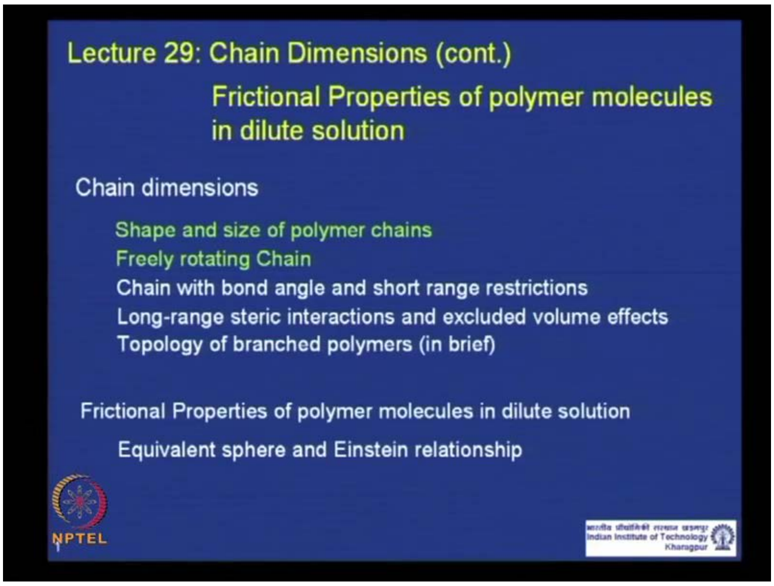
Polymer Chemistry
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 29
Chain Dimensions (Contd.) and Frictional Properties of Solution

Welcome back, now in this lecture we are going to continue our discussion, we are having in last lecture on Chain Dimensions.

(Refer Slide Time: 00:28)



Lecture 29: Chain Dimensions (cont.)

Frictional Properties of polymer molecules in dilute solution

Chain dimensions

- Shape and size of polymer chains
- Freely rotating Chain
- Chain with bond angle and short range restrictions
- Long-range steric interactions and excluded volume effects
- Topology of branched polymers (in brief)

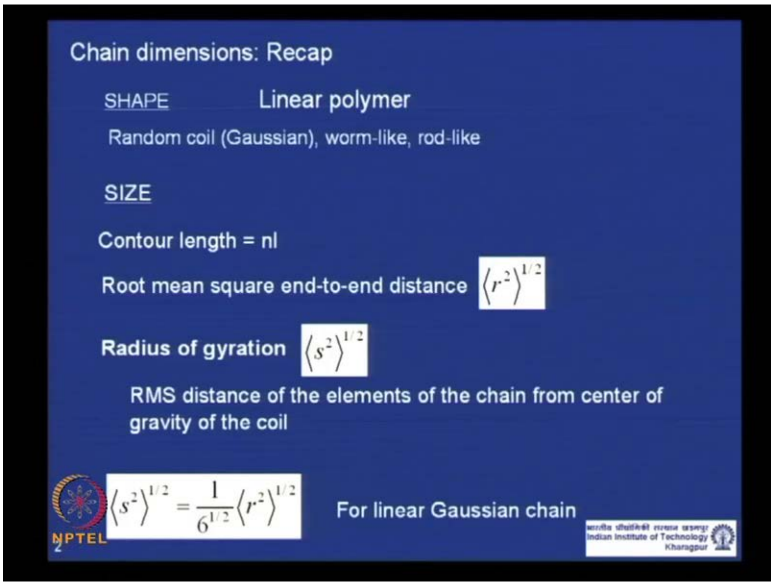
Frictional Properties of polymer molecules in dilute solution

- Equivalent sphere and Einstein relationship

And then we would move to a new topic on Frictional Properties of Polymer Molecules in dilute solution, which basically talks about mainly the viscosity of polymer solution. Now, in the topics we have completed our discussion shape and size of polymer chains, and then you also completed deducing an expression for understanding expression for freely rotating chain. Now, what we are going to discuss is how the chain dimension, the chain size namely the RMS end-to-end distance; and radius of gyration varies when we introduce the restriction on bond rotation.

And then we also, we will understand how the long range steric interactions effect the polymer chain dimension; and then the end we will start the discussion on frictional properties of polymer molecules in dilute solution.

(Refer Slide Time: 01:45)



Chain dimensions: Recap

SHAPE Linear polymer

Random coil (Gaussian), worm-like, rod-like

SIZE

Contour length = nl

Root mean square end-to-end distance $\langle r^2 \rangle^{1/2}$

Radius of gyration $\langle s^2 \rangle^{1/2}$

RMS distance of the elements of the chain from center of gravity of the coil

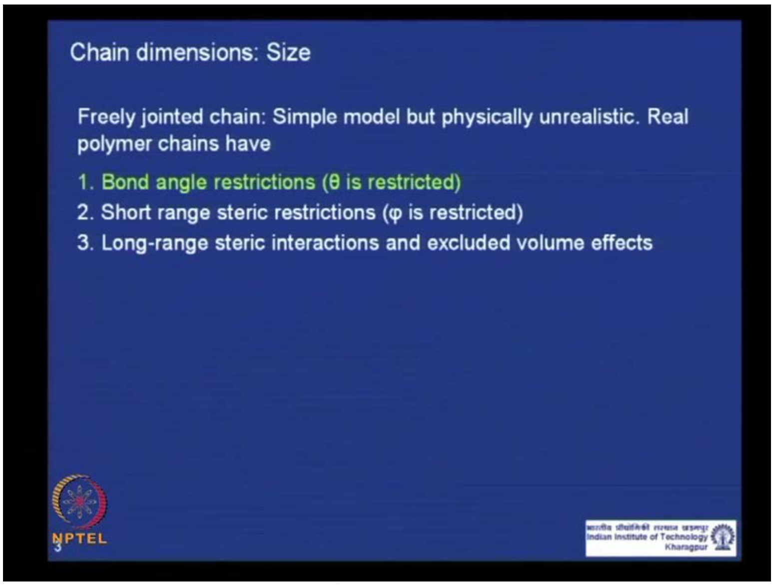
$\langle s^2 \rangle^{1/2} = \frac{1}{6^{1/2}} \langle r^2 \rangle^{1/2}$ For linear Gaussian chain

Now just recap, we had whatever discussion we had in last lecture, about the chain dimension, polymer chain dimension for a linear polymer chain we discussed that most of the polymer chains are flexible in nature; and they form random coil structure, either in solution or in merit. And we used Gaussian distribution function to get or understand the end-to-end, RMS end-to-end distance for that, then if the chain or the backbone, polymer backbone become stiff, then polymer the coil, the random coil becomes more elongated, and it is become worm like; and if it is if the backbone becomes more stiff, then ultimately the chain become like a rod, so these are the possible shapes a polymer chain can take.

In terms of size, we discussed a contour length, which is basically n multiplied by n is the number of bonds, and l is the length of each bonds. And then we introduced, we said that because the random coil is always fluctuating in because we have several conformation, numerous conformation the coil shape is always changing. So, actually you have the end-to-end distance between in a polymer coil is always changing, so you have to get a time average end-to-end distance, we introduced the term root mean square end-to-end distance, which is given by this.

And then you also discuss radius of gyration again time average quantity, which is the root mean square distance of the, elements of the difference parts of the polymer chain from the center of gravity of the coil. And you also found that there is a relation between the radius of gyration, and root mean square end-to-end distance, so if you find if you find one, the other one you can get it from this expression.

