**Polymer Chemistry**
Prof. Dibakar Dhara
Department Of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 3
Introduction to Polymers (Contd.)

In the last lecture we were discussing about the various ways of classifying polymers and at the end we came at the most important ways to, you know important way to classify polymer is based on its structure and the mechanism by which it is typically polymerized with, on the base of structure we, it was said that you can divide polymerization, polymers in addition and condensation in two ways. And in case of by the mechanism which you can synthesize polymer you can divide polymer into two classes by step polymerization or by chain growth polymerization.

Now, if you remember from the last lecture that in in case of chain growth polymers, the monomers are not started the polymerization reaction by itself, you need to have external agent which will initiate the polymer chain and once the chain starts, monomer can add one after one and thus completing the chain quickly. And in this case we have seen or we have discussed in last lecture that the rate of initiation is typically much lower compared to the rate at which the chain propagates and completes.

(Refer Slide Time: 01:58)
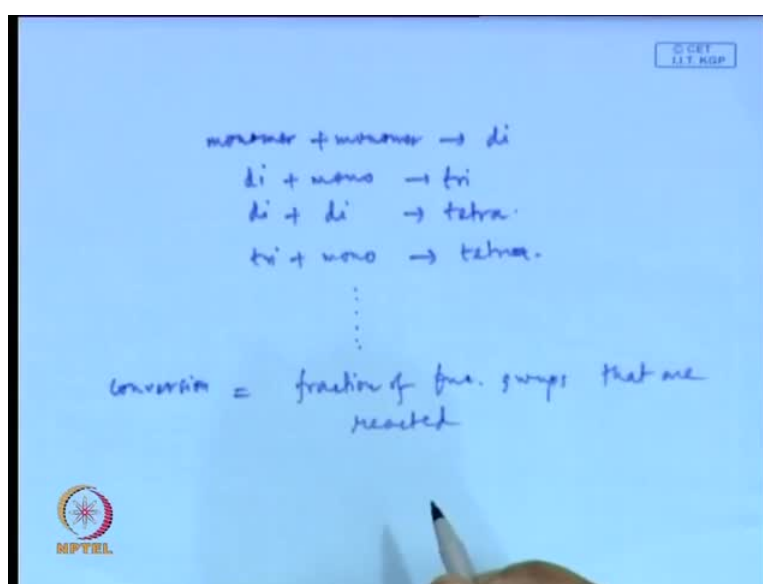
Now, in case of step growth polymerization, we also talked about that you know you typically have a monomer react with monomer at the beginning gives you a dimer. And then when the dimer is formed it can react with mono gives you trimer or it can react with itself to gives you a tetramer and this trimer can again react with monomer gives you a tetramer and so on.

So, in case of step growth polymer or step growth polymerization process the polymers are formed in various stages, no, steps first di, tri, tetra, if you stop reaction, step growth reaction after sometime before completion what will you get in the polymerization medium? If you remember or recollect from your memory in case of chain polymerization if you stop the reaction in between say after small amount of monomers got reacted, you will find that you have high molecular weight polymer as well as lots of monomers depending upon which stage you have stopped the reaction and also initiator molecules.

Now, in case of step growth polymerization if you stop in between you will see all these small molecules. These are called oligomers and and a small amount of monomer depending upon at which stage you have stopped the reaction. So, the high molecular of weight polymers in step growth polymers only form at the later stage, at the very late stage of the polymerization process. Now, what do you, what I mean by later stage.

Now, first define what is conversion in a polymerization process? Conversion is fraction of functional groups that are reacted in the process. Now, it can be expressed as a percentage or it can be expressed as the fraction.

(Refer Slide Time: 04:31)

So, let us take a example I have say 50, say 25. I have 25 A A type monomer one, another 25 B B type monomer. So, what is the total number of functional group here? Total number of functional group, groups are how much, how many? So, that is 100, total number of molecules is 50.

Now, let us, this monomers all react with each other and in the first step you have reaction monomer plus monomer gives you dimer and for simplistics imagination we just thinking that all are monomers and half of the monomers like 25 of this monomer is reacting with 25 monomers and giving a 25, dimers for our simplistic understanding we are following simply this process, this understanding. So, functional groups how many now? 25 dimers so each content two, each contains two which means functional groups are 50. So, conversion is 50 percent and what is the degree of polymerization is 2, degree of polymerization is the number of structural unit present in the polymer chain or polymer molecule.

Let us consider in the second step all these dimers reacted with each other forming tetramer. How many tetramer would be there? 12.5 on average which means you have 25. So, if I write the 12 is reacting with 12 dimer 1 is remaining which means that you had 12 tetramers plus 1 dimer left which makes it on average 12.5 tetramers, 12 tetramer plus 1 dimer which resulting at on average is 12.5 dimer. So, I can write 12.5 12.5 give it 12.5. So, how many functional group now present in the reaction term? It is 25. So, what is the

conversion? 75 percent and degree of polymerization is close to 4. You can calculate degree of polymerization from the number of tetramer and dimers present divided by total number of total molecules present in the system. So, in case of 12 so 12 multiplied by 4 plus 1 dimer 1 plus 2 divided by 12 number of molecules that is 13. So, which it gives you close to 4.

So, let us again for simplicity consider these tetramers are reacting with each other forming octamer. So, I will write say 6. 25 of this reacting with 6.25 gives you octamers. How many? So, 6.5 on average. So, how many number of functional groups now? 12.5. So, what is the conversion? Is 87.5 which is, will give you approximately a degree of polymerization of 8.

