Introduction to Polymer Physics
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Lecture – 24
Review

So, hello everyone so, in this very last lecture over course on Introduction to Polymer Physics, we will just review all the different topics that we have considered and then close this course by some after some concluding remarks.

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Week 1: Introductory Concepts

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Basic Definitions

Classification of Polymers

Definition of Molar Mass and Related Concepts:

- Number-Average Molar Mass
- Weight-Average Molar Mass
- Viscosity-Average Molar Mass
- z-Average Molar Mass
- Polydispersity Index
- Degree of Polymerization

We started off this course in the very first week by introducing some fundamental concepts about polymers, we talked about some basic definitions, different ways in which polymers can be classified. And we discussed the different types of molar masses that are defined for polymers.

So, we talked about different kinds of average molar masses the fact that polymer chain lengths are not fixed in a given polymer sample, polymers chain can have different lengths. So, that is why a fixed molar mass cannot be defined for a given polymeric material and we need to define average molar masses.

So, different kinds of average molar masses that are commonly employed those were introduced in the very first lecture. So, we talk about the number average molar mass, the weight average, viscosity average, z average molar mass. Also the concept of polydispersity index has being a ratio of the weight average to the number absolute molar mass. And very rough kind of measure of how polydispersed polymer chain length is in a given sample. Although it since it is just a number it cannot describe the exact nature of polydispersity, but it can give some idea.

Also we talked about the degree of polymerization. So, here again the since we the polymer chain lengths can be of can contain different number of monomeric units. So, we can have number average degree of polymerization or weight average degree of polymerization. So, these are the concept that we introduced in the very first lecture because, these things that that would be referred throughout this course later on.

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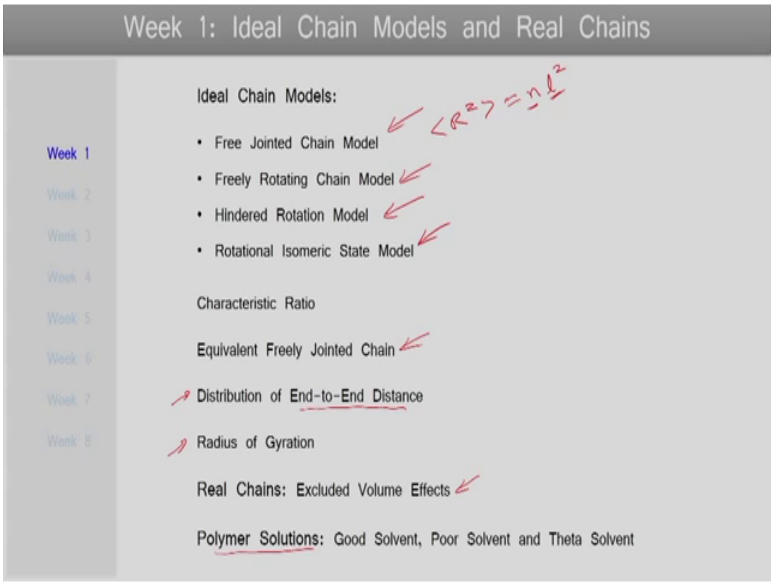

Week 1: Ideal Chain Models and Real Chains

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Ideal Chain Models:

- Free Jointed Chain Model $\langle R^2 \rangle = nl^2$
- Freely Rotating Chain Model
- Hindered Rotation Model
- Rotational Isomeric State Model

Characteristic Ratio

Equivalent Freely Jointed Chain

Distribution of End-to-End Distance

Radius of Gyration

Real Chains: Excluded Volume Effects

Polymer Solutions: Good Solvent, Poor Solvent and Theta Solvent

And from in the next couple of lectures in the very first week of this course we introduce the different models for ideal polymer chains first. So, we talked about the fact that neither polymer chain is where the chains position for chains whether well separated along the backbone they do not overlap with each other. So, even if they are on top of each other that is allowed in an ideal chain module. So, such overlaps are not expressively considered in ideal chain models.

