Science and Technology of Polymers
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Lecture - 6
Principles of Polymer Synthesis

I expected a question from you that is, what happens during synthesis of an ester from a simple alcohol, a simple acid and synthesis of a polyester from a di alcohol and a di acid. I mentioned that this polyesterification reaction occurs in large number of intermediate steps involving many intermediates. That means, I wanted to know from you is there any this question, is there any influence of there any influence of size of the reactive intermediates on the polymerization kinetics?

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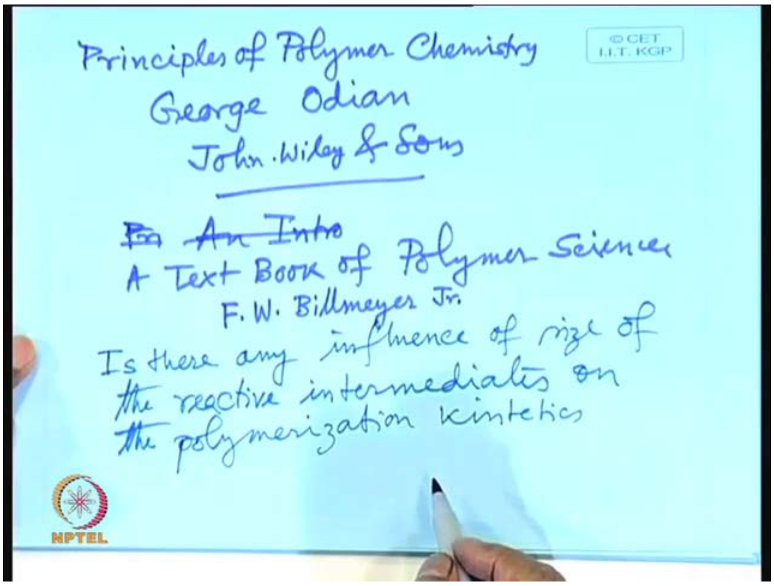

Principles of Polymer Chemistry
George Odian
John Wiley & Sons

~~An Intro~~
A Text Book of Polymer Science
F. W. Billmeyer Jr.
Is there any influence of size of the reactive intermediates on the polymerization kintetics

Then, what is that influence?

Student: (( ))

Yes.

Student: (( ))

Then ultimately, what will happen? Reactivity of the intermediates will gradually decrease. Then, one cannot expect a very high molecular rate. That is not the situation, no. No sir, you are wrong, please deliver it on this point after the class, after the class in your hostel or anywhere among you. Is there any influence of the size of the intermediates on the reactivity of the functional groups of intermediates? When it starts there are functional groups of carboxyl and hydroxyl, they are reactive to each other. (( )) that intermediate length that means the distance between two carboxyl and hydroxyl groups on carboxyl hydroxyl groups increase, increases in either the reactivity of the end groups will remain same or change. that is the question, that is the question.

Student: (( ))

That you have to ensure.

Student: (( ))

You can say, I can say, but it is to be proved, It is to be proved so I am giving you a clue you go through this audience book, there are some results and data given using some compounds of homologous higher series of gradually higher molecular rate, get it? You see the result there.

Student: (( ))

Whatever it may be, you look into all sorts of possibility, those possibilities and get the thing clarified. I want a clear answer from you in the next class.

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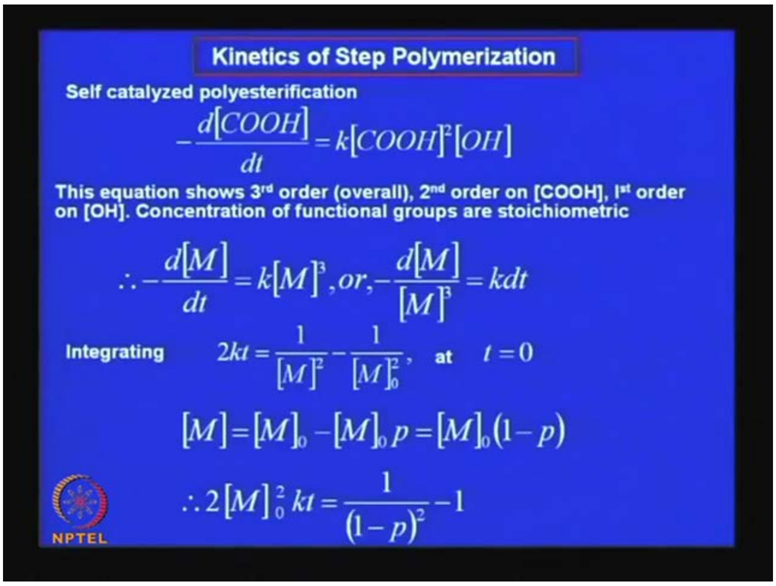

Kinetics of Step Polymerization

Self catalyzed polyesterification

$$-\frac{d[COOH]}{dt} = k[COOH]^2[OH]$$

This equation shows 3rd order (overall), 2nd order on [COOH], Ist order on [OH]. Concentration of functional groups are stoichiometric

$$\therefore -\frac{d[M]}{dt} = k[M]^3, or, -\frac{d[M]}{[M]^3} = kdt$$

Integrating $2kt = \frac{1}{[M]^2} - \frac{1}{[M]_0^2}$, at $t = 0$

$$[M] = [M]_0 - [M]_0 p = [M]_0 (1-p)$$

$$\therefore 2[M]_0^2 kt = \frac{1}{(1-p)^2} - 1$$

Now, please look into the equation, the self catalized polyesterification. Very simple kinetics overall rate minus you know the sense of meaning of the minus sign here. Since, it is depletion, so here in this equation. Second part to the carboxyl group is given and first part to the hydroxyl group is given, so it s over all third order reaction. Why this second part to the carboxyl group? Because one of the acid molecule is involved in reaction media, as a catalyst self catalized.

That is why this is second power and first power overall third order reaction. Very simple thing in term sorry placing in terms of monomer concentration, we get this is the relation. Then applying initial and boundary conditions at t is equal to 0, M becomes M 0 and to remove that integration constant integration constant we apply initial and boundary conditions, simple mathematics, you know. Ultimately we come to this final form of this rate equation. twice monomer concentration square, square of the monomer initial concentration of the monomer into red constant into t divided by square of the degree of polymerization, d p minus 1.

This is the rate equation for form of the rate equation after, in case of self catalyst polyersterification or polycondensation reaction I should say polycondensation. It may be true for the same for polyamedification also, clear? I am going for the next one, because one of the acid molecule is involved in catalysing the esterification reaction. It is not given back, where it is consumed? So, this concentration is included in the red expression. Since, acid molecule is involved in the reactant acid molecule is involved in catalysing the polyesterification reaction, so its concentration is involved in the rate expression. So, that is why it is second power to the carboxyl group.

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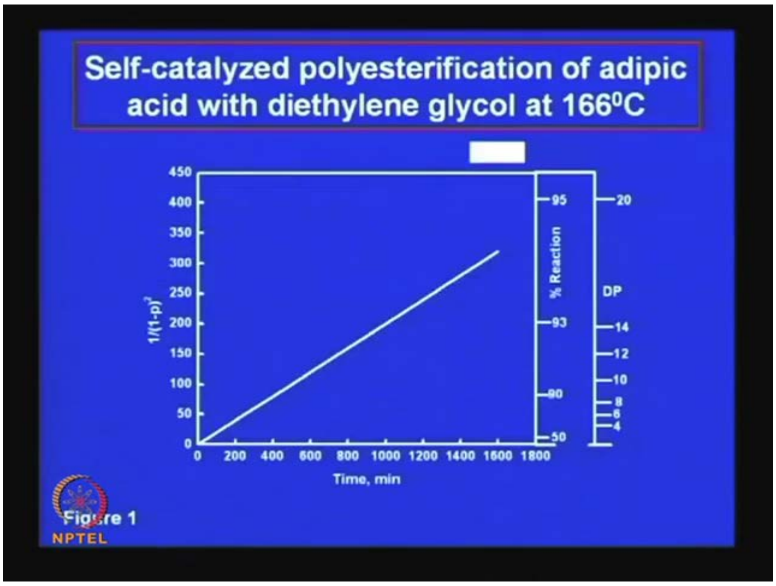

Self-catalyzed polyesterification of adipic acid with diethylene glycol at 166^0C

Figure 1

I am going to the next one. Look at the growth polymer growth. Now, this y axis this is the schematic, actually we cannot show here actual data due to copyright problem. So, here you see this is the square of the degree of polymerisation number of the degree of polymerisation versus time. So, it shows actually it is not linear overall although I have shown, overall linear for simplicity and clarity. If you please go through the books I have referred, there you will find some deviation from linearity for sure and many different regions, which are obvious from these rate expressions.

