Introduction to Polymer Science
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Lecture - 26
Polymers Chain Dimensions

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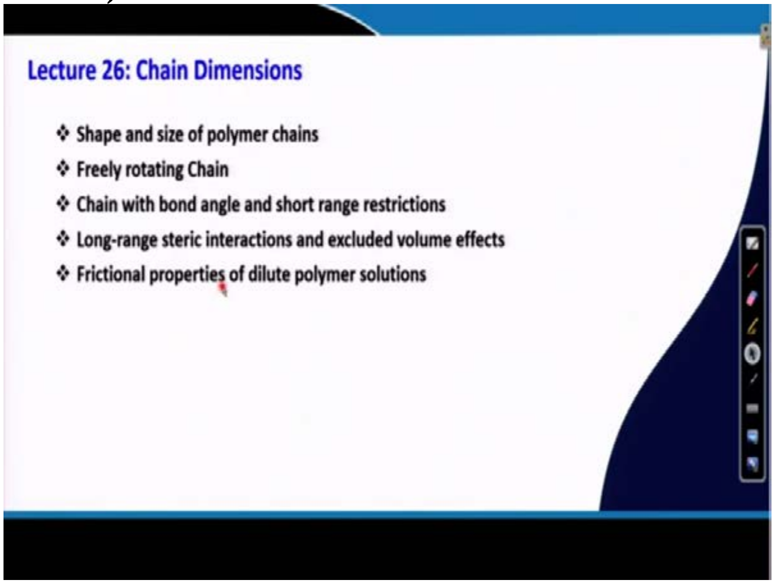

Lecture 26: Chain Dimensions

- 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
- Frictional properties of dilute polymer solutions

Welcome back. In this lecture we will discuss about chain dimensions of polymer molecules.

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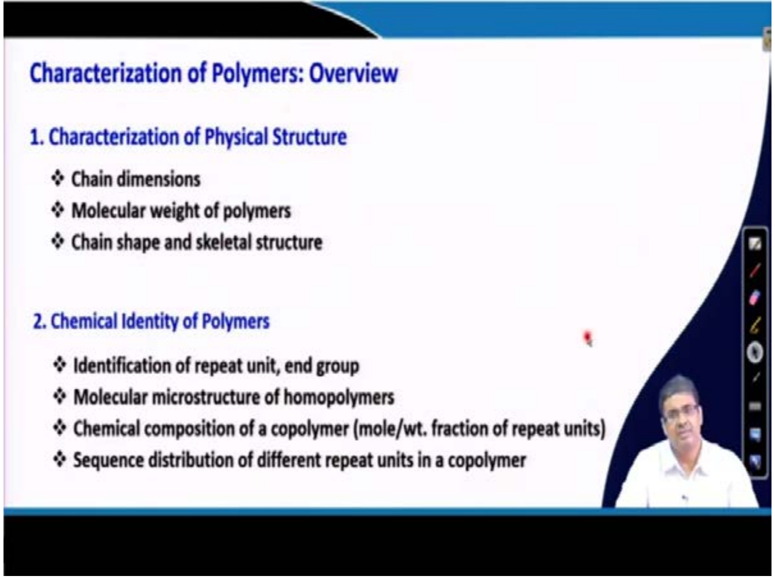

Characterization of Polymers: Overview

1. Characterization of Physical Structure
   - Chain dimensions
   - Molecular weight of polymers
   - Chain shape and skeletal structure

2. Chemical Identity of Polymers
   - Identification of repeat unit, end group
   - Molecular microstructure of homopolymers
   - Chemical composition of a copolymer (mole/wt. fraction of repeat units)
   - Sequence distribution of different repeat units in a copolymer

We are starting polymer characterization now onwards and let me give you an overview on the topic. Now, we have studied how to synthesize polymers by different methods and then we studied the solution behavior of polymers. We need to understand the nature of the polymers that we have synthesized and for that we need mainly two types of characterization; one is the characterization of the physical structure which means, we need to find out the chain dimension or molecular weight of the polymers and second, we need to determine the skeletal structure or architecture of the polymer chains. We also need to chemically identify the polymers what we have synthesized. For that we need to identify the repeating units and the end groups of the polymer. We need to find out the microstructure in case of homopolymer. For example, if we talk about tacticity whether we have syndiotactic or isotactic type polymerization, we need to find out the microstructure for the homopolymer. For copolymer, we need to find out the chemical composition of the copolymer, what is the weight fraction or mole fraction of the different repeating units in this copolymer and also, what is the nature of the copolymer, whether it is alternating, random or block copolymer. So, basically we need to find out the sequence distribution of different repeating units in that copolymer. If we can do all sorts of these characterizations, then we can satisfactorily characterize the new polymer.

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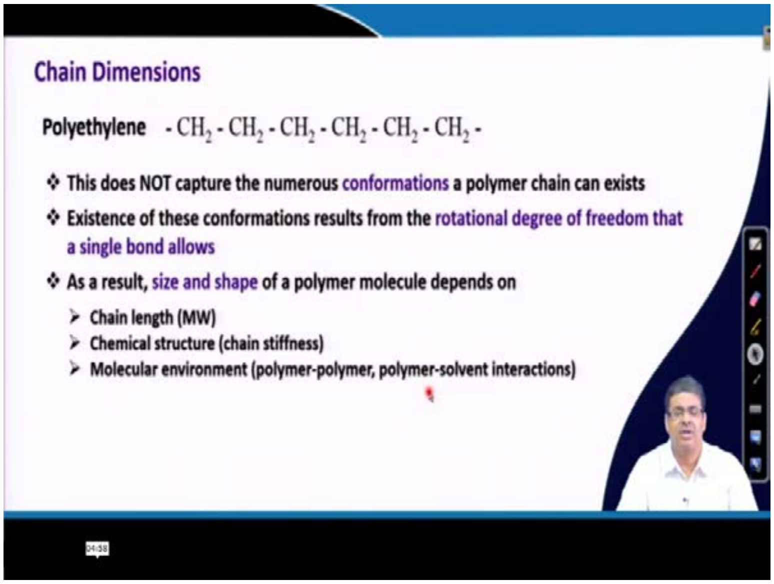