So, we consider the 4 common ideal chain models, the simplest one in the freely jointed chain model where we saw that the mean square end to end distance which is a measure of the average size of the polymer chain that was equal to nl square, n is the number of backbone bonds and say l is the length of a given backbone bond. Next we talk about the freely rotating chain model where. So, in the freely jointed chain model the angle bond angles are free to take any value whereas, in the freely rotating chain model ones angle take fixed values. And we discussed more advanced models like the hindered rotation model and the rotational isomeric state model. Where not just a bond angle, but the torsion angles were also restricted to take only certain values and not free to take any arbitrary values.

So, we discussed all these ideal chain models to describe the chain confirmations of ideal chains. And then we talked about the concepts or characteristic ratio as a measure of the mean square end to end distance of a given polymer chain divided by the mean square end to end distance of freely jointed polymer chain.

So, the characteristic ratio is a measure of the stiffness or rigidity of a polymer chain backbone. We talk about the concept of equivalent freely jointed chain. So, any ideal chain one can think of it as an equivalent freely jointed chain. So, a freely jointed can be mapped onto any ideal chain that was a concept that we discussed here. And we talked about how one can determine the number of Kuhn monomers or the equivalent monomeric units as the size of the Kuhn monomer or the Kuhn length how that can be determined mathematically. So, that was discussed.

We also talked about the distribution of end to end distance and we saw that for ideal chain the this distribution can be described by a kind a Gaussian kind of function provided that the end to end distance that we are talking about is much smaller than the fully extended chain length which will be n times that will. So, if the end to end distance is much smaller that than the counter length of the chain then the Gaussian kind of function describes a end to end distance distribution for ideal chains.

We also talked about the fact that the good measure the polymer size is actually the radius of gyration because it can describe the size of not just linear polymers, but branch as well as closed loop or cyclic polymers. So, the concept of radius of gyration was discussed. And towards the end of the first week we talked about real polymer chains.

So, in real polymer chains excluded volume affects are incorporated at so, that the different parts of the same chain cannot overlap with each other. There is some internal segment-segment repulsion within the polymer chain due to this excluding volume effects. And this repulsion actually leads to in general and expansion in the size of the real chain compared to an ideal chain.

So, the real chain excluded volume effects will consider and the size of the real chain was related to that of an ideal chain through the expansion parameter. Finally, the behavior of polymer chains in different kinds of solvents that was discussed. So, if we have a good solvent that the polymer molecules interact favorably with the solvent molecules then polymer tends to expand. In the poor solvent the solvent molecules and the polymers do not like each other.

So, the polymer will not wish to expand in such solvents and special case of poor solvent is a theta solvent where the internal segment-segment repulsion in inside the polymer chain due to the excluded volume interactions. That is counter balance by the segment solvent repulsion. Under such conditions in the polymers tends to adopt dimensions which are similar to the ideal chain dimensions. So, such theta such theta solvent was also discussed.

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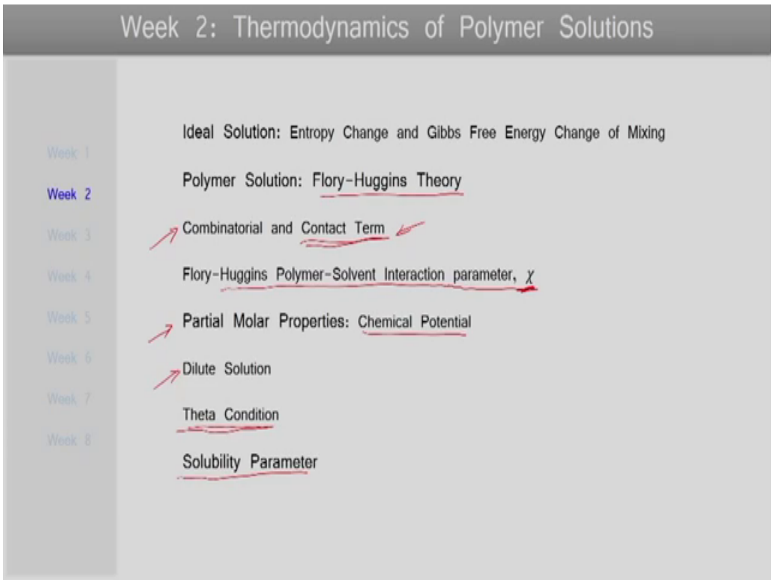

