

Polymer Chemistry
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Lecture – 21

Welcome back to this course on polymer chemistry. In this lecture, we will continue our discussion on chain copolymerization, which we began in the last lecture and the lecture before.

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Lecture 21: 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 in radical copolymerization
- Q-e scheme
- Ionic copolymerization (in brief)
- Application of copolymers (in brief)

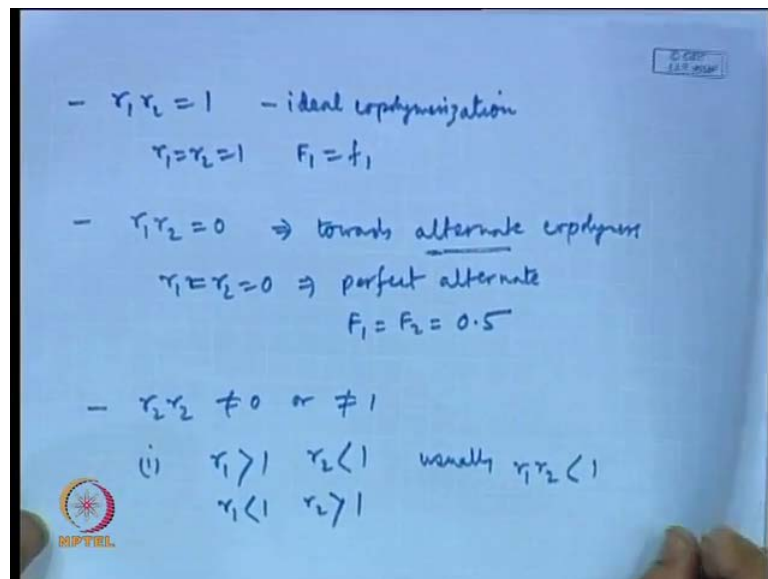
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Now, we have talked about different types of copolymers, random copolymers, (()) copolymers, alternate copolymers, block copolymers. Then, we talked about importance of copolymerization in last lecture, how we can improve the property of an existing homo polymer by introducing another co-monomer in the polymer. Then, we talked about copolymer composition equation.

We applied simple model of terminal model, where we basically we are talking about how the composition of copolymer can be predicted from the reaction, reactivity monomer reactivity ratios. We started our discussion on different types of copolymerization. Then as a result of different types of copolymerization, what are the different types of copolymer micro structure possible? We started and we are half way in that discussion.

So, we will start from this today and then move on to composition drift in a copolymer as we go on increasing the conversion in the copolymerization reaction. Then, monomer reactivity, how it depends on the different modes of chain initiation and then talk about effect of structure on reactivities, mainly in radical copolymerization. We will discuss Q-e scheme and then briefly discuss the ionic copolymerization. Then, invariably we will talk about application of the copolymers, we are talking about. Now, we continue the discussion we are having in last lecture.

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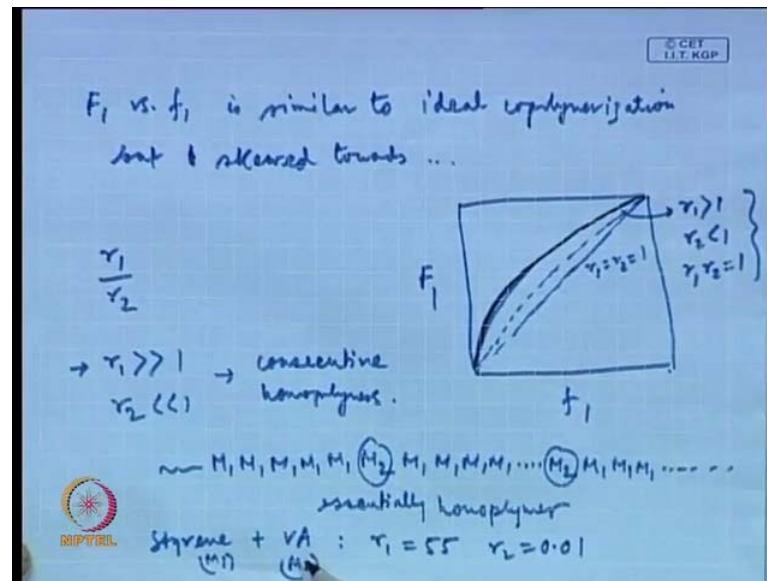


You know we have talked about different types of copolymers. For example, we have talked that in first case, if your $r_1 r_2$ is 1 it gives us ideal copolymerization. Now, this happens if the monomers have very similar structures and most of the ionic polymerizations also follow this type of behavior. There is a special case, which where both $r_1 r_2$ are 1. In that case, we have seen that F_1 is mole fraction of the monomers same as the mono fractions in the feed.

We have seen the second type, where this product is equals to 0 and which gives towards alternate copolymerization. As a special case, where $r_1 r_2$ both are 0 is perfect alternate copolymer, where basically f_1 , so as f_2 is 0.5. The closer this ratio $r_1 r_2$ to 0, it is the resulting copolymer will be more towards alternate. Now, we will talk about the third option possible, where r_1 multiplied by r_2 is neither 0 nor neither 1.

Now, this is first possibility, where one of the monomer reactivity ratios is more than 1. Another would be obviously less than 1. It could be the other way as usual. It could be r_1 could be less than 1 or r_2 could be less than 1. Usually these products, this product is less than 1. In some cases, they are slightly above 1 and possible and in the usual copolymer reaction. Now, in this case, what happened?