(Refer Slide Time: 04:06)



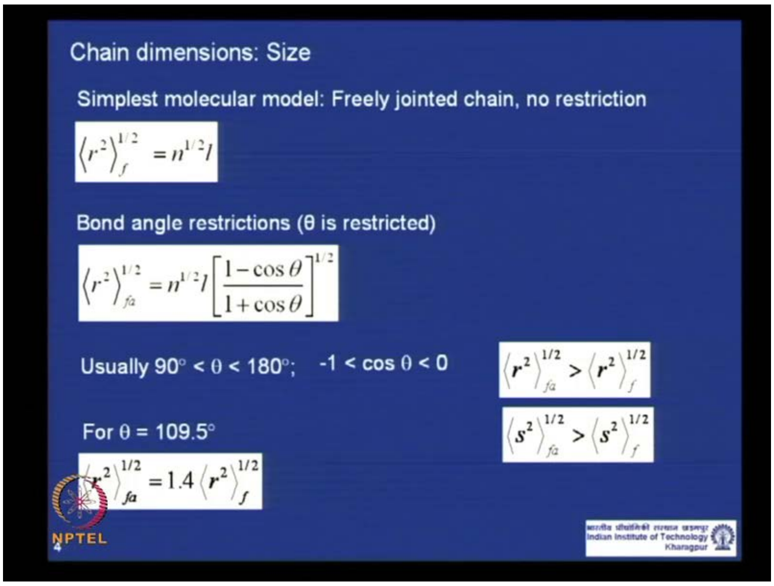
Chain dimensions: Size

Freely jointed chain: Simple model but physically unrealistic. Real polymer chains have

1. Bond angle restrictions (θ is restricted)
2. Short range steric restrictions (φ is restricted)
3. Long-range steric interactions and excluded volume effects

We discussed first the freely rotating chain, how the size the end-to-end distance, RMS end-to-end distance comes about, we found that that is n to the power half multiplied by l. And then we also discussed the effect of RMS end-to-end distance (( )), the effect of bond angles restriction on the RMS end-to-end distance, and then today we will start discussing on these two topic or in these two restrictions.

(Refer Slide Time: 04:48)



Chain dimensions: Size

Simplest molecular model: Freely jointed chain, no restriction

$$\langle r^2\rangle_f^{1/2} = n^{1/2} l$$

Bond angle restrictions (θ is restricted)

$$\langle r^2\rangle_{fa}^{1/2} = n^{1/2} l \left[\frac{1-\cos\theta}{1+\cos\theta}\right]^{1/2}$$

Usually $90° < \theta < 180°$; $-1 < \cos\theta < 0$

$$\langle r^2\rangle_{fa}^{1/2} > \langle r^2\rangle_f^{1/2}$$

$$\langle s^2\rangle_{fa}^{1/2} > \langle s^2\rangle_f^{1/2}$$

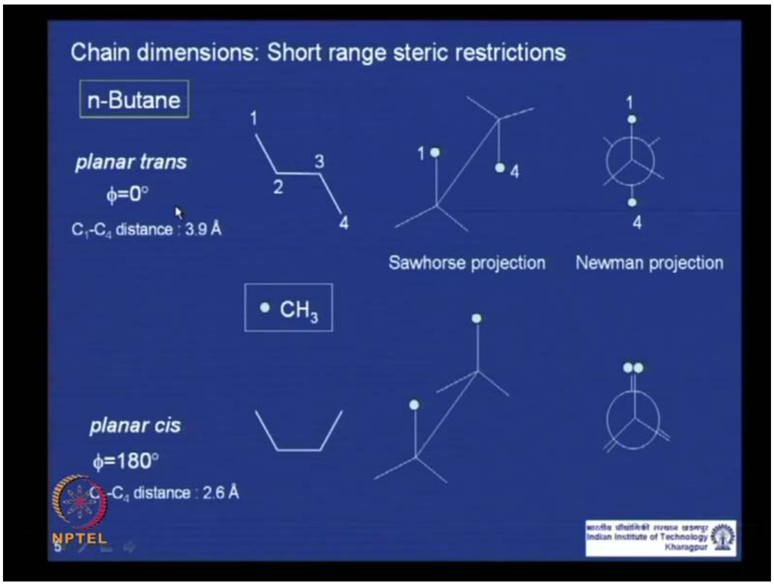
For $\theta = 109.5°$

$$\langle r^2\rangle_{fa}^{1/2} = 1.4\langle r^2\rangle_f^{1/2}$$

So, this is what you found, freely rotated, freely jointed chain there is no restriction we got RMS end-to-end distance for free chain, if as a subscript it is meaning is that it is a free rotating chain, it is given by this expression and when you have bond angle restriction, we get this expression. Now, most cases usually polymer and carbon backbone, so it has a theta between 90 to 180 which means cos theta is negative; so as expected this will be more than the end-to-end distance, RMS end-to-end distance restriction from bond angle will be higher than the end-to-end distance for freely rotating chain.

And same as the radius of gyration, most cases we have now tetrahedral bond angle is 109.5 degree in that case, this factor comes out 1.4 times. So, basically the root mean square end-to-end distance for bond angle restricted chain would be nearly about 1 4th times, 1.4 times of the freely rotating chains RMS end-to-end distance.

(Refer Slide Time: 06:18)



Chain dimensions: Short range steric restrictions

n-Butane

planar trans

$\phi=0°$

C_1-C_4 distance : 3.9 Å

Sawhorse projection

Newman projection

• CH_3

planar cis

$\phi=180°$

C_1-C_4 distance : 2.6 Å

Now, let us talk about the restriction on bond angle bond rotation, rotation about the single bond, and which we are talking about because this is this restriction comes out because of near nearby groups. So, this is this is short range steric restriction, now we start our discussion with a simple molecule of n butane, and we found out how the conformation, what are the confirmations this normal butane can take, and how the potential energy changes with different conformations.

So, what which is we know that, the word the potential energy, the chances of that being stable is higher; so this is 1, 2, 3, 4, these are four carbon atom in a butane, we are not writing the hydrogen groups here. Now, this configuration, we can put in two types configuration sawhorse projection, and Newman projection, and then in this case, this 1 methyl group and 4 methyl group is trans to each other. So, we are telling this conformation as planar trans, and we can show this conformation in Newman projection like this, this dots are CH 3 when this CH 3 groups are same side in the same plane, there are seems to each other, then we have a planar cis conformation, and this is shown by Newman projection in this.

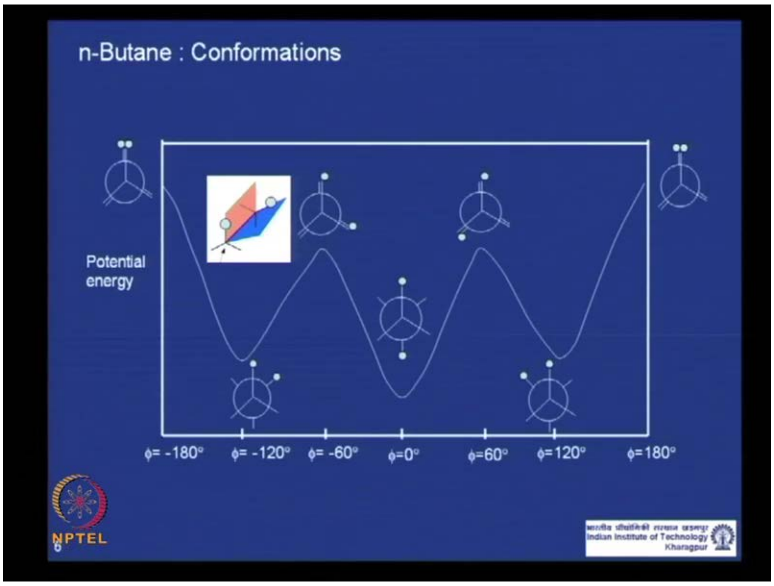
Obviously this here, because of short range steric interaction is lower, this will be much stable, much more stable than this is conformation where the short range steric interactions are higher between the two methyl group. Now, in this case, we are defining the dihedral angle is 0, dihedral angel is the angle between two planes, one plane is going through c 1, c 2, and c 3; so this plane 1, 2, 3, the plane going through this three carbon 1, 2, 3 that is one plane, and second plane is between 2, 3, and 4.