Chain Dimensions

Polyethylene $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$

- This does NOT capture the numerous conformations a polymer chain can exists
- Existence of these conformations results from the rotational degree of freedom that a single bond allows
- As a result, size and shape of a polymer molecule depends on
  - Chain length (MW)
  - Chemical structure (chain stiffness)
  - Molecular environment (polymer-polymer, polymer-solvent interactions)

Let us focus on chain dimension and let us consider the simplest molecule polyethylene, which can be written by this way CH_2-CH_2 and so on. Now, this does not capture the numerous conformations of a polymer chain that can exist. Now, we have discussed conformations before and just to repeat that these conformations result from rotation around the single bond of the polymer backbone. As this rotation takes place around the single bond, polymer can exist in different size and shape in a solvent or in a solution. So, the size and shape are kind of a dynamic structure of polymers. Structures are not rigid; their shape and size keep on changing when they are in a solute in solution. So, we talk about average size or average dimension of polymer molecules in solution.

Now, these size and shape depends on the chain length or molecular weight. Obviously, the higher the molecular weight, higher would be the size of the polymer, given other factors remain same. Chemical structure; if the chain stiffness increases, it means that rotation around the single bond becomes more difficult, then the polymer becomes more stretched or more elongated. It also depends on the molecular environment which means polymer-polymer and polymer-solvent interactions.

As you can guess that if the polymer interacts with the solvent favorably, then the polymer chain or polymer dimension will expand because a polymer wants to interact more and more with solvent molecules. Whereas, if the solvent is not good i.e. it is poor solvent, then the polymer will become smaller in dimension, because it will try to avoid the solvent molecules.

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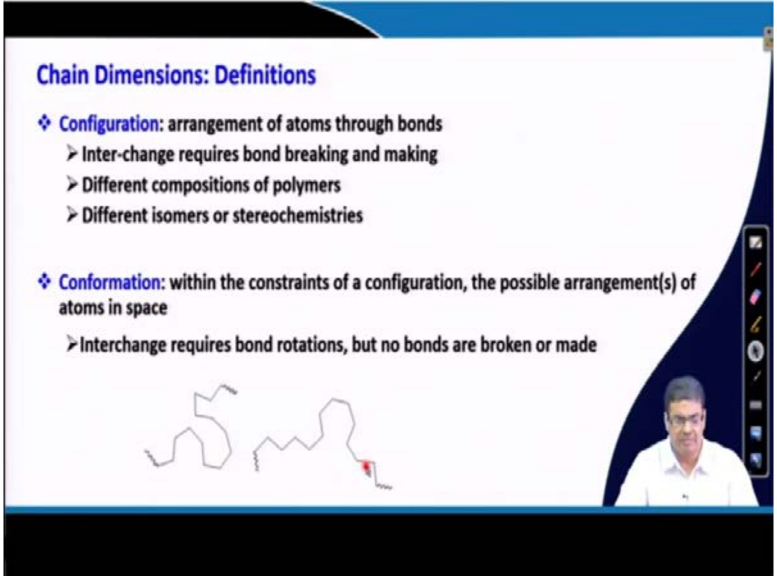

Chain Dimensions: Definitions

- Configuration: arrangement of atoms through bonds
  - Inter-change requires bond breaking and making
  - Different compositions of polymers
  - Different isomers or stereochemistries
- Conformation: within the constraints of a configuration, the possible arrangement(s) of atoms in space
  - Interchange requires bond rotations, but no bonds are broken or made

Now, we come back and just redefine or revisit these 2 terms, configuration and conformation. Configuration is the arrangement of atoms through bonds and to interchange between different configurations we actually require bond breaking and making. Different configurations correspond to different compositions of polymers for a common molecular structure, which is possible because of different isomers or different stereochemistry of the rigid unit. On the other hand, conformation means, for given configuration, the possible arrangement of atoms in space and different conformation does not require any bond breaking or bond making. It requires rotation around single bond in the polymer backbone. So, these 2 are examples of different conformations which can be obtained by rotating the single bond in the polymer backbone.

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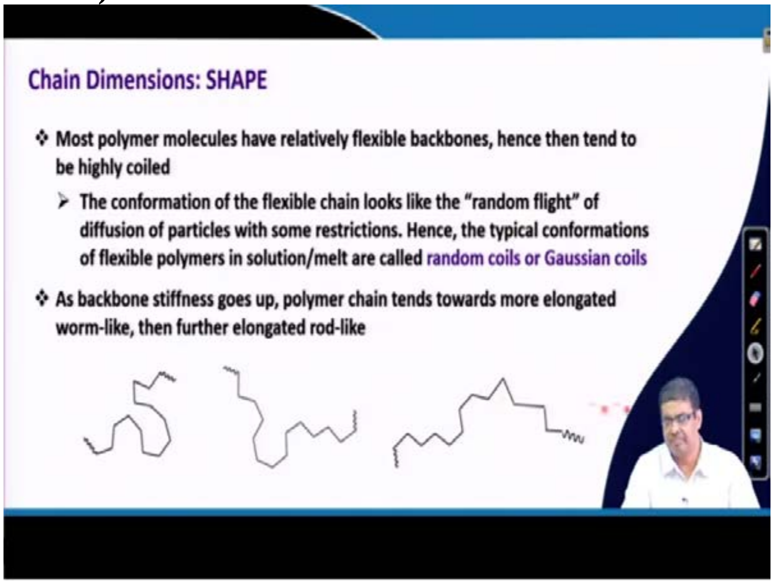