Week 2: Thermodynamics of Polymer Solutions

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Ideal Solution: Entropy Change and Gibbs Free Energy Change of Mixing

Polymer Solution: Flory-Huggins Theory

Combinatorial and Contact Term

Flory-Huggins Polymer-Solvent Interaction parameter, χ

Partial Molar Properties: Chemical Potential

Dilute Solution

Theta Condition

Solubility Parameter

And in the next week we started a discussion of the thermodynamics of polymer solution. So, in the beginning we just briefly introduced the concept of ideal solutions and derive the expression for its entropy change of mixing and delta g of mixing. And then we discussed a polymer solutions are actually different from ideal solutions. Because, the polymer size of the polymer change is much larger than the size of the solvent molecules. And the volume chain is also can have different interactions with the solvent molecules than with themselves.

So, based on the size disparity between the solute and solvent as well as interactions present polymer solutions were identified as being different from ideal solutions. And, we discussed that the Flory Huggins theory is a good theory for a qualitative discussion and a description of polymer solutions. So, while discussing Flory Huggins theory and it is derivation we talk about the combinatorial and contact term. So, combinatorial term is a purely entropic and so, the change in entropy due and due to the change in the different number of arrangements that the polymer solvent system can take. That was the communitorial term and contact term was due to the interactions present in the system.

So, combining these 2 terms we obtain the Flory Huggins equation for polymer solutions and we introduce Flory Huggins polymer solvent interaction parameter chi as an important measure of the interaction between the polymer and the solvent and, the Flory Huggins equation describing an expression for the gives energy change of mixing of a polymer in a solvent that was developed. And later on we also discussed the concept of partial molar properties especially chemical potential and we applied Flory-Huggins theory to develop expression for chemical potentials using Flory-Huggins theory for polymer solutions.

We also consider the case of dilute polymer solutions and although we discussed that Flory Huggins theory is not a good theory for dilute solutions till we applied it and obtained some expressions for chemical potentials for dilute solutions. As these would be required later on then we talk about detonation of polymer more than mass where mostly dilute solutions of polymers are employed.

We also talked about the theta condition here again as a condition at which the internal segment-segment repulsion within the polymer chain is balance where the external solvent segment repulsion. And, the polymer chains adopt the unperturbed the ideal chain dimensions and the polymer solution as a whole tends to behave like an ideal solution.

So, we discussed this theta condition. So, for a given polymer solvent system there will be a certain temperature at which condition can be realized. So, finally, the concept of solubility parameter was introduced and discussed as a useful measure of obtaining a estimate of whether a given polymer and given solvent are soluble in each other. So, we can estimate the solubility parameters of the polymer as well as the solvent and compare then and see if there close enough to each other, we can say that they are soluble in each other. And the solubility parameter approach can also be used for estimating the stability of 2 different polymers in polymer-polymer blend.

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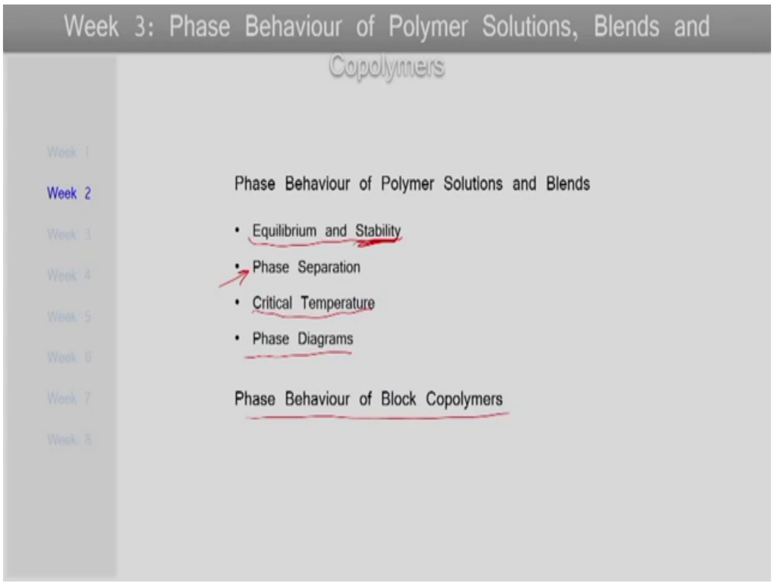

