Polymer Physics

Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 01
Introduction to Polymers

So, welcome to this course on Polymer Physics. The area of polymer physics primarily deals with the study of how the structure the interactions in the dynamics of polymer molecules at the molecular scale how these factors affect the behavior and properties of polymers. So, for this course with regards to prerequisites, no formal background in polymer science is required. Basic knowledge of fundamental course on engineering mathematics and some concepts from chemical thermodynamics are that are required as prerequisites for this course.

So, before we begin this introductory lecture let me just go through the course plan of this course. So, in this course we will begin by an introductory lecture on polymers in general to just discuss some concepts related to polymers and polymer science. Then will move on in the next lecture to discussion of models of ideal polymer chains in how such models can be used to describe the polymer chain conformations.

Next will discuss the behavior of real chains and the effect of excluded volume interactions on such behavior, in the lectures after that will look into the thermodynamics of polymer solutions. So, in particular will focus on theory that describes the thermodynamics of polymer solutions and the theory is called polymer theory is called Flory Huggins theory.

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COURSE PLAN

- **WEEK 1:** Introduction to Polymers; Models of Ideal Polymer Chains; Real Chains and Excluded Volume Effects
- **WEEK 2:** Thermodynamics of Polymer Solutions; Flory-Huggins Theory; Phase Behaviour, Miscibility and Solubility Parameter
- **WEEK 3:** Thermodynamics of Polymer Blends and Block Copolymers; Determination of Polymer Molar Mass: Osmometry
- **WEEK 4:** Determination of Polymer Molar Mass: Light Scattering; Frictional Properties and Viscometry; Size Exclusion Chromatography
- **WEEK 5:** Branching, Network Formation and Gelation
- **WEEK 6:** Crystalline and Amorphous Polymer Phase; Mechanical Properties
- **WEEK 7:** Viscoelasticity, Maxwell and Voigt Models; Non-Newtonian Behaviour and Rheology; Rubber Elasticity
- **WEEK 8:** Unentangled Polymer Dynamics, Rouse and Zimm Models; Entangled Polymer Dynamics, Reptation

So, will discuss this theory in detail and will also study the phase behavior and miscibility solubility behavior of polymers in solvents will also look at the thermodynamics of polymer blends and that of block copolymers, because such the behavior of such materials is of interest, next will look into the determination of polymer molar mass to different techniques? Now the polymer molar mass of polymers is very important it has profound effect on different properties of polymeric materials.

So, knowledge of the polymeric molar mass is important from that aspect. So, will be discussing various different techniques to determine different types of polymer molar masses. So, today what will see is that polymer molar mass cannot be uniquely defined they are different ways in which average molar masses are defined. So, different types of such average molar masses can be measured using different experimental techniques.

So, will be focusing primarily on osmometry light scattering and viscometric measurements as experimental techniques for determination of polymer molar mass, will also look at the measurement of distribution of polymer molar mass through the use of size exclusion chromatography, that is gel permeation chromatography. After that will look at the branching network formation and the physics behind and theory behind theory of Gelation of (Refer Time: 03:25). So, in this case will be primarily focusing on of course, branch poly polymers as well as network polymers.

So, normally polymeric materials are composed of crystalline phase as well as amorphous phase, so most of the polymeric materials are semi crystalline. So, will next look at the detailed behavior of both this crystalline and amorphous phases in detail. Will also study the mechanical properties of polymeric materials will look into the viscoelastic behavior of polymers specifically will discuss two models which has simple, but which are useful in describing some aspects of viscoelastic behavior of polymers. So, these models are Maxwell model and Voigt model will also briefly touch upon the non-Newtonian behavior and rheology of polymers. And will also talk little bit about the theory of rubber elasticity which is useful for describing the behavior of elastomeric materials.

Finally towards the end of this course will be talking little bit about polymer dynamics. So, polymer dynamics in self is highly mathematical in advance course will just be looking at the basic aspects of this topic. So, will begin our discussion on entangled polymer dynamics that is the dynamics of polymer change with their not entangled, with each other. So, such nature of changes is found in dilute polymers solutions there where the polymer changes are essentially isolated.

Will also briefly look upon the dynamics of more concentrated polymer solutions and that of polymer melts whether polymer changes are invariably entangled and entertained with each other which makes their dynamics more complex. So, that will be the final part of this course, so again before starting of this introductory lecture let us look little bit at the different reference texts that will be using in this course.

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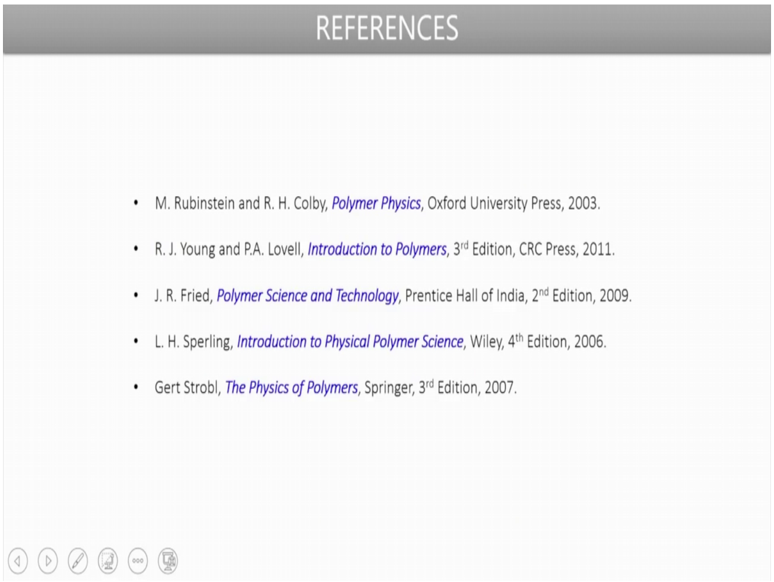

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- M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, 2003.
- R. J. Young and P.A. Lovell, *Introduction to Polymers*, 3rd Edition, CRC Press, 2011.
- J. R. Fried, *Polymer Science and Technology*, Prentice Hall of India, 2nd Edition, 2009.
- L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, 4th Edition, 2006.
- Gert Strobl, *The Physics of Polymers*, Springer, 3rd Edition, 2007.

So, the primary books that will be use as reference in this course are one the first one is the polymer physics by Rubinstein and Colby, which is the main source of material for this course next will also refer to the book introduction to polymers by young and Lovell to some extent. And other books like polymer science and technology by fried introduction to physical polymer science by sperling and the physics of polymers by strobl.

These are the some of the other books that from time to time will be using material from, but for this course the material that will be introduced through the slides and the lecture that will be enough and if somebody interested in further reading then such students are referred to the books that have been showed.

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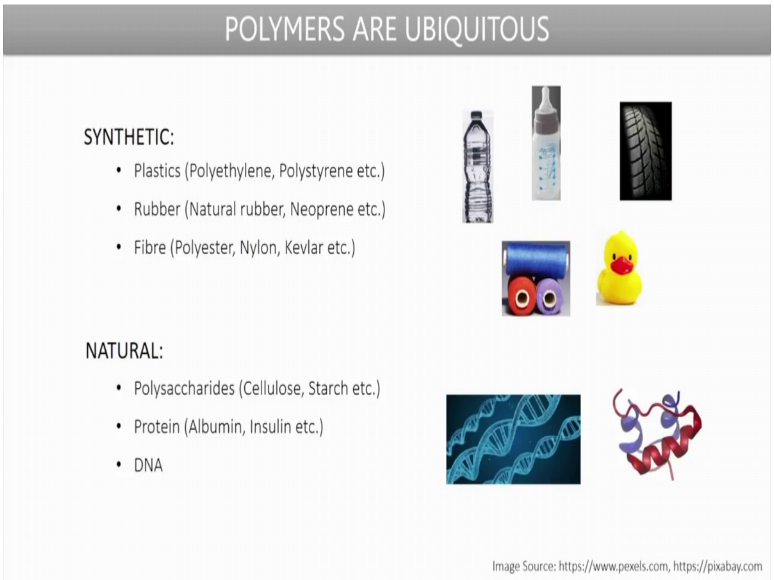

POLYMERS ARE UBIQUITOUS

SYNTHETIC:

- Plastics (Polyethylene, Polystyrene etc.)
- Rubber (Natural rubber, Neoprene etc.)
- Fibre (Polyester, Nylon, Kevlar etc.)

NATURAL:

- Polysaccharides (Cellulose, Starch etc.)
- Protein (Albumin, Insulin etc.)
- DNA

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So, the polymers as we all know are found everywhere. So, whether it is synthetic polymers natural polymers we are touched upon our lives are touched upon by polymers in one way or the other all most every day. So, some of the common synthetic polymers which we regularly encounter are polyethylene and polystyrene and many such other plastics, which are commonly used for packaging applications and many other applications, rubber like materials like natural rubber neoprene etcetera are also found everywhere. So, automobile tyres; tyres are primarily composed of rubbers as many of you might know.

Ah fibres like polyester nylon Kevlar, so these materials are also commonly encountered and are in wide spread use. So, many such synthetic polymeric materials regularly we regularly encounter in our lives. Apart from that they are many other polymers which are natural polymers which are not synthesized by synthesized by man, but which occur which occur naturally in nature.

So, examples of such natural polymers are polysaccharides or examples of which was cellulose in. So, starch these are basically polymers that the monomeric units are monosaccharaides like glucose. So, both cellulose and starch are basically composed of glucose as the monomeric unit, but the way in which the polymer architecture in the two materials is different.

Apart from that proteins are another very common example of natural polymers or biopolymers. So, proteins are basically polymers of amino acids. So, these are polypeptides where various amino acids are attached through amid linkage with each other to form long chain polymeric materials, which are called proteins. DNA is which we all know are vital to life and are the genetic contain the genetic code. So, these are also actually polymeric materials which are basically can be considered as polymers of four different types of monomeric units which are the different nucleotides.

