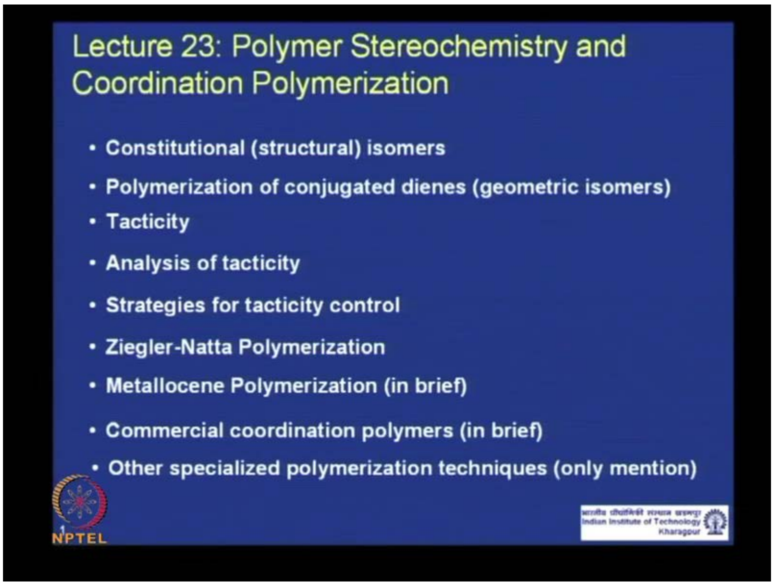
Polymer Chemistry

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

Lecture - 23
Polymer Stereochemistry and Coordination Polymerization

(Refer Slide Time: 00:28)

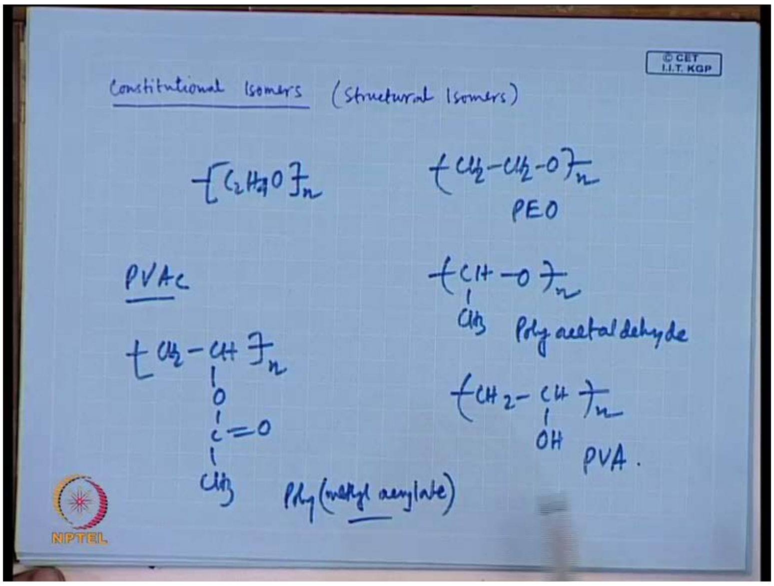


Lecture 23: Polymer Stereochemistry and Coordination Polymerization

- Constitutional (structural) isomers
- Polymerization of conjugated dienes (geometric isomers)
- Tacticity
- Analysis of tacticity
- Strategies for tacticity control
- Ziegler-Natta Polymerization
- Metallocene Polymerization (in brief)
- Commercial coordination polymers (in brief)
- Other specialized polymerization techniques (only mention)

Welcome back to this course on polymer chemistry and in this lecture we are going to begin our discussion on polymer stereochemistry and then follow by our discussion on coordination polymerization. Now, we will start with our discussion on constitutional or structural isomers and then going to polymerization of conjugated dienes which will give some insight about geometric isomerization of polymers. And then going to different types of tacticity possible in polymers, how to analyze those tacticity and how we control or we can preferentially synthesize a polymer with desired tacticity. And then we will talk about Ziegler-Natta polymerization and then we briefly talk about metallocene polymerization and give some example of commercial coordination polymers. Now this we will cover in this lecture and the next lecture which is lecture number 24.

(Refer Slide Time: 01:49)



Constitutional Isomers (Structural Isomers)

$-[C_2H_4O]_n-$

$-[CH_2-CH_2-O]_n-$ PEO

$-[CH(CH_3)-O]_n-$ Polyacetaldehyde

$-[CH_2-CH(OH)]_n-$ PVA.

PVAc

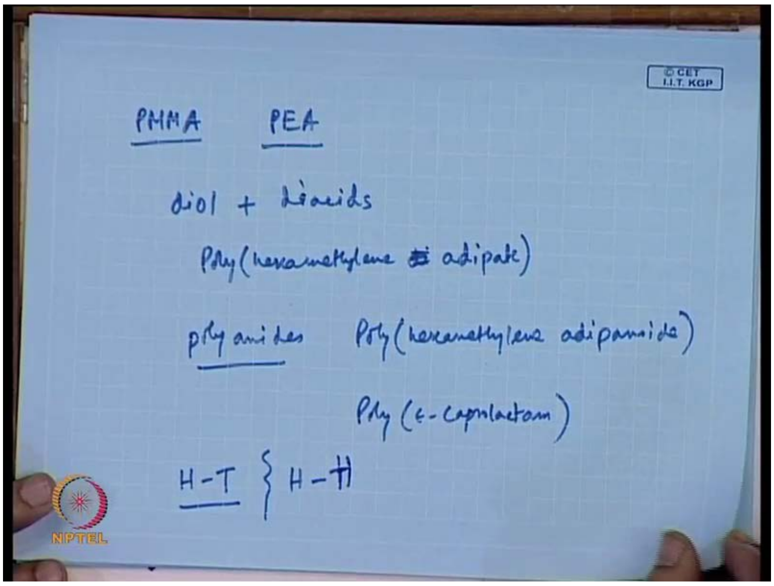
$-[CH_2-CH(O-C(=O)-CH_3)]_n-$

Poly(methyl acrylate)

Now, let us start with our discussion on constitutional isomers which sometimes also called structural isomers. Now, let us consider a polymer having repeat unit molecular formula of C 2 H 4 O and that is the formula of the polymer repeat unit. Now what are the polymers possible with this molecular formula? We can write something like this which is PEO polyethyleneoxide or we can think of a polymer like this, which is polyacetaldehyde or we can also think something like this which all of these three we have now written; they have all same molecular formula, this is polyvinyl alcohol.

