Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture - 39
Solutions: Properties

Hello, in these weeks of polymers course, our focus remains on properties, as we have been looking at mechanical properties and looking at how to analyze the response of polymers under glassy state and rubbery state and look at what happens if blends and composites are formed. And now in the next few lectures, we will continue this journey and look at the variety of properties that are important for polymeric systems.

In this particular lecture, we will look at solutions. Polymers are used for example, while making a thin film polymer solution may be used, while wet spinning of fibers polymer solutions are used. But this is again where solutions are important only during processing. But there are applications such as drag reduction in pipelines, where a small amount of polymer is added to reduce the friction between the liquid that is being transported and the pipe. So, in this case, the polymer solution itself is the product and many of course, thickening applications in foods and sauces and ketchups and so on thickeners polymers are again used in solutions, so solution properties are important. And one of the key features associated with the solution property is also dilute solution property where the amount of polymer is very less and example of this drag reduction that I mentioned polymer added is extremely small quantities. So, therefore, dilute polymer systems are good to look at from the point of view of interaction between polymer and solvents, but also relevant from a practical point of view.

So, looking at properties of solutions is what we will do in this lecture.

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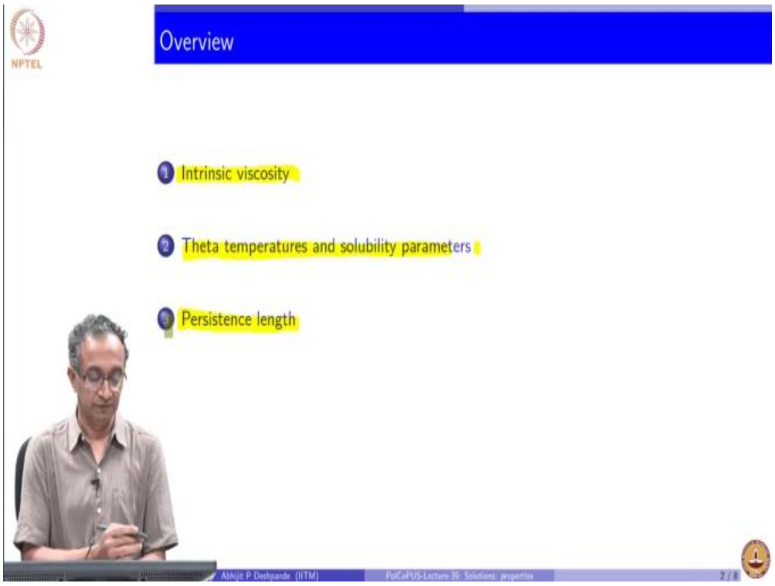

Overview

1. Intrinsic viscosity
2. Theta temperatures and solubility parameters
3. Persistence length

And we will define something called intrinsic viscosity, which is a very good indicator of the interactions between macromolecule and the solvent. And we will look at also some values of the theta temperatures and solubility parameters, which again indicate interactions between polymer solvent systems. And one of the key features associated with a macromolecular chain in terms of its rigidity is quantified in terms of persistence length. And this is very important in biological domain as well as any processing work that we do with these solutions. So, we will take a look at that, in terms of the property of the solution.

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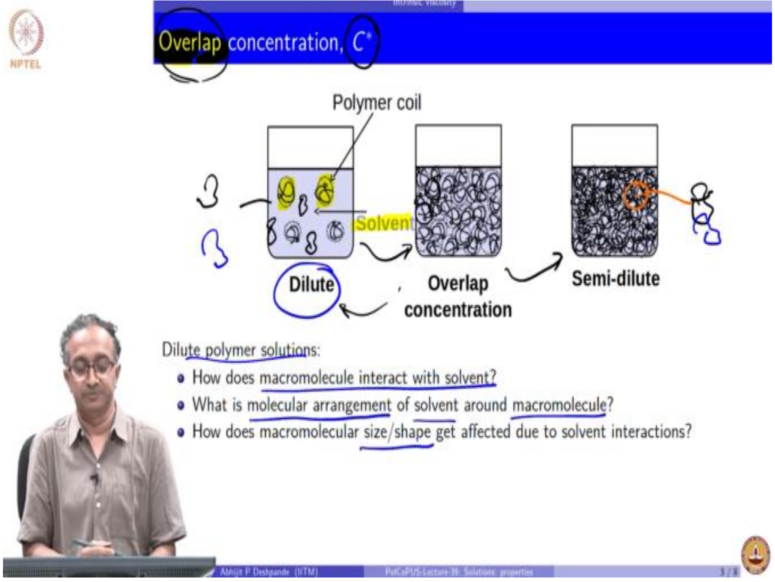