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The F_1 versus f_1 monomer composition curve is similar to ideal copolymerization, but skewed, but skewed towards the composition of the copolymer richer in the repeat unit resulting from the more reactive monomer. So, it is similar to the ideal composition copolymerization. If I plot F_1 with f_1 , in case of ideal, we have seen that is r_1 is r_2 is equal to 1. This is r_1 greater than 1, r_2 less than 1. What r_1 r_2 is equal to 1? Now, if this is not equals to 1 and if r_1 is the more reactive monomer compared to r_2 , M_1 is the more reactive monomer compared to M_2 , and then it will be skewed. This was for ideal.

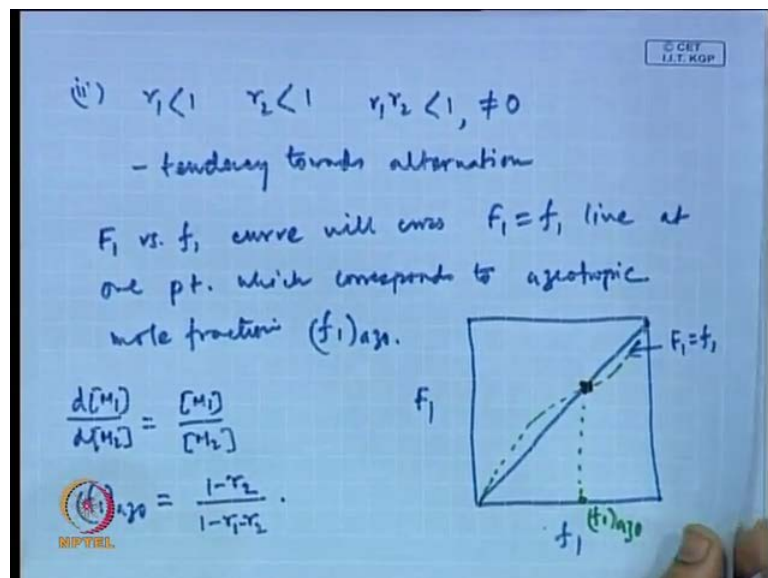
Then, it this will be skewed towards, it will be skewed towards the more reactive monomer. The higher this ratio, this r_1 by r_2 , the higher this ratio of r_1 r_2 , the higher the longer is the continuous sequence of M_1 type monomer in the copolymer and shorter is the sequence of the M_2 , M_2 monomer. So, if this is higher means the M_1 will have a longer sequence in the copolymer, and M_2 you have a shorter sequence in the co

monomer. In extreme case, if r_1 is very high and r_2 is very, very low, then the tendency would be to make consecutive homo polymers because this is very high.

Then, you will get something like and r_2 is very small. So, in some cases, you might get M 2 getting in and then again may be one more at M 2. So, basically M 1 will have a much higher tendency to more polymerize, whereas M 2 has little tendency to move polymerize. Whatever tendency it has to react, it will make copolymer towards copolymer. So, if the situation is like this, then you are going to get a polymer like this, which is essentially a homo polymer because it is mostly M 1 with sometime M 2 here and there entering in the copolymer.

Example is that styrene and vinyl acetate. I write VA. The ratio of reactivity ratios are r_1 if this is M 1, this is M 2. r_1 is 55 in case of radical polymerization and r_2 is 0.01. This is for a radical polymerization. So, basically styrene have much higher tendency to homo polymerize compared to copolymerized with vinyl acetate, where as vinyl acetate has very little tendency to homo polymerize. So, you will get essentially homo polymer of styrene at the beginning at the beginning. Then once the styrene is consumed, and then you will get the homo polymer of vinyl acetate.

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Now, the second options in this case would be where r both both r_1 is less than 1 and r_2 is less than 1. Now, obviously $r_1 r_2$ is less than 1, both not equals to 0. Now, this because both of these are less than 1, so both of these monomers have a tendency to

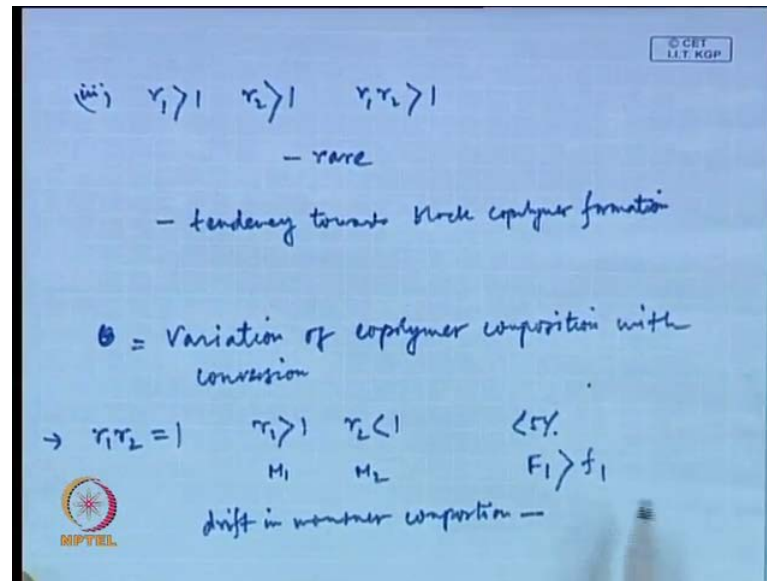
more tendencies to copolymerize compared to homo polymers. As a result, there would be tendency to towards alternation rather than forming homo polymers. F_1 versus f_1 curve will cross; F_1 is equal to f_1 curve line rather at one point, which corresponds to azeotropic mole fraction f_1^{azo} .

Now, again if I plot, so that is the line corresponds to $F_1 = f_1$ which happens when $r_1 = r_2 = 1$. Now, in this case, if both are less than 1, you will get a line like this which will cross over in this point. So, this composition is corresponding to f_1^{azo} . Now, the term azeotropic mole fraction is coming because we know azeotropes were mole fraction of 2 liquids in vapor phase equals to the mole fraction of the 2 liquids in liquid phase.