So, basically these are the examples of constitutional or structural isomers as we know from our knowledge basic organic chemistry knowledge. Similarly we can write other structural or constitutional isomers like we can write polyvinyl acetate which is having structure. Now this is the structure of polyvinyl acetate. Now you think poly methylacrylate. Now poly methylacrylate; you can yourself write down the structure and then find out that this has the same molecular formula as poly methylacrylate.

(Refer Slide Time: 03:54)



© CET I.I.T. KGP

PMMA PEA

diol + diacids

Poly(hexamethylene adipate)

polyamides Poly(hexamethylene adipamide)

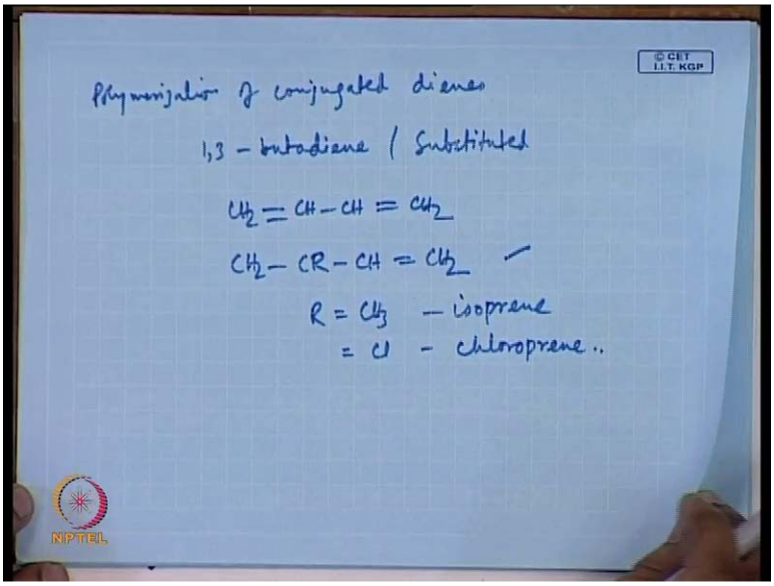
Poly(ε-caprolactam)

H-T } H-H

We can give other examples like poly PMMA poly methyl methacrylate and polyethylacrylatethey all examples of structural isomers. Now we can also have other types of examples; for example we know polyamide. We can have polyamides from the diol plus diacid. Then for example we have, say, from hexanediol plan adipic acid we form poly hexamethylene adipate. We form this polyester. Now we can get the same polyester by ring-opening polymerization of cyclic lactones. We also can form similar condensation polymers like polyamides. Now in case instead of diol if you use hexanediamine and use that adipic acid, we will get poly hexamethylene adipamide.

Now this same polyamide having polyamide having same molecular structure, molecular formula, we can get it from ring-opening polymerization of caprolcatam. So, basically these two are again examples of structural isomers in case of polymer chemistry. Now we also have seen during our discussion of chain polymerization synthesis that always it is the head-tail arrangement when polymer chain propagates. It is a head-tail arrangements always preferred almost exclusively over an arrangement like head-head. Now if you can form polymers having head to tail and head to head structure, then those will also give same molecular formula, but we know that we always get head to tail polymers in case of chain polymerization.

(Refer Slide Time: 06:54)



Polymerization of conjugated dienes

1,3 - butadiene / Substituted

$CH_2=CH-CH=CH_2$

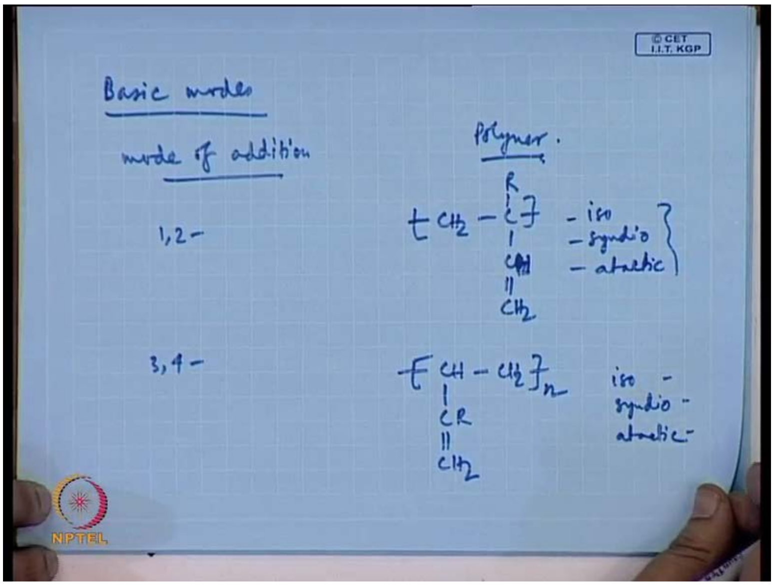
$CH_2-CR-CH=CH_2$

$R = CH_3$ - isoprene

$= Cl$ - chloroprene..