Overlap concentration, C^*

Dilute polymer solutions:

- How does macromolecule interact with solvent?
- What is molecular arrangement of solvent around macromolecule?
- How does macromolecular size/shape get affected due to solvent interactions?

One of the key features while trying to think in terms of dilute versus not a dilute polymer system is to think in terms of what is the concentration below which I can call polymer solvent system a dilute solution. And this is basically done using what is called an overlap concentration. So, if I start increasing polymer concentration and start adding these polymer coils, what you can notice is in the sea of solvent, these polymer coils are all separated with respect to each other. But if I start adding more and more polymer, then basically what I have is a situation where all these polymers basically are just overlapping each other and that is called the overlap concentration. So, below this concentration, which is usually denoted using C star, we have dilute systems and above this concentration we have semi dilute system. So, if you zoom in on any spot here, what you will notice is that one macromolecular coil is now interacting closely with another macromolecular coil. While in the dilute case we have one macromolecular coil and other macromolecular coil are not interacting with each other. So, polymer solvent interactions are key in the dilute and so, therefore, dilute polymer solutions is very useful to understand how is macromolecule interacting with solvent? And what is the molecule arrangement of the solvent around the macro molecule? We saw in the lecture related to miscibility that if solvent is solvating around the macromolecules then we have an expanded chain.

So, therefore, molecular arrangement of solvent around macromolecule is a key determinant of the shape and size and size shape how does it get affected will determine the other properties such as viscosity or any other performance that we are related. For example, in case of biological domain we have seen diffusion of protein molecules. So, all of those get determined based on size and shape of macromolecules.

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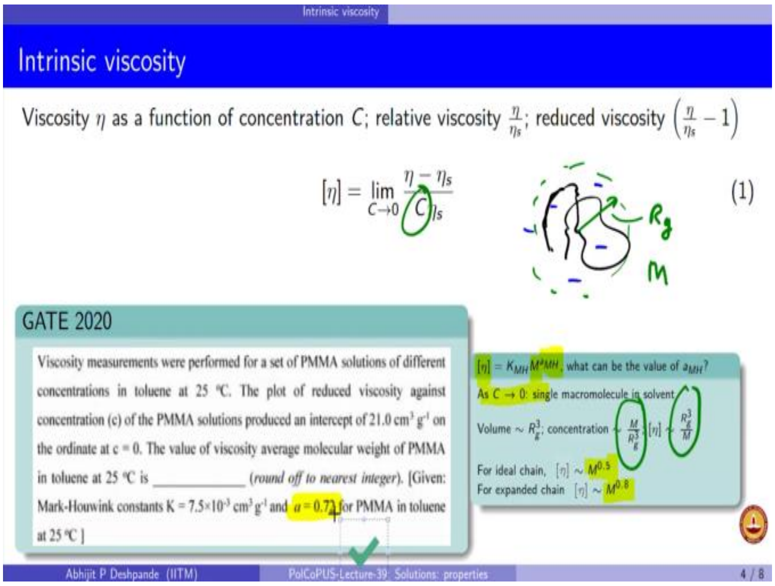

Intrinsic viscosity

Intrinsic viscosity

Viscosity η as a function of concentration C; relative viscosity $\frac{\eta}{\eta_s}$; reduced viscosity $\left(\frac{\eta}{\eta_s} - 1\right)$

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_s}{C \eta_s} \qquad (1)$$

GATE 2020

Viscosity measurements were performed for a set of PMMA solutions of different concentrations in toluene at 25 °C. The plot of reduced viscosity against concentration (c) of the PMMA solutions produced an intercept of 21.0 cm³ g⁻¹ on the ordinate at c = 0. The value of viscosity average molecular weight of PMMA in toluene at 25 °C is ____________ (*round off to nearest integer*). [Given: Mark-Houwink constants K = 7.5×10⁻³ cm³ g⁻¹ and *a* = 0.72 for PMMA in toluene at 25 °C]

$[\eta] = K_{MH} M^{a_{MH}}$, what can be the value of a_{MH}?