Let us take another step where you are taking these octamers reacting with octamers forming this 16 mar which is of, which will come around 125 numbers gives you 6.25 functional group 93.75 conversion percentage and degree of polymers is 16. So, what I am trying to make you understand, following the simple process where now we just considering the highest in a maximum possible sizes, dimer reacting dimer gives you tetra, tetra reaction with reacting with tetramer gives octa, octa reacting with octamer gives you 16 mar.

So, in this case you can see how the degree of polymerization which relates to the size of the polymer chain or polymer molecules varying with conversion. So, even at very low conversion I mean low d p you have a high amount of conversion. So, this emphasize even for example, at say 94 percent conversion you have only 16 d p which is not a polymer yet, it is a still a oligomer. Now, remember this is I am just following the simple reaction these tetramer can react with dimer, monomer and trimer further reducing the chains.

So, finally, this d p will even at this conversional rate actual d p will be lower than this 16, 8 and 4 or 2, I am just talking about the one simplistic case where following the simple reaction.

(Refer Slide Time: 10:35)
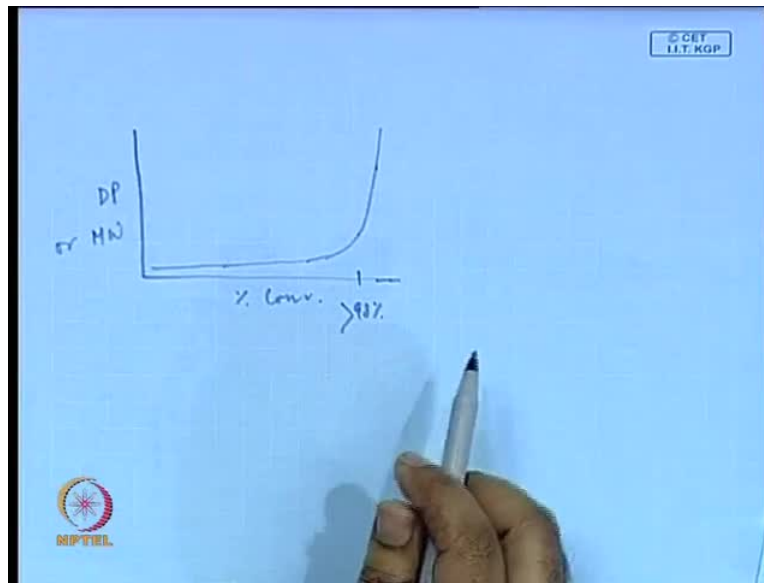
So, you can now understand that if I plot say percentage conversion with d p degree of polymerization or say molecular weight or molecular weight in case of step growth polymerization, it will only start from a slow… So, in a very low conversion you know the high the the polymer chains only will be achieved, you know high molecular polymer chains will be only achieved at very high conversion close to 98 percentage above.

So, this will clearly give you understanding that in case of step growth polymerization you can have the high molecular weight which is the practical polymer, polymers, which is useable polymers can be achieved only when the conversion is quite high, very high more than 98 percent and so.
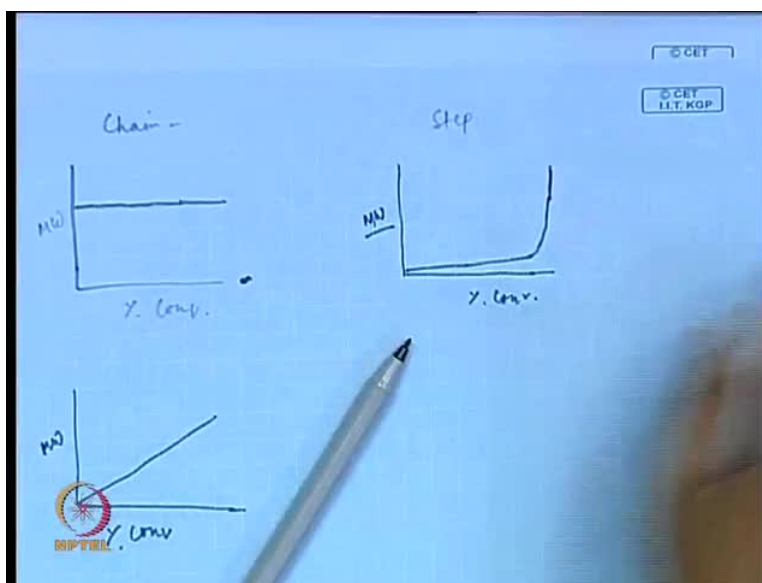
So, if I want to compare between the chain and step growth polymerization, percentage conversion verses molecular weight. In case of chain polymerization you had situation like this where you can achieve the high molecular weight at the beginning and the time goes or the more or monomer get converted, monomer get reacted you get the amount of high molecular weight polymers more and more with time.

And in case of step polymers you get the high molecular weight only at very high conversion. Now, in some cases the chain polymerization can gives you a situation like this where the molecular weight increases linearly with the conversion. It arises situation where the rate of initiation is faster compared to rate of propagation and also the reactions which were responsible for terminating a reactive species, reactive chain were absent in this case.

So, in the first case, in this case which is the normal you know which is, most of the general the chain reaction the initiation is slower compared to the propagation, chain propagation or the formation of polymer chain which means as the chain gets initiated it completes very fast. So, you get high polymer, high molecular weight polymer at the beginning and as time goes more and more chains get initiated. So, you get more and more polymer with average molecular weight remain same.