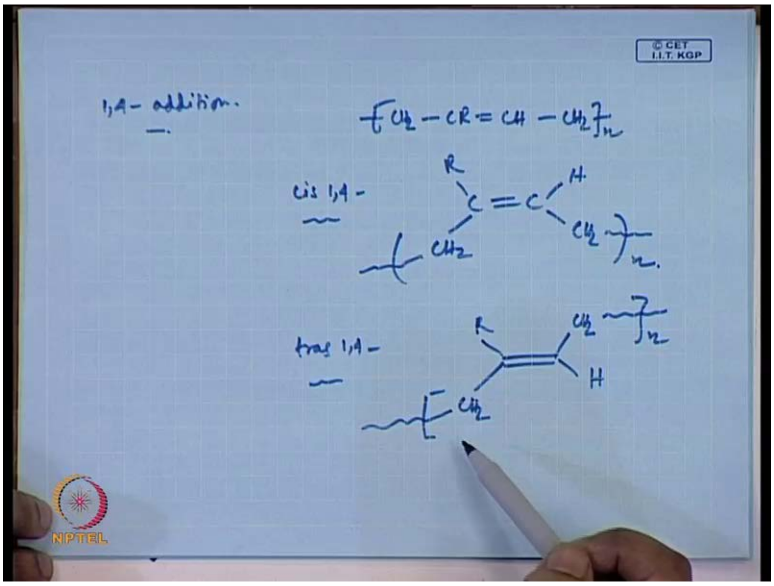
Now we can have let us talk about the polymerization of conjugated dienes. This will gives us the idea about geometric isomerization. Now let us consider the simplest of the dienes which are 1, 3 butadiene. Now you can have substituted 1, 3 butadiene as well. Now we can write general formula like this or we can write if it is substituted we can write a R instead of H and we can write this if R is CH 3, then it is isoprene; if R is chloride, then it is chloroprene. Now how when you do a chain polymerization on these types of monomers, how can you imagine what are the possible polymers these monomers are forming. For example, let us take example of this general structure and see how we can think of a different polymers producing getting produced from these general 1, 3 butadiene type monomers.

(Refer Slide Time: 08:38)



Now let us take out a basic mode by which this monomer can polymerize. Now if this is a 1, 2 addition, then we will get a polymer like this. If it is a 3, 4 addition, we can recall the molecule; this is one, this is two, this is three, and this is four. So, if you have a 3, 4 addition, then you will get a molecule like this.

(Refer Slide Time: 10:08)

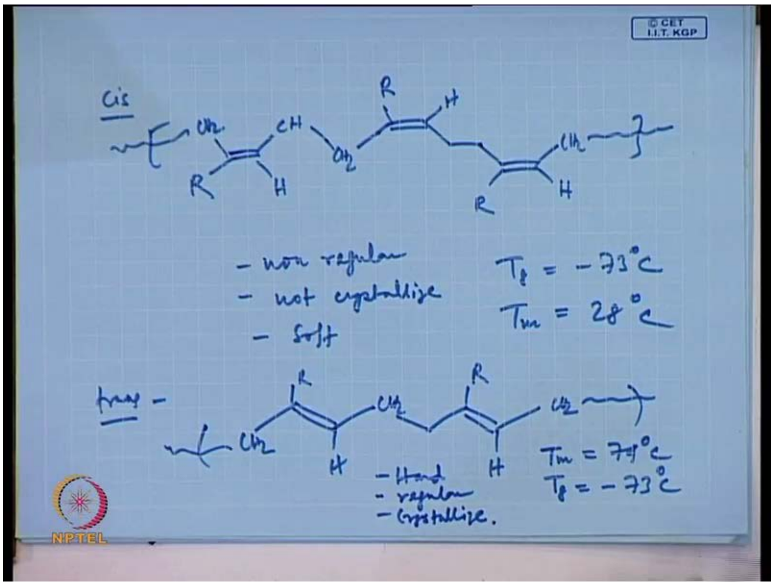


Now there is another possibility of 1, 4 addition. In this case you get the product as this. Now this polymer every monomer unit can stay as cis 1, 4 polymer which gives; you can write like this. Now they can have a trans arrangement as well. This is cis 1, 4 addition;

this is trans 1, 4 addition. Now in the case of 1, 2, 3 and 4 addition, this polymer chain also can have three possible tacticities. We will come in the discussion about tacticity in a minute, but for time being, you take my word as that these polymers which have a stereo center to acidic carbons, they can exist as three form; isotactic, syndiotactic and atactic.

So, basically you can have three possible arrangements for these same as here. So, you can now imagine how many possible isomers or isomeric form you can get by polymerization of this butadiene molecule 1, 3 butadiene molecule. Now what is the difference between these two; this is cis arrangement of the repeat units whereas this is a trans arrangement of the repeat unit. Now if you extend this polymer chain, you can write a cis structure like this.

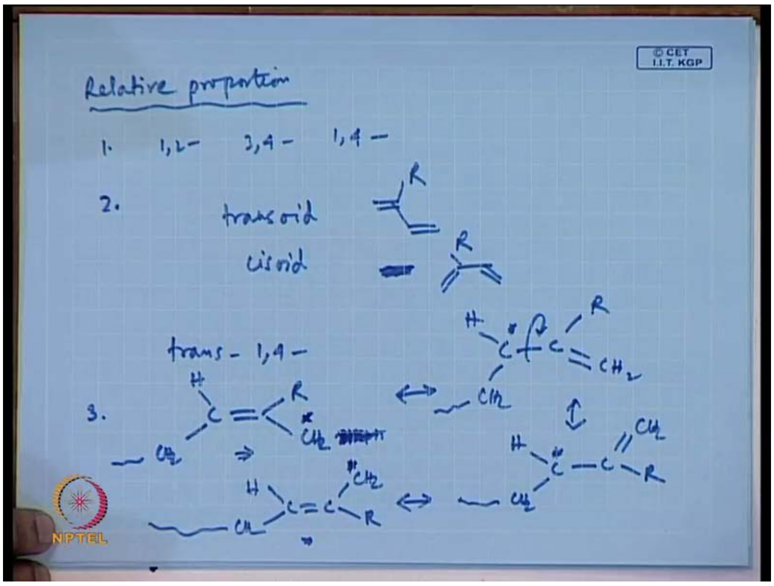
(Refer Slide Time: 12:54)