As $C \to 0$: single macromolecule in solvent

Volume $\sim R_g^3$; concentration $\frac{M}{R_g^3}$; $[\eta]$ $\frac{R_g^3}{M}$

For ideal chain, $[\eta] \sim M^{0.5}$

For expanded chain $[\eta] \sim M^{0.8}$

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So, intrinsic viscosity is one of the key parameters, which determines the interactions between the polymer and the solvent. And this is done with the measurement of viscosity of dilute solutions. So, what we do is we make solutions of different concentrations and measure viscosity, we could then calculate what is called the relative viscosity. What is the viscosity of the solution with respect to viscosity of the solvent? So, η_s is the solvent viscosity and so, this ratio of course, is 1 when there is no polymer added and then it increases more than 1 as more and more volume is added. And then therefore, we can talk of a reduced viscosity which is increase in viscosity over and above what is there in the solvent. So, therefore, $(\eta - \eta_s) / \eta_s$ is the reduced viscosity and then we divide this with the concentration that is being added and plot this as a function of concentration. And our objective is to ask the question in a following way that what happens to the viscosity of a polymer solution when exceedingly small amount of polymer is added? And that's because, in if I just had very few molecules of polymer, basically, it's a polymer molecule surrounded by sea of solvent. So, then these interactions will determine what is the size and shape of this macromolecules and therefore, the viscosity.

$$[\boldsymbol{\eta}] = \lim_{C->0} \frac{\boldsymbol{\eta} - \boldsymbol{\eta}_s}{C\boldsymbol{\eta}_s}$$

So, intrinsic viscosity therefore, is a key indicator of polymer solvent interactions and what is the shape and size of the macromolecule given us solvent which is surrounding it. So, if you take data at different C and plot them and then extrapolate it to C = 0, this is what the intrinsic viscosity is. Those of you who have looked at thermodynamics of solutions may have heard of this concept called infinite dilution activity coefficient. Generally infinite dilution activity coefficient is used as a key determinant of how two molecules A and B interact with each other. This is also intrinsic viscosity is modification to the viscosity of a solution at infinite dilution. So, it's just determining based on the interactions between polymer and solvent. Viscosity therefore, if we measure like this, in this case, for example, the question that has been asked is PMMA solutions in toluene and the reduced viscosity as we mentioned is plotted against the concentration and the intercept is given by this. So, basically intrinsic viscosity is given and we have seen this that the intrinsic viscosity depends on the molar mass of the polymer system. So, this can be used to determine the molar mass also. And so, if parameters which signify the interactions between the polymer and the solvent system and this is unique to each and every polymer solvent system, if we know these then we can find the molar mass. So, you can use the Mark-Houwink relation and plug-in numbers to get the answer. But one of the questions that I want to pose here is can we justify what is the value of such slopes? So, is this totally empirical that I do these measurements of intrinsic viscosity and then find viscosity as a function of different molar masses and then get Mark-Houwink parameters or having learnt about behavior of single macromolecules and its size and shape? Can I at least get order of magnitude figures regarding what this exponent will be? How should intrinsic viscosity depend on molar mass of the molecular chain?

So, the question that I am posing is what is the value of a K_{MH}, where intrinsic viscosity is a function of molar mass. So, as C tends to 0 because intrinsic viscosity is defined only when concentration goes to 0. So, in this case basically what we have is a single macromolecule because concentration is so low that it's only one macromolecule which is surrounded by solvent. So basically what's the concentration of in this case? So concentration in this case, we know that the size of this macromolecule can be approximately related to what we call this spherical shape. And the radius of this sphere is, if you think about how we define size and shape, we define end to end distance and radius of gyration. So, this is basically a sphere of radius of gyration R_g. So this determines the basic volume of this macromolecular system. So in this volume, we have mass which is given by the molar mass of macromolecules, because there is only one macromolecule in the system there is only dilute C going to 0. So therefore, concentration of polymer is just molar mass divided by R_g, because R^3_g is the volume, M is the mass contained in this volume. And so, intrinsic viscosity is inverse of concentration. And so it's related to R^3_g / M, where M is the molar mass.