Now, in this case they basically (( )) above this line, and other one lies below this line, so we are telling this is a dihedron angle of 0 degree, and in this case obviously, dihedron angle of 180 degree. Now, some books, some texts follow that this is 0 degree, so do not confuse, in this course telling this is 180 degree, and this is 0 degree because we will use this phi in the expression of RMS end-to-end distance as well, so this phi is equal to 0, and this is phi is equal to 180 degree.

So, the end-to-end distance in this case, distance between two ends, two carbon atoms present in the ends at 3.9 ampere, and in this case 2.9 ampere and as you have, you can understand and this is more stable conformation than this. So, obviously the end-to-end distance would be more closer to this, compared to this; and if there was no restriction, for a free rotation it would have been somewhere in the middle.

If there are no restriction on one rotation obviously, it would have been somewhere in between in middle, exactly in middle, but because this gives when you go from middle towards the planar trans conformation, you get lower energy, lower potential energy whereas, you can go towards cis conformation you get higher energy. So, it is always likelihood that pure end-to-end distance will be higher, compared to when there was no restriction of potential.

(Refer Slide Time: 10:53)



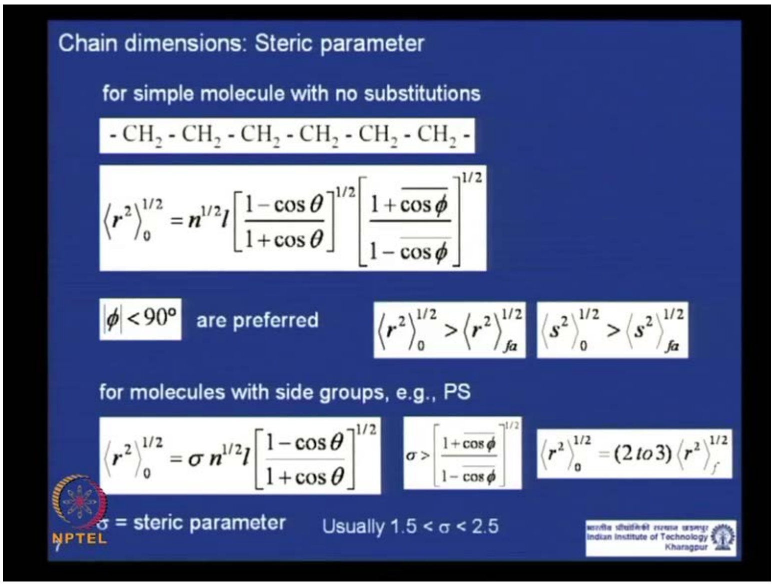
n-Butane : Conformations

You can show schematically, how this potential energy varies with different conformation, which is obtained by changing the dihedron angle, this one is the planar trans conformation which as I showed, because these two methyl groups are extremely apart, they have the least potential energy. And you can rotate the, you are looking from front side, so this is 1, this is 2, this circle is 3, and this is 4 these are the four carbon atoms, so you are looking from front side if you rotate the c 2, c 3 single bond then you will get all this from other conformation. If you if you rotate the c 2, c 3 on clockwise direction, you will get this conformation, if you put in anticlockwise direction, you will get this other conformation.

For example, if you rotate this, you take this corner and rotate 60 degree, then this methyl will come here, this methyl will come here, and this bond will come here, and this bond will go there. Now, these are this conformations are eclipse conformations, and these three are (( )) conformations, and most specifically this is trans conformation, and these are gauss conformations. So, obviously, the polymer chain or in butane will have in this case n-butane will more likely to be somewhere here, which will have higher distance between c 1, and c 4 ends.

Now, you can imagine, now if you now go from n butane, to n pentane and then slowly increase the number of carbon atoms to make a polymer, to how how this potential energy will look like. If you imagine that, it will be more more towards this region, the minima will be or the least energy would be, for larger polymer molecule, they will be more such conformations; and the lowest energy conformations will be around here, will be around say 0 degree to 90 degree range, so you can imagine that, there is numerous possible conformations for a linear polymer.

(Refer Slide Time: 13:45)



Chain dimensions: Steric parameter

for simple molecule with no substitutions

$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$

$$\langle r^2 \rangle_0^{1/2} = n^{1/2} l \left[\frac{1-\cos\theta}{1+\cos\theta}\right]^{1/2} \left[\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}\right]^{1/2}$$

$|\phi| < 90°$ are preferred

$\langle r^2 \rangle_0^{1/2} > \langle r^2 \rangle_{fa}^{1/2}$ $\langle s^2 \rangle_0^{1/2} > \langle s^2 \rangle_{fa}^{1/2}$

for molecules with side groups, e.g., PS

$$\langle r^2 \rangle_0^{1/2} = \sigma n^{1/2} l \left[\frac{1-\cos\theta}{1+\cos\theta}\right]^{1/2}$$

$$\sigma > \left[\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}\right]^{1/2}$$

$$\langle r^2 \rangle_0^{1/2} = (2\ to\ 3) \langle r^2 \rangle_f^{1/2}$$

σ = steric parameter Usually $1.5 < \sigma < 2.5$

Now, that is very difficult to you know get the end-to-end distance, due to that rotational restrictions, short range rotational restriction, it is difficult to get theoretically, it is possible for simplest molecule which is like a polyethylene, which keeps this term. So, this is additional term appearing, and this o is for the subscript for end-to-end distance, for a chain RMS end-to-end distance for a polymer chain which has both one angle rotation, and also short range steric, rotational restriction due to short range steric interactions.

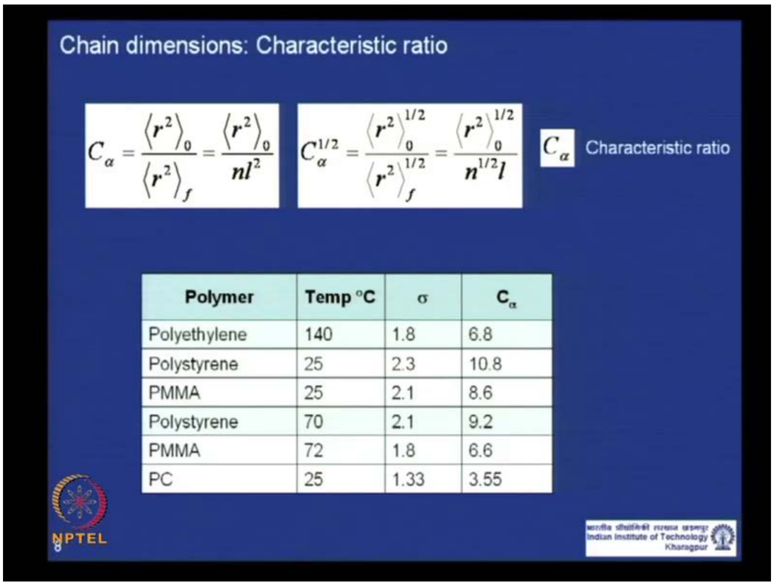
Now, as we said the least energy would preferred around dihedron angle 0 and or both the sides, so in that case you can, this term would be more than one, so this term due to bond rotational restriction will be higher than the term, which was for the other end-to-end distance, where it has only bond angle restrictions (Refer Slide Time: 14:59). So, the molecules, now we just talked about this theoretical number or this expression for this simple polyethylene molecule; now if you have side groups obviously, this rotational restriction will be higher, because the polymer will be much more stiffer than polyethylene molecules, so rotational restriction will be higher.