Basically, the liquids, 2 liquids actually vaporized in the same mole fraction in the vapor phase. So, here the composition in the free monomer is same as in the co-polymer, copolymer. So, if you take a particular composition and polymerize, then we will get always the same concentration or same composition of the co-polymers. Here and if I write this, so in this case, the M_1 now at this point, the copolymers and the feed compositions are same. Co-polymers occur without changing the composition in the feed ratio.

That is why we call this as an azeotropic composition. We can get these from our r_1 r_2 expression we derived in the last lecture as this. So, if you know the reactivity ratios r_1 r_2 , then we can get the azeotropic composition at which we can get an azeotropic co-polymerization. So, if you do a co-polymerization starting for a composition monomer composition here, then the corresponding copolymerization will be termed as azeotropic co-polymerization. Now, there is a third possibility in this set.

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Here, you have both r_1 and r_2 greater than 1. Obviously, $r_1 r_2$ would be greater than 1. Now, in this is very rare. It is not very usual thing observed for a monomer pair, but if that is the case, then both the monomer has a greater tendency to homo polymerize compare to copolymerize. So, these would be having tendency towards block copolymer formation. Now, basically we have covered almost all possibilities of different combination of r_1 and r_2 values.

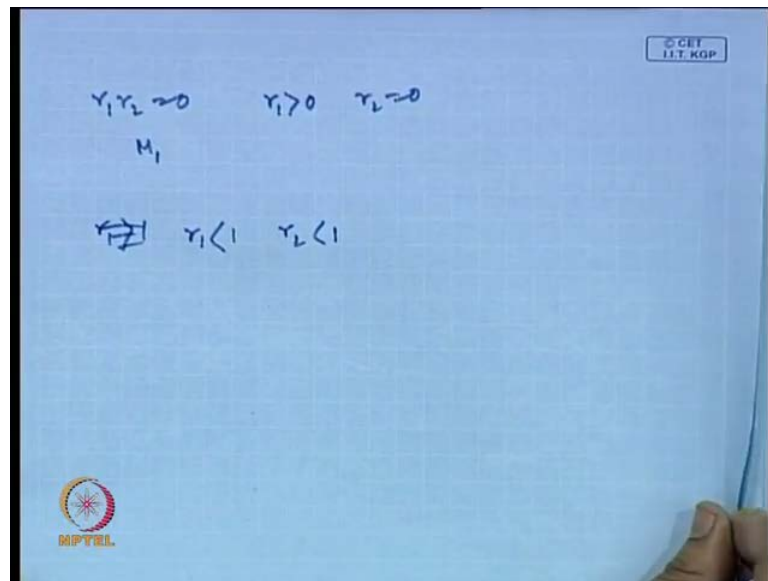
Now, let us see how these different types of copolymers would result in a variation in composition. So, how this different set of values of $r_1 r_2$, how that would be changing the combination of our copolymer composition with conversion? Now, if we take say an ideal copolymerization where $r_1 r_2$ is 1 if r_1 is higher than 1 and r_2 is less than 1, then 2 monomers will get into the chain in random fashion, but monomer M_1 will be entering in the chain at the faster rate as compared to M_2 .

This means in the beginning of the reaction, if we stop the copolymerization reaction, at this lower say less than 5 percent conversion, and then you will get a copolymer, which is having a higher mole fraction of the M_1 unit in the copolymer compared to that is in the feed. So, as a result, what will happen? With time, with conversion, the monomer composition the monomer composition will have less and less M_1 because M_1 is getting incorporated in the chain in faster rate. So, you will have a drift in drift in

monomer composition with time. As a result, you will get drift in the copolymer composition as well.

So, if you want to avoid this drift in copolymer composition, you should be restricting your copolymerization reaction to very lower level of conversion, so that the feed ratio the monomer ratio in the reaction medium does not alter too much compared to the feed ratio. Now, if you compare the other cases like r_1 and r_2 is 0.

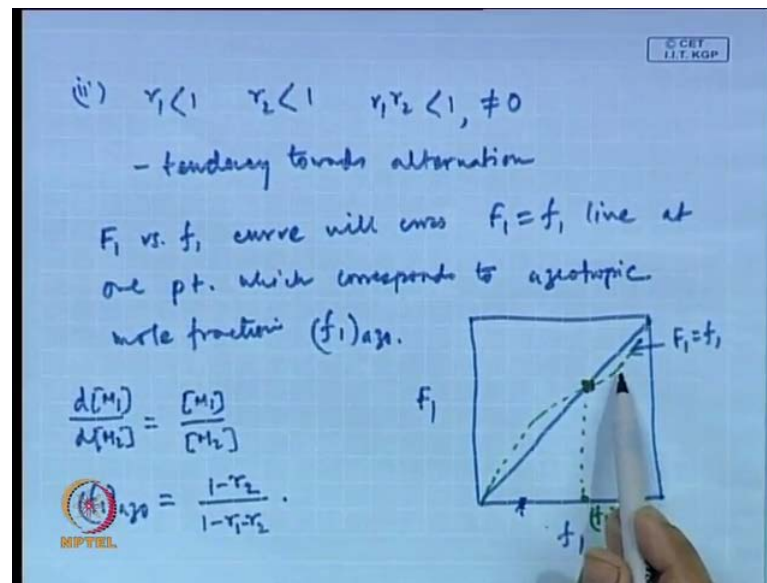
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Now, in this case because this is a more of an alternate copolymer as long as that more reactive monomer in this case say, r_1 is greater than 0 and r_2 is 0. As long as M_1 is remaining in the reaction medium, they will form alternate copolymer, but once M_1 is consumed, even if there are free M_2 present in the reaction medium, they cannot undergo homo polymerization because r_2 is 0. So, basically at the end in during the most of the reaction time, you will get same composition of the resulting copolymers. At the end, if there are excess M_2 , you get free monomers. If you start with excess M_1 , then at the beginning, you will get alternate copolymers.