Now, how does R_g depend on M? This depends on whether it's expanded chain or ideal chain, and I leave you to actually do this quick calculations and I get the how the intrinsic viscosity depends on molar mass? And for ideal chain it is .5 and for expanded chain it is .8. And look at the value which is there for a real polymer system PMMA and toluene .72. So with very simple models of ideal chain and expanded chain and a single macromolecular system, we are able to get answers to viscosity and intrinsic viscosity and how it depends. So clearly PMMA in toluene is a good solvent system where interaction between toluene and PMMA are favorable and it's an expanded chain given that we see that it agrees more with the expanded chain model.

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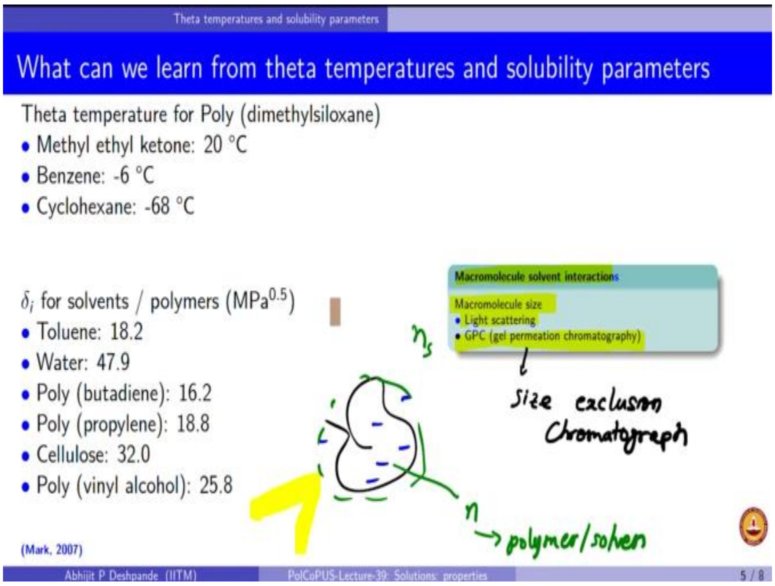

Theta temperatures and solubility parameters

What can we learn from theta temperatures and solubility parameters

Theta temperature for Poly (dimethylsiloxane)

- Methyl ethyl ketone: 20 °C
- Benzene: -6 °C
- Cyclohexane: -68 °C

δ_i for solvents / polymers ($MPa^{0.5}$)

- Toluene: 18.2
- Water: 47.9
- Poly (butadiene): 16.2
- Poly (propylene): 18.8
- Cellulose: 32.0
- Poly (vinyl alcohol): 25.8

(Mark, 2007)

Macromolecule solvent interactions

Macromolecule size

- Light scattering
- GPC (gel permeation chromatography)

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So, continuing further, what are the things we can learn by looking at such parameters of interaction between polymer and solvent, for example, we define already the theta temperature where the chain is ideal chain, and you can see that the theta temperature for let’s say PDMS, the silicon based polymer is different depending on the solvent. So, the temperature, this is the temperature at which polymer solvent interactions are just balancing each other out. If we change the temperature one way, then we will have collapse chain, if we change the temperature another way we have expanded chain. So clearly different solvents have different interactions. Similarly, solubility parameter, which again is an empirical parameter depending on the interaction energy between polymer and solvent is very different value. For toluene for example, it’s 18 and polypropylene is also it’s 18. So, whenever the solubility parameters are close to each other, they are likely to be miscible. And water clearly has a very different solubility parameter. And PVA which is soluble in water, you can see that the solubility parameter values are a guideline but not exact, because cellulose which has a solubility parameter, which is closer to water, but because of the extensive hydrogen bonding, it is not as soluble. And so cellulose ends are being not soluble in water as well as in many organic solvent. So it’s a challenging material in terms of reprocessing. And in fact, that’s the strength by which it gives mechanical rigidity to all the plant worth.