Chain Dimensions: SHAPE

- Most polymer molecules have relatively flexible backbones, hence then tend to be highly coiled
  - The conformation of the flexible chain looks like the "random flight" of diffusion of particles with some restrictions. Hence, the typical conformations of flexible polymers in solution/melt are called random coils or Gaussian coils
- As backbone stiffness goes up, polymer chain tends towards more elongated worm-like, then further elongated rod-like

Now, when you talk about polymer shape, most polymer molecules have relatively flexible background because most of the polymers we generally talk about have C-C backbone. Even if there are heteroatoms, most of these bonds are single bonds and that is why the rotation around this bond is feasible. As a result, the polymer chains tend to be highly coiled. That is why when we write polymer structure, generally we tend to write a coiled structure and not a straight line or a zigzag line. Most of the polymers have flexible backbone. So, generally when we write polymer, we write as a coiled structure. Now, the conformation of the flexible chain looks like the random flight that is the typical conformation of flexible polymers in solution or melt. They are called random coil or Gaussian coil. As the backbone stiffness goes up, which means, the rotation around the single bond become more and more difficult. The polymer chains actually tend to become more elongated or worm-like or a rod-like structure. If this rotation becomes difficult then we have a longer size and it becomes even a rod-like or more elongated structure as the rotation becomes more and more difficult or the stiffness goes up.

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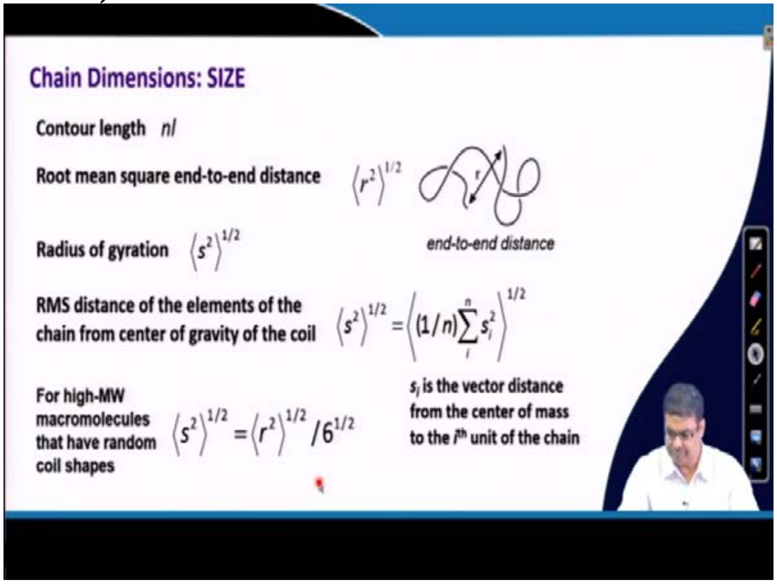

Chain Dimensions: SIZE

Contour length nl

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

end-to-end distance

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

RMS distance of the elements of the chain from center of gravity of the coil $\langle s^2 \rangle^{1/2} = \left\langle (1/n)\sum_{i}^{n} s_i^2 \right\rangle^{1/2}$

s_i is the vector distance from the center of mass to the i^{th} unit of the chain

For high-MW macromolecules that have random coil shapes $\langle s^2 \rangle^{1/2} = \langle r^2 \rangle^{1/2} / 6^{1/2}$

Now, when we talk about the size, the first thing we need to know is the contour length, which is nothing but n × l, n is the number of bonds in the polymer backbone and l is the length of each bond. So, if I talk about a polyethylene molecule, then if we talk about 10,000 bonds in the backbone, so, which is equals to n, then each C-C bond length will be 1.5Å. So, the contour length would be 10,000 multiplied by 1.54 Å. So, 15400 Å given by this structure.

Next we need to talk about is the root mean square end to end distance which is represented as this $\langle r^2 \rangle^{1/2}$. We generally write polymer as a coiled structure and the distance between 2 ends is called end to end distance. Now, as I explained that this is not a rigid chain structure, there is always rotation around the single bond. As a result, the structure is dynamic i.e. in one instant the polymer may remain in one shape and in next instant it can assume another. Thus we have different end to end distances. So, it means that the polymer chains are not static chains, there are always different conformations appearing because of the rotation around a single bond. As a result, we consider a time average dimension. Now, we generally do not write average r, but we write root mean square because, if we write r then we need to also consider the direction, which may be positive or negative direction. So, averaging will be difficult. So if we take a square term, then we need not to consider this sign then we can make it a squared term and then take a square root. This is the standard practice we do when this end to end distance or other chain parameters are considered. So, this is the time average or root mean square end to end distance.

Another parameter that we can basically bring into is the radius of gyration $\langle s^2\rangle^{1/2}$ which is a root mean square distance of the elements of the chains from center of gravity of the coil. If I have a coil structure like this and I have a center of gravity and the different elements at different distances $S_{i,}$ then we make a square and then take an average and then take a root of that.

$$\langle s^2\rangle^{1/2} = \langle\left(1/n\right)\sum_{i}^{n}\langle \mathrm{Si}^2\rangle\rangle^{1/2}$$

Here S_i is a vector distance from center of mass to the i^{th} unit of the chain. Again, the square term is done to avoid the sign of the vector. If we did not, if we had just averaged the absolute value with a sign, then sign of the vectors would complicate the matter. To avoid that it is done by root of the mean of the squared term. Now, the radius of gyration and the rms end to end distance are linked mathematically and for high molecular weight macromolecules having random coil set, these two quantities are linked by this expression.