I have shown in the mechanism of polyesterification involving acid carobxyl group etcetera, different rate constants. So, all those are involved there. So, if you want to know those so who is interested who are interested they can see audience book for detail. Now, here you see if it is linear, then square of the degree of ploymerisation and this axis shows person reaction and this is the degree of ploymerisation. So, here it is 400 so it is 20. So, up to say 1800 say 16 out of 1700 minute time only in d p of 20 could be achieved or less than that, very small.

So, every action is very slow, this indicates the polymerisation reaction ployes polyestrification reaction using self catalyst reaction, following self catalyst reaction this ploymerization is slow. Please you are, are you following these things? Electronics following, okay? So, this is here is a proof that self catalyst polyesterification reaction ployesterification reaction is a slow process. So, the productivity of the polymer if you want to go for industrial manufacter of a polyester without using any external catalyst, so it will take large time. Productivity will be less, the cost of the productivity very high.

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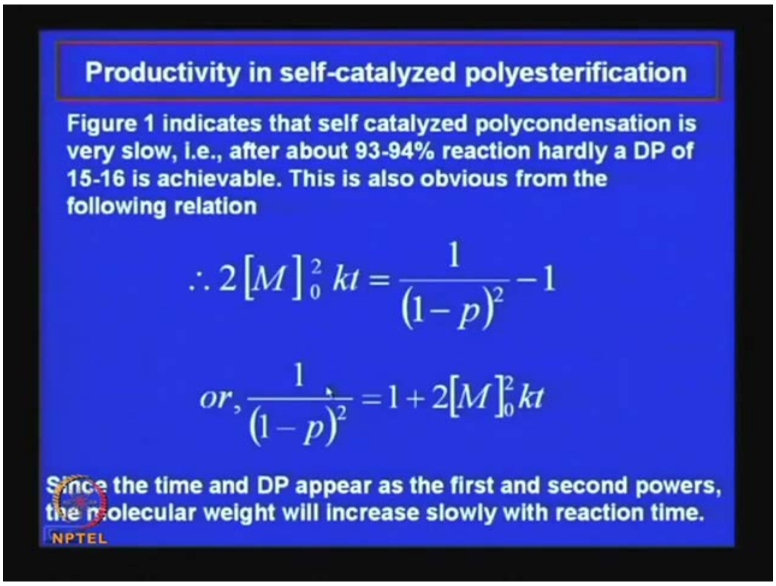

Productivity in self-catalyzed polyesterification

Figure 1 indicates that self catalyzed polycondensation is very slow, i.e., after about 93-94% reaction hardly a DP of 15-16 is achievable. This is also obvious from the following relation

$$\therefore 2[M]_0^2 kt = \frac{1}{(1-p)^2} - 1$$

$$or, \frac{1}{(1-p)^2} = 1 + 2[M]_0^2 kt$$

Since the time and DP appear as the first and second powers, the molecular weight will increase slowly with reaction time.

Here you see, this is related to the first part of time, square is related to the first part of time. So, the d p of polymerisation is, sorry the growth is very slow. This indicates growth is very slow. So, this thing I have already explained in the previous graph, showing the previous graph.

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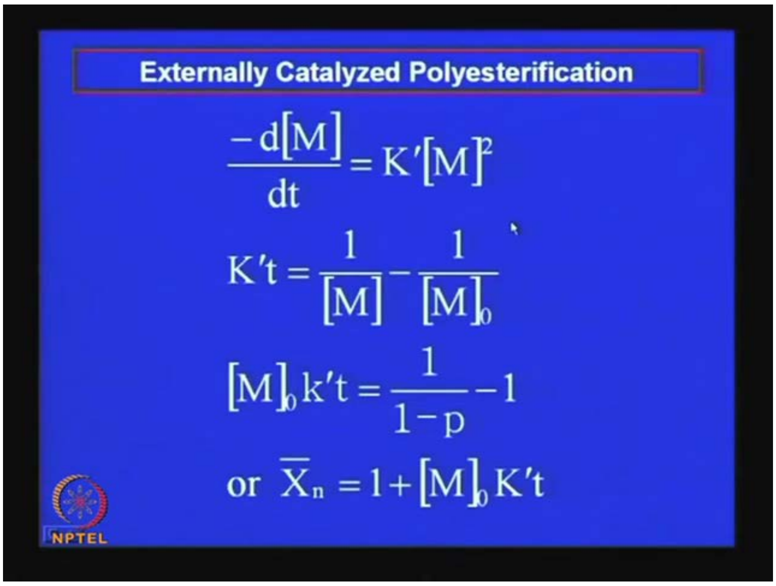

Externally Catalyzed Polyesterification

$$\frac{-d[M]}{dt} = K'[M]^2$$

$$K't = \frac{1}{[M]} - \frac{1}{[M]_0}$$

$$[M]_0 k't = \frac{1}{1-p} - 1$$

$$or \ \overline{X}_n = 1 + [M]_0 K't$$

Then, externally catalized polyesterification. The same kind of rate expression where you see this concentration of either carboxyl or sorry, carboxyl involving carboxyl and hydroxyl both both, but since some external acid is used as a catalyst, the concentration of acid is not involved in this rate expression. It is not included here, so it is square. So, this rate is second order reaction, this is second order reaction. First with first order on each of the functional groups either acid or alcohol and applying initial and boundary conditions ultimately you can get degree of polymerisation. You can do 1 plus M 0 k time t. Here you see degree of polymerisation is directly related to t, with increase in time there will be growth of molecular size X n bar, okay?

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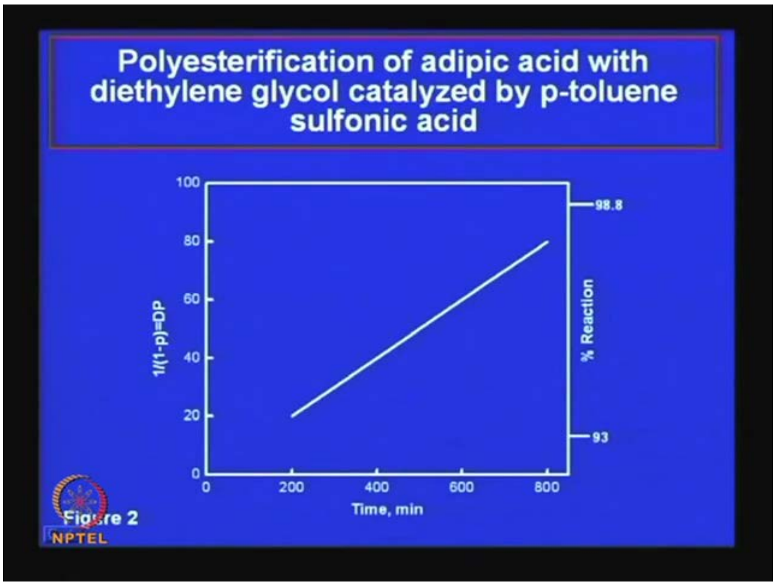

Polyesterification of adipic acid with diethylene glycol catalyzed by p-toluene sulfonic acid

Look at this curve, there you saw that for a growth of a d p of 18 only 18 to 20, it need it needed say 1600 minute time here, with array. See within 800 minute, half a minute you can get much higher growth higher growth. Say d p is 90 or 95 like that. So, this external use of external catalyst, increases the polymer production rate, polymer synthesis rate. So, in a small time in a less time you can produce huge quantity of polymer. So, this process is faster if you use an external acid as a catalyst.