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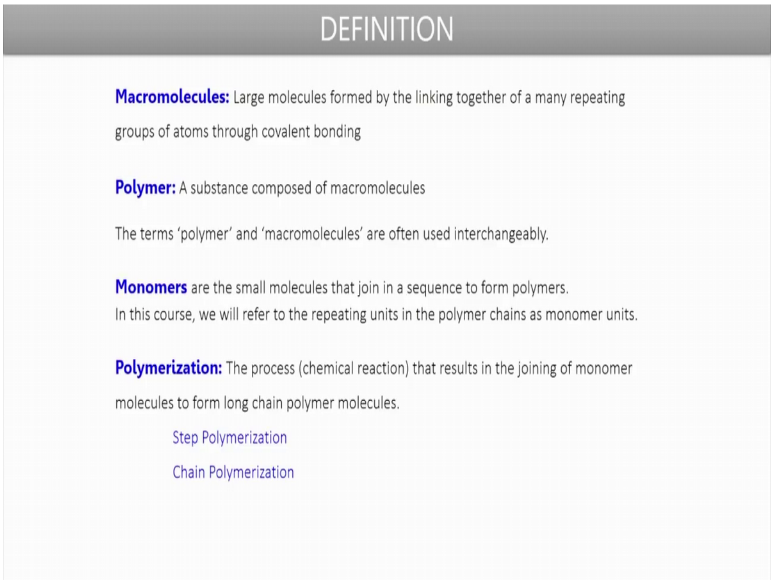

DEFINITION

Macromolecules: Large molecules formed by the linking together of a many repeating groups of atoms through covalent bonding

Polymer: A substance composed of macromolecules

The terms 'polymer' and 'macromolecules' are often used interchangeably.

Monomers are the small molecules that join in a sequence to form polymers.
In this course, we will refer to the repeating units in the polymer chains as monomer units.

Polymerization: The process (chemical reaction) that results in the joining of monomer molecules to form long chain polymer molecules.

- Step Polymerization
- Chain Polymerization

So, we now understand the polymers are present everywhere. So, next let us look at some of the definitions of common terms associated with polymers. So, first of all strictly speaking the large molecules which basically constitute the polymers are referred to as macro molecules. So, macro molecules can be defined as large molecules that are found by the linkage of many repeating groups of atoms and these linkages are formed through covalent bonding normally. So, now the polymers again strictly speaking a substance which are composed of these macro molecules. But often the terms polymer and macro molecules are used interchangeably in that the molecules long chain molecules that are present in the polymeric substance those are also referred to as polymers.

So, in this case course also will not make a distinction between formal distinction between macro molecules and polymer. And anytime we talk about these long chain molecules will refer to them as polymers instead of macro molecules, next these long chain molecules are actually composed of several repeating units. So, monomers are basically small molecules that join together to form these long chain polymer molecules.

So, in this course will be referring to the repeating units that comprise polymer molecules as monomeric units. Next the process by which these monomer molecules basically combine to form polymer chain molecules is referred to as polymerization. So, it is basically chemical reaction in which covalent bond form bonds form between different, different monomer molecules which in turn results in the formation of polymer molecule.

So, polymerization can be of two types usually or polymerization typically can be broadly divided into two types one is step polymerization the other is chain polymerization. So, step polymerization is where the process of polymerization happens step by steps. So, initially two monomers will react to form a dimer another monomer can react with this timer to form a trimer and so on. So, then two dimers can react to for a tetramer trimer and dimer can react to form a pentamer and so on.

So, we see that polymerization proceeds in a step by fashion and the other type of common type of polymerization is chain polymerization where monomers successively add to an active center, which is present at the end of a propagating chain. So, monomers keep adding to the end of the propagating chain and chain keeps growing and the active center the nature of the active center can be of radical type or an iron.

So, based on the again the nature of the active center the chain polymerization can again be broadly classified into radical polymerization or ionic polymerization. So, next the last definition that will look at is that of the degree of polymerization. So, this is nothing, but the number of repeat units that present in a given polymer chain.

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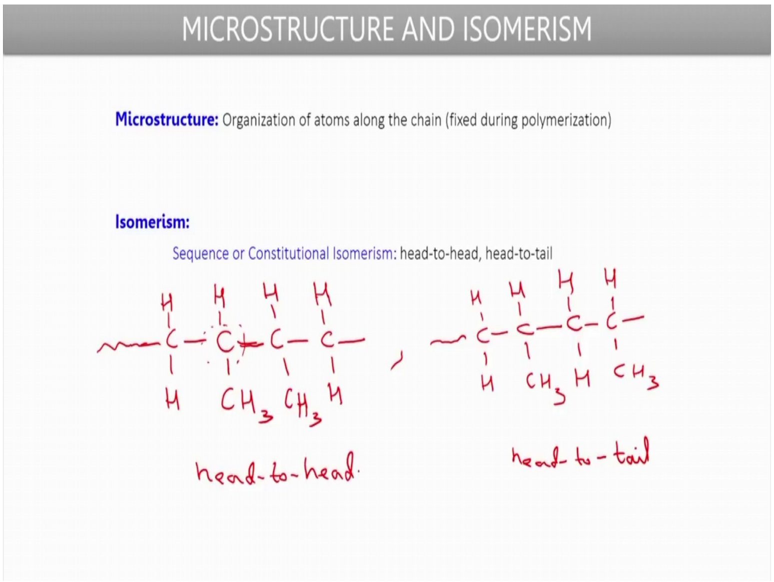

MICROSTRUCTURE AND ISOMERISM

Microstructure: Organization of atoms along the chain (fixed during polymerization)

Isomerism:

Sequence or Constitutional Isomerism: head-to-head, head-to-tail

So, before we go into other details let us first discuss the concept of micro structure and the different types of isomerism's that can be found in polymer structures. So, micro structure is nothing, but the organization of atoms along the polymer backbone which is fixed during the polymerization reaction. So, just by the twisting or change in conformation of polymer change the inherent micro structure cannot be changed ok.

So, let us look at the some of the common types of isomerism that are found in polymeric materials. So, the first type of isomerism that will discuss is called sequence or constitutional isomerism. So, this basically is can is also referred to as the head to head or head to tail type of isomerism. So, here it is easier to basically illustrate this with an example instead of discussing it verbally. So, I will just consider the case of polymer polypropylene and try to illustrate were the different type of isomeric forms that are possible ok.

So, in polypropylene the repeat unit can basically be represented like this. So, this the repeat that propagates throughout to form the polymer backbone. So, we see that we have a carbon, carbon bond in the backbone single bond and we have CH 3 groups, that is connected to one of the carbons ok. So, now, let us say if we have this chain like this and this end here is the active center to which another monomer adds ok. So, the next repeat unit of for polypropylene can add in two ways and the way in which it adds basically gives two different type of polymers one will be the head to head configuration the other will be the head to tail configuration.

So, let us say the carbon to which this methyl group is attached this methyl side group is attached. Let us say let us refer to this carbon as the head group of the head of the this repeat unit and the other carbon let refer to the other carbon as a tail of this repeat unit. So, now, if the next repeat unit comes and attaches like this ok, we see that the head carbon is gets connected to the head carbon of the next repeat unit. So, that the CH 3 groups the pendent or the hanging CH 3 groups are un are un adjacent carbon atoms.

So, if we have this kind of arrangement or this kind of configuration this is referred to as a head to head configuration. And if on the other hand let say again we have our up growing polypropylene chain ok. And let us draw the head carbon here connected to the CH 3 side group and the when the next repeat unit comes and connects. In such a way that the tail carbon of the next repeating unit connects to the head carbon of the previous repeat unit like this, then this kind of configuration is referred to as head to tail.

So, this will be referred to as head to tail in the first one that, we drew that was head to head. So, this is what sequence or constitutional isomerism looks like for a common polymer like polypropylene and anytime you have a polymer which has a side group where the repeat unit has the side group you can basically get such kind of isomeric forms.

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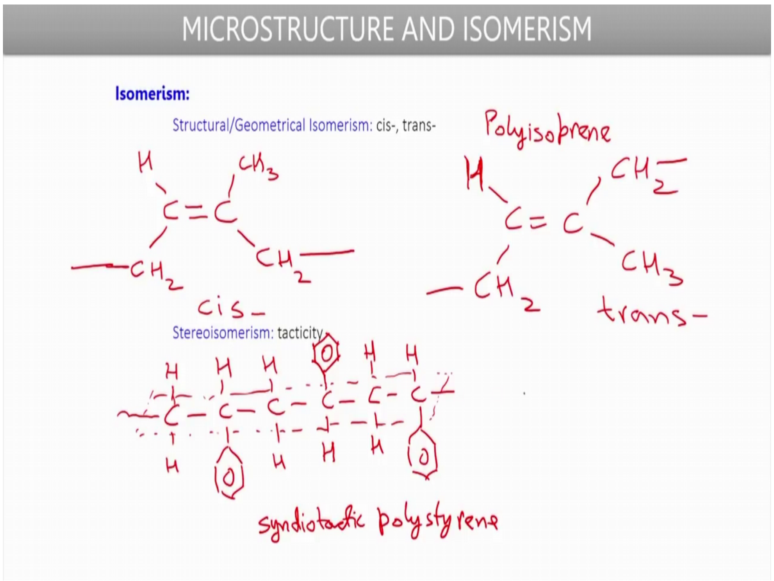

MICROSTRUCTURE AND ISOMERISM

Isomerism:

Structural/Geometrical Isomerism: cis-, trans-

Stereoisomerism: tacticity

So, next let us look at another kind of isomerism which is commonly found in which is referred to as structure or geometric isomerism. So, here the isomeric forms are referred to as cis and transform. So, so if we consider the example of polyisoprene, so the example that will consider polyisoprene ok.

So, let us first draw the two forms and then will discuss further. So, polyisoprene basically the cis form. So, these to long bonds on either side of this repeat unit basically represent the propagation of this chain in either direction. So, we see that this cis form is where the chain basically is propagating on the same side of the double bond ok. So, this is our cis polyisoprene next if we consider the transform, here what happens is the chain basically is propagating on two different sides of this double bond this we can refer to as a transform. So, this the kind of structure geometrical isomerism that is commonly observed and the nature of the isomer as profound effect on the properties of the actual polymeric material that is formed.

So, the cis polyisoprene that we see hear that basically is the form, that is formed in natural rubber. And due to the bent kind of arrangement of polymer chains these materials does not crystalize. And at normal temperature it is found as an elastomeric material which is amorphous and soft on the other hand if you look at the Trans isomer. So, the polymeric material compose of the tri primarily the trans isomer referred to as gataparcher and due to the more regular arrangement change can basically align in a better way and they can crystalize the material that we get which is gatapercher is hard material and as a high degree of crystalinity. So, basically the type of isomeric form strongly effects the properties of the actual material actual polymer material ok.

So, so next will discuss stereoisomerism. So, stereoisomerism basically is a kind of isomerism which again depends on the spatial arrangement of atoms in molecules or groups of atoms. So, here basically the when we talk about stereoisomerism of polymers that is related to the concept of tacticity in polymers. So, we will again illustrate this topic this type of isomerism through an example.

And we will consider poly styrene as a typical example for polymer that displays stereoisomerism. So, so let us first draw repeat unit of polystyrene. So, repeat unit of polystyrene will look like this. So, we again have a carbon with two hydrogen another carbon, which has this hanging phenyl pendant group and of course, the chain basically propagates in either direction.