And those situations become much more complicated, and those are basically very difficult to get impossible to get theoretically, so what is done instead of getting expression for the contribution due to the rotational restriction, for short range steric interaction, we have introduced a new term which is called steric parameter, which take care of the, who takes care of the rotational restriction term. So, this was equivalent to this term for simple polyethylene molecule, for a much stiffer molecules like polystyrene, we cannot get such expression what we are introducing instead of this term, we are (( )) steric parameter.

So, you can guess obviously, you can expect that this term would be higher than this term, because this was for polyethylene molecule, and this is for more stiffer chains, so this term would be higher than this expression, and this term is usually comes around 1.5 to 3.5. So, if you compare this dimension, which is basically we are calling this 0, this whole meaning that the RMS end-to-end distance for polymer chains which is both bond angle restriction, and also rotational restriction around the single bond, due to short range steric interaction; and this terms we are calling as unperturbed dimension, they are 1.4 times, and multiplied by this time, so it will be around 2 to 3 times.

This was expression for the freely rotating chain, this contributes about 1.4 times, and this contributes to 1.5 to say 2.5 times, so this comes around 2 to 3 times. So, if there is no restriction, no restriction in the chain, no restriction of bond angle and bond rotation, then whatever dimension the RMS end-to-end distance you would have got, in actually you consider the bond angle restriction, and also the bond rotation restriction that would be having the RMS end-to-end distance about 2 to 3 times, more than that.

(Refer Slide Time: 18:58)



Chain dimensions: Characteristic ratio

$$C_\alpha = \frac{\langle r^2\rangle_0}{\langle r^2\rangle_f} = \frac{\langle r^2\rangle_0}{nl^2}$$

$$C_\alpha^{1/2} = \frac{\langle r^2\rangle_0^{1/2}}{\langle r^2\rangle_f^{1/2}} = \frac{\langle r^2\rangle_0^{1/2}}{n^{1/2}l}$$

C_α Characteristic ratio

Polymer	Temp °C	σ	C_α
Polyethylene	140	1.8	6.8
Polystyrene	25	2.3	10.8
PMMA	25	2.1	8.6
Polystyrene	70	2.1	9.2
PMMA	72	1.8	6.6
PC	25	1.33	3.55

Now, we the stiffness can be also measured by, if you get this term, this term is basically the ratio of the unperturbed dimension divided by the dimension for a freely rotating chain. So, basically this term gives you the increase in the end-to-end distance, or increase in the dimension, because of the steric restriction both bond angle, and the rotational restriction, which means this is a parameter which predicts or which gives the idea about the stiffness of the chain.

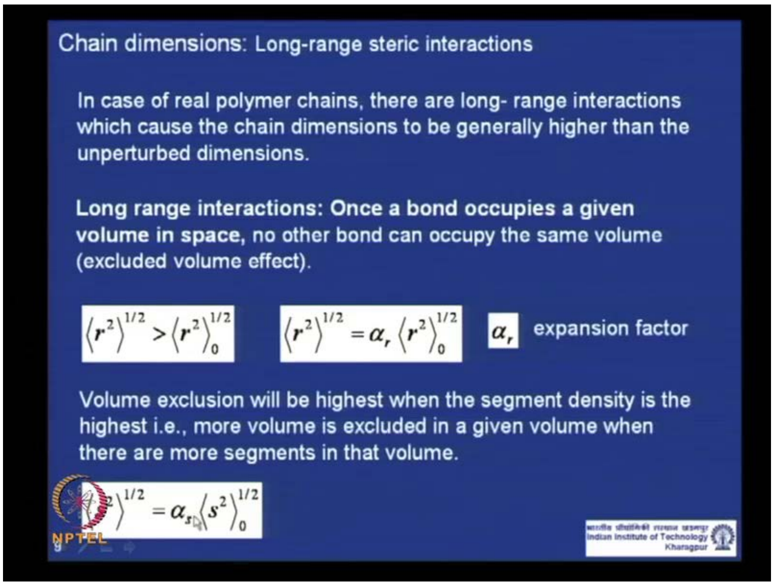
See, in this call characteristic ratio, so the higher this value you will the polymer chain you would expect would be much more stiffer, let us compare few numbers, (( )) numbers for this steric factor, and characteristic ratio for polymers at different temperature. Now, obviously, as we discussed we would expects polyethylene to be much less stiff than a polystyrene molecule, so this these are the steric factor and the characteristic ratio, they are higher than polyethylene, PMMA has less bulky side group, so it is expected to be lowest, you know having lower lowest stiffness than polystyrene, so it has it has this numbers lower than polystyrene.

Now, if you compare different temperature, so you take polystyrene at 25 degree centigrade, and polystyrene at 70 degree centigrade; obviously, temperature goes up you expect that, the restriction for single bond rotation will be coming down, because you have more kinetic energy, because higher temperature, obviously, the rotational the restriction around the single bond would come down. So, polymer actually become less stiff, and if you can you compare this numbers, numbers are also telling that polystyrene is 2.1 here, and at higher temperature and characteristic is 9.2 compared to a temperature, which is lower.

Same is the case for PMMA, if you compare PMMA, if you compare the number between 25 and 72; PMMA is less stiff at higher temperature, because the rotational restriction comes down as we increase the temperature. Now, look at this number of polycarbonate, this stiffness is even lower, now what is the use of this stiffness, now when you have a polymer coil or a polymer substance, now if you impact, if you have a substance if you impact on that matrix or on the polymer substance; obviously, the chains are flexible, then it can absorb the energy (( )) applying, so it will not break.

And if it is very stiff obviously, it will break immediately or it will break easily, as you can example glass, because glass is very stiff it breaks as soon as you hit it, whereas if you have rubber or a soft polymer, if you hit it, it would not break, it absorbs the energy because the glass chains are much stiffer compared to a rubber chains, where the rubber consists of flexible polymer chains, so they absorb the energy. Because the polymer can change the conformation and as of the energy, now polycarbonate having lowest stiffness given by this number, so polycarbonate should be as you explains much much more impact resistance polymer compared to say PMMA or polystyrene, and which is a fact among PMMA, among PMMA polystyrene PC, polycarbonate has much more impact resistant property than the other two polymers.

(Refer Slide Time: 23:54)



Chain dimensions: Long-range steric interactions

In case of real polymer chains, there are long- range interactions which cause the chain dimensions to be generally higher than the unperturbed dimensions.

Long range interactions: Once a bond occupies a given volume in space, no other bond can occupy the same volume (excluded volume effect).

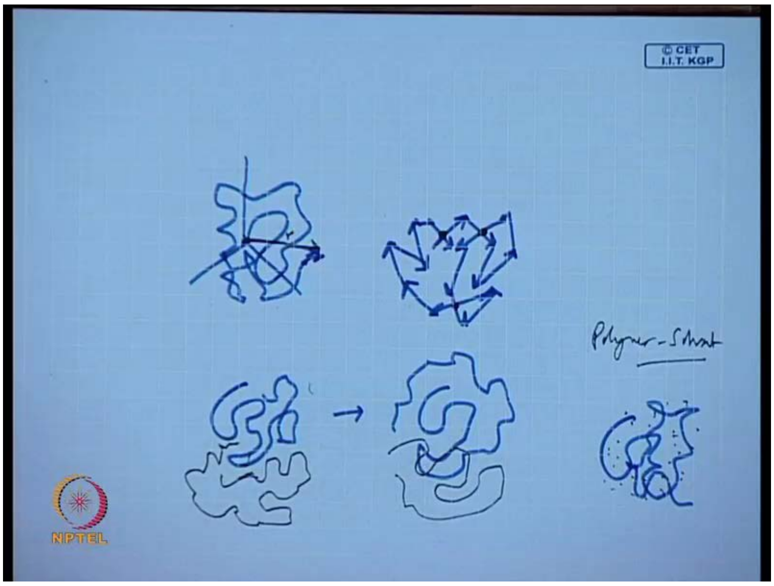
$\langle r^2 \rangle^{1/2} > \langle r^2 \rangle_0^{1/2}$ $\langle r^2 \rangle^{1/2} = \alpha_r \langle r^2 \rangle_0^{1/2}$ α_r expansion factor

Volume exclusion will be highest when the segment density is the highest i.e., more volume is excluded in a given volume when there are more segments in that volume.