So, catalized polyesterification, catalized polyamedification reaction or any condensation reaction, if that needs a catalyst it is better to use the catalyst in order to (( )) ploymerisation in order to increase the productivity. Not only that, the reaction condition also reaction condition should be mild. Otherwise you have to use harsh reaction conditions, harsh polymerisation conditions. So, these considerations are there.

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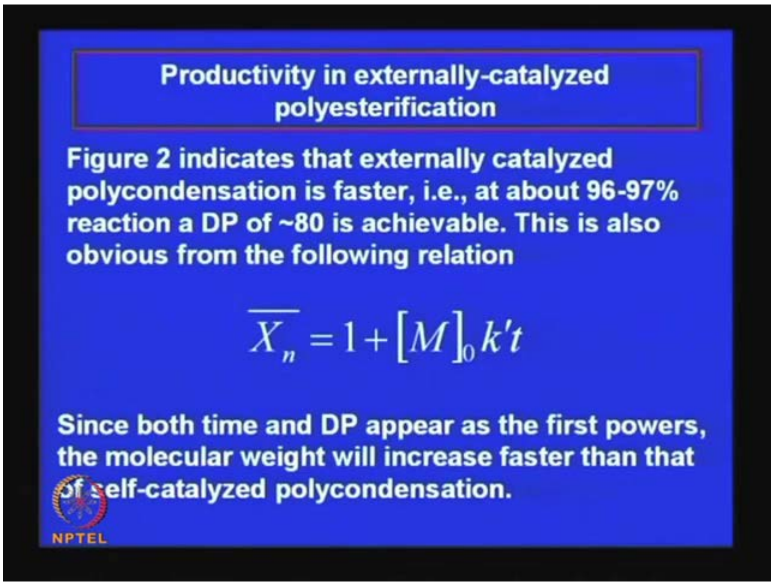

Productivity in externally-catalyzed polyesterification

Figure 2 indicates that externally catalyzed polycondensation is faster, i.e., at about 96-97% reaction a DP of ~80 is achievable. This is also obvious from the following relation

$$\overline{X_n} = 1 + [M]_0 k't$$

Since both time and DP appear as the first powers, the molecular weight will increase faster than that of self-catalyzed polycondensation.

As before it explains that, this degree of polymerisation is related to the first power of the time. Now, I am showing these relations, you can go for you should go for demerital calculations, you will find that how much time is required for a synthesis of a polymer from starting point? You can theoretically calculate with the help of this (( )) and this reaction kinetics. If you know the value of of course this is known initial concentration is known, rate constant you have to evaluate by some other experiment. So, if you know the rate constant, polymerisation rate constant, if you know the initial concentration, then in order to get a DP.

Suppose, you want to manufacture a polymer say degree of polymerisation is in 1000, then how much time is required for that achieving that 1000 DP degree of polymerisation, you can easily calculate. Suppose, you are employed in a polymer manufacturing unit, your boss has told you make a project, make a time calculation. that how much time will be required to produce say 100 metric tonne of this polymer product, then you have to calculate. You have to follow this thing, follow this principle, follow this process, you can easily calculate. For that you have to find out the data, this constant of that particular polyesterification reaction. Then you can easily calculate, okay?

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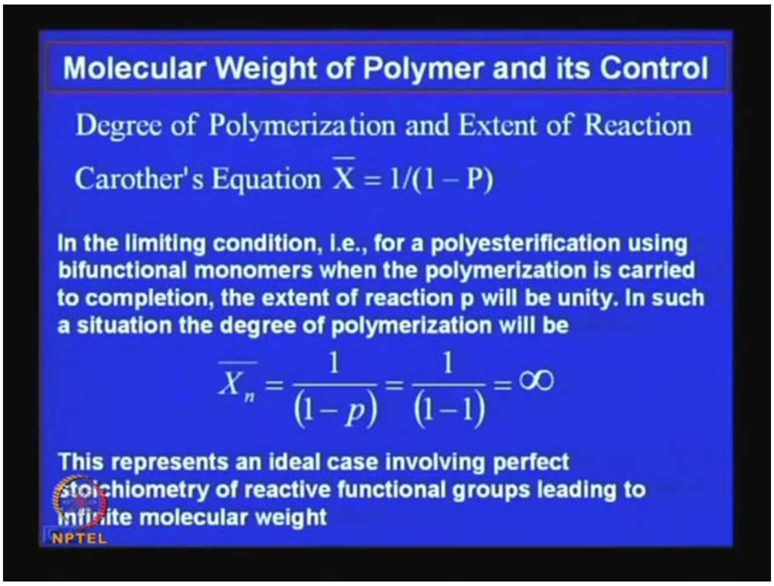

Molecular Weight of Polymer and its Control

Degree of Polymerization and Extent of Reaction

Carother's Equation $\overline{X} = 1/(1-P)$

In the limiting condition, i.e., for a polyesterification using bifunctional monomers when the polymerization is carried to completion, the extent of reaction p will be unity. In such a situation the degree of polymerization will be

$$\overline{X_n} = \frac{1}{(1-p)} = \frac{1}{(1-1)} = \infty$$

This represents an ideal case involving perfect stoichiometry of reactive functional groups leading to infinite molecular weight

Then these are certain limiting situation as I have told. Molecular weight of polymer and its control. Degree of polymerisation and extent of reaction, you know all these things. carother’s equation this 1 by 1 minus P simplest form of carother’s equation. Please do not forget, this is related to, this relates parameters of degree of polymerisation and extent of reaction involving bi functional monomers, bifunctional monomers and instoichiometric ratios. Instoichiometric amounts, instoichiometric amounts meaning that reactants are used in 1 is to 1 molar ratio, equivalent molar ratio.

Same molar ratio, please do not confuse, because there are certain things will be coming later, those will be sufficient for you to confuse yourself. That is why I am telling you please do not forget thant X n bar is equal to 1 by 1 minus P the simplest form of carother’s equation involving bi functional monomers strictly control of between the reactants. If that is 1 by 1 minus P provided the extent of reaction is P, okay? From that you can calculate the molecular weight, calculate the degree of polymerisation and you know the limiting situation I have already told. How it becomes infinity?

Infinite molecular weight? In this juncture, let me tell you one corollary, that is suppose you have taken natural rubber, I told you this is thermoplastic material. Dry natural is ore thermoplastic, but when the dry natural ore is mixed with sulphur and other functional compounds functional additives, it forms a mass which is reactive. Then after application of heat and pressure it converts to a thermoset product known as vulcanized rubber. So, when you started with the molecular weight of natural ore was 5,00,000 suppose. After vulcanization, what will be the molecular weight of the vulcanized product? Will it remain 5, 5,00,000 or will it increase to 10,00,000 or will it decrease lower than 5,00,000 increase to what value?

Student: (( ))

Will it be, suppose he has used 2 percent, you have used 5 percent. So, in case of 2 percent what will be the molecular weight? In case of 5 percent sulphur what will be the molecular weight? If it is 30 percent what will be the molecular weight? If it is 20 percent what will be the molecular weight? Are those will be different or same? If different, if it is different how much difference? This is a question, keep this question as a home work assignment. Next day come with the submit me the assignment. I am not giving very huge assignments, so one question I gave this is the second question. What will be the molecular weight of the vulcanized rubber, after it is converted from thermoplastic to thermoset?