So, now if we talk about stereoisomeric forms or the nature of tacticity in these this material which is polystyrene. The way the; this pendant phenyl group is placed with respect to the polymer backbone on alternating on or on different repentance that basically defines different types of stereoisomers for this material polystyrene.

So, so that is that is now consider longer part of the chain of polystyrene. So, let us say let us consider another repeat unit here and let us consider one more repeat unit, so we see that the way we have drawn it. So, now, let us imagine that the polymer backbone which is basically this carbon, carbon which is constituted by this carbon, carbon linkages.

So, let us consider that this polymer backbone is lies in the same plain for simplicity ok. So, now, and let say all the hydrogen's that we have up here. So, on the top are lying above this plane and all the phenyl groups are lying below this plane in the arrangement that we have drawn here. So, this kind of an arrangement were the side groups are all lying on the same side of your carbon, carbon backbone plane. So, such an arrangement is referred to as a isotactic polystyrene ok.

So, here isotactic means at all the side groups are on lying on the same side of the carbon, carbon backbone ok. We can think of another arrangement where instead of the side groups lying on the same side the side groups could be lying could be arranged alternatively on opposite sides. So, let us see, so instead of phenyl group here let us say that in another arrangement, we have we have the phenyl group on this carbon line above the plane and hydrogen atom is lying below the plane here. So, in this case this kind of arrange and arrangement where the side groups are basically alternately arranged on either side of the carbon, carbon backbone. So, such a form is referred to as syndiotactic polystyrene ok.

So, here this is also regular arrangement, but the arrangement is alternate and not on the same side of the carbon, carbon backbone plane. And if we let say continue drawing this chain then the next phenyl group will again be above the plane and the one after that will be below the plane and so on, for the syndiotactic polystyrene. Finally, we can also have a case were these phenyl groups do not show any regular arrangement across the the backbone plane ok.

So, let us say we have an arrangement like this. Where the phenyl group the placement of phenyl groups on either side of the backbone plane is random. So, if certain phenyl group is lying below the backbone plane there is no guarantee that the next one will lie surely lie below or above. So, it can be randomly placed in next one again can have equal probability of lying on either side of the plane. So, such form where the placement of the side group across the backbone plane is random this is referred to as a tactic polystyrene.

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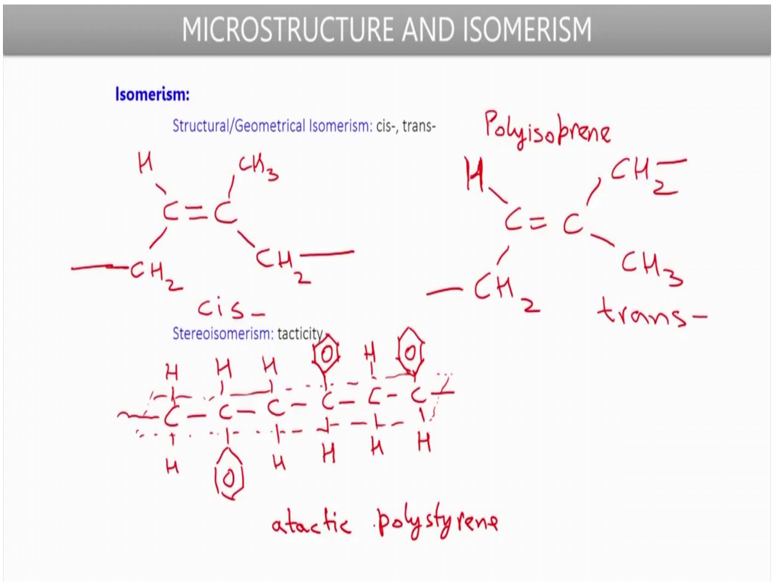

MICROSTRUCTURE AND ISOMERISM

Isomerism:

Structural/Geometrical Isomerism: cis-, trans-

Stereoisomerism: tacticity

So, here we have considered polystyrene as an example, but we can also consider any other vinyl polymer which as a side group. So, polypropylene also shows these kinds of forms where instead of the phenyl group you have a methyl hanging group. So, again in this case the type of the tacticity that is shown by the polymer actually polymer chains actually affects polymer property significantly. So, it is seen that a isotactic and syndiotactic forms, which whether arrangement of side groups is more regular. They can crystalize readily and due to the high degree of crystalinity in these materials there again the mechanical properties are superior.

On the other hand a tactic polystyrene for example, due to the random arrangement of the poly side groups they cannot align properly and they usually exists as amorous materials. So, again the nature of the isomeric form, which effects the polymer micro structure that also has significant effect on the properties of the polymeric material.

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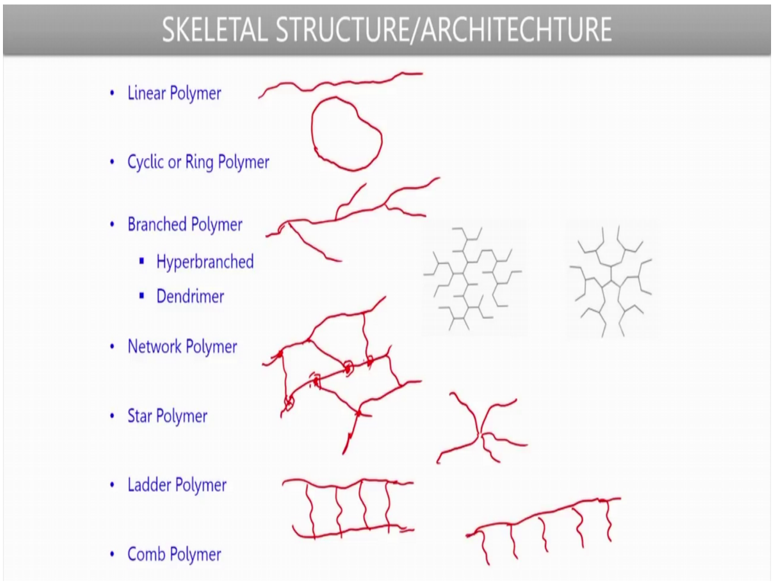

SKELETAL STRUCTURE/ARCHITECHTURE

- Linear Polymer
- Cyclic or Ring Polymer
- Branched Polymer
  - Hyperbranched
  - Dendrimer
- Network Polymer
- Star Polymer
- Ladder Polymer
- Comb Polymer

So, next let us just discuss very briefly about the different kinds of skeletal structure or the architecture of the polymer backbone that are usually seen. So, the first and the simplest backbone architecture there is that of linear polymer where the polymer backbone can be considered linear ok.

Next we can also a polymers were the backbone is in the form of a ring such polymers are called cyclic or ring polymers. So, here the backbone, basically form such kind of closed loop. So, it does not have any chain ends and it is in the form of ring if we consider branched polymers. So, here we have main backbone, but from this backbone short or long chains or branches are usually attached in this kind of polymer backbone architecture.

So, now branched polymer again there are different types of branch polymers. So, we can have hyper branched polymer where the degree of branching is very high and illustrative arrangement is shown here. So, degree of branching is high, but the branching is not very order and the material itself does not show well very well defined structure whereas, we can also have another type of highly branched polymeric arrangement which is called dendrimers. So, here if you see the material or the chain architecture is very well ordered. So, from the very core you have bonds coming out, then they further keep branching out, but very ordered arrangement is maintained.

Next we can also have network polymers where you basically have polymer chains polymer, chains interconnected with each other ok. So, these network polymers are also referred to as cross link polymers. So, so it is difficult to distinguish any main change in these polymers, the various polymers chains are basically connected to each other through what are called cross links ok. So, such connection points like the ones which are shown here. So, these are referred to as junction points and network polymers ok. And again because the mat chains are cross linked and connected with each other the properties that these polymer show are quite different from linear or branched polymers.

So, the so apart from these common types, there are many other kind of skeletal structures or architectures, that have being observed in polymers. So, some other architectures that, that can be seen are star polymer where basically the polymer chains are arranged in a start like manner, ladder polymer where again as the name suggests the polymer chains are arranged.

So, that they look like a ladder and again Kuhn polymer where you have a main chain polymer and then you have side chains which give the appearance of the polymer chain to be that of a Kuhn ok. So, these are some of the common polymer backbone architectures. Next what will do is discuss the different types of polymers based on the nature chemical nature of the repeat units that are present in the polymer chains.

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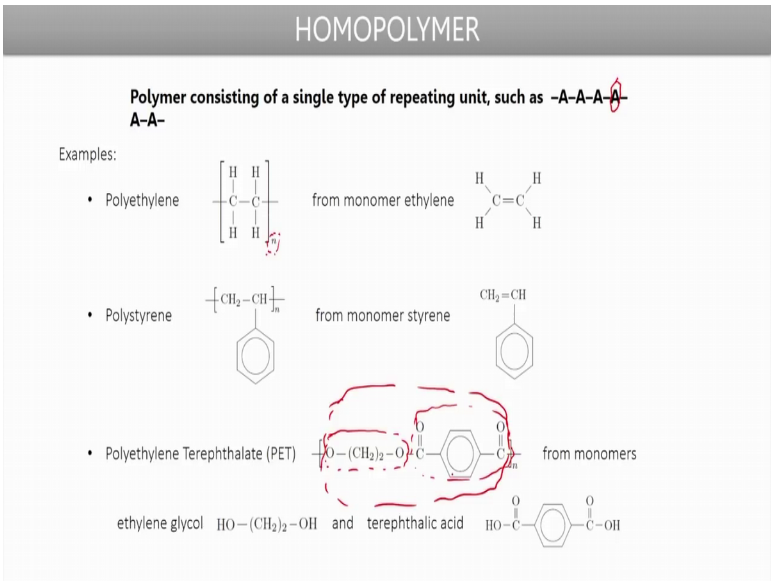

HOMOPOLYMER

Polymer consisting of a single type of repeating unit, such as –A–A–A–A–A–A–

Examples:

- Polyethylene from monomer ethylene
- Polystyrene from monomer styrene
- Polyethylene Terephthalate (PET) from monomers ethylene glycol $HO-(CH_2)_2-OH$ and terephthalic acid

So, the first type of polymer that will discuss is homo polymer. So, here the polymer basically the polymer chains consist of a single type of repeat unit. So, if a represents type of repeat unit then polymer chain can be represented a by a sequence of such a repeat units ok. So, common examples of homopolymers are polyethylene which is formed from the monomer ethylene. So and polystyrene let say which is formed from the monomer styrene.