$^2\rangle^{1/2} = \alpha_s \langle s^2 \rangle_0^{1/2}$

Now, we so far we discussed that, how we the chain dimensions which is basically you are talking about the radius of gyration, or RMS end-to-end distance, where is we introduce the bond angle restriction, and the rotational restriction due to short range interactions. Now, we have to compare, if you compare a polymer chain, how did we derive this Gaussian chain structure, the expression for the Gaussian chain remember, we used one of the chain end in the coordinate, x, y, z coordinate.

(Refer Slide Time: 24:37)



And then went randomly, did a random of fixed step length of one length, and then using radial distribution function Gaussian, what is the probability that the other end would be at a distance r from the origin. Now, doing that, what we what we consider that, this polymer molecules are volume less, we are why I am drawing this, they are several intersections, if I draw like this steps vectors like this, these are the steps random of if the polymer takes.

Then there are several intersections possible, which is basically when the which is happening after several several steps, which is basically longer, it is not immediately immediately two of the segments or two of the bonds are overlapping with each other, but it can come back, because polymer chains are flexible it can come back and occupy the same space. So, when we deduce this expression, we did not consider that these vectors have volume, so what happened the same space in this model, we consider that same space which are the intersection points can be occupied by the two two two bonds.

But, in actual sense, if you one bonds of you have said this is one bond, now what was doing in the model we were basically putting one top of it, in the same on the paper itself and we are calculating the dimension. But in actual term because this has a definite volume you cannot put on the same paper, these two cannot intersect on the plane of paper, there would be it has to expand, because this has volume. So, in real case, incase of real polymer chain there are long range interactions, these are long range interactions which cause the chain dimension to be generally higher than the unperturbed dimension.

Now, long range interactions are coming, because the fact that once a bond occupies a given volume in this space, no other bond can occupy the same volume, so if I have a bond here in the space, the same space cannot be, if I have this in this planes if you consider a bond, then you cannot, then like this let this plane is bond, you cannot occupy the same space with another bond. Because it has occupying some volume in the space, but in the model we did not consider, we considered that this space can be occupied by more than one bonds.

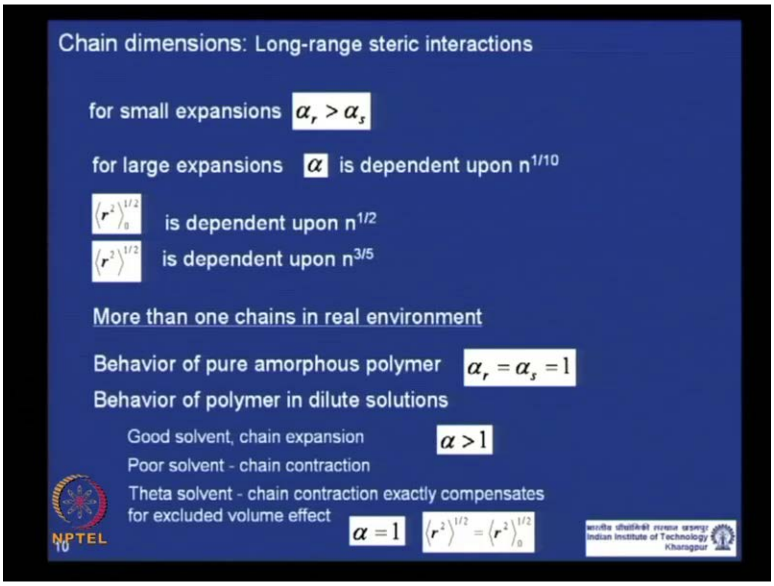
So, once a bond occupies a volume in the space, no other bond can occupy the same space basically presence of a polymer chain of or polymer segment is excluding, any other polymer segments to occupy the same volume. So, the term is used is excluded volume, this is called excluded volume effect, once a space is occupied by a polymer segment, the same space cannot be occupied by another segment, so that is the way we calling the other chains are excluded other portions are excluded from that space we are calling that excluded polymer effect.

So, obviously, now if the model was considering that this two can be overlapped in a line, obviously if they cannot the chain has to expand a little bit, or in other words the conformations which had list number of intersection, will have higher probability than the conformations which has more number of self interactions intersections. Obviously, the volume, the polymer coil will expand due to this excluded volume effect, so effectively the polymer size, or the radius of gyration and the RMS end-to-end distance will also increase.

So, in real chain the RMS end-to-end distance is actually higher than the unperturbed unperturbed dimension, when we did not consider the excluded volume effect. If we put a factor to equate them, now this has to be more than 1, and this is called expansion factor, so if this is 1, then these are equal if there are more expansion, then this will be higher than 1. Now, as you can think that this volume exclusion would be, volume expansion would be expansion or the volume exclusion would be higher, wherever the polymer chain density is much more, because if the polymer chain density is more than the chances of that two segments, or two bonds trying to occupy the same space is high.

So, the expansion would be much higher in that compared to a region, where the segment of polymer chain density is lower. So, we cannot, that is the reason we cannot equate or put the same expression factor, in in case of radius of gyration as well, so we are putting a another expansion factor, in case of radius of gyration.

(Refer Slide Time: 31:43)



Chain dimensions: Long-range steric interactions

for small expansions $\alpha_r > \alpha_s$

for large expansions α is dependent upon $n^{1/10}$

$\langle r^2 \rangle_0^{1/2}$ is dependent upon $n^{1/2}$

$\langle r^2 \rangle^{1/2}$ is dependent upon $n^{3/5}$

More than one chains in real environment

Behavior of pure amorphous polymer $\alpha_r = \alpha_s = 1$

Behavior of polymer in dilute solutions

Good solvent, chain expansion $\alpha > 1$

Poor solvent - chain contraction

Theta solvent - chain contraction exactly compensates for excluded volume effect $\alpha = 1$ $\langle r^2 \rangle^{1/2} = \langle r^2 \rangle_0^{1/2}$

For a small expansion this can be shown theoretically that a the expansion factor for end-to-end distance higher than, expansion factor for radius of gyration. And for large expansion it can also shown that, it is a approximately proportional to n to the power 1 over 10, n is the number of bonds, so basically this expansion factor is approximately proportional to the molecular weight to the power 1 by 10, where n is proportional to molecular, the molecular proportion to n, so for large expansion we will use this in future. So, please remember that for large expansion, this expansion factor is approximately proportional to the molecular weight to the power 1 over 10, and we know we knew that this unperturbed dimension was dependent on 10 to the power half.

So, the real chain, real end-to-end distance would be proportional to approximately proportional to this multiplied by this, which gives you 10 to the power 3 by 5, this is approximately proportional to n to the power 315; the RMS end-to-end distance for a real chain. Now, what happens when there is more than one chain, real scenario if you are talking about polymer solution or a polymer melt or a polymer mass obviously, there is no single chain they are many chains.

Now, what happened in that chain, so if there are more than one chains, there are more than one chain in real environment what will happen, now obviously, if you if you consider that this is a, this is unperturbed dimension, and because of excluded volume this is expanding to avoid all the intersections, self intersection it is expanding (Refer

Slide Time: 33:57). Now, what if there was another polymer here, which is the case for real case, in real case there are many polymer chains, so if you imagine this is another polymer chain; now for self intersections or intra molecular long range steric interaction, self intersection is caused by the long range steric interactions.