$$\langle s^2\rangle^{1/2} = \langle r^2\rangle^{1/2}/6^{1/2}$$

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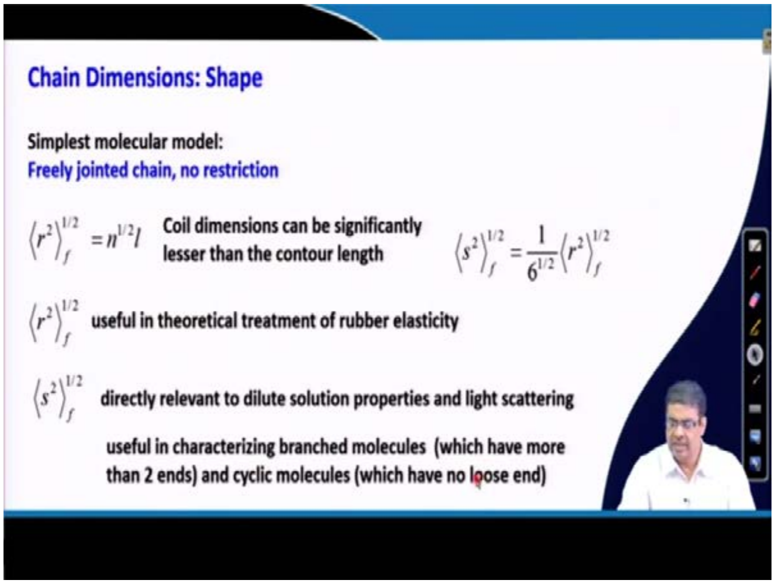

Chain Dimensions: Shape

Simplest molecular model:

Freely jointed chain, no restriction

$\langle r^2\rangle_f^{1/2} = n^{1/2} l$ Coil dimensions can be significantly lesser than the contour length

$\langle s^2\rangle_f^{1/2} = \frac{1}{6^{1/2}}\langle r^2\rangle_f^{1/2}$

$\langle r^2\rangle_f^{1/2}$ useful in theoretical treatment of rubber elasticity

$\langle s^2\rangle_f^{1/2}$ directly relevant to dilute solution properties and light scattering

useful in characterizing branched molecules (which have more than 2 ends) and cyclic molecules (which have no loose end)

The simplest model for a polymer is freely jointed chain without any restriction. The only restriction is the bond length for each link is same, which means that we can start from one end and we can continue in different direction without any restriction. Only thing we have to maintain the same bond length but, we can go any way we can. So, when you draw you need to keep this bond length fixed. This is the freely jointed chain. So, there is no restriction of bond angle or basically there is no steric hindrance between these bonds. In this case, the size or the RMS end to end distance for a freely jointed chain is given by this expression

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

Obviously, coil dimensions can be significantly lesser than the contour length. So, if we talk about the same example, we have in 10,000 bonds for polyethylene now. The value for this end to end distance n would be now a $10{,}000^{(1/2)}$ ×1.54 Å. So, it will be 100 times lower than the contour length for the same molecule, which means the coil dimension for this case significantly lesser than the contour length.

Similarly, we have this radius of gyration for freely jointed chain given by the expression below. Now, this is useful for theoretical treatment of rubber elasticity and this term is useful for this is directly relevant to dilute solution properties and light scattering properties. Since we are talking about radius of gyration is kind of radius of that coil, so it is useful in characterizing branched molecule which has more than 2 ends and cyclic molecules which have basically no loose ends.

$$\langle s^2 \rangle_f^{1/2} = \frac{1}{6^{1/2}} \langle r^2 \rangle_f^{1/2}$$

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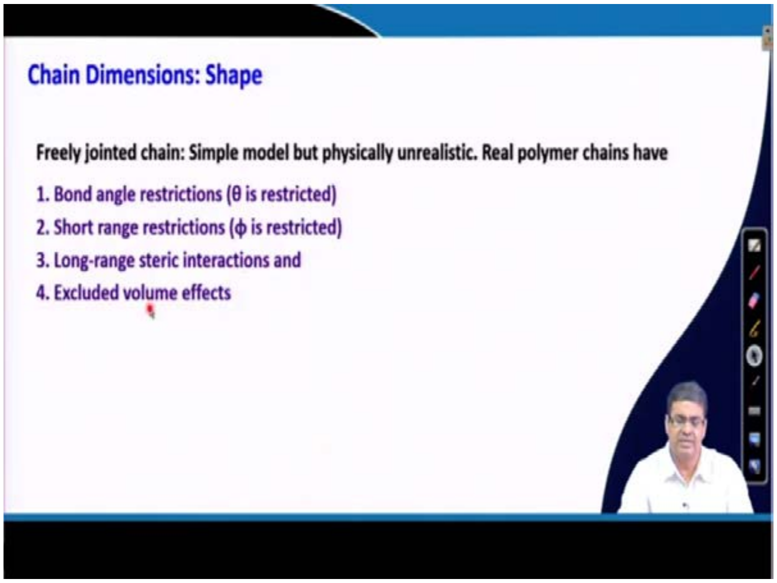

Chain Dimensions: Shape

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

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

Now, freely jointed chain is a very simple model. Real polymer chains have several restrictions. These are the following restrictions that exist for a real polymer chain, one that it has a bond angle restriction as we cannot have any angle between 2 bonds. We also have short range steric restrictions, long range steric restrictions and excluded volume effect which we will discuss one by one.