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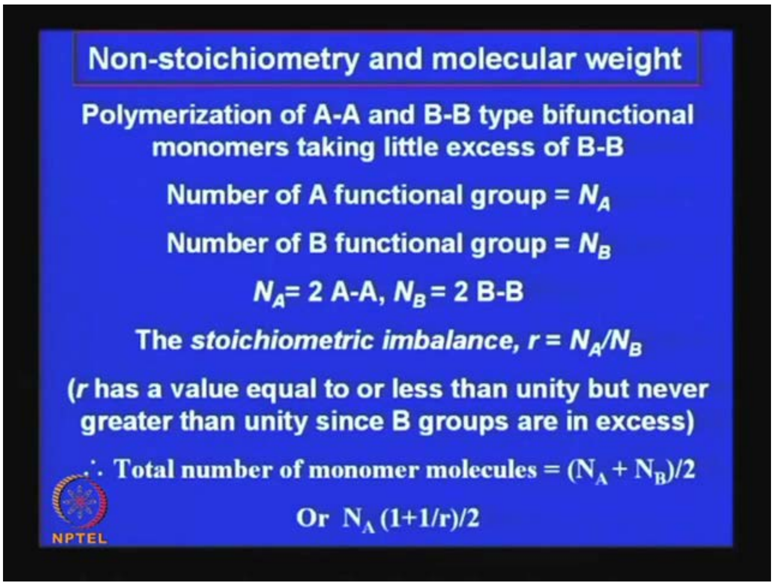

Non-stoichiometry and molecular weight

Polymerization of A-A and B-B type bifunctional monomers taking little excess of B-B

Number of A functional group = N_A

Number of B functional group = N_B

N_A= 2 A-A, N_B = 2 B-B

The *stoichiometric imbalance*, $r = N_A/N_B$

(r has a value equal to or less than unity but never greater than unity since B groups are in excess)

∴ Total number of monomer molecules = $(N_A + N_B)/2$

Or $N_A(1+1/r)/2$

Next, now let us see the music. If we move beyond stoichiometry, if we disturb the stoichiometry, of course that is the reality. Because while taking the weights of the reactants, we cannot take the weights perfectly, because I have a four place of decimal balance, you have a two place of decimal balance. You have very good balance, that cannot make a difference between 5 gram, whereas, my balance can make a difference between 5 milligram. So, you are taking weighting your balance, I am taking weight in my balance.

That was a large change in the nature of reaction. That is non stoichiometry. So, polymerisation of you consider in order to evaluate in that non stoichiometry situation ,what can happen? How to assess? How to evaluate the situation? How to monitor the situation? You have to see, so non stoichiometry means, non stoichiometry may arise out of wrong taking of weights or it may contain certain impurities. If you know from the level of the container, that the reactant is 98 percent pure, so 2 percent impurity is there. So, you have to include that impurity in your calculation.

So, instead of say 5 kg weight you have to take probably 5.2 kg weight including that impurity into consideration like this. So, you have to know what is the impurity level there? Then you have to know, what is the balance? What is the sensitivity of the balance? That you have to also include, correcting, correction factor. You cannot ignore, if you ignore you will not get a polymer. So, in case of polymerisation of two monomers having A functional groups B functional groups both are bi functional A A and B B type. Now, in that case suppose by mistake one monomer is taken in little excess say B B is taken little excess, what will be the situation. Let us see number of a functional groups are A N A designated as A N A.

Number of B functional groups designated as N B. Then total number functional groups A functional groups will be 2 into A, number of molecules into 2 because each molecule is bi functional. So, N B is equal to 2 into B B. So, stoichiometric imbalance, then if you take a little excess of B, so that stoichiometric imbalance is expressed with the help of a parameter r is equal to N A by N B and this r cannot be greater than unity. It should be less than unity or less than or equal to unity.

If it is less than unity, then N B is in excess. So, that way it has see, total number of monomer molecules then N A plus N B by 2 is a simple thing or N A into 1 plus in terms of r if you replace this, N B N A in terms of only one particular functional growth. A functional growth 1 plus 1 plus by 1 by r divided by 2 number of functional groups presents.

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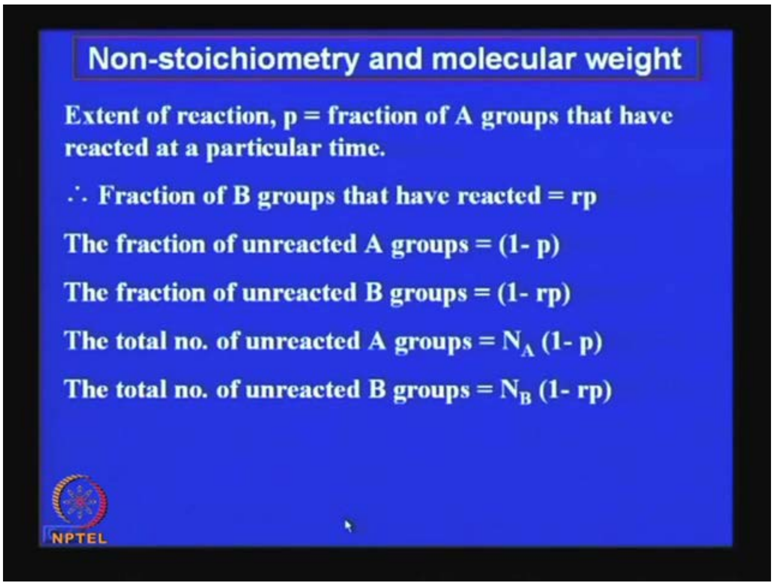

Non-stoichiometry and molecular weight

Extent of reaction, p = fraction of A groups that have reacted at a particular time.

∴ Fraction of B groups that have reacted = rp

The fraction of unreacted A groups = (1- p)

The fraction of unreacted B groups = (1- rp)

The total no. of unreacted A groups = N_A (1- p)

The total no. of unreacted B groups = N_B (1- rp)

The extent of reaction, introduce this parameter extent of reaction p. Extent of reaction p, p is equal to fraction of A groups that has reacted at a particular time t. So, the fraction of B groups that have reacted will be r p. So, fraction of un reacted A groups 1 minus p fraction of un reacted B groups 1 minus r p. Total number of un reacted A groups will be N A into 1 minus p and total number of un reacted B groups will be N B into 1 minus r p, very simple calculation, simple derivation.

So, why you are doing these things? Because we have to calculate the value of degree of polymerisation, number of degree of polymerisation or molecular weight. Because we know, number of degree of polymerisation is is equal to N 0 by N. Number molecules initially present divided by number of molecules present at any time t. So, number of molecules initially present and number of molecules present at any time t. For those two parameters, this process we are following for calculation, okay?

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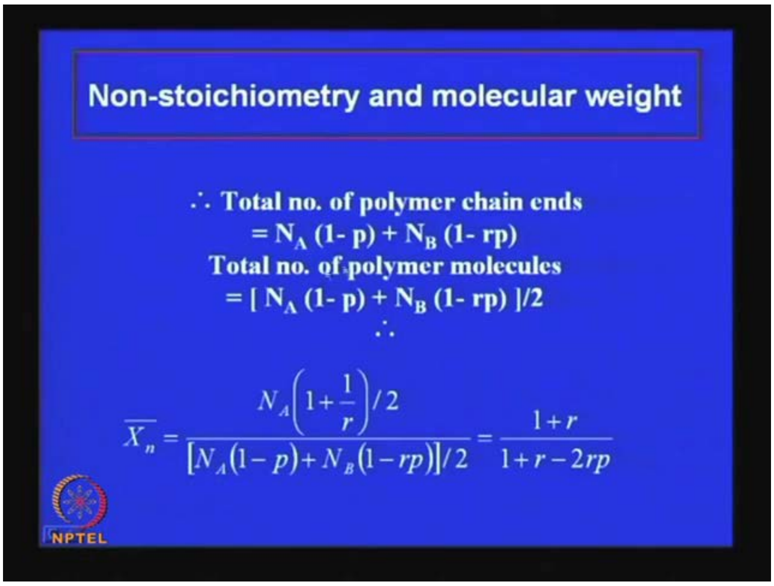

Non-stoichiometry and molecular weight

∴ Total no. of polymer chain ends
= N_A (1- p) + N_B (1- rp)
Total no. of polymer molecules
= [N_A (1- p) + N_B (1- rp)]/2
∴

$$\overline{X_n} = \frac{N_A\left(1+\frac{1}{r}\right)/2}{\left[N_A(1-p)+N_B(1-rp)\right]/2} = \frac{1+r}{1+r-2rp}$$

So, total number of polymer chain ends. Then will be because these are the any functional groups and any N B functional groups. Now, you have got the concept that polymer molecules will have 7 groups in the form of A or B groups. So, if the ends, number of ends are having A or B should total number of chain ends will be these. Number of polymer chain ends, suppose a system contain so many polymer molecules of this size, how many 1 2 3 4 5 6 7 8 9 10, 10 species are there. Each species has two ends, so total number of ends 10 into 2, 20 from that logic.