But, if you have a situation where your initiation is faster compared to the propagation of chain formation rate that means initiation happens quickly at the beginning and as your

chain or monomers get added to the reactive chain ends then your polymer chain grows linearly, as you more and more monomers get added to the reactive in chain ends more and more polymer gets added. So, your polymer chain increases linearly and in this case it has, if it has to happen, it has to, the reactions which responsible for the chain termination of, by terminating the reactive in groups has to be absent in this case so that polymer can, polymer chain can increase linearly.

(Refer Slide Time: 15:16)

So, let us compare between the two polymerization processes one more time in the chain and step polymers. In case of this left side is step polymers and this side is chain polymers. So, as you seen that step polymers happens stepwise. So, if and the reactions are between functional groups. So, reactivities of those functional is not very high and it is it is a equilibrium process, and and during the reaction you have to make sure that your equilibrium goes towards right by taking out the bi product formation from the system.

So, it takes much longer time compared to chain reactions where the reactions happen quickly in a shorter time. Obviously as the reaction, reactivity of the functional groups are lower you need high reaction temperature to overcome the activation energy, which requires your your reactions to be done at very high temperature.

Now, high temperature reaction is not only to increase the reactivities in or the equilibrium constant of the reaction, but also if you want to remove, if somebody wants to remove the bi product like say water in polyester formation or say example, a water formation water

form polyester formation to take out the water you have to increase the temperature high and put a high vacuum so that you can take out the water from the system which will give you the equilibration towards product side towards right hand side which will lead to formation of polymer molecules.

And in other case of chain reaction you can do it with lower reaction temperature as well because the reactivity of these monomers are quite high. In case of step growth polymers you generally get a bi product formation and, but if there are example where this reaction happen without formation of bi product formation and in case of chain polymers there is no bi product formation. And as I said repeatedly in case of step polymers you get the high molecular weight only at high conversion where in case of chain polymers you can get high molecular weight even at low conversion, with time or with conversion only the number of high molecular weight chains or the amount of high molecular chain increases.

In case of step polymers the monomers as you have seen from the earlier pages that monomers disappears early from the reaction whereas, in case of chain polymers the monomers disappears steadily with time and as monomers disappears you get high molecular chains forming and typically even step growth polymers you have heteroatom in the backbone whereas, in the chain polymers typically are formed by the carbon backbone. Now, this classification of step and chain growth polymers also is not completely unambiguous.

(Refer Slide Time: 19:02)
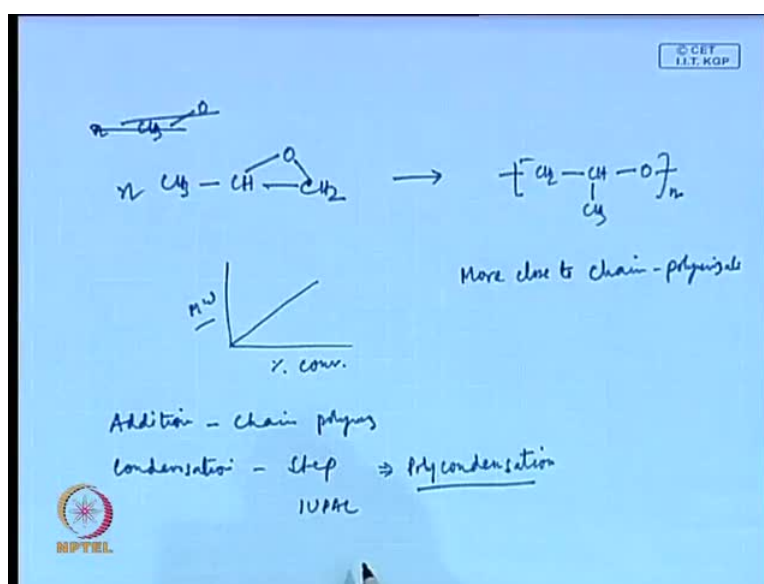
For example if I have a monomer like this, propylene oxide and I make a polymer from this. Now, by from looking at the structure of this molecule or in polymer molecule it is, because it is, has a heteroatom in the backbone with the group it seems like it is a chain growth, step growth polymers, but it is the mechanism of this polymers resembles more of a chain polymers of the type I mentioned in last page, so more close to chain polymerization.

So, this type of ring opening polymers by structure you may confuse with this, with the step growth polymers, but actually from mechanism the way it is synthesized this is more close to a chain polymerization of this type than a step growth polymers where the polymers are formed step wise, dimer, trimer, tetramer and so on. In this case the formation happens by addition of monomers towards the chain end.

More more example of such can be given where this classification is not completely unambiguous. So, what the conclusion, what the final message you should remember that this addition and chain polymers or chain growth polymers they should not be used interchangeably and so as your condensation and step polymers. So, you should remember that though this addition and chain polymers are quite quite similar in terms of the structure and most of the chain polymers are made by addition reactions and most of the step polymers are synthesized by condensation reaction, but they are different they should not be used interchangeably.

Some U, IUPAC has suggested that this should be named as poly condensation in then instead of step polymers or step growth polymerization, but step growth polymers is much more broader nomenclature compared to a term like poly condensation which is which is narrower.