Now every case if you look the structure you can write yourself; for every repeat unit you have cis arrangement here. Here there is a cis arrangement and for this double bond also you have a cis arrangement. Now you should look at these molecules, this is not very regular. As they are not very regular what happen? They cannot pack well in a crystal lattice and as a result this has soft polymer. So, it has a non-regular structure. So, do not crystallize. Hence it is a soft material. The T g for this is minus 73 C and T m is 28 degree centigrade. Now if you compare this to the trans arrangement. So basically in this case, every monomer unit has a trans arrangement.

Now you can yourself imagine this is a very regular structure which means if you have regular structures, then the polymer chains can come closer to each other and pack very well. As a result they can crystallize easily and hence the melting point is higher 74 degree centigrade compared to 28 degree C. So at a room temperature, this has a crystalline structure. Crystalline domain exists in room temperature which actually gives this polymer the strength and this is a hard material. So this is hard material, regular structure, crystallize easily.

(Refer Slide Time: 16:51)



Now, how can you think of which one is dominant product or which one is not a dominant product? So, in a polymerization what is the relative facts proportion of this all the possible structure we just discussed 1, 3 addition, 3, 4 addition and 1, 4 addition; obviously, between 1, 2, 3, 4 and 1, 4 addition; between these three obviously it will be the addition which will give the intermediate having lowest energy. Obviously, b p dominant product among these three and most cases because the 1, 4 addition gives a longer resonance stabilization in most cases, this is the preferred propagation mechanism compared to the other two.

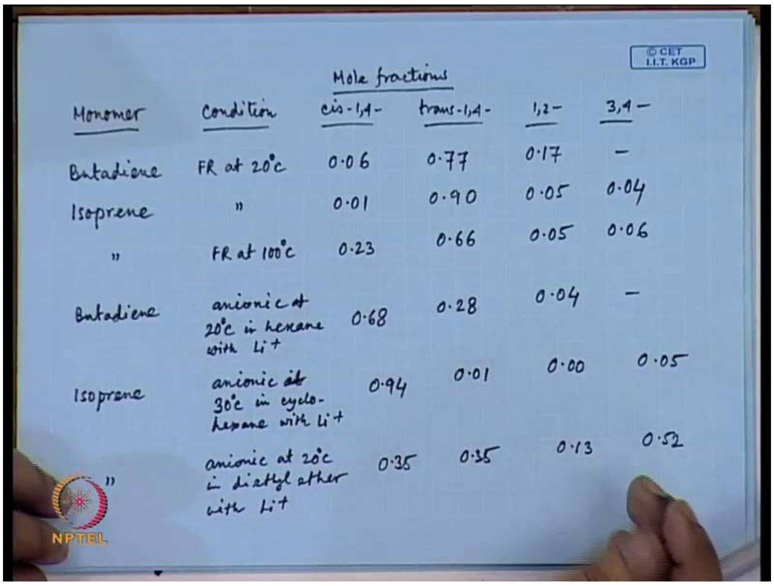
Now once you have a 1, 4 addition between cis and trans, if you just consider what is the possible structure of the monomer itself. Now you can think two type of special arrangement; one is transoid where these two double bonds are in trans and one is cisoid. Now the confirmation or the configuration of the polymer chain will be determined by the confirmation of the adding monomer which the monomer which is getting added. The confirmation of that monomer will determine the resulting polymer chain and between these two, the transoid structure is a much stable structure compared with cisoid structure.

So, unless there is a specific organization or specific mechanism occurring in normal cases, trans 1, 4 will be a predominant product compared to a cis 1, 4 product. Now there could isomerization among the intermediate states. Now if I write, so this is the propagating chain end. Now this can and this will take part in resonance and it can form. This is a chain end; this is not the polymer, this is a chain end. So, it could be radical, it could be cation or it could be an anion. This is the chain end; this monomer will come and add to this and the chain will propagate. Now this single bond can be easily rotatable. It can be easily we can rotate this around this single bond and if we can rotate we can get.

Now when this in resonance, it will form this chain end. So, basically you can have one chain end with one active center and because of resonating structures, it can actually form another geometry around the double bond and now this propagates it will form a trans polymer, if this chain polymer, this chain propagates, it will be a cis product. So, even if you have a cis chain end it can isomerize and give you a trans product. Now that depends upon the temperature. If your temperature is high, then there is this isomerization between this two monomer; these two structures are highly possible. So, there is always almost equal possibility of this propagating and this propagating which mean that the resulting polymer will be a mixture of cis and trans product at a higher temperature.

If you lower the temperature; obviously, this isomerization become less and less probable then the most stable structure which is a trans structure will polymerize which will product. Now if you have this R depending up on size; obviously, you can imagine if R is high, the more the size of R, the trans product will be more dominated because the energy difference between cisoid and transoid will be much higher as you increase the size of the R. So, if you increase size of R in absence of any specific mechanism, the trans will be higher product, and if you decrease the temperature again trans will be a higher predominant product.