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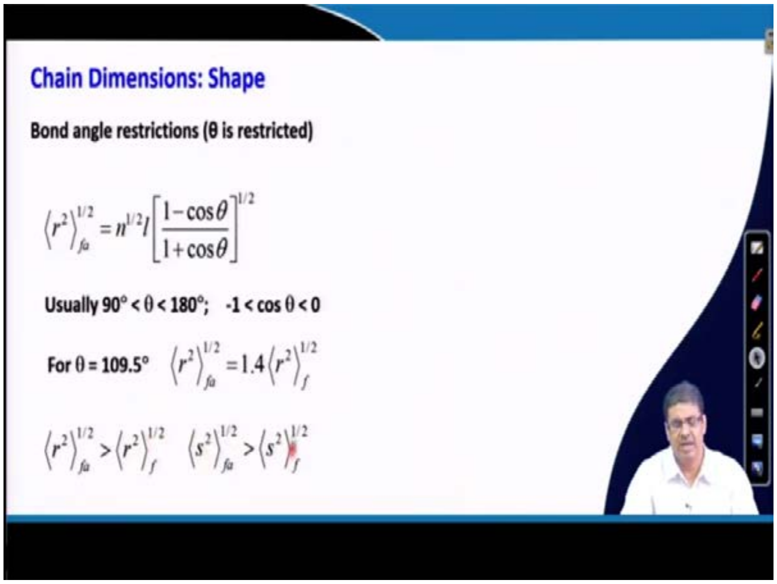

Chain Dimensions: Shape

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 $90^\circ < \theta < 180^\circ$; $-1 < \cos\theta < 0$

For $\theta = 109.5^\circ$ $\langle r^2\rangle_{fa}^{1/2} = 1.4\langle r^2\rangle_{f}^{1/2}$

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

Let us talk about bond restriction. Suppose we have 2 bonds, once we place the first bond, we will have no restriction of placing the second bond, it can be placed in any direction, all are equally probable. Then there would be an average place where the bond can be placed. Owing to restrictions, the bond angles are fixed. Thus, the actual distance between two ends will be more than when there is no bond angle restriction. So, bond angle restriction for bond angle greater than 90 actually will increase the average end to end distance. we now add a second term to bring this restriction of the bond angle.

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

So, we write ‘fa’ as superscript which is a freely rotating, there is no restriction about rotation around single bond. But there is a fixed bond angle, the fa stands for fixed bond angle. Usually, bond angles are between, say 90^{o} to 180^{o}, which means Cos θ ranges from -1 to 0 and for a tetrahedral C-C bond length, this θ is 109.5^{o}. Hence this quantity is 1.4 times than the freely rotating polymer chain as we discussed. Because of the bond angle which is higher than 90^{o}, this end to end distance becomes higher compared to freely rotating chain. So, this is higher than freely rotating chain. Similarly, the radius of gyration would be higher than the radius of gyration of freely rotating chain.

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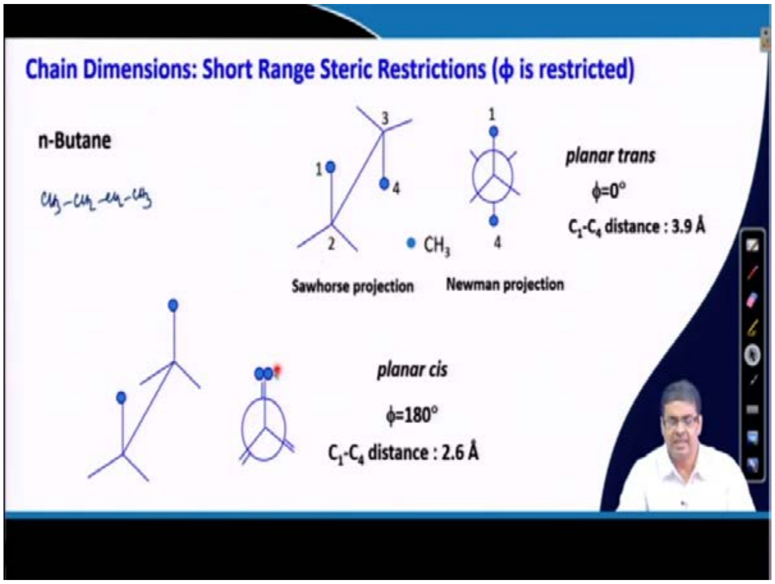

Chain Dimensions: Short Range Steric Restrictions (ϕ is restricted)

n-Butane

$CH_3-CH_2-CH_2-CH_3$

Sawhorse projection

Newman projection

planar trans

ϕ=0°

C_1-C_4 distance : 3.9 Å

planar cis

ϕ=180°

C_1-C_4 distance : 2.6 Å

Now, next we will talk about the short range steric restrictions, which is the restoration of dihedral angle. Let us talk about the simple system of n-butane which structure is we know CH_3 C H_2 CH_2 CH_3. Now, we generally represent the molecule by 2 ways - we can represent by sawhorse projection or Newman projection. So, when these methyl groups are in opposite direction as shown in these 2 projections, then we call it a trans and corresponding dihedral angle is 0. The C_1 to C_4 distance is 3.9 Å. Now, if these two CH_3 groups are in the same direction as seen from this projection, then we call this cis conformation and dihedral angle is 180^{o}. In this particular case, the distance between C_1 to C_4 end to end distance is lower, in this case 2.6 Å. As you can understand, if these 2 methyl groups in are in cis position then there will be steric hindrance among these. So, this conformation is probably less likely than this conformation where these 2 CH_3 groups are opposite to each other. So, the steric hindrance is not there or steric hindrance is absent. Now, because of this rotation around this single bond we can have many conformations and there will be many values of end to end distance between C 1 and C 4 as it rotates around this single bond and that is always happening.

In case of bond angle restriction, the bond angles are same for all the time, but in this case, because the rotation about single bond always exists, that means we are getting different conformations with time and as a result the energy of this conformation and the end to end distance will also change.