Week 3: Phase Behaviour of Polymer Solutions, Blends and Copolymers

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Phase Behaviour of Polymer Solutions and Blends

- Equilibrium and Stability
- Phase Separation
- Critical Temperature
- Phase Diagrams

Phase Behaviour of Block Copolymers

In the next week we can continued that this time arranges of polymer solutions and we discussed the phase behavior of polymers solutions and polymer blends. So, here we initially talk about the concept of equilibrium and stability. So, for a polymer solution to form the delta g of mixing should be negative. And if the polymer solution is being formed at given temperature and pressure the equilibrium condition is that the delta g should be a minimum. It should be negative and g should be a minimum.

And we disused that this, the condition for stability is given by the second derivative of the Gibbs energy of mixing with respect to composition. We also discussed the concept of phase separation. So, if the stability conditions are not satisfied then in that case a given polymer how many this polymer solution can phase separation in 2 different phases to further lower its Gibbs energy.

So, we discussed those we talk about the concept of critical temperature and depending on the type of polymer solution or blend we have we can have a upper critical or lower critical solution temperature and we also discuss the phase diagram.

So, typically for such cases the phase diagram is where temperature is plotted against composition which is typically the polymer volume fraction. So, t versus phi 2 kind of curves we discussed and the binodal as well as a spinodal curves on this phase diagram for identified those. And identified the 2 phase regions as well as, single phase regions separated by the binodal curves and the critical points has being the points of maximum or minimum on this binodal or spinodal curves.

We briefly also disused the phase we have block copolymers. So, block copolymers, in block copolymers the, if that 2-2 different blocks do not interact readily then they will not like each other. But, since there covalently bonded so, at the macroscopic scale they will not phase separate, but they will show microscopic phase separation and that could due to the formation of very interesting ordered kind of morphologies. So, that is what we discussed while talking about the phase behavior block copolymers.

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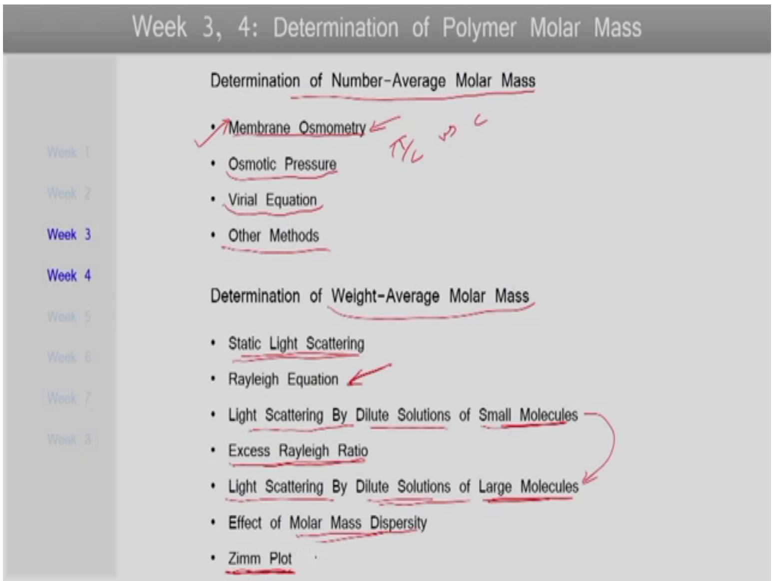

Week 3, 4: Determination of Polymer Molar Mass

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Determination of Number-Average Molar Mass

- Membrane Osmometry
- Osmotic Pressure
- Virial Equation
- Other Methods

Determination of Weight-Average Molar Mass

- Static Light Scattering
- Rayleigh Equation
- Light Scattering By Dilute Solutions of Small Molecules
- Excess Rayleigh Ratio
- Light Scattering By Dilute Solutions of Large Molecules
- Effect of Molar Mass Dispersity
- Zimm Plot

And, then towards the end of this third week we started discussion of the different techniques to measure different types of polymer, molar masses. So, we started off with techniques to determine number average polymer molar mass and here we discussed predominantly the Membrane Osmometry as the important technique. We discuss the concept of osmotic pressure which is key to this technique in an Osmometry and how osmotic pressure can be related to the number of molar mass, thermodynamic as well as other relations.