So, generally, these macromolecular solvent interactions are very important determinant of the molecular size that a polymer molecule occupies. And this is the basis for measuring the molecular weight using either light scattering or GPC. So gel permeation chromatography is also called size exclusion chromatography. So we what we do is we exclude the size of different polymer molecules based on what their size is. So we have a gel through which pores of the gel, the macromolecules continue to go. And if they are small molecules, they get trapped in pores and they come out last, while if it is a big molecule, it does not get trapped and therefore it can come out faster. So that's a way of measuring molar masses of different bulk polymer sample. And light scattering of course also is where there is a macromolecule and a solvent system and the size of this macromolecule is basically determines because the refractive index and this here will be different compared to outside. So, this is the solvent refractive index and this is the polymer solvent system refractive index. So, because of this there will be scattering. So, scattering and diffraction events will happen and therefore, by doing light scattering, we can measure the size of the macromolecules in solution.

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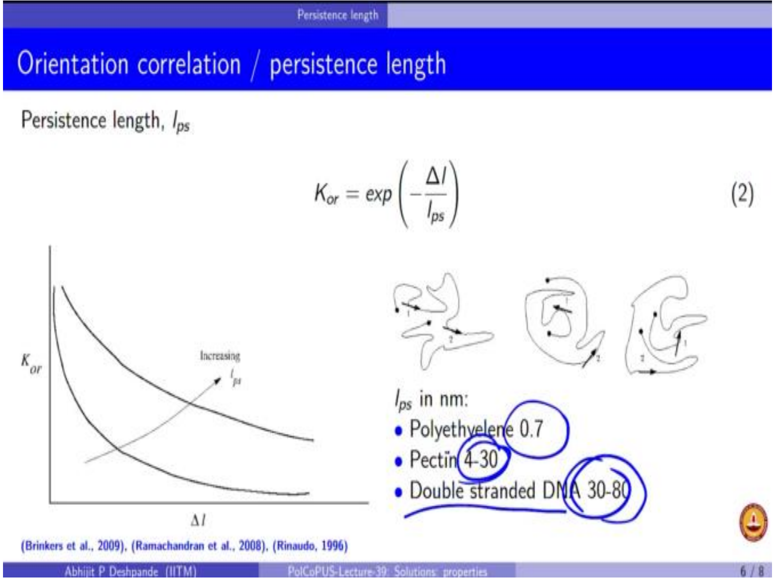

Orientation correlation / persistence length

Persistence length, l_{ps}

$$K_{or} = exp\left(-\frac{\Delta l}{l_{ps}}\right) \qquad (2)$$

l_{ps} in nm:

- Polyethylene 0.7
- Pectin 4-30
- Double stranded DNA 30-80

(Brinkers et al., 2009), (Ramachandran et al., 2008), (Rinaudo, 1996)

We will close this lecture by looking at this important property of polymer which is in terms of rigidity of the macromolecule and this is relevant not only in the form of solution where bio macromolecules, this persistence length is a very important indicator of the overall mechanical role that a macromolecules plays in the cell environment, but it is also important from a processing point of view for engineering and other polymers. So, we talk about the correlation between one part of the chain with another part. So, for example, the way we have drawn here the polymer chain what we are asking is, if I know the orientation at 1 point, what happens to orientation at some other point. So, 1 and 2 are two points on the polymer chain and we are interested in knowing, what is the relation between these two orientation.