When M_2 is getting over all the M_2 is getting incorporated in the copolymer chain, you will get rest of the M_1 s, which is remaining. They will homo polymerize. So, you get an alternate copolymer at the beginning. At the end, you get a homo polymer of M_1 . If you talk about the case, we just talked about say r_1 less than 1 and r_2 is also less than 1, what will happen?

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Look at this plot versus mole ratio mole percentage in the copolymer. In the monomer, if you start from a composition here say, this point because M 1 is getting incorporated faster. So, in this case, below this point before this point, M 1 is getting incorporated in the chain faster.

After this point, it is M 1 is getting incorporated in a slower rate. So, what will happen if you start from this point? The M 1 will get incorporated in the chain at a much faster rate. So, eventually, the concentration of M 1 in the reaction, M 1 monomer in the reaction will come down to 0. If you start a point somewhere above this point, then less fraction of M 1 would get into the chain. As a result, slowly with combustion, the concentration of mole fraction of M 1 monomer in the chain in the reaction medium would be going to 1.

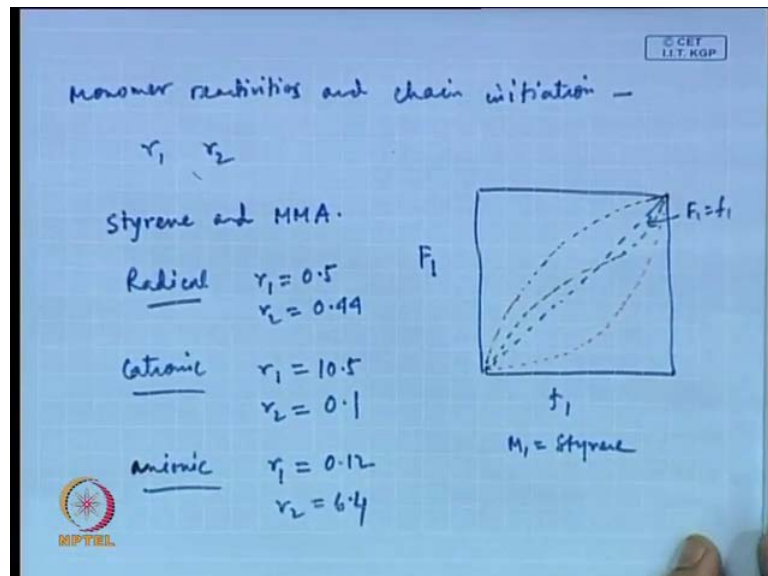
So, in this case, you you actually go through with composition, where M 1 in the M 1 the mole fraction of M 1 in the reaction medium either 0 or 1. So, accordingly, you will get drift in the copolymer composition as well. So, these are the some examples, which we are, which you can which you can now convince that there is a tendency in this copolymer. In the most, most cases except when r_1 is r_2 is equals to 1 or r_1 and $r_1 r_2$ is 0. In case of these cases, you have a drift in the composition as you increase the conversion or as the reaction progresses with time.

So, what is usually done in in practice industry in most of the applications is require that you cannot have this much of drift in the composition of your polymer sample. There is a basically, there is a control over the composition in the entire polymer sample is required. So, what is done in practice? Either you start the reaction from a known a feed ratio or stop the reaction at a very low conversion say less than 5 percent, but that is not very practical.

Then, you have to take out the polymer from that monomer mixture and restart the polymers and so on. So, that is not very practical. So, what is practically done is basically you you add the more reactive monomer, which is getting incorporated in the chain mass in a faster rate. That monomer is added in a controlled manner in the reaction medium.

So, in effect, you basically fix or you you basically remain or maintain the feed ratio, the monomer of M 1 and M 2 unchanged during the inter polymerization so that the copolymer composition also does not change during the inter polymerization. So, you basically get homogenous polymers. Now, let us talk about that, monomer reactivity, reactivities and chain initiation.

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Now, we have seen that the disc scheme what we have been talking till now is valid for radical initiation or ionic initiation, but this values, the set of values for r 1 and r 2, they are almost independent for a radical initiated chain copolymerization, but the values of

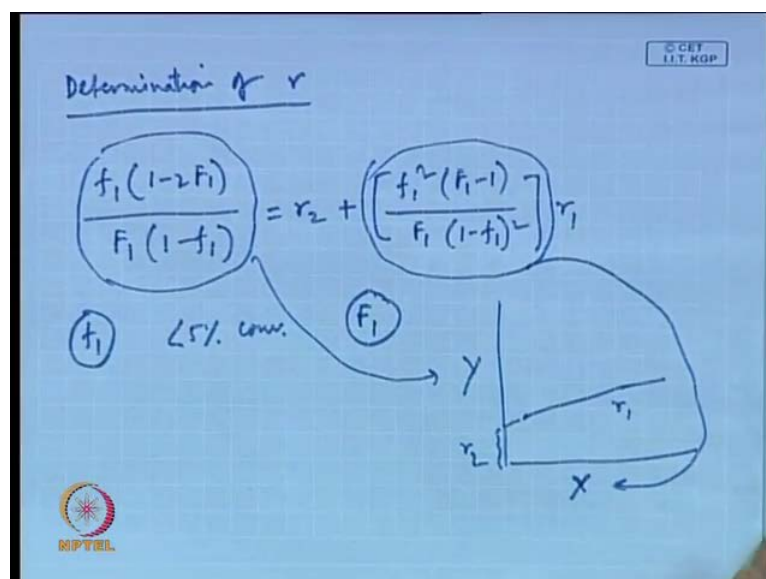
individual r_1 and r_2 could dramatically change if the mode of initiation is changed. For example, if I take a set of monomer like say, let us take an example of styrene and MMA, methyl methacrylate radical. They have more or less similar reactivity.