(Refer Slide Time: 23:47)

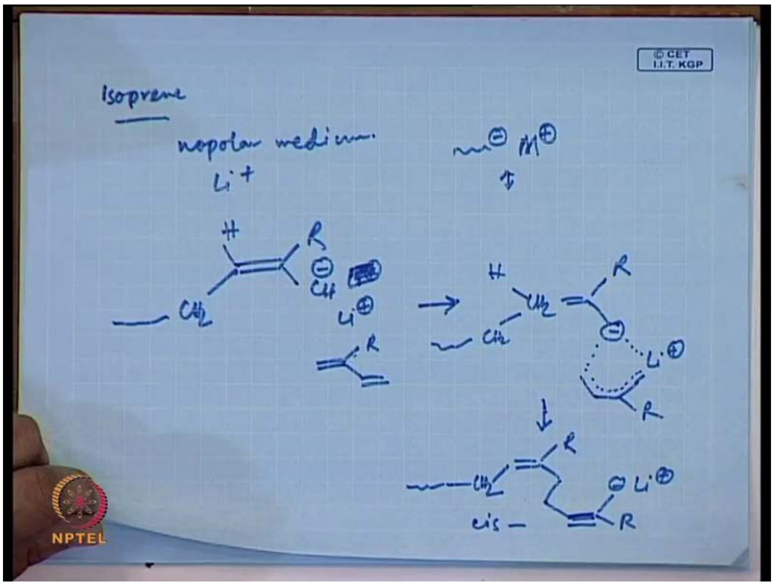


© CET I.I.T. KGP

		Mole fractions			
Monomer	Condition	cis-1,4-	trans-1,4-	1,2-	3,4-
Butadiene	FR at 20°c	0.06	0.77	0.17	–
Isoprene	"	0.01	0.90	0.05	0.04
"	FR at 100°c	0.23	0.66	0.05	0.06
Butadiene	anionic at 20°c in hexane with Li^+	0.68	0.28	0.04	–
Isoprene	anionic at 30°c in cyclo-hexane with Li^+	0.94	0.01	0.00	0.05
"	anionic at 20°c in diethyl ether with Li^+	0.35	0.35	0.13	0.52

Now let us look at some data. If you take butadiene this molecule which does not have any substitution and isoprene which has a large substitution, then if we do a free radical reaction at 20 degree centigrade, you get the trans product higher. If you increase the size of the substitution from hydrogen to metal, the size goes up. So, your trans product is become more dominating than or in comparison to the case where there was no substitution. Now this gives you the temperature; compare between these two isoprene free radical polymerization at 20 degree centigrade and isoprene free radical polymerization at 100 degree centigrade. Obviously as I explained a few minute back that if your temperature goes up the chances of isomerization provided the isomerization will be higher. So, there will be always chances of cis and trans forming together. So obviously if you compare this two, now there is a significant increase in the cis isomer as well. Now what happened in case of ionic polymerization of butadiene.

(Refer Slide Time: 25:34)



So, let us again take example of, say, isoprene. If you do in a non-polar medium and with a small counter ion, now we know in or from our knowledge about anionic polymerization that there is the anionic chain and the count; there will always be the counter ion, say, M plus. Now they can exist in different state if the polarity of the medium is higher, then they will slowly move from methide ion covalent bonding to tight ion pair then to free ion pair. If the polarity of the medium is slower, then they will become closer and closer. If you have non-polar medium they will become very tight ion pair.

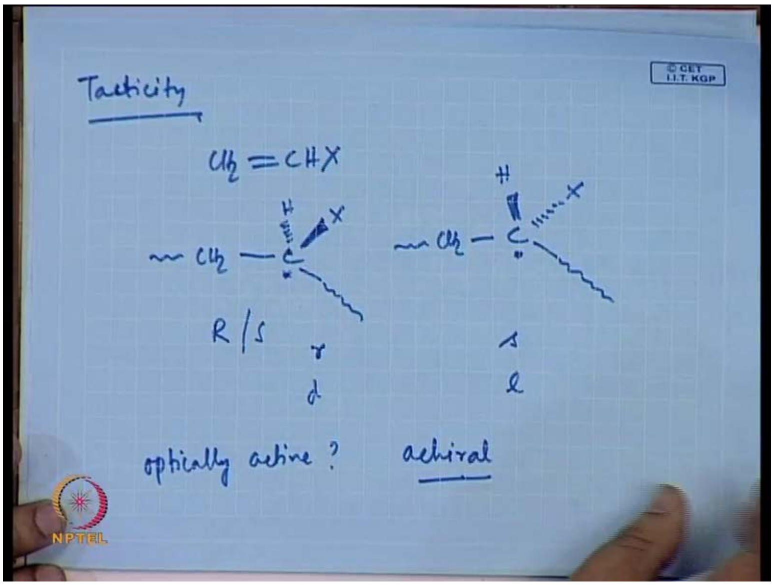
Now if have tight ion pair, then the smaller the size of this counter ion, the tighter would be your interaction between the anionic part and the cationic part. So, in this case non-polar medium and lithium counter ion, they will be remaining as tight ion pair. Now if you use this condition and make a polymerization of, say, conjugated diene this counter ion lithium, so let us write here; we will be very close, they are not isolated. So when the new monomer adds, there will be a interaction, coordination between the chain end the polymer chain end or active chain end, propagating chain end and the counter ion and the monomer like this.

So, there will be an interaction between this positive counter ion and the negative propagating chain end and the new incoming monomer. As a result now the cis this is coming from same side. So, you will form product like. So, this is a cis product. So, because there is a interaction between this counter ion and the chain end and the monomer, they will form a predominantly cis product Now, if you increase the polarity of the medium then obviously, then the counter ion and the lithium will be well-separated. And if they are well separated, obviously, there will not be any possibility of such type of intermediate formation and hence as usual the trans product will be predominant.

So, if the medium is non-polar and your counter ion size is lower, then there will be a possibility or there will be an intermediate formation by coordination between the anionic chain end and the incoming monomer. And that will lead to cis monomer formation whereas if you increase the polarity of medium, then obviously the active chain end and the counter will be well separated, well solvated; so there will be apart from each other, separated from each other. So, there will not be any possibility of this type of intermediate formation. So, as usual the trans product will be dominated. So, if you look few data's you take butadiene and isoprene; obviously, we will compare anionic at anionic polymerization 20 degree centigrade in non-polar medium hexane, anionic polymers at almost similar temperature at non-polar medium. Obviously because there will be a dominated cis product.