(Refer Slide Time: 22:40)
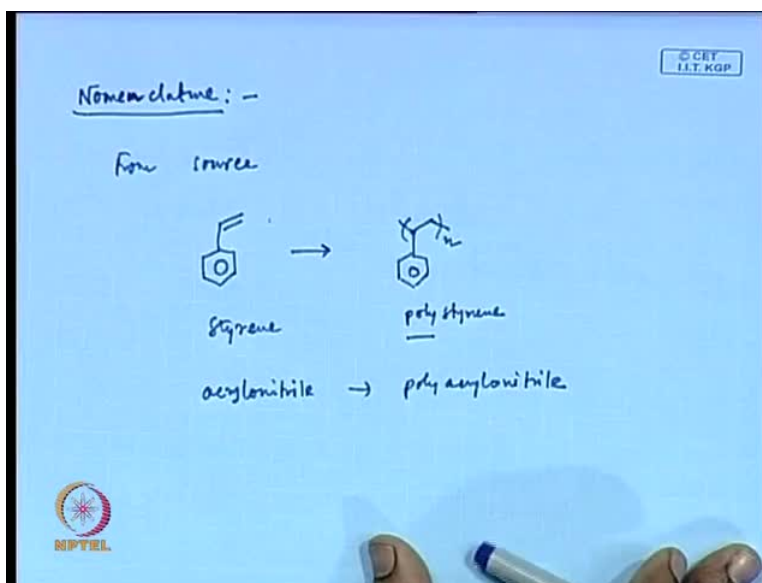
So, now I move to a a new topic nomenclature. How do you name polymer molecules? Again like the various classification ways, you know various ways of classifying polymer molecules this nomenclatural so also not very unambiguous. The most easy simple and least ambiguous method of naming polymers is from its source, from source that means if you have a polystyrene, this is styrene. So, you just prefix this term poly followed by the monomer term and you name this as a polystyrene. So, acrylo acrylonitrile would give you poly acrylonitrile and so on.

So, this is very simple where and this is done mostly from if the polymers are made from a single monomer which monomer is directly converted to the polymer, so styrene to polystyrene and acrylonitrile to poly acrylonitrile.

(Refer Slide Time: 24:32)
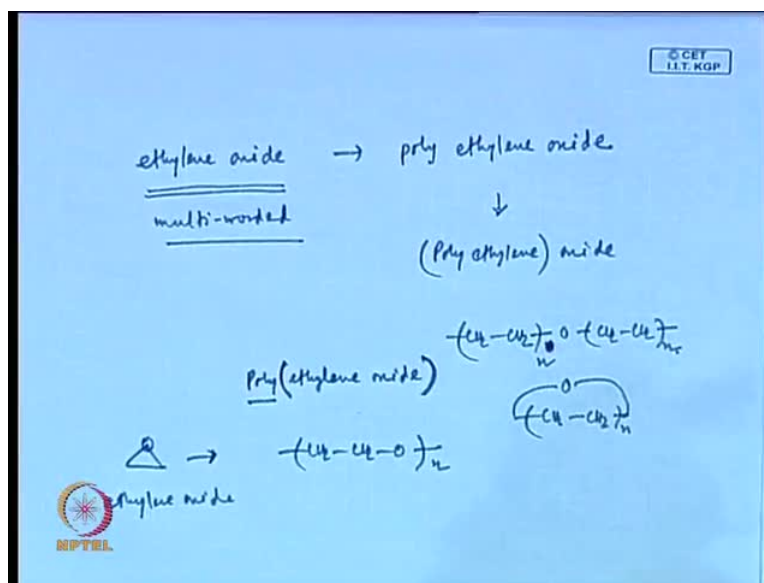
And say ethylene oxide to poly ethylene oxide. Now, if I write this poly ethylene oxide this might give you different structure depending upon how do you represent this molecule. If I write this like polyethylene oxide put a bracket, it might look like this polyethylene or a cyclic.

So, if I write polyethylene oxide that means oxide of polyethylene. It will look like this, but if I write the same molecule polyethylene oxide then it will mean this. This is polyethylene oxide which is actually what it is, this is ethylene oxide and you get a polymer from this like this. So, if you have a multi worded monomer, multi worded then you must put a bracket before prefixing the term poly. So, in this case ethylene oxide you must put a bracket that the monomer inside the bracket and then prefix the term poly. Otherwise, if you do not put a bracket it might gives you a confusion of you know which finally, which structure it is. Some other example we can give.
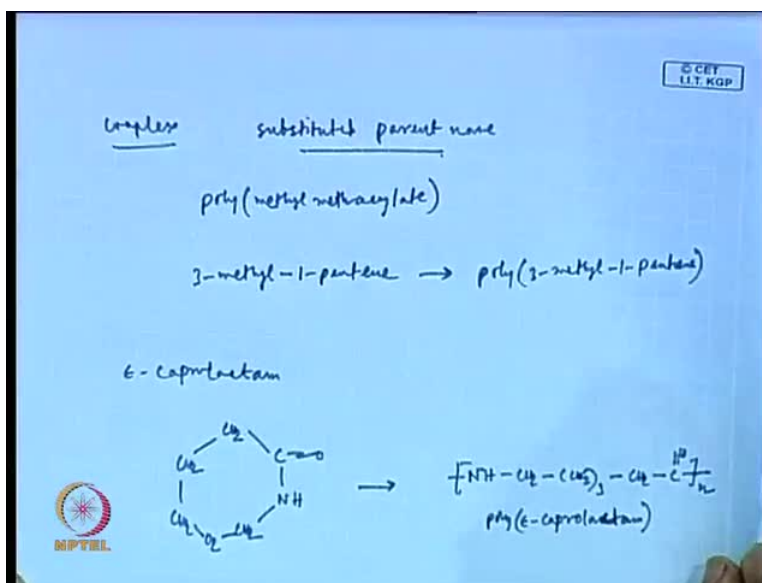
And if there is the monomer is very complex you know or it has substituted parent name also you have to put bracket before you prefix the polymer poly term. For example, poly methyl methacrylate. A polymer form from 3 methyl 1 pentene because these are substituent's. So, you have to put this monomer term within bracket.