So, r_1 has 0.5 and r_2 is 0.44. So, if I plot that f_1 where M_1 is styrene. F_1 that is the line corresponds to F_1 is f_1 . Now, in case of radical copolymerization of styrene and MMA, it would look like something like this. As you can see from this, r_1 is also less than 1 and r_2 is less than 1, but their re-activities are not very different. Now, if you do a cationic polymerization, then obviously styrene is much more reactive compared to MMA in a cationic polymerization. So, you get a curve like this.

So, in case of cationic, r_1 is 10.5 and r_2 is 0.1. In case of an ionic, you get the other way round because in case of an ionic, the reactivity of methyl methacrylate is much faster compared to styrene. So, with this, this page shows that for a given radical reaction, you know this r_1 and r_2 values are almost same. You know they do not change too much with reaction conditions like temperature and reaction medium, but if we have different chain initiation mode.

Then obviously the react monomer reactivity ratios will differ, will dramatically different, which depends on the stabilization of the resulting active center. Obviously, for these ionic, this also may depend on the solvent polarity and the counter and so on. Now, how do we determine this r_1 and r_2 experimentally we have been talking about?

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So, determination of or evaluation of reactivity ratios, so I write just like r . Now, as we, as I mentioned earlier also that this expression is we talked about this expression in the last lecture. It this is valid for no numerical number of set of monomers or pair of monomers irrespective of whether the initiation is done by radical or ionic. So, we can use this expression and from that, we can actually get the value for r_1 and r_2 . Now, this expression can be rearranged and written like this.

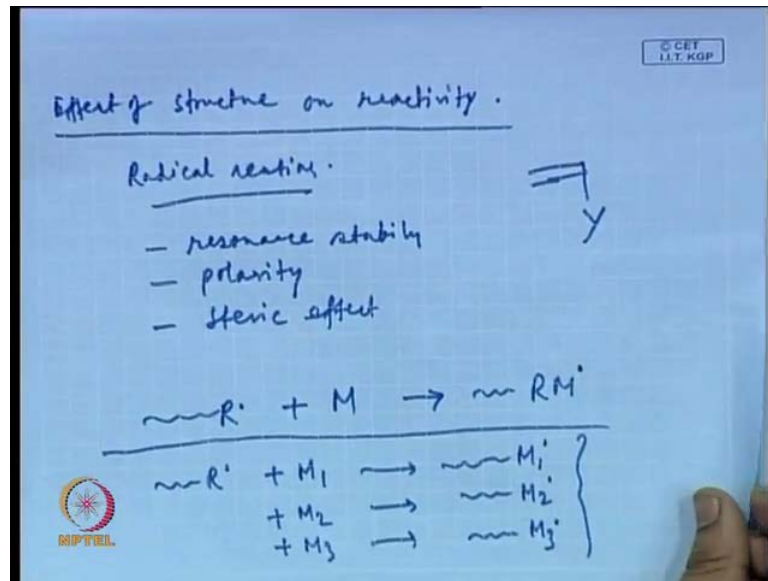
The same expression, which I just showed in the last page, we can simply do mathematical rearrangement and get an expression something like this. Now, what is what can be done is basically you do several reactions. Start with different f_1 values. You take feed monomer ratio with different f_1 values and stop the reaction say less than 5 percent conversion and quantify the amount of mole fraction of the monomer unit present in the copolymer at the end of this 5 percent or when you stop the reaction.

You can do it by spectroscopic thing mix like enema, UV or IR or even for more sophisticated cases; you can actually radio level the monomers. Actually, from the radio activity measurements, you can actually get the incorporation of individual monomers in the copolymers. Feed ratio, you can get from the like normal chromatographic analysis like h p as n g c. So, what you have now for a different state of f_1 ? You have values of capital F_1 . So, you make a plot where you put these in y axis this one and put these in x axis.

So, the slope would give you r_1 and the intercept should give you r_2 . So, that is one of the ways you can determine from experimental value, experiment different experiment with different feed ratio and stopping the reaction at low conversion and then measuring the mole fraction of different monomers in the copolymer, but this is a old method. Now days, these are not practiced. In the lab, there are more sophisticated statistical method and which are computerized.

They are used to determine r_1 and r_2 . We are not going into detail of those methods, but essentially, the concept or the principle of determining r_1 and r_2 is similar, where you do the reaction in different feed monomer ratios and then stop the reactions at low conversion and get the copolymer composition. Then, do from that, you can get the reactivities of the monomer reactivity values of r_1 and r_2 . Now, let us talk about the effect of structure monomer structure on reactivities or reactivity ratios.

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Monomer reactivity ratios (Radical copolymerisation)

M ₁	M ₂	r ₁	r ₂	r ₁ r ₂
	acrylamide	0.87	1.37	1.17
acrylonitrile	butadiene	2.0	0.1	0.2
	MMA	0.84	0.83	0.7
	styrene	0.01	0.4	0.004
	vinyl acetate	6.0	0.07	0.42
Maleic anhydride	acrylonitrile	0.0	6.0	0.0
	Methyl acrylate	0.02	3.5	0.007
	Styrene	0.005	0.05	
	vinyl acetate	55	0.01	0.55
styrene	α-methyl styrene	2.3	0.38	0.87
	monochloro tri-fluoro-ethylene	1.0	1.0	1.0
	vinyl acetate	1.35	0.65	0.88

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Now, before I going to this, let us show you some number of just to say these are tabulated from known values. Now, these are the some of the numbers of different r₁, r₂, r and their product as well. So, for example, if you compare maleic anhydride and styrene, individual individual r₁ and r₂, they are very close to 0. So, basically they do not have a tendency to homo polymerize when they are together. So, there is is a tendency to copolymerize all the time.