So, we came up with fact that if we plot this osmotic pressure over concentration versus concentration, then through that plot from that plot by hitting a straight line, the intercept can give us a measure of the number average molar mass. We also discussed virial kind of equation for the osmotic pressure and through that how again number average molar mass or the second degree of coefficient can be obtained. And we 3 talked about some other methods that also can be used for determining number average molar mass.

In the next week we started our discussion of the weight average molar mass determination. So, here the static light scattering that was discussed in detail as a method of choice for determining the weight average molar mass. So, we initially introduced this Rayleigh equation as equation that describes a scattering of some in instant electromagnetic radiation from a point scatter.

And you starting from that Rayleigh equation we built upon that discussed the scattering of light by dilute solution of initially small molecules and here we introduce the concept excess Rayleigh ratio. Because, in a solution we have not we have 2 different types of molecules present. We have the solvent and the solute molecules present to a. And to just consider the effect of scattering from solute this excess Rayleigh ratio is considered that which kind of eliminates the scattering from the solvent part.

Then later on we discussed a light scattering of dilute solution by large molecule. So, the different between large and small-small molecule light scattering is that in the large molecule different parts of the molecules can actually can scatter light in different ways and that those scatter the a radiation scanning for the interfere. So, that is the difference and we discussed that that.

And then if we have a large mole solutes which have large molecules as well as which have molar mass dispersity. So, a typical polymer change in polymer samples whether chains have different lengths. So, the effect of that molar mass dispersity was also explored. And finally, to determine the quantities like weight average molar mass or the second real coefficient or even some kind of a measure of the radius of gyration how that can be done using the Zimm plot method that was discussed in detail.

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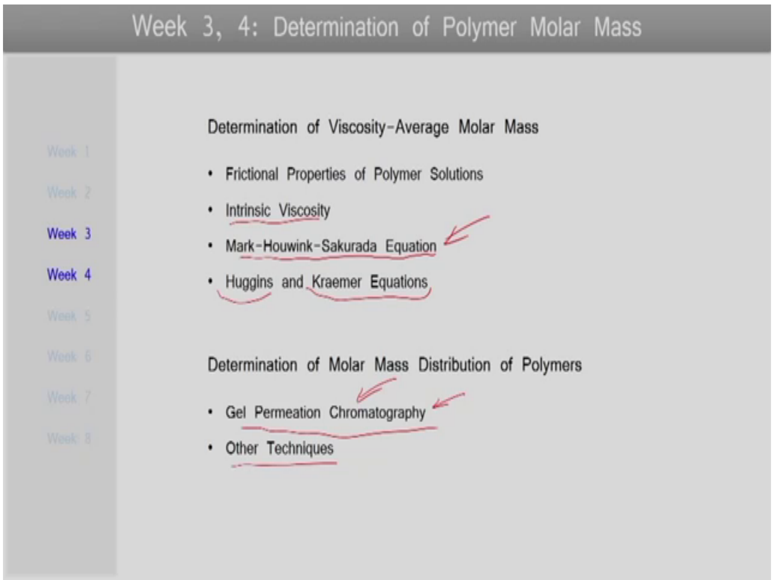

Week 3, 4: Determination of Polymer Molar Mass

Determination of Viscosity-Average Molar Mass

- Frictional Properties of Polymer Solutions
- Intrinsic Viscosity
- Mark-Houwink-Sakurada Equation
- Huggins and Kraemer Equations

Determination of Molar Mass Distribution of Polymers

- Gel Permeation Chromatography
- Other Techniques

Next viscosity average molar mass determination was discussed. So, initially the friction properties of dilute solutions where discussed were the concept where intrinsic viscosity was introduced and the mark Houwink's other equation were introduced; as a relation between intrinsic viscosity and the molar mass or the viscosity average molar mass of the polymer.