So, if I have a monomer like this epsilon caprolactam, I get a, by ring opening polymerization I can get this polymer. Now, this will, how do you name again because this just a polymer of the monomer, so poly caprolactam caprolactam.
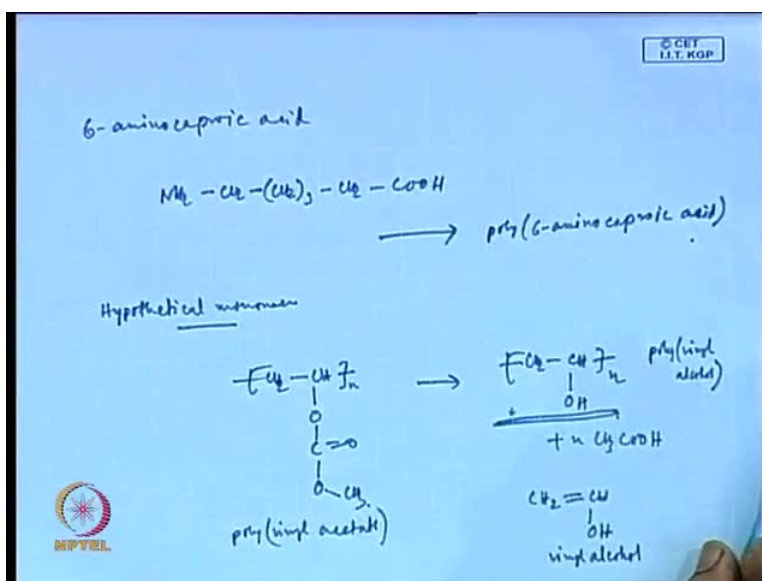
Now, same monomer can be synthesized from condensation of 6 amino caproic acid, you can get the same polymer which were shown here. The same polymer can be achieved by a ring opening polymers of epsilon caprolactam and a self-condensation of 6 amino caproic acids. So, you can also write this as 6 amino caproic acid. So, the same same structure, same polymers sometimes can be named in a different way you know. Sometimes, the polymers are named from hypothetical monomers for example, I have this polymer are generally synthesized by hydrolysis of this vinyl, polyvinyl acetate. This is vinyl acetate and I put poly term in between, it will give poly vinyl acetate.

So, this polymer is generally formed by hydrolysis of the polyvinyl acetate, but if you look without knowing that that it has synthesized from hydrolysis of these you can imagine or hypothesize that it has been synthesized from this monomer which is vinyl and alcohol. Now, you know as a matter of fact that this does not exist as such independently because it exclusively exists at its tautomer of acetyl diode, but because this polymer looks like that it has been synthesized from a hypothetical monomer like this, this is this polymer is generally named as polyvinyl alcohol. So, this is some cases where this is one of the example of where you name the polymer from a hypothetical monomer. How you typically name these step polymers?

(Refer Slide Time: 32:55)
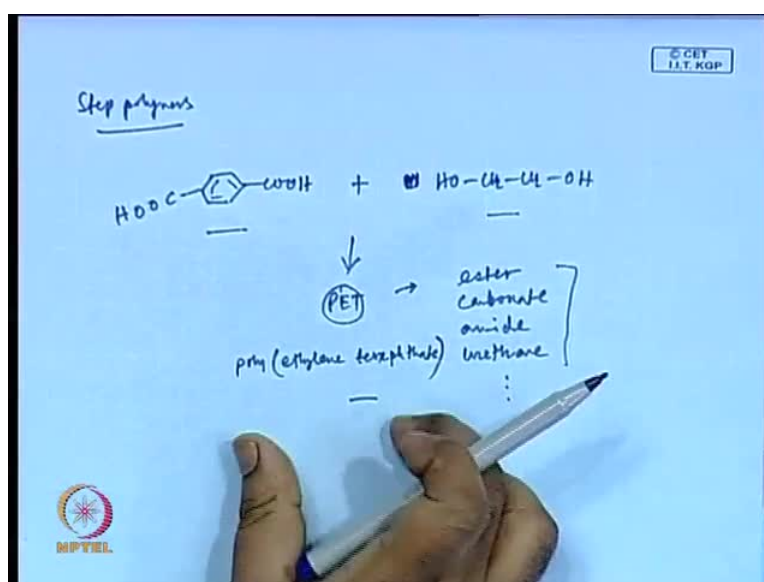
Now, we just gave example of this alpha 6 amino caproic acids condensing to 6 amino caproic acid poly caproic acid in last page, this one. So, if if this is, if the polymer is

forming from by poly condensation or step growth polymers from one monomer then you can simply write prefix poly and put the monomer name after that's, that will gives you name.