Now, when the structures are quite similar like this tetra fluoro ethylene and ethylene or tetra fluoro ethylene and mono chloro tri fluoro ethylene, their structures are very similar. So, their reactivity ratios are almost close to 1. So, they basically give a perfect ideal copolymerization. If you take a case like acrylonitrile and butadiene, then this is this is a higher number. This is a lower number. So, butadiene acrylonitrile has more tendencies to homo polymerization and butadiene will have higher tendency to copolymerization.

So, you essentially get copolymer at the beginning. They will be rich in the monomer may be right from acrylonitrile and once acrylonitrile is consumed, then you will get homo polymers of butadiene. So, basically you can get this r_1 and r_2 numbers from any standard literature and from there, you can compare this $r_1 r_2$ values and their product to get idea about how about the reactivities of the different monomers and the resulting copolymer. How the nature is, the microstructure of the copolymer from definite pair of monomers and the possible drift in the copolymer composition from these values of r_1 and r_2 .

Now, let us go back and see the effect of structure and reactivity. Now, in case of radical, first talk about the radical reaction. Now, in case of radical reactions, these copolymer reaction rates would depend on like resonance, resonance stability of the monomers or the substituent, which is present. So, basically if I talk about the monomer like this, then the ability to of the Y group to stabilize any resulting radical and then polar polarity polar effect. How these double bond is polarized, is it the electron deficient or electron rich and steric effect? Basically, it is steric effect of the substituent group.

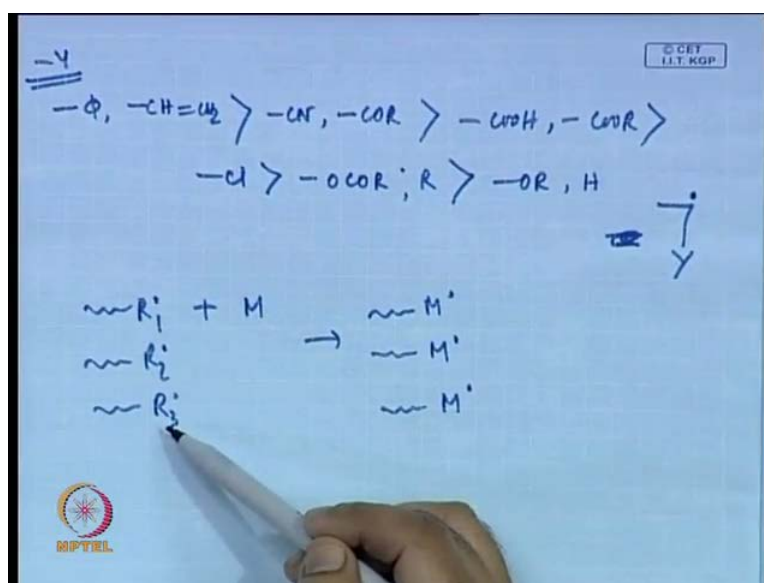
Now, what is the reaction in a in a in a basically copolymerization or radical reaction? You have radical and you have that is reacting in monomer to form another radical. So, if you want to compare reactivity of different monomer to a particular radical say, if you in this case, if I fix this radical, this polymer radical or propagating radical, let us fix this and then if I want to compare different monomers, how the reactions will look like?

So, let us keep this intact and M_1 , this will lead to $M_1 \cdot M_2$. This will lead to $M_2 \cdot$. So, what it essentially means? If you want to compare the reactivity of these different monomers, M_1 , M_2 , M_3 towards a particular radical, essentially dictate by

the stability of these 3 propagating radicals. If the propagating radical is more stable, then the reaction will go towards right hand side. If it is not that stable, then reaction will not tend to go towards right hand side.

So, basically the reactivity of different monomers towards a particular radical will depend on the stability of the resulting radical from that monomer. So, higher the stability, higher is the reactivity. So, if I want to rank different monomers, I have to rank according to their ability to stabilize.

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So, if I write Y phi, this has very strong stabilization effect on the radical. Then, this follows the ability of these substituent groups to stabilize the radical generated from this monomer. So, basically in this case, this has the least ability to stabilize a radical. If Y is H or Y is OR, that has the least ability to stabilize this radical. So, they have least reactivity towards a particular polymer radical. Now, this has a very high ability to stabilize this radical. So, they have a much higher reactivity towards a particular radical.

Now, if I want to compare the reactivity of the radicals, see if I want to compare reactivity of different radicals with a single monomer, then what it will give? So, in all the cases, it will produce the same radical. So, the stability of this resulting propagating radical will be same. Hence, the reactivity order of these different radicals towards a monomer will be inverse towards the stability of this radical.

So, the monomer which is or the radicals which is least stabilized, they will have the highest reactivity towards a particular monomer. So, in this case, the order of reactivity of the radical will be exactly reverse for what we just solved for the reactivity of monomers towards a single radical. So, one more time, this is this this order will follow for the reactivity of this monomers towards a given radical. Now, the radicals from these monomers will have exactly the reverse order, when you compare their reactivity towards single monomers. Now, let us compare some numbers.