They will try to expand, now if they try to expand, what will happen they will try to overlap with this chain, if they expand obviously, they will try to occupy the space which is already occupied by this chain. Now, then they have they do not time, because there is already one segment is present, it will not allow, it will exclude the portion from the other chain to come and occupy the same space, where this will exclude any volume from the other segments.

So, obviously, the intramolecular long range interactions, steric interactions try to expand the chain, whereas intermolecular long range interactions are basically try to contract, the chain and to bring in to the unperturbed dimension. So, there is two opposite effect when you have multiple number of chains, consider single chain intramolecular interactions long range interactions try to expand the chain, to avoid the self intersection, whereas to avoid the intersections between the segments of different polymer chain, intermolecular long range steric interactions try to compact the chain.

And that is nullified in a pure, so basically in a pure amorphous polymer this gets nullified, and your dimension becomes same as, the actual dimensions becomes same as the unperturbed dimensions. So, in case of pure amorphous polymer, the expansion factor becomes 1, because there is two opposite in effect causing one intramolecular causing the chain to expand, whereas the intermolecular is trying to cause the chain to compact. What happened in the dilute solution, now in dilute solution you have polymer there are not many polymer, when you have dilute polymer chain, I wrote this this two, because you are talking about pure amorphous polymer there is no solvent.

Now, in case of dilute polymer solvent, there is unlikely that two polymer chains should be so close, so polymer polymer interaction would be this exclusion will be will be less in low probability. So, the interaction will be between polymer and solvent, dilute solution will be interaction and polymer and solvent, now if there are if there are favorable interactions between the solvents and the polymer, compared to a solvent solvent interactions. Obviously, the chain will expand you can you can anticipate that if the interactions between polymer solvents is favorable compared to the main interaction between solvent solvent and polymer polymer.

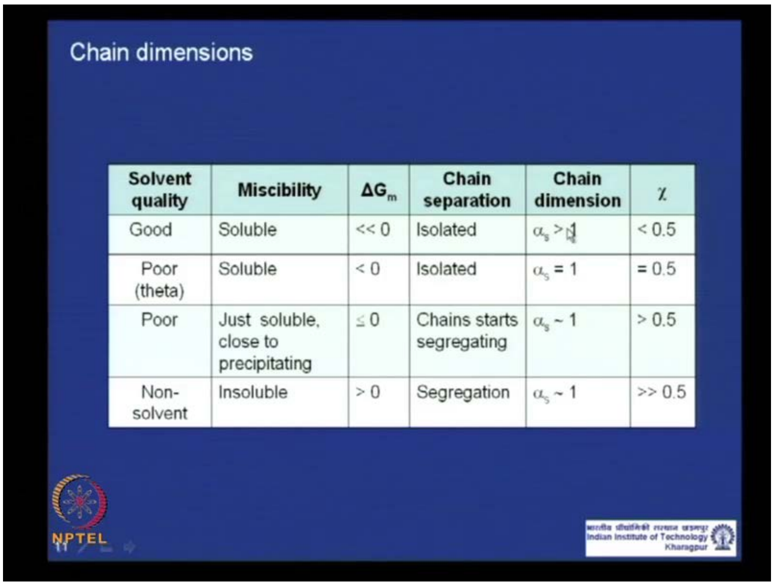
The polymer will try to maximize the number of polymer solvent contacts, which means it will try to expand the coil dimensions, so that you get maximum number of polymer solvent interaction, instead of solvent solvent interaction. So, if you have good solvent, where the polymer solvent interaction is favorable compared to a solvent solvent interaction then polymer chain will expand, if you have a poor solvent where solvent solvent you know, solvent polymer interaction are not favorable. Then what will happen, again the intramolecular intramolecular intersections or intramolecular long range interactions will try to expand.

But, on expanding it has to come in contact with the solvent molecules, with the solvent molecule (( )) solvent molecules do not like, so they will try to compact the polymer chain. So, incase of poor solvent, a single polymer chain is tried to, because of excluded volume effect tried to expand whereas, polymer solvent interaction, because they are unfavorable to compact. And when these two becomes equal, the polymer chain dimension is become same as the unperturbed dimension, and you have equal that solvent as a theta solvent, which basically nullified these two effects.

So, good solvent chain expansion, the expansion factor is more than 1, if you have poor solvent chain contraction happened. And if it is the solvent is such that, the theta solvent where the chain contraction due to unfavorable polymer solvent interaction exactly compensate, the excluded the expansion due to excluded volume effect, and you get that the expansion factor is 1. So, the real dimension of polymer chain becomes same as the dimensionless unperturbed that chain; that means it is not perturbed by any other polymer or solvent.

This now you can justify the where this term unperturbed is coming, as if it is present alone, it is not perturbed by any other external molecule, whether it is another polymer molecule or a solvent molecule. So, theta solvent again, so theta solvent and if your amorphous polymer, the dimension of a real polymer chain is same as the dimension of unperturbed chain.

(Refer Slide Time: 40:50)



Chain dimensions

Solvent quality	Miscibility	ΔG_m	Chain separation	Chain dimension	χ
Good	Soluble	$<< 0$	Isolated	$\alpha_s > 1$	< 0.5
Poor (theta)	Soluble	< 0	Isolated	$\alpha_s = 1$	$= 0.5$
Poor	Just soluble, close to precipitating	≤ 0	Chains starts segregating	$\alpha_s \sim 1$	> 0.5
Non-solvent	Insoluble	> 0	Segregation	$\alpha_s \sim 1$	$>> 0.5$

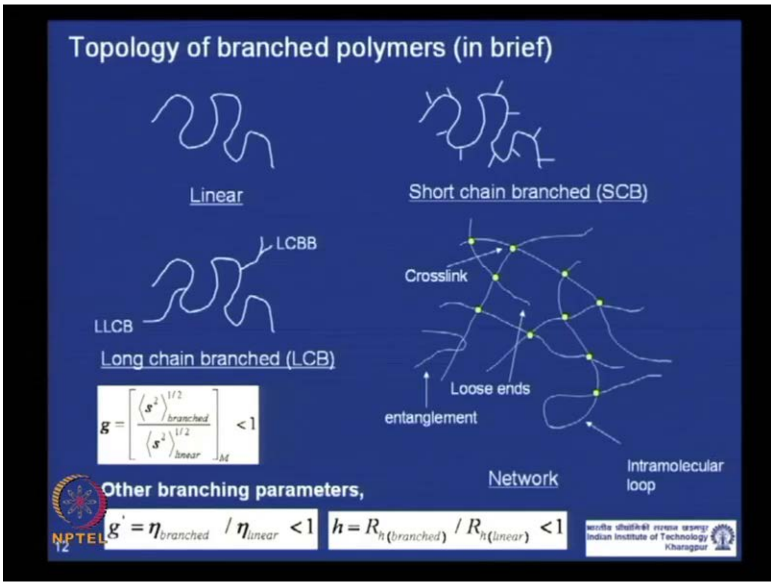
So, in summary if the solvent quality is good obviously, miscibility is high, the delta g mixing is less, and if solvent quality is good in a dilute solution this change will separate, they will be isolate to each other. And chain dimension the expansion factor will be more than 1, so real chain end-to-end, RMS end-to-end distance will be higher than the RMS end-to-end distance for unperturbed chain. And chi the polymer solvent interaction is be lower than 0.5, they are all inter limited, for theta solvent chi is 0.5 expansion factor is 1.

So, there is a still isolated and Gibbs free energy mixing, now comes from only the combinatorial entropy, which is basically small for polymer solvent system, but still negative combinatorial combinatorial entropy is positive. So, it contribute negatively it favors the mixing process, so in theta conditions still the mixing is possible favorable and you get a soluble mixture of polymer and solvent.