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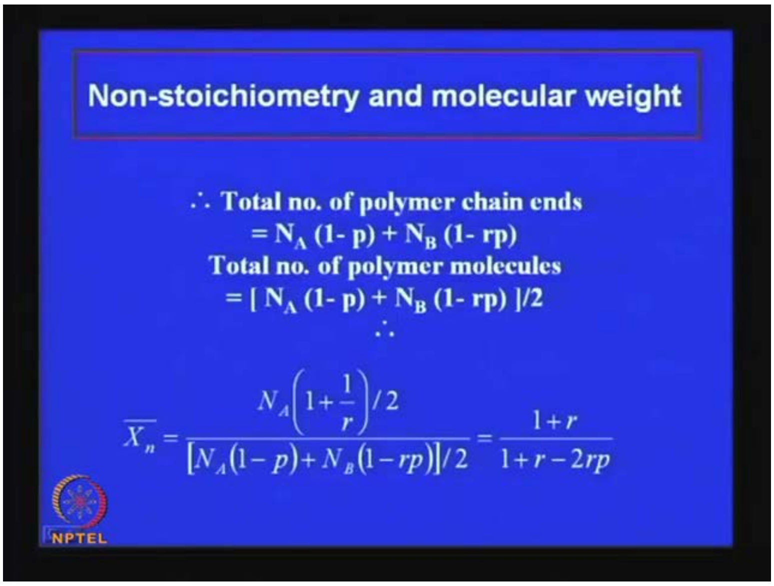

Non-stoichiometry and molecular weight

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So, total number of polymer chain ends, then if you know the total number of polymer chain ends, we can experimentally evaluate. We can experimentally determine that thing, we can experimentally determine how many end groups are there, this side and this side by stoichiometric estimation or by some other spectroscopic technique. So, total number of ends we can calculate, then total number of polymer molecules divided this number, total number of end groups by 2 you will get number of polymer molecules. Then you substitute those values here X n bar is equal to X n bar is equal to number initially present, number present at any time t. So, from there you have already seen N A into 1 plus 1 by r.

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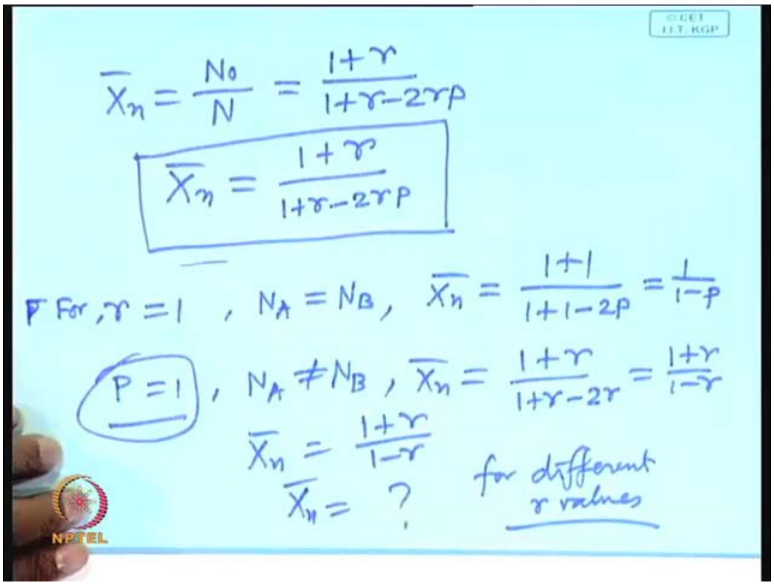

$$\bar{X}_n = \frac{N_0}{N} = \frac{1+r}{1+r-2rp}$$

$$\boxed{\bar{X}_n = \frac{1+r}{1+r-2rp}}$$

For, $r = 1$, $N_A = N_B$, $\bar{X}_n = \frac{1+1}{1+1-2p} = \frac{1}{1-p}$

$P = 1$, $N_A \neq N_B$, $\bar{X}_n = \frac{1+r}{1+r-2r} = \frac{1+r}{1-r}$

$$\bar{X}_n = \frac{1+r}{1-r}$$

$\bar{X}_n = ?$ for different r values

Ultimately these leads to 1 plus r divided by 1 plus r minus twice r p. So, this is a relation involving stoichiometric imbalance r. Extent of reaction p where you have used bi functional monomers in which one of the monomers are taken in excess or there are certain impurity materials. Those impurity materials are counted as some functional groups or something like that. There are various other considerations if you go through that ordience book you will get those details.

But for all of you it is not necessary, those who are interested you are referred to that book for details of information’s there. But if you are intelligent enough, looking at this relation you can evaluate you can, you can derive many things. Now, here limiting situations might be r may be is eqaul to 1, that means N A can be equal to N B, perfect stoichiometry. In that case for for r is equal to 1 that means N A is equal to N B X n bar is equal 1 plus 1 divided by 1 plus 1 minus 2 p.

So, for equimolar quantities of reactants, the characteristic equation is 1 by 1 minus p. When p is equal to 1, but N A is not equal to N B, then X n bar is equal to 1 plus r divided by 1 plus 1 plus r minus twice r. So, it will be equal to 1 plus r divided by 1 minus r. So, even if you continue up to cent percent reaction, the degree of polymerisation is equal to 1 plus r by 1 minus r. Now, here this value of r we can have several situations, you can test, take again this as your home work assignment for different values of r 0.98, 0.97, 0.9, 0.99 like this, you have to do the value of degree of polymerisation.

That means if one of the reactant is used 0.1 mole percent excess or 0.5 mole percent excess or 1 mole percent excess, then what happens to this degree of polymerisation? You get that value, am I clear? There will be numerical calculations, so please have a practice in the evening hours for different values of... This is the one case, another case when p and r both varies, different p and different r, what can happen? It is very difficult to achieve 100 percent reaction; it will take very, very long time. So, before that you have to stop the polymerisation. In that case if again there is some mistake in r, then we may not get a polymer product.

So, what is that situation you have to choose, you have to theoritically achieve. If there is any problem in polymer manufacturing in your industry, you find molecularity is very low, your quality control department has given you a feedback. The product charge, your feed charge your charge to the reactor, with that feed charge this is the product, this is the molecular weight, then the entire responsibility lies on you to find out the fault, where is the fault? Where lies the fault? So, you have to go for calculation, for this thing this calculation is necessary, okay?