And then to obtain intrinsic viscosity from experiments this Huggins and Kneemers equations were introduced. And once we have this intrinsic viscosity by plotting appropriate data using either Huggins or Kneemers equation. Then from the intrinsic viscosity using the mark Houwink Sakurada equation the molar mass viscosity, average molar mass can be determined.

And finally, in this week we also discussed briefly that determination of the distribution of molar mass. Not just the specific average molar mass, but the entire distribution that we discussed can be obtained from this gel permeation chromatography technique. And there are other technique as well which can be employed the GPC is the most preferred method of choice for determination of molar mass distribution.

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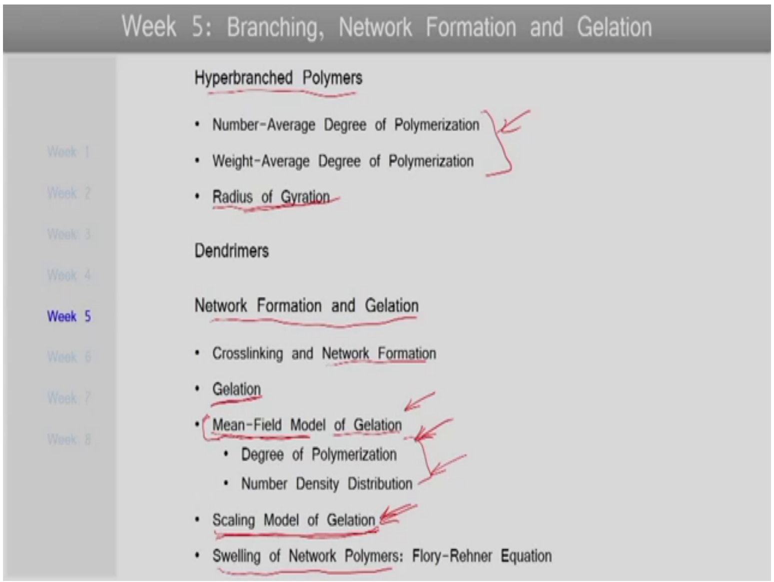

Week 5: Branching, Network Formation and Gelation

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Hyperbranched Polymers

- Number-Average Degree of Polymerization
- Weight-Average Degree of Polymerization
- Radius of Gyration

Dendrimers

Network Formation and Gelation

- Crosslinking and Network Formation
- Gelation
- Mean-Field Model of Gelation
    - Degree of Polymerization
    - Number Density Distribution
- Scaling Model of Gelation
- Swelling of Network Polymers: Flory-Rehner Equation

Next, in the fifth week we focus our attention on branch and network polymers. So, initially we talk about branch polymer specially hyper branch polymers and we derived expressions for number average and weight average degree of polymerization of this hyperbranched polymers.

We talked about the fact that the radius of gyration of this branch polymers. The expression is such that the scaling of the radius of gyration with the number of monomers present is much bigger than what we have for radial linear polymer. So, a given branch polymer having the same number of monomeric and degree of polymerization has linear polymer will have a much smaller size.

We also discussed dendrimers which are also highly branched polymers, but here the branching is such that the structure is very ordered and one can identify that dendrimers has consisting of different generation; so, internally a core or a 0 generation and then successive generation growing outwards from this core.

So, it we discussed some concepts related with dendrimers and then we moved on to the network polymer case and the concept or network formation and gelation. So, here we discussed the fact that if the monomer functionality is such that we can have formation of cross links between different polymer change present. Then ultimately that can lead to the formation of networks, where a network is giant molecule that is spans the entire sample of the polymer. And that network formation typically leads to gelation and onset of gelation leads to significant change in the properties of the polymeric material.

We can consider 2 some models of this gelation as well. So, we primarily focused on this mean field model of gelation has proposed by Flory and Stockmayer. And here we derive expression for the degree of polymerization as well as number density distribution of using this mean field model of gelation.

We also briefly talked about scaling model of gelation where we identified some critical exponents. And we saw that the scaling of model relation gives results that are a bit different from the mean field model of gelation. But, and specifically if we are talking about gelation in different dimensions then the scaling model predicts different critical exponents. But, if the gelation is happening in high dimension then the results from the scaling model reduce to those from the mean field model of gelation.