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Rate constants (k_{12}) for Radical-Monomer Reactions:

Monomer	Polymer radical			
	Styrene	MMA	acrylonitrile	vinyl acetate
1,3-Butadiene	280	2060	98000	230000
Styrene	165	1130	13100	154000
MMA	314	515	46000	46000
Acrylonitrile	413	422	1960	18100
Vinyl chloride	9.7	52	720	2300
Vinyl acetate	3.4	26	230	2300

$$R_1 + M < R_2 + M_2 < R^* + M < R^* + M_2$$

$$\text{Sty}^* + \text{VA} < \text{Sty}^* + \text{Sty} < \text{VA}^* + \text{VA} < \text{VA}^* + \text{Sty}$$

$M_1 = \text{Sty}$
 $VA = M_2$
 $r_1 = 55$
 $r_2 = 0.01$

This is the rate constant for radical monomer reactions for different monomers and different polymer radical. So, if I compare different monomers with a particular radical say like styrene in this case or MMA in this case, so you will see that these numbers lower in this, which means the order of reactivity of these monomers following this order, which we just showed in the last page for a particular radical.

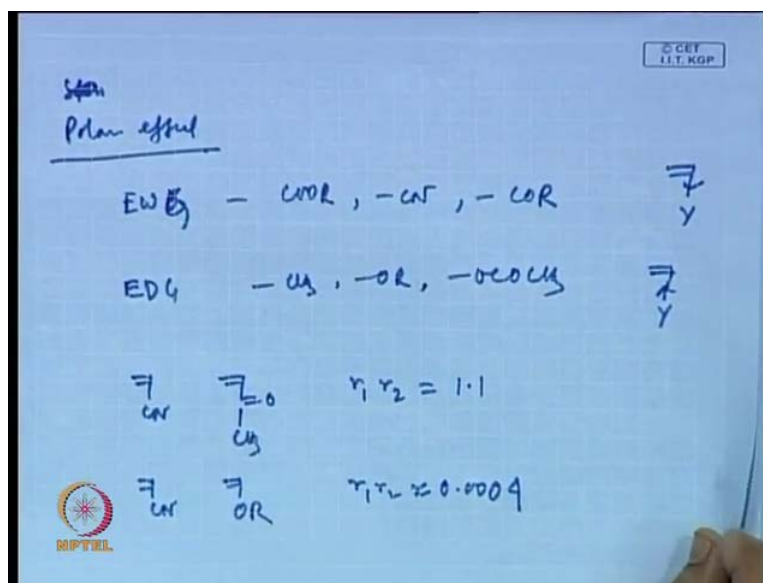
So, if you are doing reaction of this monomers towards say styrene radical, then they will follow this strength and the radicals towards a particular monomer, say like say acrylonitrile. All the radicals will follow the reverse strength. So, vinyl acetate will have the highest reactivity compared to the other polymer radicals for particular monomers. So, in this case, if I take acrylonitrile, vinyl acetate has much higher reactivity compared to acrylonitrile and methyl methacrylate and styrene.

So, basically if I want to compare, differentiate where you have a stabilized radical and a not stabilized monomer, stabilized radical plus a stabilized monomer, a not stabilized radical and not stabilized monomer, not stabilized radical and a stabilized monomer. Now, in this case, you have the highest reactivity, most stable monomer. A stabilized monomer will have more reactivity towards a particular radical and radicals, which are unstabilized. They will have higher reactivity towards a particular monomer.

So, the reactivity order would be this. So, if you compare the reaction of styrene plus vinyl acetate, this radical form vinyl acetate high reactive and in this case, styrene monomer. So, this is a vinyl acetate radical plus styrene monomer, vinyl acetate radical plus vinyl acetate monomer, styrene radical plus styrene monomer, styrene radical plus vinyl acetate monomer. A stands for stabilize. So, styrene is stabilized monomer and styrene radical generated from styrene is a stabilized radical.

So, this will have highest tendency. So, if we have a vinyl acetate radical in the reaction medium, then it will always copolymerize. If you have styrene radical in a medium, then it will always homo polymerize. So, basically if you have a reaction radical reaction, radical copolymerization between styrene and vinyl acetate, these are the 2 products of the reaction propagating dominantly. So, it will be homo polymers of styrene and some alternate of copolymer of vinyl and vinyl acetate and styrene. That is why the reactivity ratios are so different. M 1 is styrene and vinyl acetate is M 2. Now, these are these are all about steric resonance effect. You can also have steric effect polar effect.

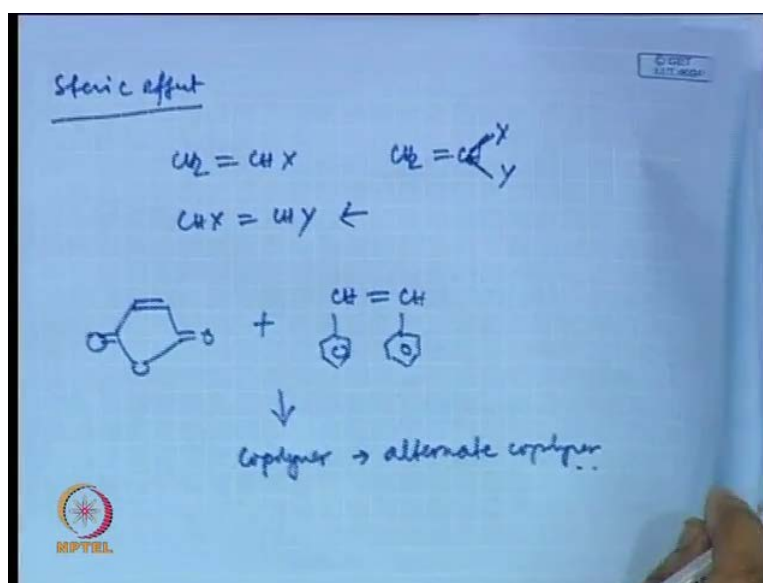
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Let us talk about the polar effect first. Now, if you have electron withdrawing groups like in the monomers like say COOR, CN or COR, you could have electron donating group like CH₃, OR. If your electron withdrawing group, then this double bond will be electron deficient. So, basically there will be effectively positive and if you are electron donating group, basically it will be electron rich double bond. So, if you have monomers which are very different in their polarity of the double bond, then they will tend to form alternate copolymers.