If it is form from two monomers likes this terephthalic acid plus ethylene glycol you get polyethylene terephthalate. In this case you indentify in the polymer structure in which class it belongs for example, whether this belongs to a ester class or a carbonate or a amide or urethane. So, you first identify the polymer, look at the polymer and identify which class it it belongs and then name accordingly from which this polymers is synthesized.

So, when you make a polyester from this two monomer terephthalic acid and ethylene glycol you get a polymer which is polyester. So, you know how esters are named. So, name accordingly. How do you name this then ester form from terephthalic acid and ethylene glycol? So, you name it ethylene terephthalate and because it is a polymer so you are writing this poly ethylene terephthalate. So, similarly, you can name other step growth polymers as well where you have to first indentify the functional group or the class in which they belong and then accordingly you name the polymer.

So, so a polymer which is found forms abscisic acid and hexamethylenediamine, abscisic acid and diamine acid and amine which will you have to put name as a amide. So, hexamethylenediamine plus abscisic acid you will call that polymer as a polyhexamethylene abscisic amide, you understand. So, if it is a polyester, you have to name as a polyester like polyethylene terephthalate, if it is a amide you have to name as a amide.

(Refer Slide Time: 36:15)
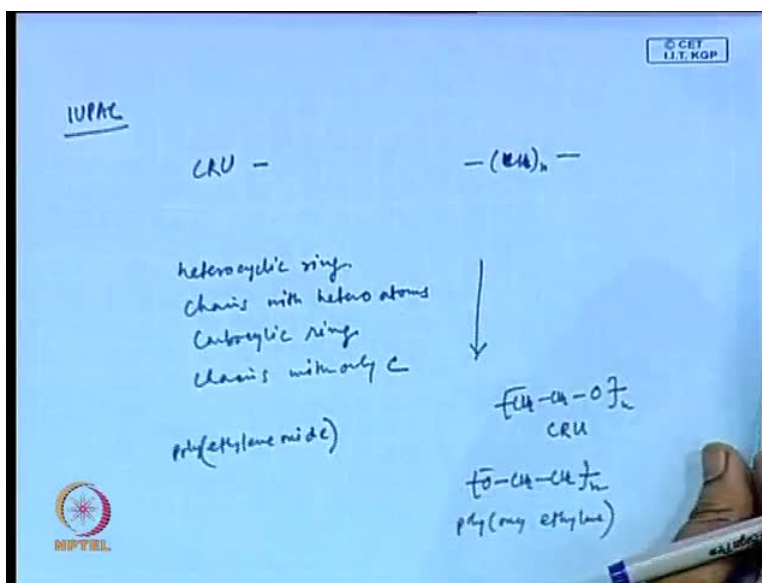
Now, IUPAC because there is so many confusion or about naming polymers IUPAC has given a guideline how to name polymers. For that you have to first identify the constitutional repeat unit of the polymers. The repeat unit we talked about that means if you write a polymer structure and the bracket you have put n that means you have to find the the portion thus unit which is repeating. So, if you build a polymer structure which which structure has to be repeated.

So, in case of polyethylene, if you want to write polyethylene you know this is repeated and once you identify the constitutional repeat unit then you have to place this different parts of this repeat unit according to the seniority from left. You identify the, you already identified the repeating unit and how do how do I name the repeat unit? You have to place the repeat unit such a way that the seniority the one, the part which is senior most gets the, you put in the extreme left hand side. Now, how do you determine seniority? You follow the order like heterocyclic ring chains with hetero atom, carbocyclic ring and chains with only carbon.

So, if I I have polyethylene oxide. Now, IUPAC suggest that we have, I have indentified this is the repeat unit, constitutional repeat unit in this polymer polyethylene oxide, but according to the seniority you have to write this as this. So, name has, will be polyoxyethylene instead of polyethylene oxide.
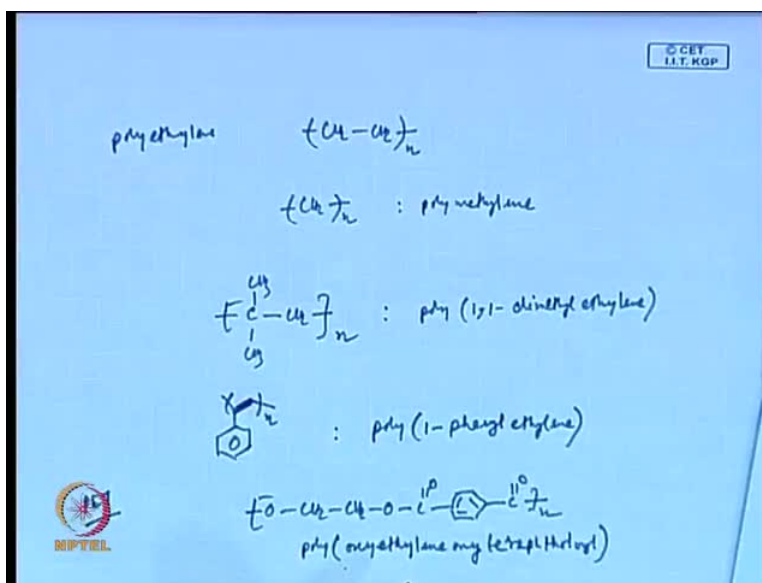
So, though we name polyethylene because we know that this polymer has been made from ethylene molecule, but because the constitutional repeat unit is this then according to IUPAC you have to say this as a poly methylene. So, how do you name this one? Now, in commonly it is known as polyisobutylene, but according to IUPAC it will be poly 1 1 dimethyl ethylene. What about this? Very common polystyrene, accordingly IUPAC it will be poly 1 phenyl ethylene.