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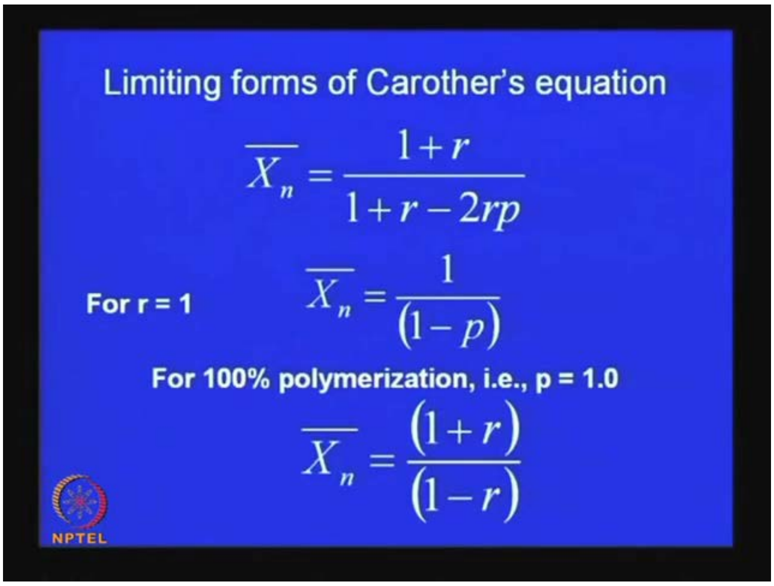

Limiting forms of Carother's equation

$$\overline{X_n} = \frac{1+r}{1+r-2rp}$$

For r = 1
$$\overline{X_n} = \frac{1}{(1-p)}$$

For 100% polymerization, i.e., p = 1.0

$$\overline{X_n} = \frac{(1+r)}{(1-r)}$$

I have already told you limiting forms of this Carother's equation.

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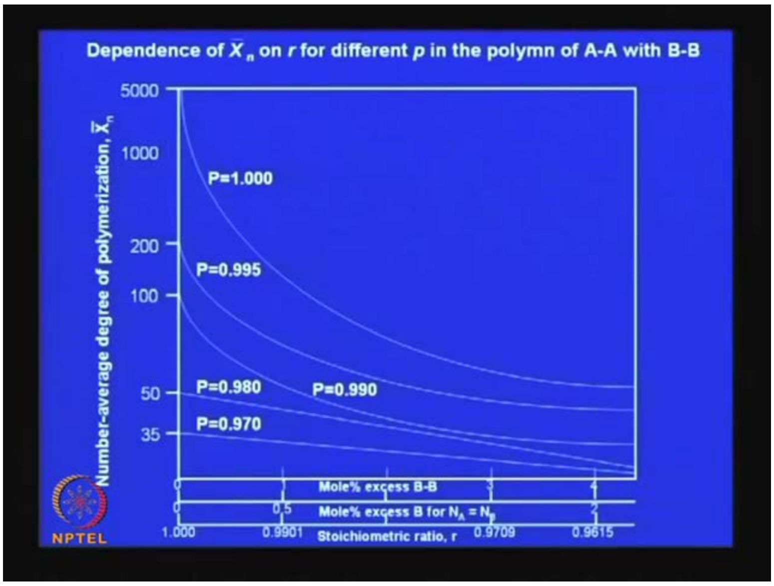

Dependence of $\overline{X}_n$ on r for different p in the polymn of A-A with B-B

Again this is a schematic diagram; this is drawn by me, only for convincing you. Now, y axis you see number average of degree of polymerisation. x axis, x axis shows three different axis, in different situations. In one case you see the font is little smaller, I could not accumulate mole percent excess B B. That means the degree of polymerisation changes with excess B groups 1 mole percent, 2 mole percent, 3 mole percent, 4 mole percent. You see on one particular case you see how this extent of reaction changes? So, with the change in extent of reaction and along with this stoichiometry, what is the molecular weight?

Here you see, you can have very high molecular rate, provided you continue the reaction after cent percent conversion. Then only you have to take very small amount of B groups in excess. As you go increasing the B groups, then you will end up with about molecular weight DP 50 or even less than 50, you understood? Try to give some time on this schematic diagram. This diagram utilises extent of reaction and one of the monomers in excess. If you go on increasing the concentration of the monomer, excess monomer, then you have to compromise with the degree of polymerisation. Provided even if you carry out the reaction through cent percent completion, do you understand? The top card, look at the top card.

Suppose, you are satisfied with your N group analysis, that you have correct the polymerisation reaction to completion because you have achieved p is equal to 1, but your product molecularity is very less, your diagnosis will be locating the fault, will be in this impurity or during weight. That means role you have taken one of the monomers in large excess. Either 2 mole percent you have taken, excess if you are here is the DP less than 100, so definitely you have taken 2 mole percent excess of the monomer B. Other cases mole percent excess of B is N A is equal to N B this is another case.

Stoichiometric ratio r, if it is expressed in this way. One perfect stoichiometry r is equal to 1, N A is equal to N B, then dividing from this stoichiometry to lower values our value is 0.96. You see the degree of polymerisation. Mole percent excess B you see here, you can add some mono functional compound. It signifies that you have started with A A and B B both are bi functional. How to control the molecular weight? Suppose, those groups are very reactive and you have to stop the polymerisation, you can stop it chemically by adding a mono functional component.

Suppose, you have taken say ethylene glycol and adific acid, if you want to stop the polymerisation you can add formic acid or acetic acid. In that case, mole percent excess of B only, even if you have taken N A is equal to N B, even if you have taken N A is equal to N B, then you can control the polymerisation by taking a mono functional agent, that acetic acid or formic acid or a methanol or ethanol.

Student: (( ))

Stoichiometry of the monomers A and B B, suppose you have taken ethalene glycol and aectic acid. Those monomers to take part in polymerisation equal stoichiometry.

Student: (( ))

For that case you can have a situation, that you have to control the molecular weight, you have to limit the molecular weight not a DP of say 1000 you do not want a DP of 1000, you want a DP of say 100 for sudden purpose. It is necessary, it is necessary it is not always true that you have to lead to molecular polymer of highest molecular weight, not necessarily. That depends on the properties you want. You may use that product in some painting for your surface coating purpose for making a film. In that case you need a low molecular weight product.

Whereas, for mechanical application for load bearing application; you may need a very high molecular weight product. Those things I have not explained, structure property relations. First of all let me complete this synthesis principles part, principles of synthesis part, then I shall discuss those things, then it will be clarified. Where is a very good question you have asked, that what is the necessity of this thing? Mole percent excess B means, you have to stop the polymerisation using monofunctional agent having B functional group, am I clear? Is it clear?

This diagram is very informative because you can you can calculate the amount of reactants for synthesizing any polymer as well as you can know, how much time should be continued for this polymer growth? How much time should be allowed for getting a suitable quantity of polymer as well as desired molecular weight level? So, you please do some numerical calculations, taking different ratios of the reactants. That means r value or you can use one of the reactant in little excess or you can use here. You see, you can use some mono functional reactant also mono functional reactant.

I mean that if you take say acetic acid and ethylene glycol for getting polyethylenetriethalate, great polymer. In order to stop the polymerisation at any stage, you can either add to the reactor a mono functional compound like acetic acid or methanol or ethanol. So, that way by adding some mono functional compound at one time say after 5 hour or after 2 hour like that, then you can know how much will be the molecular weight? If you want a specific molecular weight, then you can find out the time required for that growth as well as how much amount of mono functional reactant is to be added at what time, so that will stop the polymerisation.

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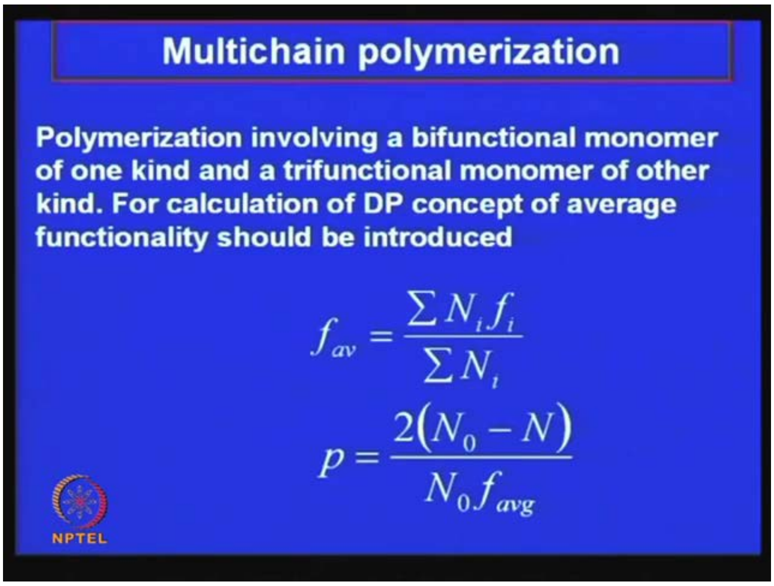

Multichain polymerization

Polymerization involving a bifunctional monomer of one kind and a trifunctional monomer of other kind. For calculation of DP concept of average functionality should be introduced

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$

$$p = \frac{2(N_0 - N)}{N_0 f_{avg}}$$

Now, let us pass on to multi chain polymerisation. What do you mean by multi chain polymerisation? As you have seen that the minimum requirement of possibility of this monomers, lies in the ratio of the two reactants as well as the bi functionality of the monomers. Strict control of bi functionality as well as strict control of stoichiometry molar ratio of the reactants leads to a linear polymer structure, linear chain polymer. Now, if there is certain impurity, that impurity can affect the molecular structure of the polymer. It may not be linear, it may be branched or it may be even cross linked. Now, there are certain polymers polymerisation reactions or certain polymers, where we deliberately use a bi functional monomer with a tri functional monomer.