So, in both of these cases we see that there is a single repeat unit that is replicated many times to form the polymer chain. So, in the structure formula that we have shown here the repeat unit is shown in side square brackets. And the n the subscript n here basically represents that this unit is repeated many number of times to give you the polymer chain. So, same is to polystyrene and many other polymers like polypropylene, polyvinyl chloride and so on.

So, here we have shown the structure of polyethylene terephthalate, which is also considered home polymer. And the reason why it shown here is if we look at it carefully its actually come made by the reaction of two different monomers one is ethylene glycol and one is terephthalic acid. So, unlike polyethylene or polystyrene shown above this pet is formed by the polymerization of two different monomers. But although they are two different monomers that polymerize to give pet it is normally considered a homo polymer, because the monomer units that results from the two monomeric spices and which are shown here. These two monomeric units are connect to a covalent bond and they always repeat in the same sequence.

So, this whole combination of atoms basically can be considered as the repeat unit of this polymer and hence pet can be considered as a homo polymer with the repeat unit that shown here ok. So, apart from homo polymers the other type of polymers that are there are called heteropolymers. And in these polymers the; these polymers are basically formed by the combination of more than one type of repeat unit. So, if the number of different types repeat units present is to then the heteropolymer is referred to a copolymers.

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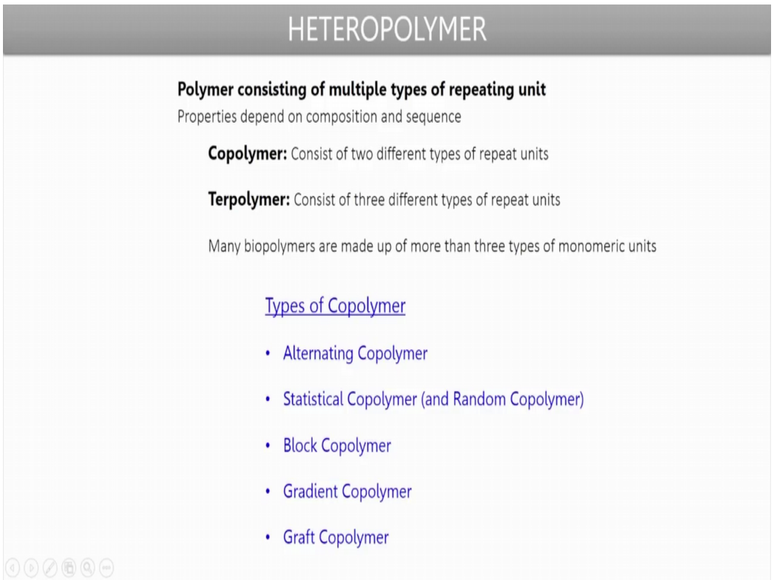

HETEROPOLYMER

Polymer consisting of multiple types of repeating unit

Properties depend on composition and sequence

Copolymer: Consist of two different types of repeat units

Terpolymer: Consist of three different types of repeat units

Many biopolymers are made up of more than three types of monomeric units

Types of Copolymer

- Alternating Copolymer
- Statistical Copolymer (and Random Copolymer)
- Block Copolymer
- Gradient Copolymer
- Graft Copolymer

If the number of repeat units is three then it can be referred to as a terpolymer and so on. But many times irrespective as number of different types of repeat units many times heteropolymers just simple refer to as copolymers as well.

So, if we talk about copolymers many of the biopolymers that we discuss initially like proteins and DNA they are actually made up of more than three types of monomeric units. So, for example, proteins are made up of amino acids and they can be many different types of amino acids present in a given chain of protein molecule Similarly, DNA is made up of four different types of monomeric units, which are the four nucleotides. So, the different types of heteropolymers that are commonly there one can broadly classify the different types as alternating copolymers statistical copolymers where random copolymer is a subset of that. Then we can have block copolymers we can have gradient copolymers and we can also have say graft copolymers.

So, next few slides will briefly discuss all these types of copolymers in slightly more detail, so if we talk about alternating copolymers ok.

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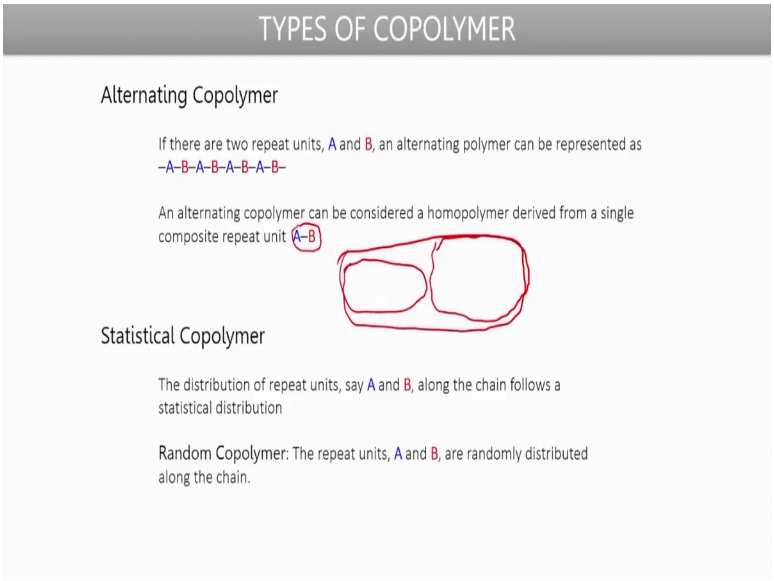

TYPES OF COPOLYMER

Alternating Copolymer

If there are two repeat units, A and B, an alternating polymer can be represented as –A–B–A–B–A–B–A–B–

An alternating copolymer can be considered a homopolymer derived from a single composite repeat unit A–B

Statistical Copolymer

The distribution of repeat units, say A and B, along the chain follows a statistical distribution

Random Copolymer: The repeat units, A and B, are randomly distributed along the chain.

So, they usually we have two types of repeat (Refer Time: 32:08) let us say the repeat units are A and B. Then an alternating copolymer can be represented simply as sequence in the form of A B A B A B A B and so on as shown here. So, basically the repeat units are alternating. So, if we look at the sequence in alternating copolymer carefully what will see is that the alternating copolymer can actually be considered as a homopolymer which is derived from a single composite repeat unit A B. So, if we consider A B as a single repeat unit then essentially an alternating copolymer can equivalently be thought of as a homopolymer. Where the A B unit together is a single repeat unit and that is that is the one which is get getting replicated.

So, the example of pet that we showed earlier in for homopolymer that actually can be thought of an alternating copolymer as well. So, the pet chain that we should if we consider that as an alternating copolymer. Then this is one repeat unit derived from one monomer and this is the other repeat unit derived from the other monomer. But as we just discussed we can also consider this as homopolymer derived from this whole repeat unit here.

Next let me talk about talk about statistical copolymer. So, statistical copolymer basically is a copolymer in which you have the repeat units A and B which are connected in a sequence that follows some statistical law ok. So, random copolymer is basically a subset of statistical copolymer, where the arrangement of A and B follows the random distributions. So, the sequence of these repeat units are A and B is does not follow any order and it is completely random.

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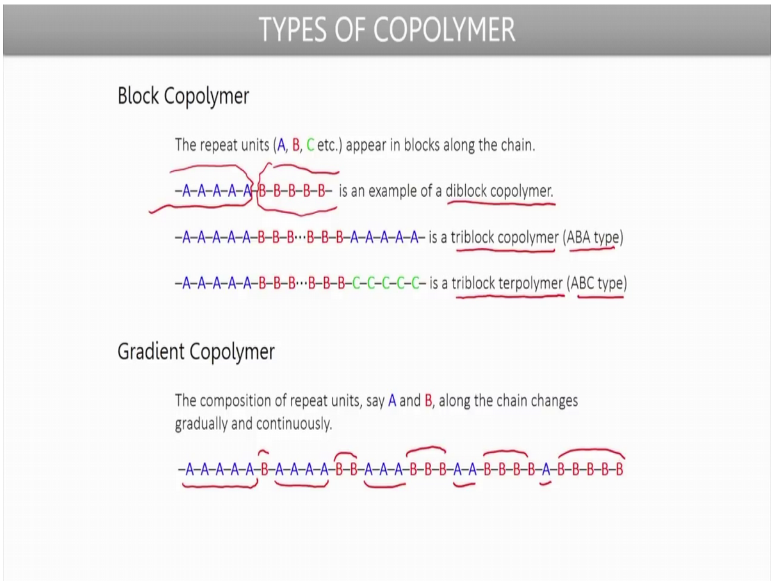

TYPES OF COPOLYMER

Block Copolymer

The repeat units (A, B, C etc.) appear in blocks along the chain.

–A–A–A–A–A–B–B–B–B–B– is an example of a diblock copolymer.

–A–A–A–A–A–B–B–B···B–B–B–A–A–A–A–A– is a triblock copolymer (ABA type)

–A–A–A–A–A–B–B–B···B–B–B–C–C–C–C–C– is a triblock terpolymer (ABC type)

Gradient Copolymer

The composition of repeat units, say A and B, along the chain changes gradually and continuously.

–A–A–A–A–A–B–A–A–A–A–B–B–A–A–A–B–B–B–A–A–B–B–B–B–A–B–B–B–B–B

Next we if we look at block copolymers. So, block copolymers consist of two three or more number of repeat units, which are arranged in large blocks along the polymer chain backbone. So, if we look at the first case here, so here we have a block of A which is connected to a block of B ok. So, this is an example of a dibook block copolymer similarly here we have an block of A connected to a block of B, which is again on the array side connected to a block of A. So, this is an example of what is called triblock copolymer and this is called ABA type triblock copolymer

If we look at the next example here we have a block of A followed by a block of B, then followed by a block of another type of repeat units C. So, this is also an example of a triblock heteropolymer, but since a number of different types of repeat units is three will call it triblock terpolymer and the type is ABC. If we talk about gradient colpolymers, so, here unlike block copolymer the composition of repeat units A and B along the chain backbone that actually changes gradually and continuously and it does not change abruptly as in the case of block copolymer.

So, if we look at the sequence shown here, then and if we follow the sequence along the polymer chain. Then initially we have the number of repeat units of type A is large and then it decreases from 5 to 4 and then 3 2 and 1. Whereas the number of repeat units of type B that actually is slowly increasing along the polymer chain from left to right from 1 to 2 to 3 to 4 5 and so on. So, basically the difference from block copolymer is that the repeat units base change gradually along the polymer chain they do not abruptly change from A to B.