So, if I have a rod like molecule, molecule which prevents any flipping back and forth of macromolecule, then I will have basically a chain like this and then if I choose two points on it, if this is orientation, it will be orientation, same orientation, because let's say this macromolecule can orient overall, but again the point 1 and 2 will be in the same orientation. So, in this case, point 1 and 2 are correlated perfectly. The orientation of point 1 and orientation at point 2 are correlated with respect to each other. On the other hand, if we have a flexible chain like this, and the way we have I have drawn here, see the orientation at point 1 and 2 are completely random with respect to each other, which means that the orientation is not correlated. So, generally, the points which are closer to each other will always have correlation, which is stronger, because in the end, we have seen that this is based on the covalent bonds. So, the orientation between this and this, the 2 subsequent bonds will always be perfectly correlated. For example, this angle is 109 in case of butane and close to 109 in case of polyethylene and many other olefinic polymers. So, therefore, orientation correlation the answer to the question that if I know orientation at 1 point, and if I start travelling along the chain and start asking what is the orientation at that point, these 2 orientations, how are they correlated with each other. So, if these 2 points are close to each other, then correlation will be good, if we travel away, then correlation will fall and there will come a time when correlation will go to 0. And so, this is a signature of a flexible chain, and polyethylene and many other polymers are flexible, the fact that correlation dies away. We can have another extreme where correlation never dries, dies. And that is the example of a perfectly rigid macromolecule. Because one side no correlation at one point, no matter how far down do I go, I know the correlation of other points also and so, of course, polymers in between vary show different types of persistence length, persistence of the correlation. So, in this case, persistence length is infinite, if we have a polymer where there is no correlation at all; then persistence length is smaller.

So in general, we can use an exponential function to describe this decay of orientation as a function of the distance along the macromolecule. So delta l is distance along macromolecule. And so, as we travel from 1 point to the other along the macromolecule, what happens to correlation? And so l_{ps}, which is part of this exponential determines how fast or slow this decays as a function of space.

$$\boldsymbol{K_{or} = \exp\left(-\frac{\Delta l}{l_{ps}}\right)}$$

And just looking at these correlation numbers in terms of three different polymeric systems for polyethylene, the persistence length is just .7 nm and therefore, polyethylene is a very good example of flexibility. On the other hand double stranded DNA if you look at it’s 30 to 80 nanometers and pectin, which is another biopolymer, which we have seen frequently, it is somewhere in between.

So, therefore, based on this persistence length, we can classify the polymers as flexible, semi flexible or rigid polymers and how they change their conformations? How can they induce elasticity? How easy it is to for them to stretch and bend? So, all these will determine their overall mechanical response in a given situation.

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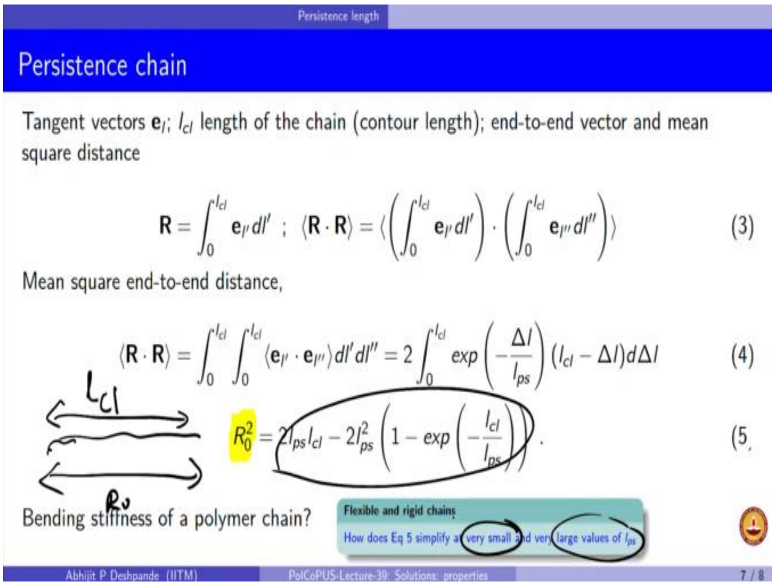

Persistence length

Persistence chain

Tangent vectors $\mathbf{e}_l$; l_{cl} length of the chain (contour length); end-to-end vector and mean square distance

$$\mathbf{R} = \int_0^{l_{cl}} \mathbf{e}_{l'} dl' \; ; \; \langle \mathbf{R} \cdot \mathbf{R} \rangle = \langle \left(\int_0^{l_{cl}} \mathbf{e}_{l'} dl' \right) \cdot \left(\int_0^{l_{cl}} \mathbf{e}_{l''} dl'' \right) \rangle \tag{3}$$