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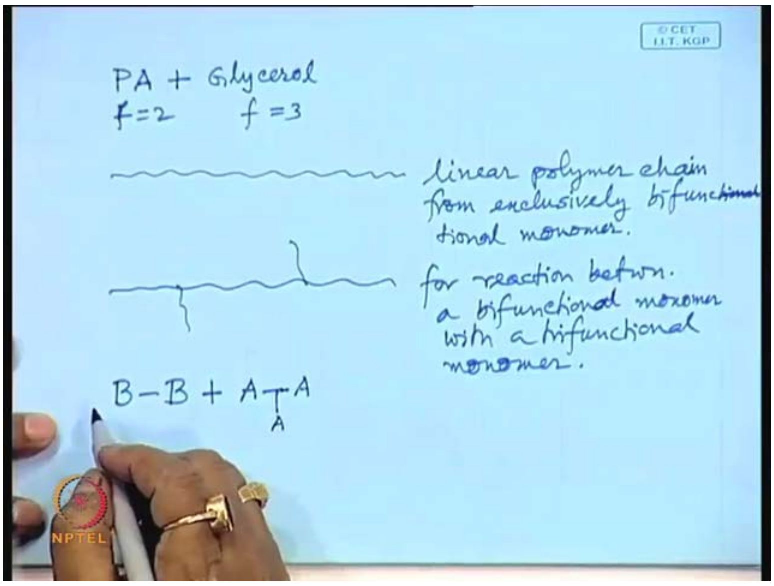

PA + Glycerol

f=2 f=3

linear polymer chain from exclusively bifunctional tional monomer.

for reaction betwn. a bifunctional monomer with a bifunctional monomer.

$$B-B + A\underset{A}{\top}A$$

Say you can react ethylic anahydride or ethylic acid and glycerol, now this is ethylic anahydride is a bi functional. f is equal to, f is equal to 2, here f is equal to 3, what will happen? Now, in case of exclusively bi functional monomers, you will get a linear polymer chain from exclusively, sorry exclusively bi functional monomer. But if you take some quantity of tri functional monomer along with this bi functional monomer, having the same kinds of functional groups, then you can get a branched polymer. How it happens? How it happens? Say suppose, you want to synthesize a polymer taking a bi functional monomer having functional groups B, then you take a tri functional monomer like this, having functional groups a three functional groups are there, so you can get a polymer from this like...

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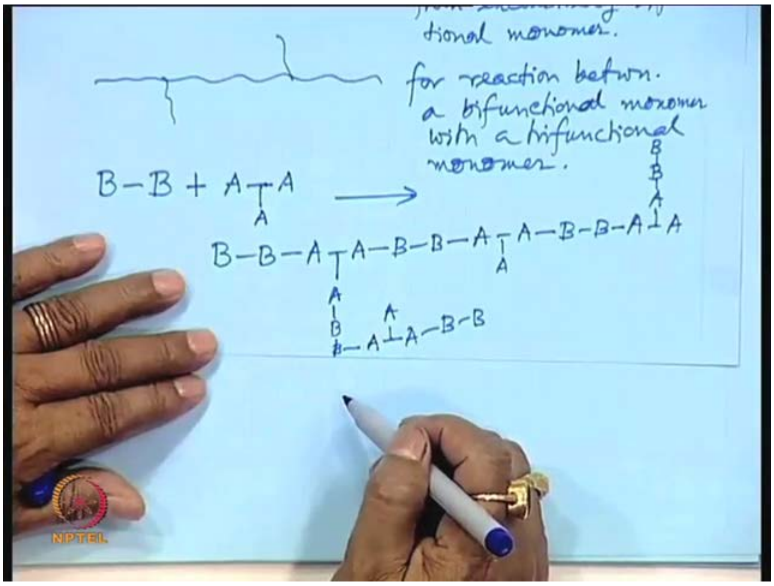

Sorry, I am sorry B A B B, then it may again link to A B B like this. Here it will continue so here and so forth, do you understand? So, this why you can, there is a possibility of formation of branch beyond that. It can lead to a cross linked three dimensional network system of polymer, three dimensional network of polymer that thing we will discuss today.

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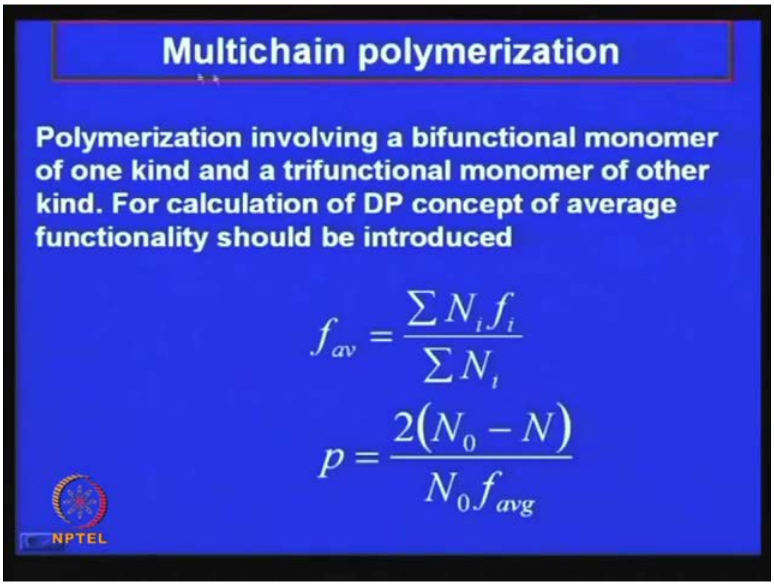

Multichain polymerization

Polymerization involving a bifunctional monomer of one kind and a trifunctional monomer of other kind. For calculation of DP concept of average functionality should be introduced

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$

$$p = \frac{2(N_0 - N)}{N_0 f_{avg}}$$

Now, this multi chain polymerisation and the polymerisation involving a bi functional monomer of one kind and a tri functional monomer of other kind for calculation of degree of polymerisation. Concept of average functionality should be introduced otherwise, how we can calculate? So, here this function in case of bi functional monomers functionality s 2 f is equal to 2. Now, if we take a mixture of bi functional monomer with a tri functional monomer like.