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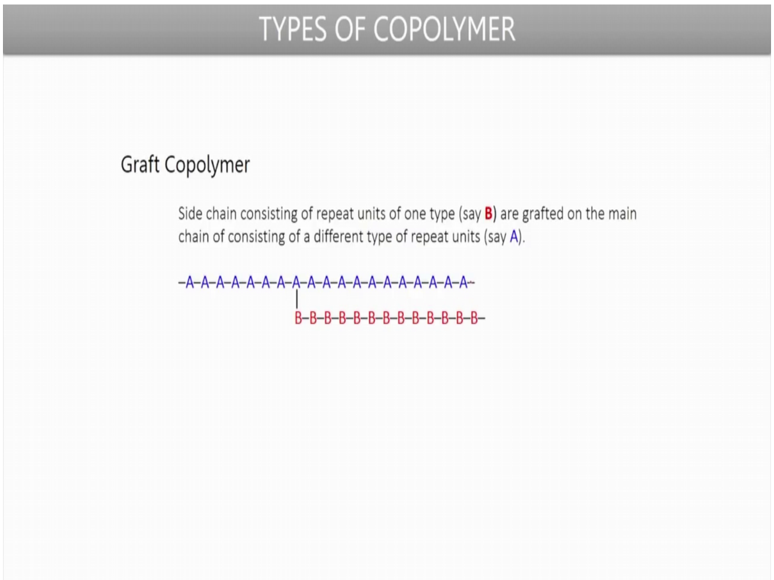

TYPES OF COPOLYMER

Graft Copolymer

Side chain consisting of repeat units of one type (say **B**) are grafted on the main chain of consisting of a different type of repeat units (say A).

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

B-B-B-B-B-B-B-B-B-B-B-B-B-

The last type of copolymer that will discuss is graft copolymer. So, here there is a type of branched polymer, where we have can have a main chain consisting of given type of repeat unit let say A. And another chain or chains are basically grafted or connected as side chain or branches to this main chain and this side chains will be made up of different type of repeat units. So, common example of graft polymer copolymer as shown here as a main chain consisting of only A repeat units and a side chain consisting of only B repeat units.

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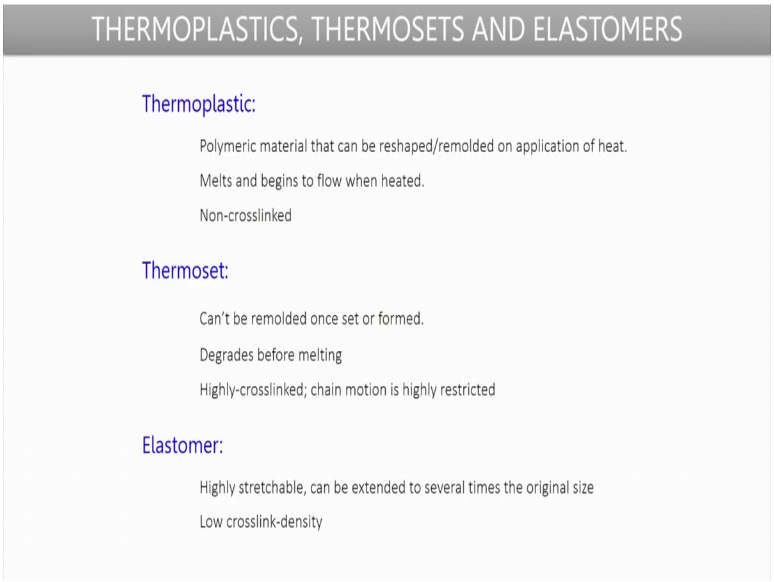

THERMOPLASTICS, THERMOSETS AND ELASTOMERS

Thermoplastic:

Polymeric material that can be reshaped/remolded on application of heat.

Melts and begins to flow when heated.

Non-crosslinked

Thermoset:

Can't be remolded once set or formed.

Degrades before melting

Highly-crosslinked; chain motion is highly restricted

Elastomer:

Highly stretchable, can be extended to several times the original size

Low crosslink-density

So, another kind of classification for polymers is basically is based on there molecular structure as well as a properties that they display. So, we can have this classification into three different categories one is thermo plastic other is thermosets or thermosetting plastic and third one is elastomer.

So, when we talk about thermoplastics. So, thermoplastics are basically polymeric materials, which can be remolded or reformed into different shapes again and again upon the application of heat. So, once you let say give the thermoplastic material a particular shape, then later on by the application of heat by melting you can again reshape it into different product.

So, from the molecular prospective thermo plastic basically consist of polymer chains which may be linear or branched, but which are not cross linked with each other. If we talk about thermosets or thermosetting plastics, here these materials once they are formed they cannot be remolded or reshaped. And the final shape that they are given that is given to them at the time of let us say processing that that shape is cannot be changed with the application of heat.

So, they cannot be remolded, so if heat is sufficient heat is applied in before actually flowing or melting tend to actually degrade. And the reason for this behavior is that at the molecular level the chains are highly crossed linked with each other.

So, because of the high cross link density upon application of heat the chains basically are not free to move about hence the materials does not flow. And if the amount of heat supplied is large enough the covalent bonds actually break and the material degrades, the third type here is referred to as elastomer. So, these are materials which show a very high degree of extensibility.

So, they can basically be their length can basically be extended to multiple times original dimension and when the applied load is removed, then they can regain their original dimension. So, such elastomeric materials like rubber at the molecular level these also consist of chains which are cross, cross linked similar to the thermosets, but the degree of cross linking is not as high. So, these are these seems actually lightly cross linked only which allows them to be extended to high extension ratios.

So, next in the remainder of this lecture what will do is discuss the concept of polymer molar mass. So, polymer molar mass is actually different from the molar mass of small molecules. In the sense that there is no unique molar mass that can be ascribed to polymeric sample. And the reason for this is poly given polymer sample or poly polymer material, usually consist of polymer chain molecules that are of different lengths ok.

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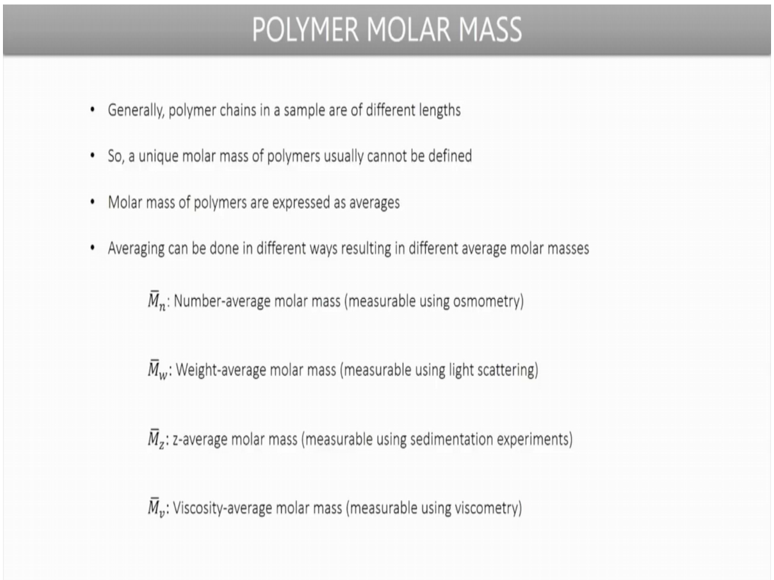

POLYMER MOLAR MASS

- Generally, polymer chains in a sample are of different lengths
- So, a unique molar mass of polymers usually cannot be defined
- Molar mass of polymers are expressed as averages
- Averaging can be done in different ways resulting in different average molar masses
  - $\bar{M}_n$: Number-average molar mass (measurable using osmometry)
  - $\bar{M}_w$: Weight-average molar mass (measurable using light scattering)
  - $\bar{M}_z$: z-average molar mass (measurable using sedimentation experiments)
  - $\bar{M}_v$: Viscosity-average molar mass (measurable using viscometry)

So, you can in a given polymer sample you might have chains of many different lengths and because of this a unique polymer molar mass cannot be defined because each, each individual chain will have its own molar mass. But since you have so many chains and each chain is different in length the respective molar mass of the polymer chains are also different, and we can only talk about average molar mass of the entire polymer sample. So, for this reason polymer molar masses are defined actually as averages and no single unique polymer molar mass is usually defined.

So, when we again talk about average polymer molar mass there are many place in which the averaging can be done. So, based on the way in which averaging is done we can have different types of molar masses. We can have number of average molar mass which can be measured using osmometry experiments; we can have weight average molar mass which is measureable using light scattering experiments.

We have z average molar mass which can be measured using sedimentation experiments and finally, we have viscosity average molar mass, which is measurable using viscometry experiments. So, of course, other types of molar masses can also be defined, but these are the common ones because these are can be measured using experiments radially.

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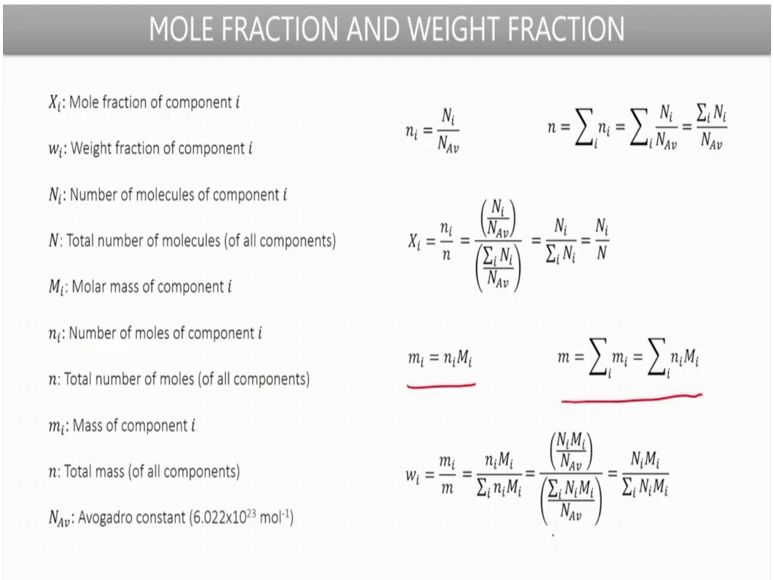

MOLE FRACTION AND WEIGHT FRACTION

X_i: Mole fraction of component i

w_i: Weight fraction of component i

N_i: Number of molecules of component i

N: Total number of molecules (of all components)

M_i: Molar mass of component i

n_i: Number of moles of component i

n: Total number of moles (of all components)

m_i: Mass of component i

n: Total mass (of all components)

N_{Av}: Avogadro constant (6.022×10^{23} mol^{-1})

$$n_i = \frac{N_i}{N_{Av}} \qquad n = \sum_i n_i = \sum_i \frac{N_i}{N_{Av}} = \frac{\sum_i N_i}{N_{Av}}$$

$$X_i = \frac{n_i}{n} = \frac{\left(\frac{N_i}{N_{Av}}\right)}{\left(\frac{\sum_i N_i}{N_{Av}}\right)} = \frac{N_i}{\sum_i N_i} = \frac{N_i}{N}$$

$$\underline{m_i = n_i M_i} \qquad \underline{m = \sum_i m_i = \sum_i n_i M_i}$$

$$w_i = \frac{m_i}{m} = \frac{n_i M_i}{\sum_i n_i M_i} = \frac{\left(\frac{N_i M_i}{N_{Av}}\right)}{\left(\frac{\sum_i N_i M_i}{N_{Av}}\right)} = \frac{N_i M_i}{\sum_i N_i M_i}$$

So, let us first go through some basic nomenclature and definitions before looking at the mathematical definitions equations of these molar masses. So, in this course the nomenclature that will use for mole fraction weight fraction number of molecules molar mass, number of moles mass of a component Avogadro constants. So, all those are shown here, so for example, X i capital X i will be used to denote the mole fraction of a component i in a given mixture W i will be used to represent the weight fraction of component i and so on. So, based on the nomenclature that we have defined here let us look at how quantities like the mole fraction, weight fraction etcetera can be defined in terms of the other quantities here.

