation, the variation in both the comonomer feed composition as well as the variation in the copolymer composition. So, this then gives you the overall idea about, what is the composition of the copolymer as a function of conversion?

So, that explains then we are now trying to understand little bit in a deeper way, how the copolymer composition changes? As you understand the logical way of the lecture, it goes from instantaneous copolymer composition. Very small conversion to the question, if you do the conversion continuously, the conversion goes to higher and higher value. How the copolymer composition changes? It is not the same as your instantaneous copolymer composition because, the composition might drift also. In order to know the system better, you have to actually have an idea of this drift, which system is becoming richer with, what? If your monomer feed mixture is becoming richer with one of the monomers, how does that affect your copolymer mixture? I mean the copolymer composition with time those things you need to know, otherwise you do not know everything about your system.

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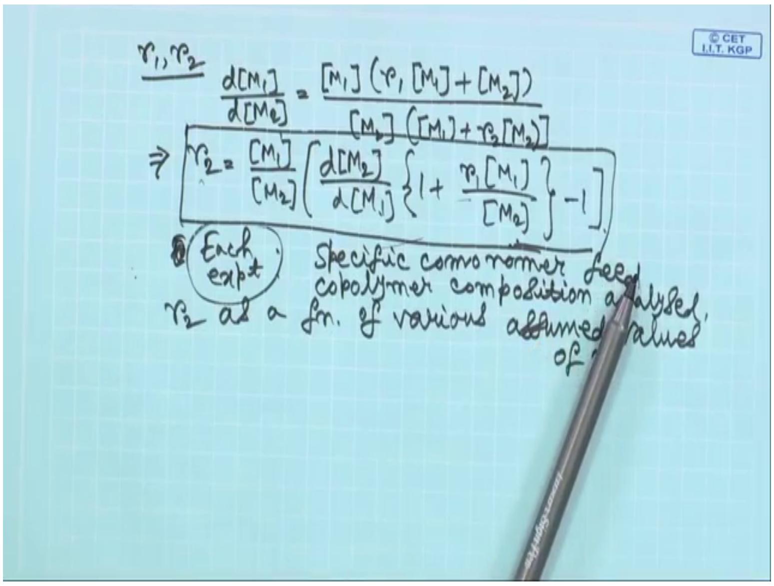

r_1, r_2

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])}$$

$$\Rightarrow \boxed{r_2 = \frac{[M_1]}{[M_2]}\left[\frac{d[M_2]}{d[M_1]}\left\{1+\frac{r_1[M_1]}{[M_2]}\right\}-1\right]}$$

Each expt. Specific comonomer feed copolymer composition analysed, r_2 as a fn. of various assumed values of

So, I hope that has explained this thing in little bit detail. Now the next question that we want to consider here is the following.

We have been talking about this r1 and r2, quite a lot and they seem very important going by, what I have been telling you the reactivity ratios of monomer and 1 and monomer2. But, I did not tell you about how to determine experimentally these values?

So, let us say we are trying to have an analysis towards that direction now, we will start with this instantaneous copolymer composition this expression, dM1 divided by dM2 equals to M1 into r1M1 plus M2 divided by M2 into M1 plus r2 M2.

Now, this particular expression, if you do the rearrangement you can write it down like this, I am not doing the full analysis you can work it out by yourself. R2 is equal to M1 divided by M2 into dM1, actually this dM2 goes here. So, dM2 dM1 into 1 plus r1 M1 divided by M2 minus 1. So, this is the expression of r2 here.

So, what you can do is that, your r2 and r1 are linear in this particular expression. So, you can plot your what you start with is you do separate experiments several experiments and, each experiment that you do, you start with a specific comonomer feed. So, you know the value of M1 by M2 this is a co monomer feed composition and then, after doing the reaction for a slight extent of converses less than 5 percent, you analyze the co polymer composition. And then that will give you a dM2 by dM1, you can directly analyze the copolymer composition.

Now so, copolymer composition analyzed. So, in this particular equation other than r1, you know then everything. So, these 2 are linearly related. So, what you do then you plot for each experiment, you plot r2 as a function of various assumed values of r1. So, you get a straight line.

Now, you do another experiment, where you change the comonomer feed and corresponding you see you get another copolymer composition. And then again, you put in this equation and then, again you plot r2 as a function of various values of r1. So, all these lines that you will get, the intersection of these lines will give you, the best values of r1and r2. That is how you can determine the values of r1and r2 from this particular system.

So, you start with a particular comonomer feed composition and, you do the reaction to less than 5 percent conversion, you analyze the copolymer, when you say feed you are talking about comonomer feed composition. So, you analyze the copolymer and then, you fit in this equation. So, your r2 is linear with r1 and, you put various assumed values of r1. So, you have a straight line accordingly, you generate several such straight lines, when you are putting different values of, to start with when you are saying, you are starting with a different comonomer feed. So, you will get corresponding copolymer composition and, you get another straight line. So many straight lines will come and then, the best feed values of r1 r2, the best values of r1 and r2, will be the intersection of these lengths. So, that will be the best values of r1 and r2.

Now, what I will go into in the next class is, to talk about the microstructure of the copolymer. So, what do we mean by microstructure of copolymer? We have already talked in detail about copolymer composition, we talked about the instantaneous copolymer composition, we talked about the comonomer composition feed. And we said that instantaneous is not enough, we have to understand how it conversion the copolymer composition is changing. So, we understood that also in terms of the you know, equations and all and then we have experimentally determined r1and r2. So, what else remains to be known, something very important that we have not talked about is, what we call as microstructure.

So, we know you have a system. So, your system may not be ideal copolymerization it may not be r1 r2 equals to 1; means it may not be r1 equals to 1, equals to r2. It may be r to some value and r1 some value say r1 is 10 r2 is 0.1, that is my pet value that I have already talked about, and I have explained all the things with that or maybe, you have an alternating copolymerization where r1 and r2, both are not equal to 0, but they are less than 1, but one of them is higher than 1, one of them is lower than 1.

So, the question then is, what is the sequence length distribution? Suppose your M1 has gone into the polymer and, M2 has gone into the polymer the 2 monomers. Now they are distributed, let us say you are talking about a random copolymer, let us say you are talking about an ideal copolymerization, r1 and r 2 are not equals to 1. They have some different values r1 greater than 1, r2 less than 1 then, the question is of course, say M1 which is more reactive, it will go in more proportion to the copolymer, but both of them will be placed in random placement.

So, what I would like to ask here is, let us say you are talking about a triad M1, M1, M1 when you say triad; that means, it is M1, M1, M1 unit, both sides they are M2. So, this is the separate M1, M1, M1 unit in the copolymer. How many such M1, M1, M1 units are? There in other ways what is the number distribution of this M1, M1, M1 units. What is the probability that we will have an M1, M1, M1 unit? Or the same way, what is the probability we will have a pintat M1, M1, M1, M1, M1? Or a (Refer Slide Time: 28:44) say, M1 M1 we can talk about M1, like this we could talk about M2 also like this.

So, even in random placement, they will have different proportions like this, because the reactivities are different. So, if you are talking about the diad (Refer Slide Time: 29:02) say, M1, M1 or say M2, M2. What is the distribution number of distribution? How many such (Refer Slide Time: 29:10) are there of M1, in the whole polymer chain on an average. How many triads are there? How many tetrads are there? How many n units consecutively together flanked by the other monomer both sides are there? This gives you the complete understanding of your copolymer composition. And that is what is necessary and, that is why it is necessary, to talk about what you call as microstructure or in specific terms sequence length distribution. So, this is precisely the thing that we are going to talk about in the next class, until then.

Thank you and goodbye.