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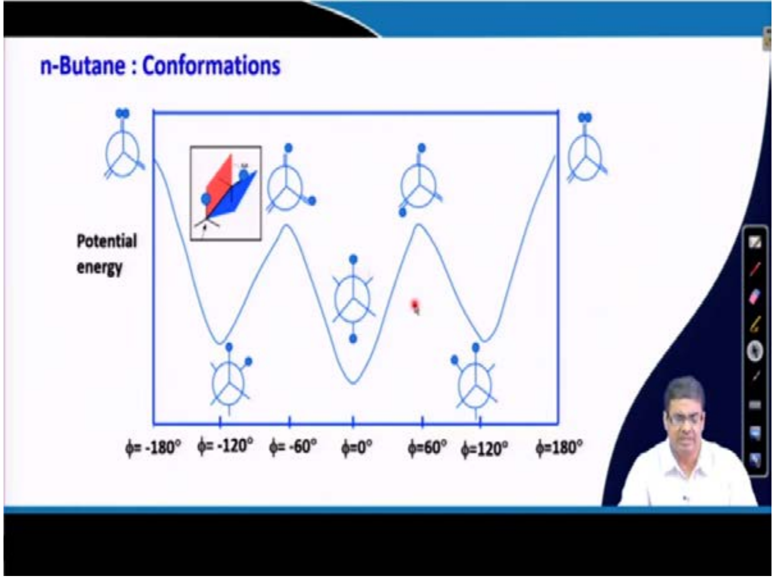

n-Butane : Conformations

We can plot the potential energy from one end to another end as we are rotating. From one end when the 2 methyl groups are overlapping with each other then we rotate 360^{o} starting from -180 to +180. When these 2 methyl groups are farthest apart, dihedral angle is 0, the potential energy minimum and there are other gauche conformations. All these things that you have already studied in your first year chemistry courses. So, as you can see, this cis conformation has highest energy and the trans conformation has lowest energy. So, given a chance, conformation will try to remain here, but because free rotation is possible. Hence, it is not that the conformation will always be like this, but there will be other conformations, but most of the time the molecule will stay in conformation which has lower energy.

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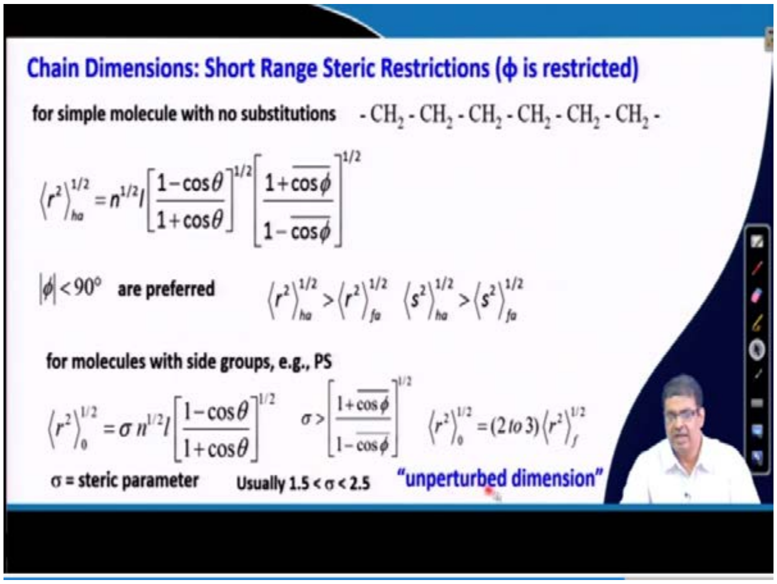

Chain Dimensions: Short Range Steric Restrictions (ϕ is restricted)

for simple molecule with no substitutions -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-

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

$|\phi| < 90^\circ$ are preferred $\langle r^2\rangle_{ha}^{1/2} > \langle r^2\rangle_{fa}^{1/2}$ $\langle s^2\rangle_{ha}^{1/2} > \langle s^2\rangle_{fa}^{1/2}$

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

$$\langle r^2\rangle_{0}^{1/2} = \sigma n^{1/2} l \left[\frac{1-\cos\theta}{1+\cos\theta}\right]^{1/2} \quad \sigma > \left[\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}\right]^{1/2} \quad \langle r^2\rangle_{0}^{1/2} = (2\ to\ 3)\langle r^2\rangle_{f}^{1/2}$$

σ = steric parameter Usually $1.5 < \sigma < 2.5$ "unperturbed dimension"

So, for this restriction, we are adding this second term. If there is no restriction, then it is between 0° to 180° which means if there is no restriction the average would have been 90° and cos 90° is 0. So, this term $\left[\frac{1+\overline{cos\phi}}{1-\overline{cos\phi}}\right]$ would be = 1. If there was no steric hindrance, which are called short range steric hindrance, $\left[\frac{1+\overline{cos\phi}}{1-\overline{cos\phi}}\right]$ would be = 1, but because there are steric hindrance, the average value of ϕ will not be 90° but it will be less than 90°. So, preferred $|\phi| < 90^{\circ}$. So, $\left[\frac{1+\overline{cos\phi}}{1-\overline{cos\phi}}\right]$ will be higher than 1. Now, in this case we are writing *ha*, *h* is for hindered rotation, and *a* for fixed bond angle. Now, this would be obviously higher than when there was no hindrance for rotation around single bond. So, this will be higher than this as we discussed that the dihedral angle will be less than 90°.