So, ni is the number of moles of component i small n i. So, we can define this small n i is capital N i by the Avogadro number where capital N i is the number of molecules of component i. So, if we if the number of molecules of component i is capital N i Avogadro constant basically is the number of molecules present in one mole. So, their ratio gives a number of moles of component i present. So, next just small n which is the total number of moles of all components present that just denoted by the summation of n i over all the components.

So, the summation with the index i actually runs over all the components in the mixture. And then since small n i is the related to capital N i through the Avogadro number we can further define the total number of moles as summation of capital N I divided by the Avogadro number.

Similarly, mole fraction is just a number of moles of a component i divided by the total number of moles present in the entire sample. So, X i is small n i by n and again based on the definitions that we are just discussed. We can actually show that X i is also equal to capital N i by capital N, which is the mole fraction or also can be represent as a ratio of the number of molecules of component i divided by the total number of molecules present in the sample. Similarly, if we talk about the mass of component i present in the sample that can be written as the number of moles of component i multiplied by the molar mass of component i.

So, total mass of the sample again can be represented as a sum of the individual masses of the different components as shown here. So, based on these definitions again the weight fraction one can define as the weight fraction of component i can be defined as the mass of component i present in the sample, derived by the total mass of the sample. So, again based on the definition for m i and m here we can rewrite the weight fraction in this form.

And finally, after again writing the number of moles in terms of numbers of molecules Avogadro number all those things. Finally, the expression for the weight fraction in terms of the number of molecules is just capital N i m i derived by summation over capital N i M i. So, the mole fraction and the weight fraction that we have derived in terms defined here in terms of the number of molecules that is what will be using in the next slides next few slides to discuss the polymer molar mass definitions.

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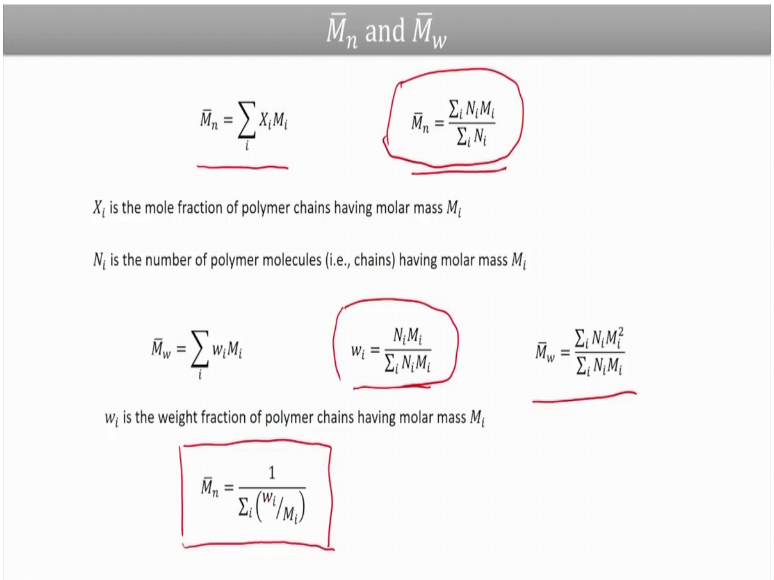

$\bar{M}_n$ and $\bar{M}_w$

$$\bar{M}_n = \sum_i X_i M_i \qquad \bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

X_i is the mole fraction of polymer chains having molar mass M_i

N_i is the number of polymer molecules (i.e., chains) having molar mass M_i

$$\bar{M}_w = \sum_i w_i M_i \qquad w_i = \frac{N_i M_i}{\sum_i N_i M_i} \qquad \bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

w_i is the weight fraction of polymer chains having molar mass M_i

$$\bar{M}_n = \frac{1}{\sum_i \left({w_i}/{M_i} \right)}$$

So, now let us talk about the definitions of the number average molar mass and the weight average molar mass. So, the umber average molar mass basically can be defined as the sum of the product of the mole fraction of a individual component and the molar mass of the individual component. So, when we talk about polymer sample then the individual components in a given mixture that we are talking about a basically the individual polymer chains of a certain length ok. So, for given polymer sample can be considered as an mixture of polymer chains of different lengths. And the different components present in this mixture basically polymer chains having certain length.

So, in so from that perspective the number of molar mass is just a product of mole fraction of polymer chains having a certain molar mass m i multiplied by the respective molar masses. So, that is definition that shown here and again based on the definition of the mole fraction X i. In terms of the number of molecules the way the number average molar mass can also be written in this form, it is a ratio of two summations. Similarly, the weight average molar mass can be expressed as a product of the weight fraction of polymer chains having a molar mass m i multiplied by the corresponding molar mass m i.

Now, weight fraction again as discussed previously can be defined in terms of the number of molecules in this way. So, combining these two the weight average molar mass can also be written in the form that shown here. Finally, by combining the definition of M N bar shown here. And the weight fraction shown here by combining these two definitions, we can also express the number average molar mass in terms of just a weight fraction and the individual molar masses of polymer chains of different lengths.

So, next let us discuss all these definitions through the use of certain examples to make these concepts bit clearer.

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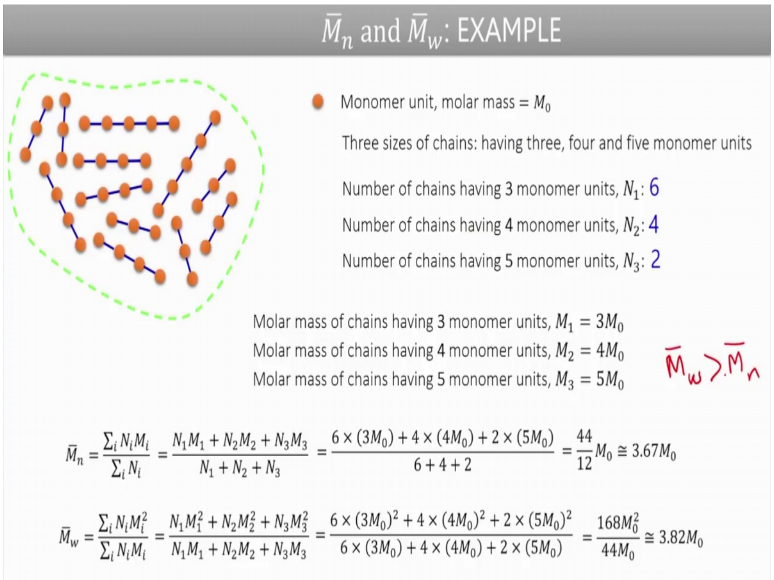

$\bar{M}_n$ and $\bar{M}_w$: EXAMPLE

● Monomer unit, molar mass = M_0

Three sizes of chains: having three, four and five monomer units

Number of chains having 3 monomer units, N_1: 6

Number of chains having 4 monomer units, N_2: 4

Number of chains having 5 monomer units, N_3: 2

Molar mass of chains having 3 monomer units, $M_1 = 3M_0$

Molar mass of chains having 4 monomer units, $M_2 = 4M_0$

Molar mass of chains having 5 monomer units, $M_3 = 5M_0$

$\bar{M}_w > \bar{M}_n$

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} = \frac{6 \times (3M_0) + 4 \times (4M_0) + 2 \times (5M_0)}{6 + 4 + 2} = \frac{44}{12} M_0 \cong 3.67 M_0$$

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} = \frac{6 \times (3M_0)^2 + 4 \times (4M_0)^2 + 2 \times (5M_0)^2}{6 \times (3M_0) + 4 \times (4M_0) + 2 \times (5M_0)} = \frac{168 M_0^2}{44 M_0} \cong 3.82 M_0$$

So, let us consider a small very small representative polymer sample, which consist of different polymer chains of different lengths. So, if we look at the polymer sample that shown here. So, it can consist of basically three different types of polymer chains one polymer chain which has only three monomer units another type of polymer chains having four monomer units and another type having five monomer units.

So, the orange dots that are circles started shown in this sample are basically represent the mole monomer unit. And let us say the mono molar mass of the monomer unit is let us represent that by M naught or M 0. So, in this sample we have three sizes of chains having three 4 and 5 monomer units respectively.

So, now let us say count the number of chains having 3 monomer units and let us call that as N 1, capital N 1. So, number of chains having 3 monomer units is 6 as shown here. Similarly, number of chains having 4 monomer units is four as again shown here. And the number of chains having 5 monomer units which where representing by N 3 that that number is two again as highlighted there.

So, now, that we have the numbers, numbers of change seven different monomer units now that we have identified those. Next the molar mass of chains having 3 monomer units that we are representing, representing by M 1 and since these chains have only 3 monomer units the molar mass is three M naught. Similarly for those having 4 monomer units the molar mass is 4 M naught. And those having 5 monomer units the molar mass is 5 M naught and these are this being represented respectively by M 1, M 2 and M 3.

So, now if we try and write out the expression for M N bar, so the starting from the definition for the number average molar mass of this polymer sample these are definition. And if we expand the numerator and denominator for this particular case we have three types of polymer chains. So, the summation basically will consist of three terms as shown here.

So, the numerator will be capital N 1 M 1 plus N 2 M 2 plus N 3 M 3 and denominator will be just N 1 plus N 2 plus N 3, which is just a total number of chains present in this sample. So, substituting the all the values that we have for this particular sample, sample shown. So, this is the expression what we get which after simplification finally, gives the value as 3.67 M naught. So, the number of average molar mass of this sample is 3.67 times the molar mass of our monomer unit.