If you have similar polarity, then they will tend to form an ideal polymerization. So, if I compare acrylonitrile and say methyl phenyl ketone, then they will have almost ideal polymerization copolymerization. If you compare taking to different groups, where they are this electron deficient and this is electron rich, then they will tend to be forming alternate copolymers. So, if you choose 2 sets monomer from 2 different sets, then they will form alternate copolymer. If you choose monomers from same sets, then they will tend to form a ideal polymer.

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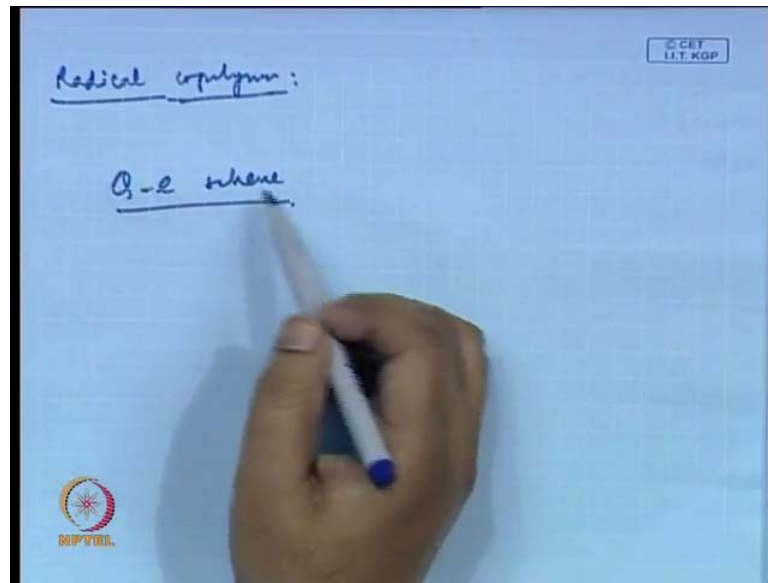


You can have also steric effect affecting the monomer ratios. For example, if you have like compare these two, this basically have very low reactivity because they are 1, 2 substituent. If you compare these with X and Y, then this steric does not play much role. Then, the resonance stabilization actually raditive, when they are present in a same carbon atom whereas, they are 1 2 substituent, then steric actually have a very detrimental effect.

So, reactivity actually comes down very much. Now, some cases, this polarity, this steric effect, the polarity effect actually can help in polymerize or we overcome the steric effects. For example, if I take a monomer of this sort. Like take maleic anhydride and stacked Sullivan. Because of steric effect, these 2 individual monomers, they cannot homo polymerize because they are 1 2 substituent. They are steric problem. But, their polarity is different. This is highly electron deficient and this is highly electron rich.

So, what happens? These polarity effects actually help them to form copolymer. They will be from different groups as we mentioned from electron donating groups and withdrawing groups and one from electron donating groups. So, you will have alternate copolymer forming just to give you some number about the steric effect. If I take, let us keep that for time being.

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Now, in case of radical polymerization, in radical copolymerization, the reactivity does not depend too much on the reaction medium. However, if because of the medium, if the availability of monomers are different, then they actually affect or they affect their availability in copolymerization. As a result, you can get effective different composition, which is not predicting from their r_1 and r_2 values.

For example, if we have two monomers and then copolymerize them in ball power solution, then compare their copolymerization behavior in heterogeneous polymerization system like emulsions or suspension. Then, what happens there is some time, there is a possibility that one of the monomers will preferably partition in the core for say emulsion polymerization. If the partition is more for one of the particular monomer, then that monomer will be available for copolymerization more, than the other monomer.

So, basically increasing reactivity ratios may not be different. But, because their availability in terms of copolymerization is different, as a result, their partition ability in the reaction point or the reactor, then the r_1 and r_2 might be different, r_1 and r_2 could be different if the monomer structure changes. For example, if you have Carboxylic acid like acrylic acid and then compare its copolymerization behavior over acryl amide, then we change in ph of the medium.

If there is acidic ph, for example, ph 2, then acrylic acid remain as COH and if it is a basic ph like ph 9, then we have a COO minus group. As a result, you have different

monomers altogether. You have the reactivity to be different, the r_1 and r_2 values for acrylic acid would be different at different pH. If there, the copolymer is not soluble in the resulting monomer, then also there could be a complicated behavior of the 2 reactivity ratios.

Now, what we are going to discuss next is the Q and e scheme. Now, because all these, there are 3 different type of effectives. We have just studied resonance effect and polarity effect and steric effect, which might alter the reactivities of the different monomers. It is very difficult to predict. They are very complicated. They are very difficult to predict or estimate the reactivity ratios and as a result copolymer composition from given monomer structures.

So, what is done is a semi empirical scheme. This Q e scheme, which basically takes care of the resonance stabilization and the polarity part and basically have values for different monomers and from that values, we can actually predict the copolymerization behavior of the 2 different pair of monomers. Now, what we will do in the next lecture? We will start from this Q e scheme, briefly talk about this and briefly talk about the ionic copolymerization and very briefly on the application part of this copolymerization and start. Now, in the second half of that lecture, we will start the ring opening polymerization.