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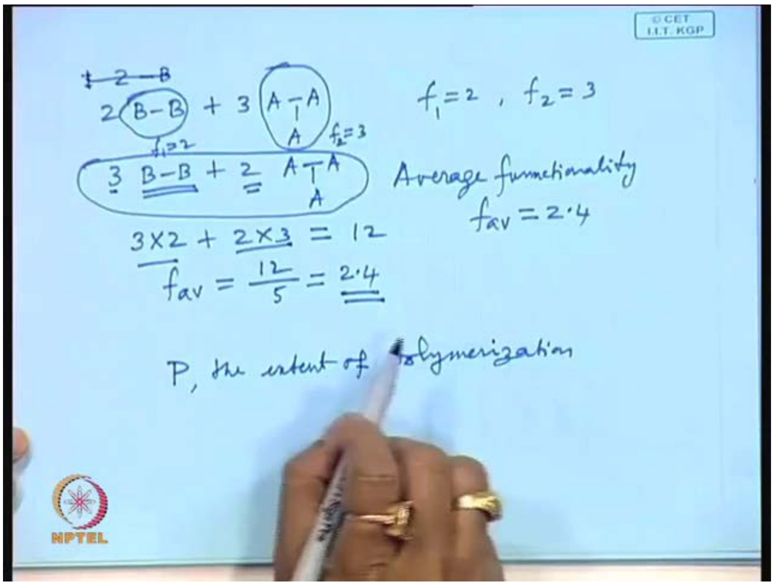

$2\ \text{B-B} + 3\ \text{A-A(A)}$ $f_1 = 2$, $f_2 = 3$

$f_1 = 2$, $f_2 = 3$

$3\ \text{B-B} + 2\ \text{A-A(A)}$

Average functionality $f_{av} = 2.4$

$3 \times 2 + 2 \times 3 = 12$

$f_{av} = \frac{12}{5} = 2.4$

P, the extent of polymerization

1 mole of or 2 mole of say bi functional monomer and sorry, 2 mole of bi functional monomer with 3 moles of tri functional monomers or or three moles of bi functional monomers plus 2 moles of trifunctional monomers. Let us see what happens now? Here in this case f is equal to 2, say f 1 is equal to 2 and f 2 is equal to 3. For this one f 1 is equal to 2 and f 2 is equal to 3, then what is the average functionality? That average functionality can be calculated from this relation.

How if you take 3 moles of this bi functional monomer, 2 moles of this thing? So, it will be 3 into 2 functional groups plus 2 into 3 functional groups. So, this equals 12, so average functionality f average is equal 12 by how many moles? 5 moles, so it is coming around 2.4. So, for this system, for this system average functionality f average is equal to 2.4. This is very simple, once you calculate this thing, then you can calculate the extent of polymerisation p...

Student: (( ))

Average number of functional groups present in the system; I have shown this calculation, if you take a bi functional monomer B B, where you have taken 3 moles, 3 moles of B B. So, total number of functional groups is in this case six and tri functional 2 moles of tri functional monomer, A A A. So, average number of functional groups here 2 into 3 is 6 total is 12. So, how many moles are there 3 plus 2, 5 moles. So, what you have done? Total number of functional groups present in the system divided by total number of moles of monomers you have taken.

So, this is the average functionality. That can be calculated with the help of this formula, of this formula. So, then then from this thing by taking the help of average functionality, we can calculate the extent of p, the extent of polymerisation. Extent of polymerisation, which is related to this average functionality as well as this is related to the degree of polymerisation X n bar.

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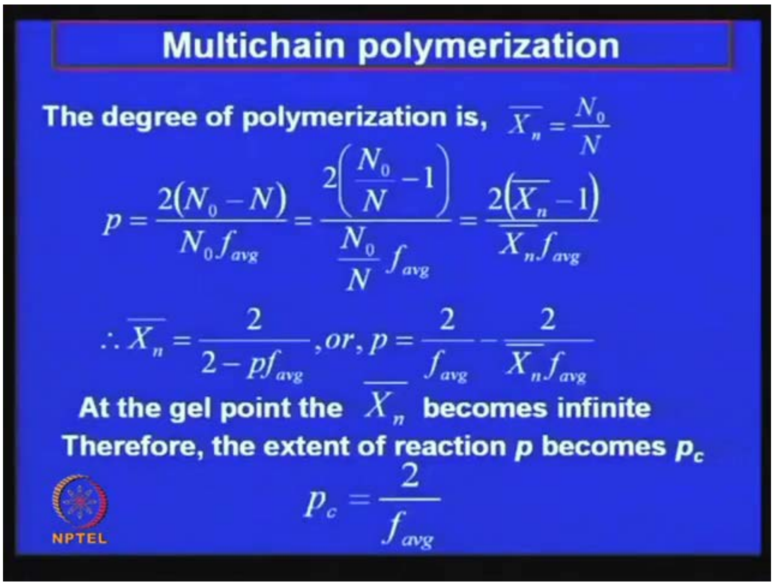

Multichain polymerization

The degree of polymerization is, $\overline{X}_n = \frac{N_0}{N}$

$$p = \frac{2(N_0 - N)}{N_0 f_{avg}} = \frac{2\left(\frac{N_0}{N} - 1\right)}{\frac{N_0}{N} f_{avg}} = \frac{2(\overline{X}_n - 1)}{\overline{X}_n f_{avg}}$$

$$\therefore \overline{X}_n = \frac{2}{2 - pf_{avg}}, or, p = \frac{2}{f_{avg}} - \frac{2}{\overline{X}_n f_{avg}}$$

At the gel point the $\overline{X}_n$ **becomes infinite**

Therefore, the extent of reaction *p* becomes p_c

$$p_c = \frac{2}{f_{avg}}$$

How? Now, from the definition of the extent of reaction, extent of reaction you see here, N 0 is the initial number of moles present in the system. N is the number of moles reactants. So, number of moles remaining is this total number of functional groups for each monomer. If it is a bi functional not not that, for each event of reaction between two opposing functional groups, say one hydroxyl and one carboxyl group will react. So, this is the total number of functional groups reacted divided by functional groups present.

That is the extent of reaction, the initial number of functional groups present because this is the f average is the average functionality multiplied by the total number of moles present initially. Then this is the moles present at any instant of time, moles of reactants present at any instant of time instant of time functional groups. So, the ratio of this 2 is the extent of reaction. Any ambiguity, any doubt? Once again I am repeating, p is the amount of reaction occurred at any instant of time, that means number of functional groups that has reacted or fraction of functional group that has reacted or percent of reaction that has happened at any particular instant of time.

To express this phenomenon mathematically, we can see, we can define this way. So, this is the initial number of functional groups present, what we have taken by multiplying the average functionality f average by the original number of molecules. This N 0 is the initial number of moles, N has reactant. So, remaining N 0 minus N sends since, each event of reaction between a carboxyl and hydroxyl groups, two groups will be consumed. One hydroxyl and one carboxyl, so these two factor has come, this two factor has come. So, this receives the extent of reaction. Now, one simple derivation, it comes equal to 2 into X n bar minus 1 divided by X n bar f average. X n bar is number average degree of polymerisation.

So, on rearranging you can get X n bar is equal to 2 by 2 minus p into f average or p is equal to 2 by f average minus 2 by X n bar f average. There is a chance, there is a there is a chance of analysing the situation, what will happen if molecular weight or degree of polymerisation becomes infinite? So, if X n bar value is infinite, then this term will vanish with 0. So, it will be 2 by f average. So, at the start of duration at the start of cross linking, once the cross linking reaction has started inter molecular linkage between molecules has started, entire system is gelled, means it is cross linked.

So, last day I told you if it is gels or if it forms cross linked structure, the molecular weight becomes infinite. So, at the incipient of gelation at the moment of gelation, we consider that the entire system has converted to a single molecule and its molecular weight is inifinite. From that concept, this term vanishes and this pc is the extent of reaction, critical extent of reaction. pc becomes the critical extent of reaction beyond which one should not continue the polymerisation. If somebody continues, then your polymer mass will be a gelled, you cannot apply that.

You cannot process that, you cannot convert that product into that polymer, into a suitable product, like tin or a bucket or anything, you cannot. Because that has converted to a gel, cross linked. That will be neither soluble in a solvent nor you can melt it. If it is not soluble in a solvent, you cannot make any product or if it is not meltable, you cannot make any product through processing using different machineries, say (( )) or injection moulding or any other machine where it needs to be heated for increasing the flow by heating, do you understand? So, at the it should be stopped below the gelation to start. Before it starts gelation, the polymerisation should be stopped. So, that critical extent of reaction is pc which is equal to 2 by f average.

Thank you.