If this solvent becomes more poor or poorer, it becomes, the polymer solvent interaction parameter becomes more than 0.5 and chains starts segregating and it is just close to, it is very close to your, so basically the contact interaction is positive, which is nullifying the entropy, favorable entropy contributions towards Gibbs free energy; the favorable combinatorial entropy towards Gibbs free energy. So, the nullify is that precipitating, and in case of non solvent when polymer segregates, Gibbs free energy mixing is positive, the polymer is insoluble, and chi, the polymer solvent interaction polymer solvent is higher than 5.

Now, what about this, in a non solvent what about this, the polymer solvent interaction parameter becomes 0.5, but expansion factor you can now imagine or you can think cannot be less than 1, because it is the unperturbed dimension if you are talking about a single chain. The unperturbed dimension is because of, the bond angle restriction and the bond rotation restriction, now you cannot have a more compact chain than that, for linear chain you cannot have a situation where there is more compact (( )). Because this is inbuilt to polymer chain you cannot compact, then your bond angle has to be lower, and rotational restriction has to be lower, so you cannot bring down the expansion factor, so it starts precipitating, with expansion factor of close to 1.

(Refer Slide Time: 44:10)



Topology of branched polymers (in brief)

$$g = \left[\frac{\langle s^2 \rangle^{1/2}_{branched}}{\langle s^2 \rangle^{1/2}_{linear}} \right]_M < 1$$

Other branching parameters,

$g' = \eta_{branched} / \eta_{linear} < 1$ $h = R_{h(branched)} / R_{h(linear)} < 1$

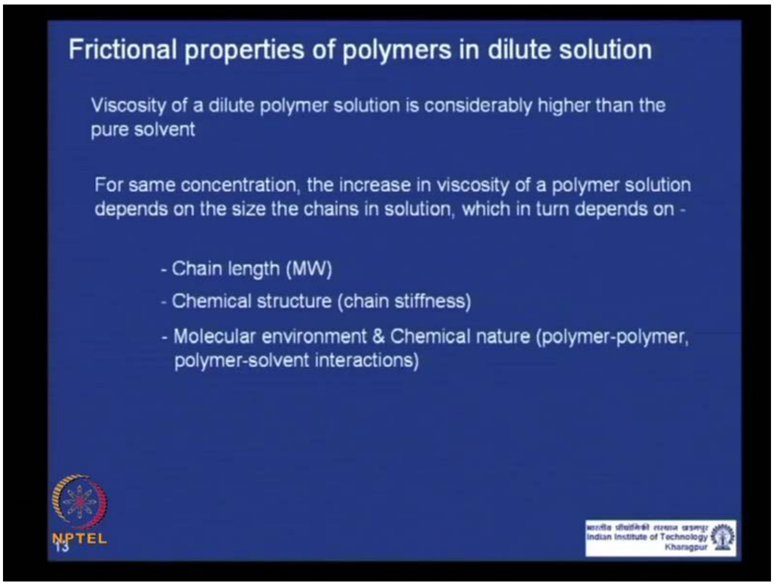
Now, let us move just have a deep discussion of the, just now we talked about whatever discussion we have about the dimension is mainly or mostly all about linear polymer, which is shown here this (( )); now you can have branches also, you can have short branches, and you can also have long branches. Now, long branches can have further branch from itself, so it is a long chain branching with branches, long chain branches with branches or you have a linear chain branching here or you can have a network.

Now, network have cross links points, lose ends entangled, this is entangled especially entangled between two chains, physical entanglement, there is no chemical cross linking here, it is basically one chain here entangled in another. When you call long chain, long or short how it distinguish between whether the branch is long or short, if the branch, length of the branch is more than the entanglement chain length of the entangled molecular weight for entanglement chain length they, what is the entanglement chain length is the length between two entangled portions.

So, if the length of the branch is higher than the entanglement molecular weight, then you call that as a long chain branch, how you characterize or define the sort of gives the parameter, describe the branching; obviously, the branched for same given molecular weight, if you have same molecular weight, because the branches the size, radius of gyration will be lower as you can expect. So, S for the branch, you know radius of gyration for the branch will be lower than the linear for same molecular weight, so this g would be lower than, so if you can calculate these two, you can get the extent of branching, the lower is the value of g, the higher is the extent of branching.

Now, other branching parameters, you can also define is the intrinsic viscosity of branched by linear, we will have more discussion on that or the hydrodynamic radius of the branched divided by the linear ones. So, basically if the molecular are same then because of branches are presents the chain, the polymer chain will be much more compact, so the radius, hydro dynamically radius of the radius of gyration, or the viscosity will be lower compared to linear polymer chain having the same molecular weight. And you can, if you get this property like this viscosity or radius of gyration of these two, then you can find out the extent of branching in polymer.

(Refer Slide Time: 47:34)



Frictional properties of polymers in dilute solution

Viscosity of a dilute polymer solution is considerably higher than the pure solvent

For same concentration, the increase in viscosity of a polymer solution depends on the size the chains in solution, which in turn depends on -

- Chain length (MW)
- Chemical structure (chain stiffness)
- Molecular environment & Chemical nature (polymer-polymer, polymer-solvent interactions)

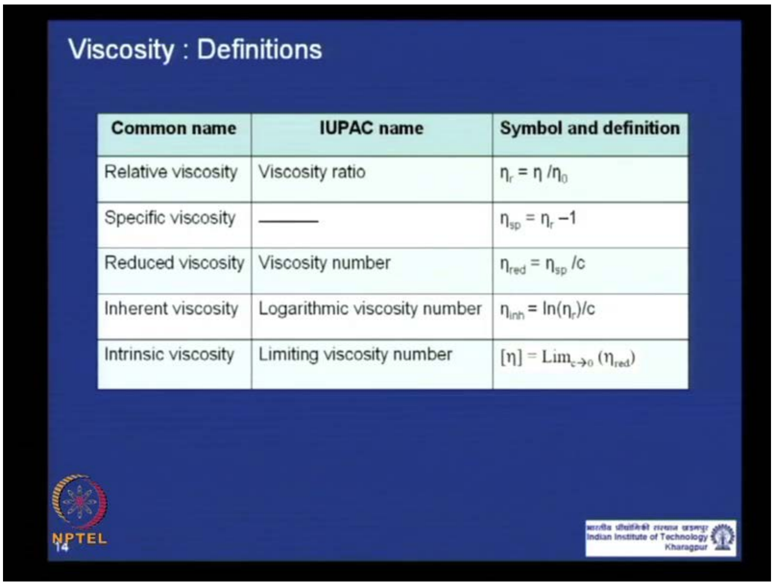
Now, let us move to the next topic, which is frictional properties of polymer solution, we will basically keep our discussion limited to our dilute solutions, now we talk about frictional properties, first thing comes in our mind is viscosity. Now, viscosity of a dilute polymers you can, you must have experienced viscosity of dilute polymer solution is considerably higher compared to solvent. Now, that is because you have large difference in size of a solvent molecule, and the polymer molecule, because the size difference you get this large increase in the viscosity of the solvent, and that increase the extent of increase by addition of a polymer molecule.

For a given concentration would be higher if the size of the polymer goes up, so if you if you add same amount polymers of different molecular weight, in the same solvent at same temperature, then the polymer which have the hard molecular weight or higher size, it will have, the solution will have higher viscosity. For the same for the same concentration the increase in viscosity of a polymer solution, depends on the size of the suspension in the solution, the size more size higher the size, the higher is the viscosity as we discussed.

And the size in terms depends on the chain length of the molecular weight, as we have discussed earlier, chemical structure; chain stiffness the more higher the stiffness, the dimension of the size goes up. And the molecular environment and chemical nature, and how what is the constitution, chemical constitution of polymer and that determine, what is the solvent given that determines how good is the polymer polymer, and polymer solvent interactions.