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

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

Similarly, the radius of gyration would be higher than the freely rotating radius of gyration, $\langle s^2\rangle_{ha}^{1/2} > \langle s^2\rangle_{fa}^{1/2}$. Instead of butane molecule if you have a polymer molecule which has bulky side groups like aromatic groups in polystyrene, then this becomes more complicated and getting a proper expression for this steric restriction become difficult. So, in that case, all these short range steric restrictions are accommodated in σ, which is called steric parameter which is the term that is multiplies with the dimension of the freely rotating chains with fixed bond angle to get the dimension of chain with two restrictions. So, the actual value of the static parameter would be higher than this, as we have bulky side group and this generally varies between 1.5 to 2.5. This value, which we are writing 0 or naught here, which means this is obtained experimentally and not determined theoretically and this is approximately 2 to 3 times of the RMS end to end distance for a freely rotating polymer chain and this dimension we call unperturbed dimension.

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

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

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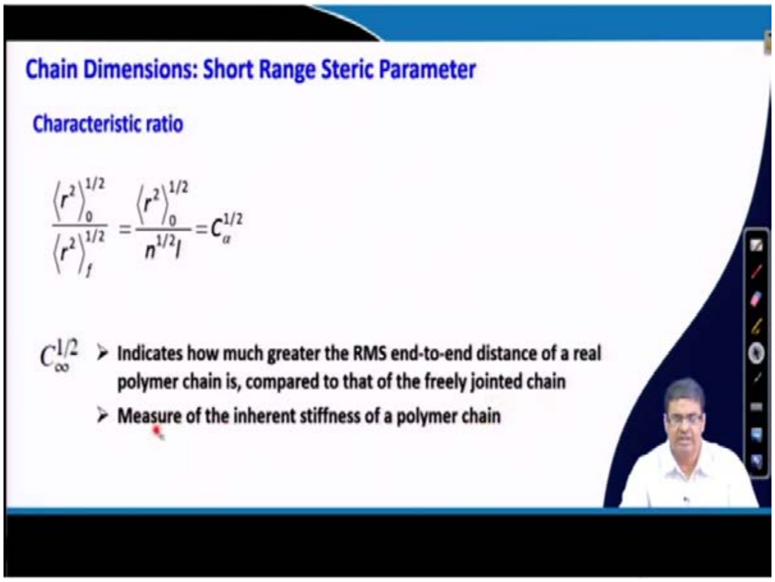

Chain Dimensions: Short Range Steric Parameter

Characteristic ratio

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

$C_\infty^{1/2}$
- Indicates how much greater the RMS end-to-end distance of a real polymer chain is, compared to that of the freely jointed chain
- Measure of the inherent stiffness of a polymer chain

Next, if we compare the unperturbed dimension and this freely rotating or free polymer chain which did not have any restriction of bond angle or dihedral angle, then this ratio gives the stiffness of the polymer chain which is mentioned as characteristic ratio. So, this value of characteristic ratio indicates how much greater the RMS end to end distance of a real polymer chain compared to that of a freely jointed chain. So, it is the measure of inherent stiffness of a polymer chain.

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

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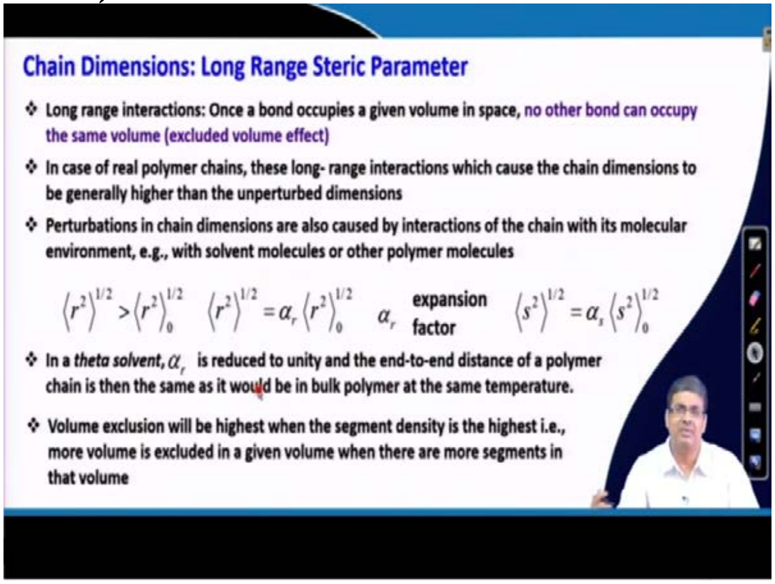

Chain Dimensions: Long Range Steric Parameter

- Long range interactions: Once a bond occupies a given volume in space, no other bond can occupy the same volume (excluded volume effect)
- In case of real polymer chains, these long- range interactions which cause the chain dimensions to be generally higher than the unperturbed dimensions
- Perturbations in chain dimensions are also caused by interactions of the chain with its molecular environment, e.g., with solvent molecules or other polymer molecules

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

- In a *theta solvent*, α_r is reduced to unity and the end-to-end distance of a polymer chain is then the same as it would be in bulk polymer at the same temperature.
- 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

Next, we will go to the long range steric parameter. Once a bond occupies a given space in the given volume, no other bond can occupy the same volume, we call this as a excluded volume effect. Basically if I write a polymer chain like this, then once it occupies that particular space, then the second fragment or second polymer cannot occupy the same place and this we call excluded volume effect.