In both the cases the cis product is dominating. If you take or increase the polarity of the medium, if you compare these two the temperature is almost closed. If you instead take a cycloid hexane, you take diethyl ether, increase the polarity of the medium keeping any other thing, then look at this; cis product is not that dominating now. If you increase the polarity further then cis product will become lower and lower increasing the polarity of the medium. Now I think with this we have completed discussion on conjugated monomer polymerization of conjugated monomers.

(Refer Slide Time: 32:17)



Now let us talk about the tacticity. If you take a simple monosubstituted monomer and then consider what happens when this polymerize; now we can consider a polymer where you can have two types of stereo chemistry, you can have this. So, these two carbon atom where you have four different substitutions. So, as you know from our knowledge if carbon has four different substitution then this is a stereo center or stereogenic center; sometimes we also call this is an asymmertric center and it is a chiral also. It is in chiral, the chiral center as well. Now you can write you can name whether it is r and s. Now that will depend up on which get priority whether this one or this one. Now that will depend up on which is having higher length, whether there is a functional group or not.

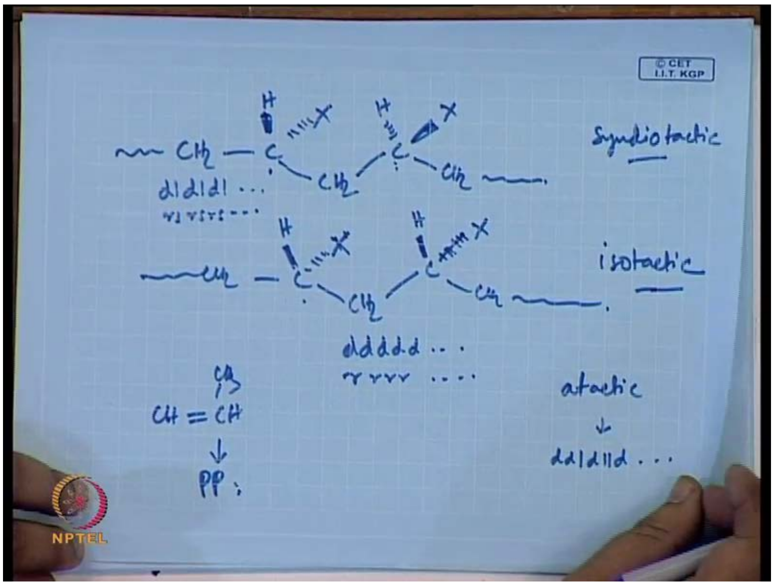
So, we do not know; from this structure we know whether this r and s but at least we know, if this r then this is will be s or if it s this will be r. So, to avoid confusion sometimes it is written at small r lower case r and sometimes this is written as s. And some cases or some people also prefer to write this is d l or we know this is d or l but if it is d then this is l; if it is l then it is d. So, these are the other type of nomenclature we use. Now this cannot be this two configurations cannot be interchanged by simple rotation of around the single bond. Now will that be optically active. By definition this should be a chiral molecule. So, this will be optically active.

Now if you claim that the optically activity is a very short range phenomena and that only depends upon first may be first one or two atoms or groups around this stereo center or asymmetric center. Now in this case in a polymer, there are hardly any differences between, say, first two group or atom in this two case. So, basically though in true sense it is a stereo center and a chiral molecule but because these are long molecules and first few molecules are same, they basically do not show any optical activity. So, they are basically achiral in nature. So, they do not show any optical activity. Now you can argue that the carbon which is almost at the end and on near to the end group and obviously in the end, there will be some functional group and the other side will be the rest of the polymer chain.

So, that symmetric carbon should have some optical activity. You are right saying that the acidic carbon atoms at the end which has one of the functional group associated instead of a polymer chain, this should be chiral and show some activity but their concentration in the polymer is so low that in practically they do not contribute any optical activity or you do not see. Their contribution is so low that you do not see any optical activity when you get to measure the optical activity of the stereo polymers. Now polymer also show optical activity if they are a optically active conformation.

In a macro sense, if your polymer has a, say, helical structure or something like this biomacro molecules, then their conformational structure cannot have any symmetry element which will result in the optimal activity. Now, that happens in case of biomacro molecules where you have exclusively one such conformation present in the sample. But in case of synthetic polymers, now these conformations, there are many conformations polymer conformations possible for single polymers and in a polymer sample the average doubt and you do not see any effective optical activity for that optically active conformation. So, if you add the next monomer what would be the arrangement now.

(Refer Slide Time: 38:14)