Mean square end-to-end distance,

$$\langle \mathbf{R} \cdot \mathbf{R} \rangle = \int_0^{l_{cl}} \int_0^{l_{cl}} \langle \mathbf{e}_{l'} \cdot \mathbf{e}_{l''} \rangle dl' dl'' = 2 \int_0^{l_{cl}} exp\left(-\frac{\Delta l}{l_{ps}} \right) (l_{cl} - \Delta l) d\Delta l \tag{4}$$

$$R_0^2 = 2l_{ps}l_{cl} - 2l_{ps}^2 \left(1 - exp\left(-\frac{l_{cl}}{l_{ps}} \right) \right). \tag{5}$$

Bending stiffness of a polymer chain?

Flexible and rigid chains

How does Eq 5 simplify at very small and very large values of l_{ps}

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So, with this, we will just look at the overall on mathematical expression for this model of chain, we have seen expanded chain and ideal chain and similarly, we have this model of a polymeric system which is called persistence chain where the end to end distance is nothing but summation of tangent vectors throughout the length of the chain. And so, end to end distance mean square distance is nothing but ensemble average of the end to end vector R. And if you carry out some algebra, you can show that in the end, end to end distance is given by the persistence length and the contour length, and contour length is basically the overall length of the macromolecule. And one of the questions you can think of is what happens to this R 0, the end to end distance when l_{ps} is small or l_{ps} is very large. If l_{ps} is very large, you remember that it is a rigid chain.

$$\boldsymbol{R_0^2 = 2l_{ps}l_{cl} - 2l_{ps}^2(1 - \exp\left(-\frac{l_{cl}}{l_{ps}}\right))}$$

So, therefore, if l_{ps} is very large the polymer molecule will be like this then the end to end distance which is R 0 will be same as l contour length. So, can you play around with algebra in this expression and try to justify for very small and very large value of l_{ps} what happens. When you have l_{ps} very small you should get the ideal chain behavior, where the contour length to square root should be the end to end distance, while a rigid rod polymer where the contour length and end to end distance are proportional to each other. So, I will leave you to do this exercise.

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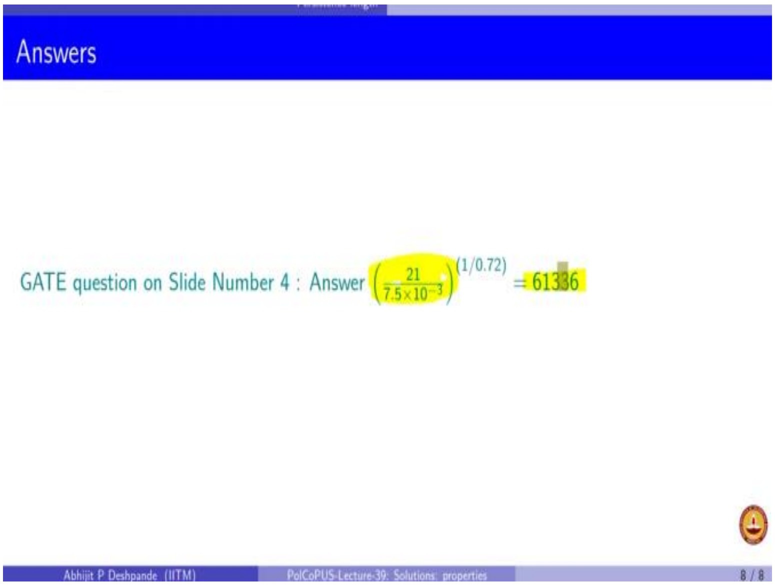

Answers

GATE question on Slide Number 4 : Answer $\left(\frac{21}{7.5\times10^{-3}}\right)^{(1/0.72)} = 61336$

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And with this we will close the answer to the question that was posed based on the exam is just application of the Mark-Houwink relation to get the molar mass and which is a good way of measuring the molar mass of polymer solvent system. So, with this we close the discussion of polymer solutions. And we will continue our journey related to properties of different kinds of polymeric systems in the remaining part of the week. Thank you.