Next if you try to calculate the weight average molar mass of the sample, will start with the definition that we discussed previously and again substitute all the values. So, again since we have three types of chains present in this sample will have three terms in the summation. And once we substitute the values of these terms the expression that we get is shown here. And finally, upon simplification we get final value of the weight average molar masses 3.82 M naught. So, what we observe is that the weight average molar mass comes out to be larger than the number average molar mass for this case.

And just because of the way in which this average molar masses have been defined it turns out that the weight average molar mass is in general always larger than the number average molar mass for polymer samples. So, not just for this particular case for any polymers sample the weight average molar mass always comes out to be larger than the number average molar mass. And the only case in which the two can be equal is if for hypothetical case if all the polymer chains have the same length.

So, in that case the weight average number average molar mass is will be the same for all other cases the weight average molar mass is always larger than the number average molar mass.

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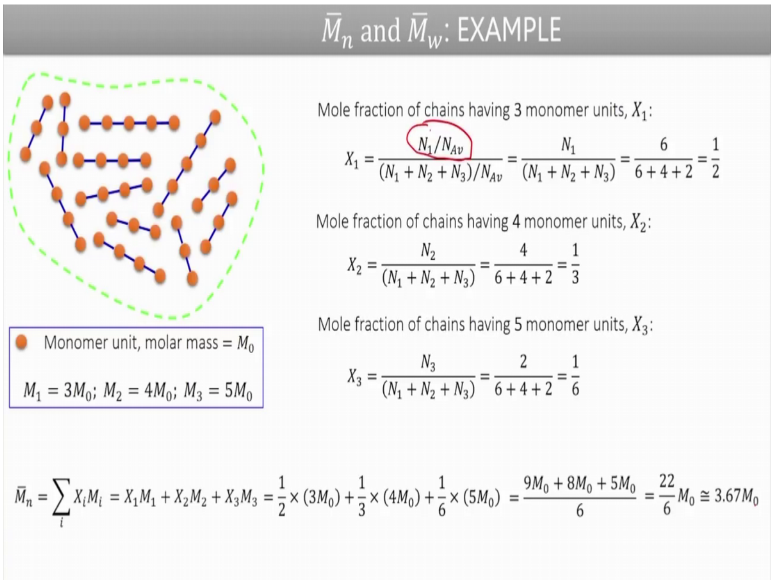

$\bar{M}_n$ and $\bar{M}_w$: EXAMPLE

● Monomer unit, molar mass = M_0

$M_1 = 3M_0$; $M_2 = 4M_0$; $M_3 = 5M_0$

Mole fraction of chains having 3 monomer units, X_1:

$$X_1 = \frac{\boxed{N_1/N_{Av}}}{(N_1+N_2+N_3)/N_{Av}} = \frac{N_1}{(N_1+N_2+N_3)} = \frac{6}{6+4+2} = \frac{1}{2}$$

Mole fraction of chains having 4 monomer units, X_2:

$$X_2 = \frac{N_2}{(N_1+N_2+N_3)} = \frac{4}{6+4+2} = \frac{1}{3}$$

Mole fraction of chains having 5 monomer units, X_3:

$$X_3 = \frac{N_3}{(N_1+N_2+N_3)} = \frac{2}{6+4+2} = \frac{1}{6}$$

$$\bar{M}_n = \sum_i X_i M_i = X_1M_1 + X_2M_2 + X_3M_3 = \frac{1}{2}\times(3M_0) + \frac{1}{3}\times(4M_0) + \frac{1}{6}\times(5M_0) = \frac{9M_0+8M_0+5M_0}{6} = \frac{22}{6}M_0 \cong 3.67M_0$$

So, next let us continue this example and let us see that by using the other definitions of M N bar and M W bar that we had earlier, whether we can arrive at the same results as we did earlier. So, the other definition of m n bar is based on the mole fraction of the different chains that are present. So, let us first find out the mole fractions of the chains present in this particular sample.

So, X 1 which is the mole fraction chains having three monomer units that can be defined as number of moles of chains having three monomer units divide by the total number of moles of all the chains present. So, here the number of moles of chains having three monomer units if we represent that by small N 1 as we have decided in the nomenclature. Then we know that this small N 1 is just the number of molecules derived by the Avogadro number and that is what we have used here directly. And similarly if the number of moles have being converted into number of molecules in the denominator as well in the definition of this mole fraction through the use of Avogadro number.

So, essentially the mole fraction again as we discussed earlier instead of being expressed in terms of number of ratio of number of moles. We can also express in terms of terms of ratio of number of molecules which we get here. And finally, for chains having three monomer units that ratio comes out to be half, next if we represent the number of or the mole fractions chains having four monomer units as X 2. Then again X 2 can be defined as the ratio of the number of molecules of chains having 4 monomer units divided by the total number of molecules present and that comes out to be 1 by 3.

Similarly, the mole fraction for those chains having 5 monomer units comes out to be 1 by 6. So, we again use the other definition of n bar sigma X i M i substitute all the values then we get this kind of an expression, which upon simplification again leads us to value 3.67 M naught, which is what we got earlier. Similarly for M W bar if we want to again check whether the other definition M W bar in terms of weight fractions if that also should give us the same answer. So, to check that let us just calculate the weight fraction of the different chain type present first.

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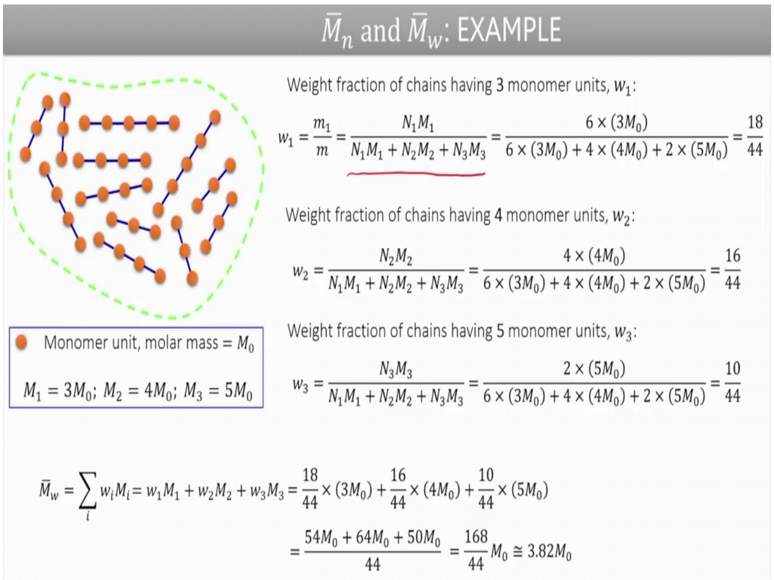

$\bar{M}_n$ and $\bar{M}_w$: EXAMPLE

Weight fraction of chains having 3 monomer units, w_1:

$$w_1 = \frac{m_1}{m} = \underline{\frac{N_1M_1}{N_1M_1 + N_2M_2 + N_3M_3}} = \frac{6 \times (3M_0)}{6 \times (3M_0) + 4 \times (4M_0) + 2 \times (5M_0)} = \frac{18}{44}$$

Weight fraction of chains having 4 monomer units, w_2:

$$w_2 = \frac{N_2M_2}{N_1M_1 + N_2M_2 + N_3M_3} = \frac{4 \times (4M_0)}{6 \times (3M_0) + 4 \times (4M_0) + 2 \times (5M_0)} = \frac{16}{44}$$

Weight fraction of chains having 5 monomer units, w_3:

$$w_3 = \frac{N_3M_3}{N_1M_1 + N_2M_2 + N_3M_3} = \frac{2 \times (5M_0)}{6 \times (3M_0) + 4 \times (4M_0) + 2 \times (5M_0)} = \frac{10}{44}$$

● Monomer unit, molar mass = M_0

$M_1 = 3M_0$; $M_2 = 4M_0$; $M_3 = 5M_0$

$$\bar{M}_w = \sum_i w_iM_i = w_1M_1 + w_2M_2 + w_3M_3 = \frac{18}{44} \times (3M_0) + \frac{16}{44} \times (4M_0) + \frac{10}{44} \times (5M_0)$$

$$= \frac{54M_0 + 64M_0 + 50M_0}{44} = \frac{168}{44}M_0 \cong 3.82M_0$$

The weight fraction of chains having three monomer units W 1 that is just the mass of these type of chains or the mass of chains have been three monomer units divided by total mass of the sample. So, that ratio again can be represented in this form, so capital N 1 N 1 M 1 represents the mass of chains having three monomer units this should actually divided by the Avogadro number. But since that appear that factor appears both in numerator and denominator that gets cancelled. So, this is the expression that we get and again upon substitution we get 18 by 44 as the weight fraction. Similarly for both chains having 4 monomer units the W 2 comes out be 16 by 44 and for weight fraction chains having 5 monomer units we get W 3 as 10 by 44.

So, using the definition of M W bar in terms of the weight fraction, that is the product weight fraction in the individual molar masses of the different chain types and the summation of that. So, if we expand that this is what we get and upon substituting the values that we have just calculated the final result that we get is 3.82 M naught which is again the same as what we got earlier. So, these two examples basically illustrate that the different definitions of M N bar and M W bar are equivalent.

Next let us talk about a couple of other average molar masses that are defined for polymers in general and which are measureable using experimental techniques. So, these two molar masses are the z average molar mass and the viscosity molar mass. So, the number average and weight average molar mass are the two molar masses, which are which will encounter more commonly, but the other two viscosity and z average also encounter in some cases. So, will also briefly discuss the definition here.