The more the interactions between polymer and solvent, the coil expands, so you have large size, so you have large viscosity. So, if you have more interaction between, so if you have higher size, higher chain length obviously, the size will go up, as you have seen that we discussed just now, that the chain length goes up the molecular goes up, the size will the size will be higher, so viscosity will be higher. If the chain stiffness goes up, the size will be up, the viscosity will be up, if there is more interaction between polymer and solvent, the size will be up and the viscosity will be up.

(Refer Slide Time: 50:25)



Viscosity : Definitions

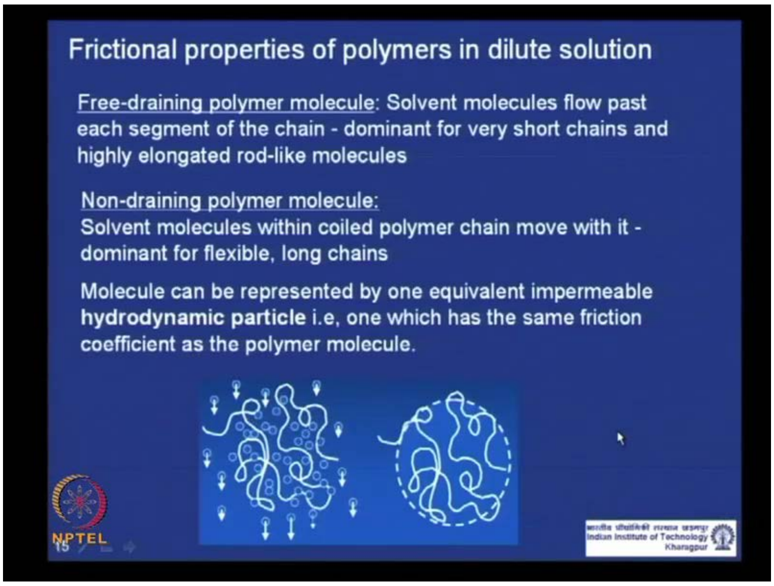
Common name	IUPAC name	Symbol and definition
Relative viscosity	Viscosity ratio	$\eta_r = \eta / \eta_0$
Specific viscosity	———	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp} / c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \mathrm{Lim}_{c \to 0} (\eta_{red})$

Now, there are few definitions of viscosity you should know this, these are common name of different viscosity, and these IUPAC name, these are most still now common names are used by many people, actually more people uses this common name than the IUPAC names. This is eta is the viscosity of the solution of a concentration, of a polymer concentration C at a given solvent and given temperature, whereas eta 0 is the viscosity of that solvent that particular temperature, so this eta by eta 0 or the relative viscosity is gives by the extent of increase, in the viscosity by the addition of polymer at a concentration C.

And you, these are the self expanded, this expression which you can look at, specific viscosity reduced viscosity inherent viscosity, intrinsic viscosity is talked about the ability, intrinsic ability of polymer chains to intrinsic, increase the viscosity of a solvent. So, that is, it gives us very important parameter which will be using several times in determining the molecular weight, so intrinsic viscosity relates to the intrinsic ability of a polymer, to increase the viscosity of a particular solvent at a given temperature.

Because, it is an intrinsic ability, the intrinsic viscosity is very gives lot of useful properties, lot of useful information, and which will be utilized in determine molecular weight, and other things which will discussed in next lecture.

(Refer Slide Time: 52:26)



Frictional properties of polymers in dilute solution

Free-draining polymer molecule: Solvent molecules flow past each segment of the chain - dominant for very short chains and highly elongated rod-like molecules

Non-draining polymer molecule:
Solvent molecules within coiled polymer chain move with it - dominant for flexible, long chains

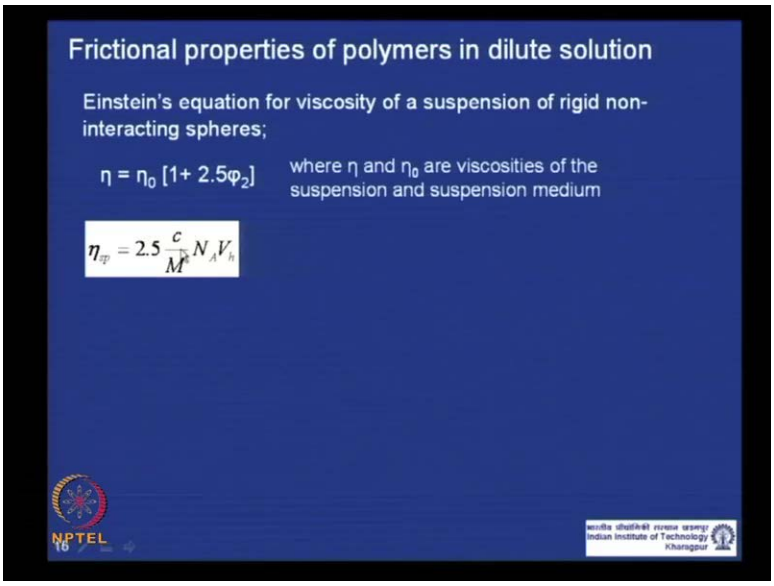
Molecule can be represented by one equivalent impermeable **hydrodynamic particle** i.e, one which has the same friction coefficient as the polymer molecule.

Now, the two types of polymer chains can be imagine, one is free draining polymer chains, where the solvent molecules, when you when polymer chains moves in a solvent in a solution, polymer chains moves in a solution; if the polymer chains moves without the solvent molecules, which are the associated with this, and the solvent molecules move past the polymer molecules. Then we are talking about freely drained, freely draining polymer molecules, so solvent molecules flow past each segment of the chain, and you can think that it is dominate about rod-like molecule, if you molecule is stiff, if you rod like molecule, then obviously, when it moves the solvent molecules will not be sticking to it.

It will flow the solvent molecules will flow past each other; it happens even for flexible chain if the coil size is little low, and that is dominant for this short chains. The other one is non draining polymer molecule, which is the case for most of the polymer molecules, now in a linear flexible, any flexible polymer chains are closer to non-draining polymer molecule. Non-draining polymer molecule is where, the solvent molecules will within the coil, coiled polymer chain moves along with it, so if I think this why it is the column, and the coil and these circles are solvent molecules when the polymer moves, it takes the solvent molecules along with it.

So, you can imagine that this polymer coiled solvent is like a impermeable sphere, which consists of the polymer coil and the solvent molecules, which are associated with the polymer chain. And happens that happens for large flexible polymer chains long chains and this this polymer molecule can be precipitated by one equivalent, this is equivalent hydrodynamic particle, and one has the same friction coefficient as the polymer molecule. So, this is the case, where most of the polymers will deal with deal mostly with flexible large polymer chains, so if that polymer moves to the solution, it takes the solvent molecules along with it. So, we consider most of our polymer chains is non-draining, and the polymer coil will be thought as a permeable spherical particles.

(Refer Slide Time: 55:31)



Frictional properties of polymers in dilute solution

Einstein's equation for viscosity of a suspension of rigid non-interacting spheres;

$\eta = \eta_0 [1 + 2.5\varphi_2]$ where η and η_0 are viscosities of the suspension and suspension medium

$$\eta_{sp} = 2.5 \frac{c}{M} N_A V_h$$

Now, for this suspension of this rigid non non interpenetrating sphere, Einstein's equation of viscosity of a suspension is given by this expression, again this is viscosity of the suspension of the solution of this is. If you are talking about because we are thinking the polymers as hard particles; that are why the term suspension, we are using instead of solution, but intrusion that is the solution.

So, eta is the viscosity of the polymer solution, eta 0 is the viscosity of medium, and this phi 2 is the volume fraction of the polymer chain, so what we can easily show that, this expression would give this expression. Now, what will do now, we will stop here for this class, and we will in the next lecture, we will continue our discussion from here, and deduce the expression for intrinsic viscosity of flexible polymer chains in a dilute solution.