So, the PET molecule polyethylene terephthalete we have to write according to the seniority, the constitutional repeat unit like this and IUPAC name accordingly would be poly oxy ethylene oxy, this is tere phthaloyl. The IUPAC name becomes you know very complicated, very difficult mostly for this step growth polymers. So, these all are very easy to name in our conventional way as polyethylene terephthalate. Whereas, IUPAC would suggest that you name this has poly oxide ethylene oxide terephthaloyl.

So, it has become very difficult. So, that is why IUPAC nomenclatures are not very you know used very regularly unless you are making a completed new monomer, new polymer from a new monomer or the the name of the polymers is not conventionally available like polystyrene, if I write tell polystyrene as poly 1 phenyl ethylene you know first time somebody hears the person will not be able to correlate what is, what he is talking about, what I am talking about, but if I say polystyrene it is very easy for the person who is listening, it is easy to comprehend the structure.

So, typically IUPAC nomenclature is not followed in case of polymer nomenclature. Unless you have a new structure from a new monomer then you have to name, there is no common name existing. So, you have to name according to IUPAC or is very complicated name, complicated structure where common names are very difficult like co polymers and and so on, the kind of structures are very difficult commonly then you apply this IUPAC nomenclature procedure and name the polymer. And also in case of polymer specially in case of this the polymers which are sold in large quantities they have trade names.

Trade names width, this is known commonly known in the market and the problem in case of because as I said in earlier classes that in earlier lectures that you, when you use the final a polymer material, you do not use the polymer as such from the synthesis and after it coming out synthesize you add with some other additives and then make compounding and finally, form a product out of that so that the final use of that polymer is not as such 100 percent polymer, there will be some other ingredient has to help and that that plastic or that final use of that polymer, that is no, you said the company so sell this as trade name, where the problem is in trade name that somebody who is know learning polymer chemistry or it is very difficult to remember because same polymer will have different trade names coming from different companies.

A polycarbonate would be called lexan by SABIC, makrolon by Bayer and so on. So, they flexi glass will be PMMA from one supplier, (( )) with some other company. So, it is very difficult. When somebody who is in the market, who is practicing regularly that person which is practicing polymer scientist or polymer chemist is probably useful for them to you know, necessary for them to remember the trade names as well along with the the common name or the the names which typically used for the polymer molecules.
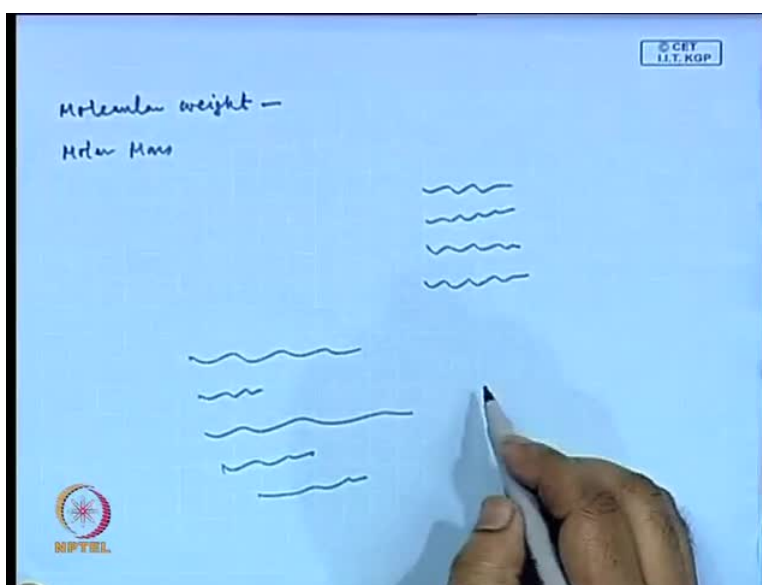
So, after this nomenclature we will move to one of the important aspect of polymer molecular weight. Now, molecular weight you know is relative term that means is a, the weight of a molecule compared to divided by the weight of isotope C 12, for sometimes it also more correctly it mentioned as molar mass which is basically the mass of 1 mol of that molecule. So, you have a unit, molecular weights are unitless whereas, molar mass has a unit gram per mol or kg per mol typically gram per mol.

So, in this course we will use this both the terms molecular weight and molar mass and as you you can understand that these are almost same you know, you can as long as you remember what the meaning is you can use this two term molecular weight and molar mass independently. Now, as I said very beginning that when you make a polymer, polymer molecules and polymer samples always comes with a distribution of molecular weight, not all the chains are of same size, there are not of same sizing, not all the polymers are same size, same (( )). So, you always have a something like a distribution big, small, medium like that.

Now, we will only see the mechanism of polymerization. We will probably more appreciate why you cannot have all the polymer chains of same size or same molecular weight. There always has to be a distribution. Now, when you have a distribution to characterize or to represent this sample having different polymer molecules of different sizes you have to mention the average mass, average molar mass, we will say the mixture

of several molar mass molecules you have to mention a average and also the distribution. Then only it will represent the actual sample what in your hand or what you are handling with.

So, how do you, the polymer are, polymer molecular weights are defined, a simple arithmetic average by total weight divided the number of molecules which gives this, gives us that number average molecular weight.