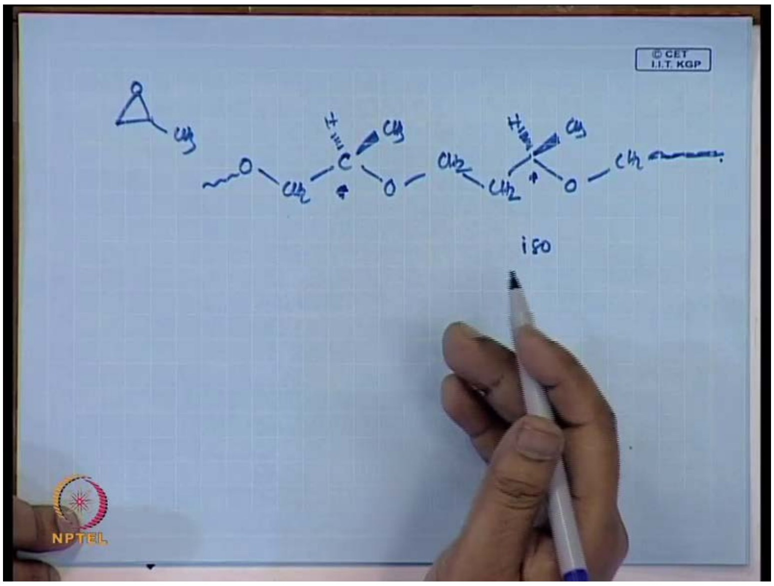


Now, it can have two types of arrangement where I can have. So, basically in this case this two molecules this two carbon atom has different configuration. If this is r then it will be s whereas in this case they have same configuration; if this is r then there also r. So, that is too possible if you can add; if you think of adding another one, you can have another two possibilities and so. Now if all these configuration of these tertiary carbon atoms are same, then we call this is an isotactic polymerization if this is all same. If you can think of that the next carbon also have same configuration and if they alternate, then they are called syndiotactic, this is isotactic and if there is no order, then it is called atactic which is basically random distribution.

So, if I can write this is ddddd or say rrrr, whatever way you write, then this will be the dl dl dl or rs rs rs type of configuration. This alternate configuration of the carbons symmetric centers and in this case it will be arbitrarily atactic would bem say, ddl dlld something like that whatever you want. This is arbitrarily; there is no order as such. Now why you are interested in knowing the syndiotic tacticity of the chain polymers? Obviously as you can expect from the structures, these two both isotactic and syndiotactic will have regular structures. They have regular structures; obviously, isotactic will be having more regular than symbiotic structure.

So, if I consider a molecule like, say, propylene and make polypropylene out of this; may be you can make a isotactic polymerization, you can make a isotactic polymer of from propylene molecule. Then isotactic polypropylene having a regular structure will slice easily and that will be hard molecule. And if you have atactic polypropylene, then again there will not be any regularity in the chain. So, the chains will not be able to slice easily and you will have a soft polypropylene which is of no use in practical sense. So, if you want to have a application practical application of utility of polypropylene molecules, then you should have a regular structures like isotactic or some cases in that atactic also able to crystallize but probably in a lesser extent compared to a isotactic polypropylene. Now we can have similar sort of tacticity in case of in case of polymers where we do not have all carbon backbone.

(Refer Slide Time: 43:19)

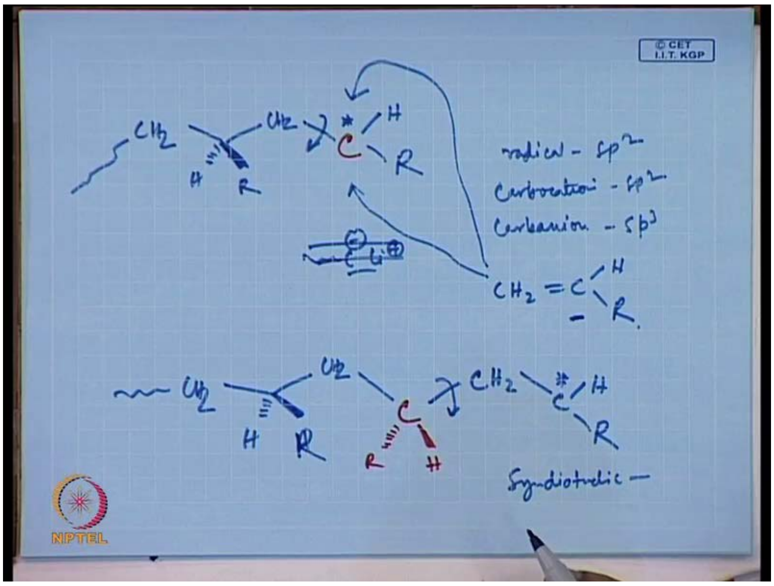


For example, if I do a ring-opening polymerization of ethylene oxide which we discussed in the last lecture. Now you can imagine placing, let us take consider propylene oxide as shown. So, here again you can have if you have same configuration of this carbons then this is like this. This is a same configuration; if you have same configuration from all the molecules you will again have isotactic, if you have alternate configurations then you have syndiotactic and if their configurations are not any regular, they are not arbitrarily placed, then you can again call this is as atactic polymers.

Now in this case unlike polypropylene or other the carbon-carbon chain polymers, if you consider these carbon which is asymmetric in nature, then in this case, this two polymer residues; in this case, this one and this one, they are actually different in nature. Unlike the polymers the chain polymers we have only carbon-carbon backbone, in this case they are different; like in this case you have oxygen next molecule atom and this is CH 2 molecule. So, in this case you expect that this will show optical activity unlike, say, molecule like polypropylene and indeed they do show optical activity. These types of polymers actually show optical activity. Now how do you synthesize; what are the ways you can synthesize, what are the strategies you can take to synthesize one particular stereo regular polymer like isotactic polymers or syndiotactic polymers?

As you know by this time that it is always recommended or beneficial to make or synthesize polymer having a definite stereo regularity whether it is isotactic or syndiotactic, they always have more helpful or more polymers which will have more utility compared to atactic polymers. Now which one of these three possible stereo arrangements which will be dominated that again determined by the medium where you are doing and of course, the initiation mechanism as a cationic mechanism or radical mechanism you have taken.

(Refer Slide Time: 46:31)



For example if I consider c s, that is the terminal carbon atom which is an active center. Let us consider this is a propagating chain whether this is an active center; now it could be radical, it could be anionic, or it could be cationic. Of course if you have a cationic then you have an anionic counter ion. If you have an anionic then you have a cationic counter ion. Now what are the geometries of these carbon atoms, what is the hybridization? If this is a radical, then obviously this is s p 2. If it is carbocation, then also it is s p 2. Now if it is carbon anion, then ideally it should be s p 3 but because you have a substituted group substitution here R, now we know this the monomers which undergo anionic polymerization, they actually get stabilized by resonance with this substitution.