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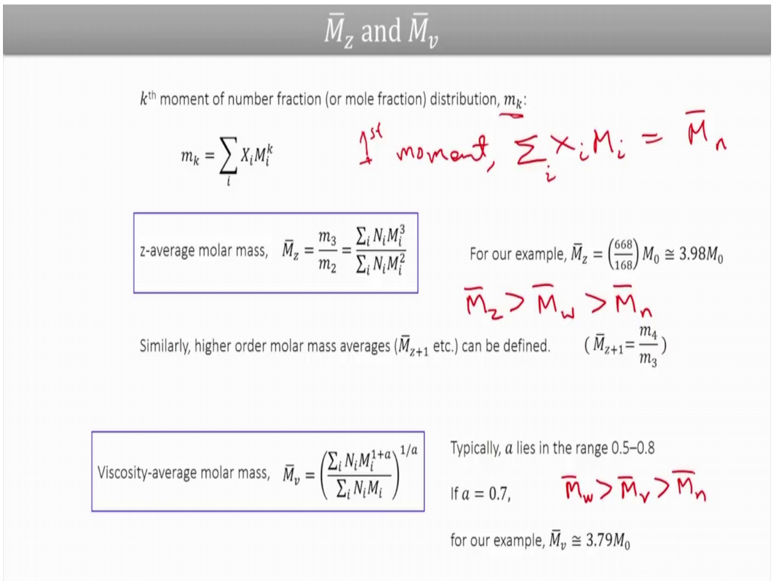

$\bar{M}_z$ and $\bar{M}_v$

k^{th} moment of number fraction (or mole fraction) distribution, m_k:

$$m_k = \sum_i X_i M_i^k$$

1^{st} moment, $\sum_i X_i M_i = \bar{M}_n$

$$\boxed{\text{z-average molar mass,} \quad \bar{M}_z = \frac{m_3}{m_2} = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}}$$

For our example, $\bar{M}_z = \left(\frac{668}{168}\right) M_0 \cong 3.98 M_0$

$\bar{M}_z > \bar{M}_w > \bar{M}_n$

Similarly, higher order molar mass averages ($\bar{M}_{z+1}$ etc.) can be defined. $\left(\bar{M}_{z+1} = \frac{m_4}{m_3}\right)$

$$\boxed{\text{Viscosity-average molar mass,} \quad \bar{M}_v = \left(\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i}\right)^{1/a}}$$

Typically, a lies in the range 0.5–0.8

If $a = 0.7$, $\bar{M}_w > \bar{M}_v > \bar{M}_n$

for our example, $\bar{M}_v \cong 3.79 M_0$

So, before going on to the definition of z average molar mass let us first define what is called the kth moment of number fraction or mole fraction distribution and this kth moment of the number fraction distribution is represented by m k. So, it is defined simply as a summation over the product of the mole fraction X i multiplied by the molar mass m I raised to the power k.

So, if we talking if we are talking about the first moment. So, in that case k will be 1 so this will simply sigma X i M i. So, we can say that the first moment is just sigma X i M i which is nothing, but as we know this is the definition of M N bar. So, the first moment itself is how the M N bar number average molar mass is defined.

So, now if we look at z definition of z average molar mass, that simply defined as the third moment ratio of the third moment to the second moment. So, summation of N i M i q by summation of N i M i square now instead of capital N i here, we can also write X i in both the terms and that will not change the definition. So, this definition and the definition using mole fractions instead of these numbers both are equivalent because will see that again in both the cases the numerator and denominator gets a common factor which can be cancelled out. So, in any case this definition that we have a this standard definition, but apart from this M z bar one can also define equivalently as X i M i q by summation X i M i square.

So, if the example that we consider earlier if we talk about that example then in that case if we use the formula shown here for the z average molar mass. It comes out to be 3.98 M naught and we see that these values are actually larger than the weight average and number molar mass that we calculated earlier. So, in general the z average molar mass is always larger than the weight average molar mass, which is larger than the number average molar mass. And all three of them will be equal in the special and of an hypothetical case were all the polymer chains have the same length, otherwise this kind of relation will always we follow.

Similarly in z average molar mass if we look at it is actually molar mass average which is one ordered higher than the weight average molar mass. Similarly, molar masses average of higher orders can also be defined like the z plus 1 average molar mass or M bar z plus 1, which we can define as the ratio of the moments m 4 by m 3.

So, M bar z 2 1 can defined as m 5 by m 4 and so on, but I mean normally these kind of higher average molar masses are not readily measureable using experiments. Finally, the viscosity average molar mass, which can be measured using viscometry experiment is defined like this. Where the parameter a that we have a exponent that have some significance, and will discuss this later on when we are talking about viscometry and the measurement of this molar mass. But for now let us just say that this parameter a is has a value that typically ranges from 0.5 to 0.8.

So, for example, if we consider, consider a case where a as a value of 0.7, then for the example again that we have discussed previously for the polymer sample that we took as an example, the calculation of m v bar results in a value of 3.79 m naught. So, we see that this value actually lies in between the value of number average molar mass and the weight average molar mass, so in general will see this kind of relationship.

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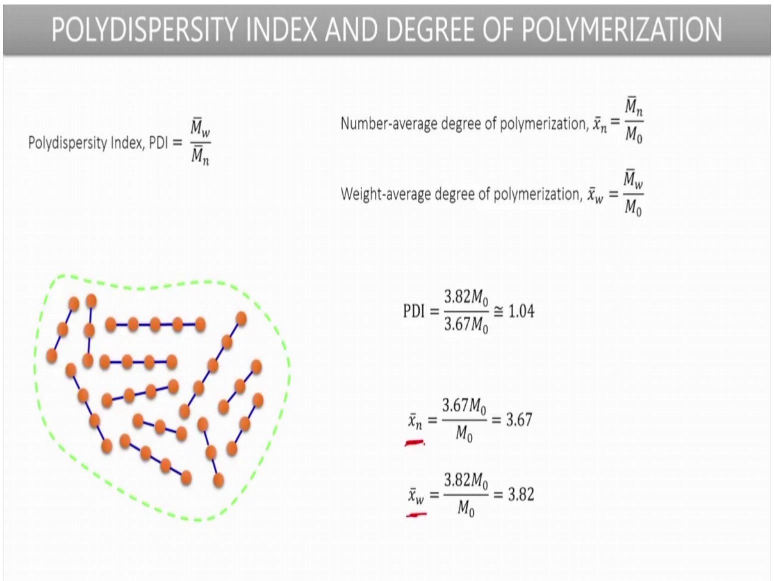

POLYDISPERSITY INDEX AND DEGREE OF POLYMERIZATION

Polydispersity Index, PDI = $\frac{\bar{M}_w}{\bar{M}_n}$

Number-average degree of polymerization, $\bar{x}_n = \frac{\bar{M}_n}{M_0}$

Weight-average degree of polymerization, $\bar{x}_w = \frac{\bar{M}_w}{M_0}$

$$\text{PDI} = \frac{3.82M_0}{3.67M_0} \cong 1.04$$

$$\bar{x}_n = \frac{3.67M_0}{M_0} = 3.67$$

$$\bar{x}_w = \frac{3.82M_0}{M_0} = 3.82$$

And before we conclude this introductory topic will just talk about couple of other terms and definitions. So, we have talked about the fact that the polymer chains samples usually show a distribution of chain lengths and hence the molar mass is also distributed. So, since the polymer chains themselves polymer samples are themselves poly dispersed.

So, the molar mass distribution has some width and it is not unique value. So, quantity called the polydispersity index is usually defined which as a ratio of the weight average molar mass and the number of average molar mass. And it gives some indication as to how write the molar mass distribution is of course, entire molar mass distribution is something that one that has to measured separately. But it gives some rough ideas to how write the molar mass distribution in a polymer sample is.

So, this polydispersity indexes I just mentioned is just defined as the ratio of weight average molar mass to number average molar mass. And also since the polymer chain lengths are not the same we have a distribution of polymer chain lengths, the degree of polymerization also is defined in terms of different averages. So, the number average degree of polymerization which is represented by represented by x n bar is defines as M n bar by M naught. And the weight average degree of polymerization represented by x w bar is represent is defines as M w bar as weight average molar mass divided by m naught which is the monomer molar mass.

So, if we again consider the example that we discussed earlier and tried to find out the values of these quantities for this particular example. The value for polydispersity index for this sample is 1.04, the number average degree of polymerization is 3.67 and the weight average degree of polymerization is 3.82. And since the weight average molar mass is always larger than the number average molar mass. The corresponding weight average degree of polymerization is also always larger than the number average degree of polymerization.

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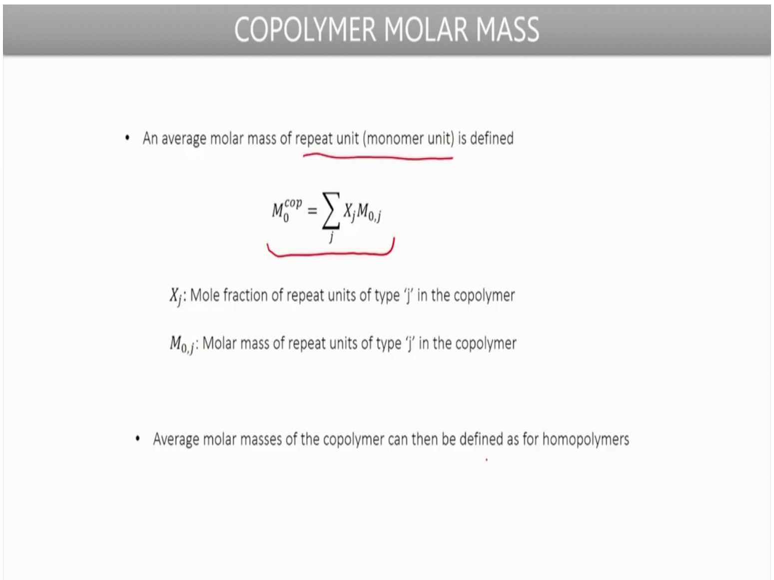

COPOLYMER MOLAR MASS

- An average molar mass of repeat unit (monomer unit) is defined

$$\underbrace{M_0^{cop} = \sum_j X_j M_{0,j}}$$

X_j: Mole fraction of repeat units of type 'j' in the copolymer

$M_{0,j}$: Molar mass of repeat units of type 'j' in the copolymer

- Average molar masses of the copolymer can then be defined as for homopolymers

Now, finally, we will discuss the keys of the molar mass of copolymers. So, till now we have been discussing the molar mass is only of homopolymers because we only define a single monomer mass which was M naught. So, now, if we consider the case of copolymers in that case also similar formulae can be used for the definition of different types of average molar masses.

The only thing is that we need to define some kind of an average or equivalent value for the molar mass of the monomeric unit or the repeat unit as well, because for copolymers will have more than one type of repeat units present that is why this is important.

So, the average molar mass of repeat unit in the case of copolymers first that can be defined in this way. So, if we have let us say many different types of repeat units present in our copolymer then an average repeat unit of the copolymer can have a molar mass defined in this following way. So, here the mole fraction of repeat units of type j in the copolymer that is represented by x j in this formula and the M naught j is the molar mass of repeat unit of type j in the copolymer and this summation will go run over all the different types of repeat units that are present inside sample.

So, now once the, this average repeat unit molar mass has been defined for the copolymer. Then all the previously defined formula for the average molar mass discussed till now. All those formula can be used with the only change that instead of the molar mass monomer molar mass the average repeat unit molar mass for the copolymer will be used. So, the average masses of the copolymer, we can just simply define in a similar way as we did for the homopolymers earlier.

So, with this discussion will conclude this first lecture which basically talked about all the different introductory aspects of polymers and polymer science. So, with these this introduction will in the next lecture start a discussion on the different types of chain models that available for ideal polymer chains.