But, for typical let us say 2D or 3D kind of gelation we get different critical exponents from scaling gelation model of gelation than the mean field model. And finally, we discussed the swelling of network polymers where the Flory-Rehner equation that was introduced to describe the swelling behavior of network polymer. So, a network polymer if the solvent is added, it will typically not dissolved, but tend to swell. So, how much swelling takes place those kind of things we discussed and introduced the Flory-Rrehner equation in that context.

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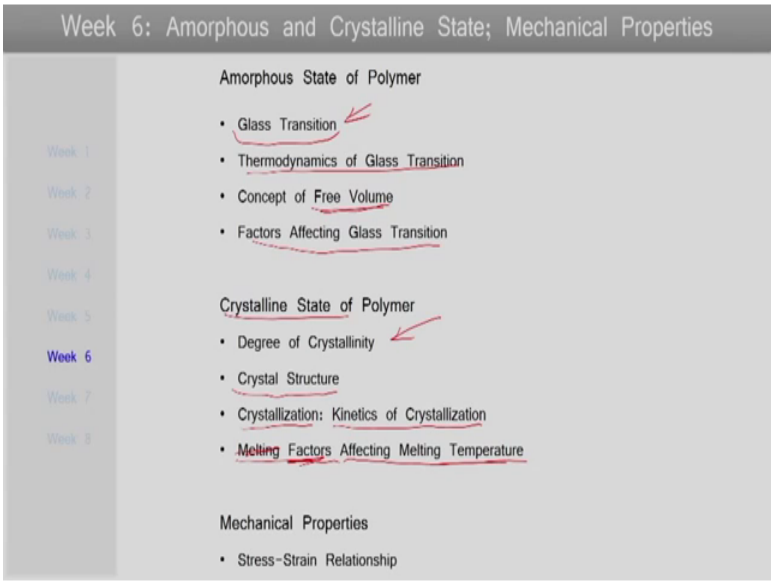

Week 6: Amorphous and Crystalline State; Mechanical Properties

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Amorphous State of Polymer

- Glass Transition
- Thermodynamics of Glass Transition
- Concept of Free Volume
- Factors Affecting Glass Transition

Crystalline State of Polymer

- Degree of Crystallinity
- Crystal Structure
- Crystallization: Kinetics of Crystallization
- ~~Melting~~ Factors Affecting Melting Temperature

Mechanical Properties

- Stress-Strain Relationship

In the sixth week we talked about the amorphous sand crystalline phase of polymer. So, for the amorphous phase we talk about this an important thermal transition called a glass transition. And we discussed the thermodynamics of glass transition in a bit of detail. We introduced the concept of free volume in the polymeric material and how it is critically associated with the concept of glass transition. And finally, we also discussed: what are the typical factors that affect the glass transition temperature.

Next we talked about the crystalline state of polymeric material because, we know that a a typical polymer actually is semi crystalline in nature which contains both crystalline and amorphous domains. So, we discussed amorphous state as well as crystalline state of the polymers in detail. So, the crystalline state we introduced a concept of degree of crystallinity which is a measure of how much crystalline domain is a portion is present in a given polymer sample. We talked about the structure of the polymer crystal that are formed. So, we discussed that the typically la polymer lamellae form where the polymer chains fold in a way such that the folds basically form a plane and this fold planes constitute the crystalline lamellae that we have.

And in the case of crystallization for melt this lamellae get arranged in such a way that we get a spherical spherulitic kind of polymeric crystals. We also talked about the crystallization phenomena and briefly discussed kinetics kinetics kinetics of crystallization as described by the avrami equation. we finally, discussed some factors that affect the melting temperature. So, some factors that affect the melting temperature that also we discussed.

And towards the end of this week we briefly talked about the mechanical properties of polymers. So, we introduced the quantities stress and strain and the typical stress strain relationship as exhibited by different types of polymeric materials. So, for a single crystalline polymer fiber so, other the Young’s modulus is quite high.

In the stress and strain relationship is different from what we get in a semi crystalline polymer or for a glassy polymer or for an elastomer where the stress strain relation is highly non-linear. So, these are the some of the things that we briefly introduced by discussing the mechanical properties. And in the next week we consider in detail.