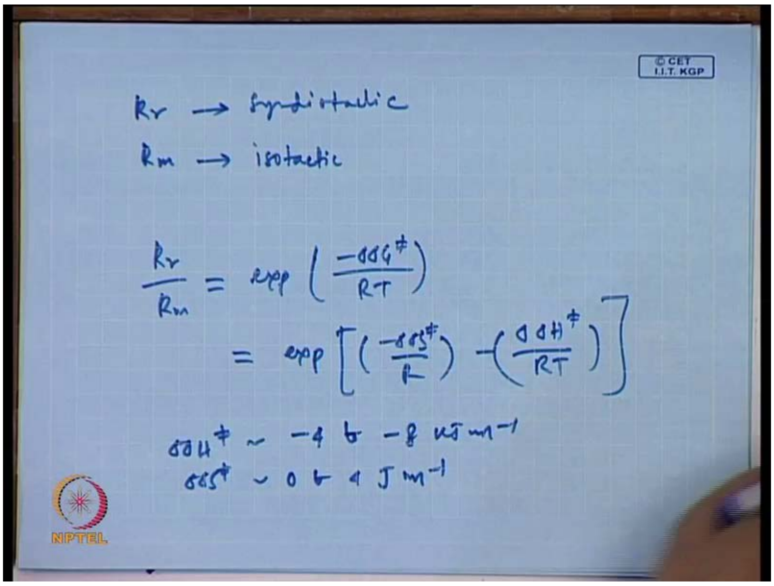
If you remember, say, acrylonitrile or methyl methacrylate where this anion charge get delocalized by resonance with the substitute group and this requirement of resonance with the substituted group again makes this as planar. So, this is actually this carbon is having a planar structure irrespective of s p 2 whether it is radical, carbocation or carbon ion. Now that will change if your counter ions are very tightly bound with the carbon atoms. If you have a anionic group and a carbon ion and if your counter is tightly bound, say, if you have lithium plus, you are doing a reaction with a n butyl lithium in a non-polar medium, then this carbon ion c minus will be having very strong tight ion pairs as we discussed in case of that conjugated diene polymerization; they will be very tight.

Now in this case, this will not be a planar. This carbon will not have a planar geometry. So, first let us discuss where either you have a radical or you have a cation, carbocation or a carbon anion where the counter ions are free; they are not tightly bound. And if they are free that happens in a polar medium, then as we discussed now, you can consider this carbon the terminal carbon as a planar molecule; it has a planar geometry. Now if it has a planar geometry, when the next monomer comes in because it is a planar it can come from both the sides. So, there is no special and so it can come from this or it come from this side as well. So, no special preference of or hindrance from one of the other side's; let us wipe it off to avoid confusion, this one.

So in general case, if you are talking about radical polymerization of or ionic polymerization where you have the counter ions are free, then the stereo chemistry of this carbon atom will be determined once the next monomer gets in. So, what happened? This is the monomer which I have written here at the end now. So, what happened for this, the configuration of this carbon? Which side now the hydrogen and R will come? Obviously, they will prefer because R is up. So, now, R will prefer to be at down and hydrogen will prefer avoid the steric hindrance.

So, unless there is a specific mechanism in normal case, there will always be syndiotactic would be a preferred tacticity. Now again this bond this bond they can fully rotate. So obviously, if the temperature is higher, then it can rotate and form the isotactic polymer as well isotactic linkage and in that case if there is a random orientation of two asymmetric carbon atom, then you are going to get a syndiotactic molecule. So, if you decrease the temperature you are going to increase the concentration, the tendency of syndiotactic formation and if you increase the temperature then their preference would be lost.

(Refer Slide Time: 53:58)



$k_r \rightarrow$ syndiotactic

$k_m \rightarrow$ isotactic

$$\frac{k_r}{k_m} = \exp\left(\frac{-\Delta\Delta G^{\ddagger}}{RT}\right)$$

$$= \exp\left[\left(\frac{-\Delta\Delta S^{\ddagger}}{R}\right) - \left(\frac{\Delta\Delta H^{\ddagger}}{RT}\right)\right]$$

$\Delta\Delta H^{\ddagger} \sim -4$ to -8 kJ m^{-1}

$\Delta\Delta S^{\ddagger} \sim 0$ to 4 J m^{-1}

So, we can write this two approaches when to rate constant when k r and k m where k r is the rate constant for the syndiotactic addition, r means racemic to consecutive carbon they will have different configuration. So, we are writing k r and k m for the measure which will give the isotactic addition; this is syndiotactic addition. Now their ratio will determine which product gets dominated and that will get determined by the difference in the activation gives few energy between the two molecule where we can write like this, where this del del l star and del del H star is the difference in the activation energy different activation entropy and this is the difference in the activation energy between the two routes.

One is syndiotactic and atactic formation and from experiment data we get this around minus 4 to minus 8 kilo Joule per mole and this we get around 0 to 4 Joule per mole. So, this is very low. So, the preference one after one over 1 would be determined by the reference in their activation energies and if they increase their temperature, there will be no preference between this two. And hence there will be tendency for any of the two stereo regularity formations which will lead to atactic molecule atactic polymer. If you reduce the temperature of previously, there will be increased tendency of syndiotactic polymer formation.

So if you increase the temperature, then we will get more of a syndiotactic polymers and again this we are talking about where you have either we are talking about radical polymerization or anionic or cationic polymerization where we are carrying out the polymerization in a polar medium where you have the counter ion and the active centers they are free as they are existing as a free ion. Now what we will do in the next lecture; we will discuss the strategy how we can and how those ionic polymerization can or would give the isotactic polymerization. As you have seen that with decrease in temperature we get preferentially syndiotactic formation; if we increase the temperature we get atactic formation. So, how to get isotactic polymers; we will discuss that in the next lecture.