(Refer Slide Time: 48:01)

Number average molecular weight. Now, again you can write number of average molar mass as well, it is, represent as sometimes like this, some books write like this. So, you can choose to write any of this and sometimes simply M n, because we know the, as a polymer person or when we using polymers in a sample that always is a average.

So, even if you write simply M n it will understand, it will be understood by all of us, we are seeing that it is a average molecular weight, so number average molecular weight. So, you can mention any of this symbol or you can simply mention M n. So, we will in this we will use M n for most of the time. It is a simple arithmetic mean so M n would be total mass or weight by total number of moles. So, we are talking about molar mass in this case, total weight you have, if you have i number of molecules you can sum with i and you can sum in the vision.

N i is the number of molecules, number of molecules in that sample. In the sample having mass of w i. So, total mass will be given by total summation of all the molecules divided by total number of moles, number of molecules in this case, it is a moles. We are talking about moles, number of moles of these things. So, we can write n i, this is M I. So, how do you get total molecular weight? Total mass of the sample n i is the number of moles having molecular rate of this.

So, you multiplied each one n i M i which will give you the weight of or mass of the, that sample and you sum over all the samples and divided by total number of moles gives you the M n 1, number average molecular weight or you can simply write this as x i M i where this x i is mol fraction of the molecules having molecular rate of M i. So, M M n number of average molecular rate is nothing but the simple arithmetic, it is the simple arithmetic mean, average of your sample. So, you get total mass n i M i dived by total number of moles which gives you molecular mass, molar mass, mass in the, mass gram per mol.

(Refer Slide Time: 51:51)

We defined the second molecular rate which is M w bar or M w or M w which is weight, molecular weight which is defined at, in last case we had this, the mol fraction multiplied by the molecular rate of individual fractions. In this case we have weight fraction multiplied by the molecular weight of the individual fractions. So, w i is the weight fraction of the molecules having molecular rate of M i. So, I can write individual molecules by total weight.

So, weight fraction by total weight of the individual fraction divided by the total weight and individual fraction is given by n i M i. So, you have another M i which will give you n i M i square. So, you get M w as this. Remember what was M n? M n was n i M i by n i. Now, in case there is another molecular weight defined M z which is M i cube M i square, this is M z and sometimes viscosity is used as to determine the molecular weight which gives you viscosity average molecular weight M v which is all the expressions are similar, close to each other.

So, this is viscosity average molecular weight. This is z average molecular weight, but most commonly this two terms are used and those are sufficient for your description of your sample and to quantify the breadth of the distribution this term is used poly dispersive index or simply sometimes dispersive index which is given by this ratio. So, the higher is this ratio higher is the poly in dispersive index that means higher is the breadth. So, if you have the polymer sample weight fraction M i like this compared to something like this, this will be, they maybe have similar molecular weight average, but they, this will be much more broader, they will highly will be DI value for this sample will be much higher compared to the value for this sample.

(Refer Slide Time: 56:10)
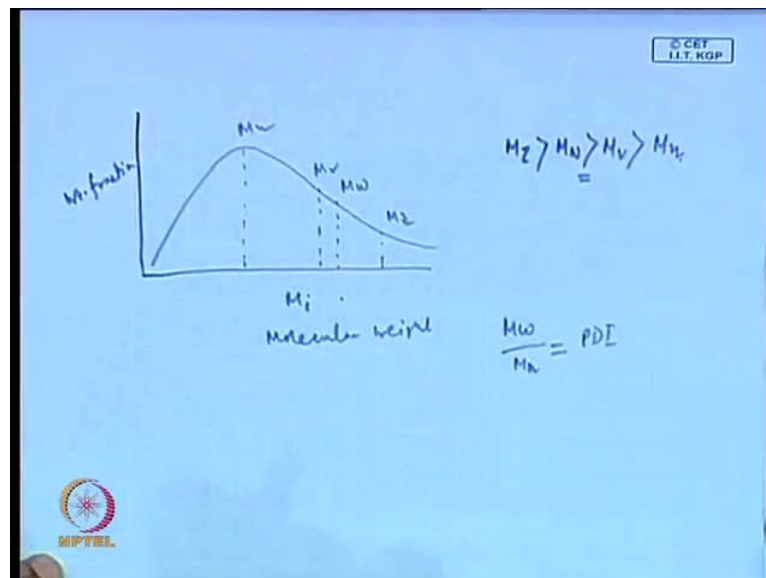
So, typically how this, what is the ranking M z is always higher than M w, then M v and M n. Now, these two are quite close to each other. M v and M w are very close to each other. So, of this all the four molecular rate we talked about M n is having the least value, M z is

the highest and then M w and M w and M v are very close within 10 to 20 percent. M v is always lower than M w, but it is very close within 10 to 20 percent.

So, if I plot weight fraction between and the molecular weight or M I, this is molecular weight the curve is, will look like this, this and this will be say M n, M w, M v and this will be M z. And M remember M w by M n is PDI poly dispersive index. So, in the next lecture I will continue, no why? What is the necessary for having more than one molecular weights for a given polymer sample? Why, cannot we just say M n? We will try to see whether, now, the necessity of, we can explain with the, why with that, what is the necessity of this define molecular weights.

So, in this lecture what we have learned? We have learned the classic continuous and classification that that detailed differences between your chain polymers and step polymers and then we studied the nomenclature. And we have studied the molecular weight and we will continue from the molecular weight and move to the step growth polymerization mechanism in next class.