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Week 7: Viscoelasticity and Rubber Elasticity

Viscoelasticity

- Creep
- Stress Relaxation
- Mechanical Models
  - Maxwell Model
  - Kelvin-Voigt Model
- Creep Compliance
- Stress Relaxation Modulus
- Boltzmann Superposition Principle
- Dynamic Mechanical Analysis

Rheology

- Non-Newtonian Behaviour
- Temperature and Molar Mass Dependence

Rubber Elasticity

- Thermodynamics
- Affine Network Model
- Mooney-Rivlin Equation

Some interesting mechanical behavior of polymeric materials; so, one was viscoelasticity. So, in viscoelasticity we introduced the concept of creep and stress relaxation. So, this time dependent kind of behavior that shown by this polymeric materials when certain load is applied to them so, the; so, that was discussed in detail.

And the some simple mechanical models like Maxwin Maxwell or Kelvin-Voigt model these were also discussed. In this week then we talk about creep compliance in the stress relaxation modulus as quantities of parameters characteristic to the creep and the stress relaxation behavior. Discussed the, we discussed Boltzmann superposition principle and finally, briefly talk about dynamic mechanical and analysis where in oscillatory load is applied and the responses observed.

We also very briefly talked about the rheology of polymers relations or polymeric materials even polymer solutions are melts and we what we discussed is that the Rheology is typically non Newtonian in nature. And in many cases shear thinning kind of behavior is seen and a power law kind of mathematical model which can be used to describe Rheological behavior. Temperature and molar mass dependence, where also briefly discussed with respect to viscosity, how the viscosity of the polymer changes with temperature and molar mass.

And finally, in this week we talk about rubber elasticity which is mechanical behavior exhibited by elastomers. So, we observed that this kind of stress and relationship that we get in rubber elasticity is highly non-linear. So, here we discussed the thermodynamics initially of this rubber elasticity we discussed the simple model which is a fine network model and sim phenomenological equation called a Mooney-Rivlin equation that also describes rubber elasticity.

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Week 8: Polymer Dynamics

Unentangled Polymer Dynamics

- Introduction
- Rouse Model
- Zimm Model

Entangled Polymer Dynamics

- Entanglements in Melt
- Edwards Tube Model
- Reptation

And finally, in the last week we discussed very briefly and at very introductory level the dynamics of polymer polymeric material so, polymer solutions as well as melts. So, for unentangled polymer dynamics we introduced some basic terminology like the diffusion coefficient, friction coefficient all that. And we talk about the Rouse model as good model for describing the dynamics of unentangled polymer melts having short chain polymeric polymers. And the Zimm model as a good model for describing dynamics of dilute polymer solutions and in the case of entangled polymer melts we discussed first the concept of entanglement what it means in a given polymer melt.

And we discussed that Edwards tube model can be used to simplify the description of this entangled polymers. And finally, using this Edwards tube model we discussed that the reptation model as proposed by deGennes to describe the dynamics of entangled formulas that was covered again at a very introductory level. So, these are the topics that we have covered throughout the course. One just quick comment regarding all the different expressions that we have developed a use in this course is that wherever the temperature appears. So, almost always that the temperature is a absolute temperature whose SI unit is Kelvin.

So, whether it is a the temperature that is appearing in the Flory Huggins equations or the temperature that appears in equations when we describe this rubbery elasticity or the polymer dynamics. So, in all these cases the temperature always has to temperature is that which always has to be the absolute temperature typically expressed in Kelvin.

So, whenever if we are solving a problems using any of these equations you have to keep in mind that the temperature that we are using even if it is given in let us say degree Celsius it has to be converted to an absolute temperature like Kelvin. So, with that small note I would like to conclude this course and I hope that this course has been good learning experience for on introductory topics related to this area of polymer physics. Of course, the area itself is quite vast and all the topics that we have touched upon we have touched upon at mostly introductory levels.

So, the hope is that this course whatever we have covered will serve as a foundation and those of you who are interested in learning some specific topic from here in more detail. So, they will at least have some idea of the basics of that topic and then more advanced text or research articles can be consulted for learning more advanced details of those topics.

So, with that we will conclude this course.

Thank you.