In case of real polymer chains, this long range interaction which causes a chain dimension to be generally higher than the unperturbed dimension, because in unperturbed dimension we did not consider these excluded volume effects. Now, because of excluded volume effect, the polymer fragments need to avoid overlapping each other which means the polymer dimension would be even higher. Perturbation of the chain dimension can also happen if there is interaction between the polymer fragments with solvent molecules. If there is a favorable interaction between the polymer and solvent molecules, then polymer will try to expand further making the size of the polymer coil even higher. So, in real polymer chain, the real polymer RMS end to end distance would be higher than the unperturbed dimension.

$$\langle r^2\rangle^{1/2} > \langle r^2\rangle_0^{1/2}$$

$$\langle r^2\rangle^{1/2} = a_r\langle r^2\rangle_0^{1/2}$$

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

We are basically considering, this as the expansion factor, which is the ratio of the actual real RMS end to end distance with the RMS end to end distance of the unperturbed dimension and this is called expansion factor. Similarly, we have expansion factor for radius of gyration. Now, in case of θ solvent, this excluded volume effect does not come and also there is no interaction, ΔH_{mix} is 0. So, there is no contact interaction between the polymer and solvent molecule. So, basically in case of θ solvent the actual dimension becomes same as the dimension of the unperturbed dimension which means the value of the expansion factor becomes 1 and if we have a good solvent, the expansion factor becomes more than 1.

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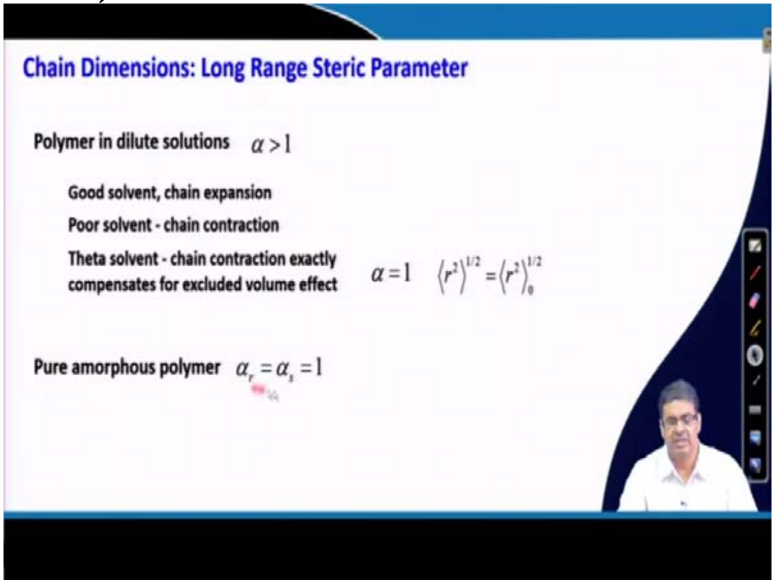

Chain Dimensions: Long Range Steric Parameter

Polymer in dilute solutions $\alpha > 1$

Good solvent, chain expansion

Poor solvent - chain contraction

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

Pure amorphous polymer $\alpha_r = \alpha_s = 1$

For polymer in dilute solution, generally these expansions factor is more than 1 and in good solvent we have chain expansion, poor solvent we have chain contraction. In θ solvent, the chain contraction exactly compensates the excluded volume effect, and we have alpha or expansion factor is equal to 1. This is true for pure amorphous polymer also, where also the expansion factor for RMS end to end distance and the radius of gyration is 1.

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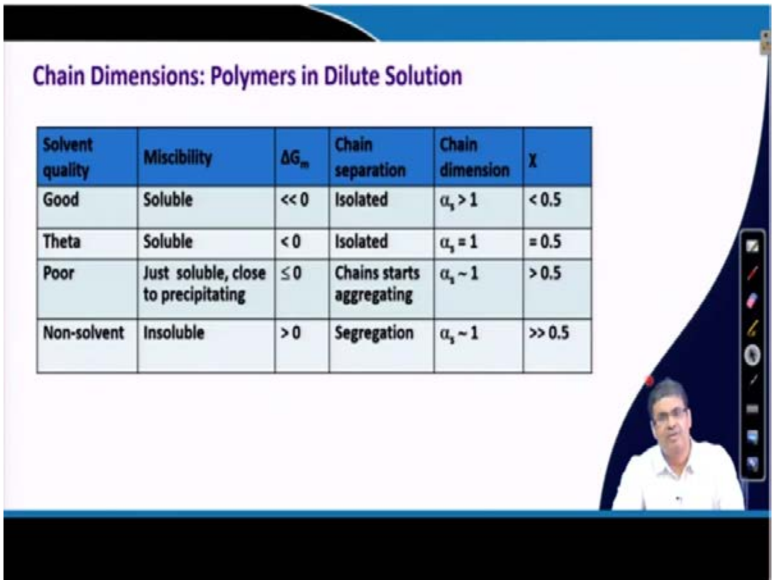

Chain Dimensions: Polymers in Dilute Solution

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

In summary in case of chain dimension, if we have good solvent then the polymer and solvent will be miscible and we get a soluble polymer and ΔG_{mix} is negative. As we are talking about dilute solutions, so the chains are well separated from each other and expansion factor is more than 1 and polymer solvent interaction parameter is less than 0.5 or less than half. In case of θ solvent, the polymer is miscible or soluble in the solvent, ΔG_{mix} is less than 0, polymer chains are separate from each other, the expansion factor is 1 and the polymer solvent interaction parameter is equal to half. For poor solvent the polymer is just soluble and is very close to precipitating out, with $\Delta G \leq 0$ and the chain starts slowly aggregating. Now, the polymers have already reached the unperturbed dimensions. So, it is not possible to further compact the polymer because of the restriction of bond angle and bond rotation. Hence, the expansion factor remains close to 1, but the polymers start basically aggregating with each other leading to precipitation. When this happens, then the polymer solvent interaction parameter value has less than or greater than 0.5

Now, if this goes much higher than 0.5, then the solvent is actually non solvent. Then the polymer is insoluble, ΔG_{mix} is positive and polymers are segregated. The chain dimension are just like pure amorphous polymer and the expansion factor is close to 1. So, with this we come to the end of this lecture on chain dimension and this next lecture we will discuss frictional properties of polymer solution.