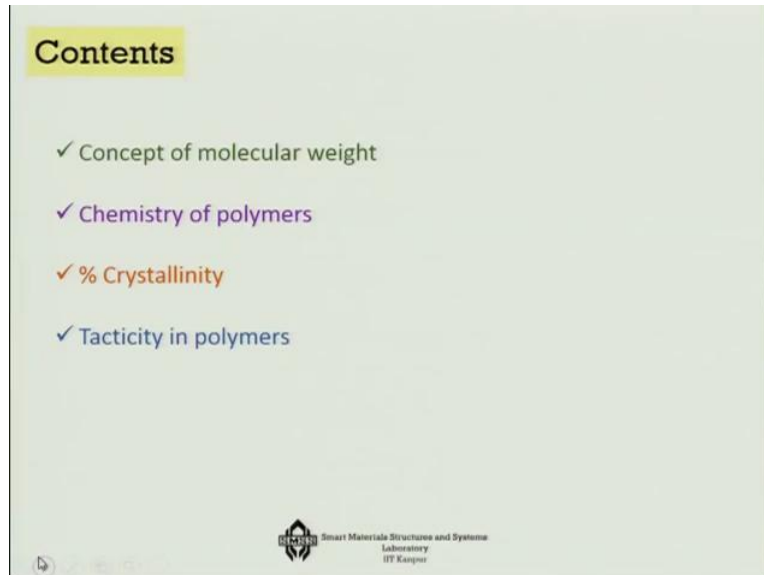


Nature and Properties of Materials
Professor Bishak Bhattacharya
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Lecture 17
Polymer Structure

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Good morning, today we are going to talk about polymeric structures. So the topics that we will be covering today are the concept of molecular weight because that is what will actually tell us about this polymeric structure, so concept of the molecular weight we are going to talk about. And then we are going to talk about the chemistry of the polymers and then the crystallinity, how it actually is affected by the molecular weight and then we will talk about the tacticity in polymers that also have effect in terms of the crystallinity in the polymer.

Overall, we will remain today in the domain of polymeric structure. Now the first thing whenever we talk about polymer is that, if you consider a polymer (())(1:11) a metal, what we call is the density of a metallic sample no matter whatever part of a sample you take, the bulk density and the density at a point hardly departs between one another, the reason being that all the molecules so to say metallic molecules are uniformly distributed over time entire volume that it occupies.

But the same thing, you cannot talk about suppose if we consider this to be a polymer and then if we want to, if you take a small little part of it let us say the microstructure of the polymer and then if I want to find out that what is the density of it, that with respect to the bulk density may vary a lot.

And the reason is because of the molecular weight of the polymer and that molecular weight is not a single molecular weight why, because when you look at a polymer, it is hardly about one single material, but it is many mers or many polymerisation of units that are actually involved in a polymer. So it is the molecular weight distribution, which is important particularly in polymers like thermoplastics.

Now, there are 2 types of polymers I already told you. One is the thermoplastics and other is the thermosets. Thermosets if you remember that they have network kind of structures right, chemical network. So for thermosets, you cannot really isolate one individual species, so it is more homogenized in that sense. And as a result, thermosets have infinite molecular weight that means there is no sense in terms of defining the molecular weight.

But for thermoplastics which may have suppose a long chain, a short chain, a medium chain, again a long chain, so it has many conglomerations of different types of chain links, there is this concept of molecular weight is very important. Now, there are various ways in which we can define this molecular weight. The 1st one we call a Number average of molecular weight.

So here, what we way we define is that total weight of all the polymer molecules in a sample divided by the total number of polymer molecules in a sample, so this gives you some kind of an average weight. That means, suppose there are 10 numbers of samples of a particular molecular weight, 5 number of something else, et cetera. Then you sum of all this weights together and simply divide them by the total number of the sample.

However, dividing all of them by the total number of the sample means you are giving equal weight age to all the species, which is not fair because some polymers are actually heavier than the others particularly those which are having very long chain lengths, they are not the same as those which are having short chain length, so there is a different concept also for that, that is known as Weighted average molecular weight, where instead of $\Sigma M_i N_i$, this we put it as $\Sigma M_i^2 N_i$ and instead of dividing it by ΣN_i , we divide it by $\Sigma M_i N_i$.

So that is the difference between M_w and M_n in terms of number average, we do not give weightage for the heavier molecular weight chains. On the other hand, for weighted average molecular weight M_w , we give due weightage to the heavier molecule weight of the samples.

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Degree of Polymerization

$$DP = \frac{\bar{M}_n}{m}$$

where, \bar{M}_n = Number average molecular weight
 m = repeat unit molecular weight (no. of atoms x atomic wt.)

Example: Suppose for Polyvinyl chloride, $\bar{M}_n = 21,150$ g/mol
Then, repeat unit molecular weight, $m = 2 \times 12 + 3 \times 1 + 1 \times 35$
 $= 62$ g/mol

$$DP = \frac{21,150}{62} = 341$$

Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed

Effect of Molecular Weight

Graph showing Property vs. Molecular weight, degree of polymerization. The x-axis is logarithmic with markers at 10^4 and 10^7 . The y-axis is Property. Two curves are shown: 'Tensile and impact strength' (red) and 'Viscosity' (blue). A vertical dashed line at 10^7 is labeled 'Commercial polymers'.

Chemical structure of PVC: $\left(\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C} - \text{C}- \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array} \right)_n$

Repeat unit contains - 2 carbon, 3 hydrogen and 1 chlorine atom

PVC

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Graph showing Melting Temperature vs. Degree of Polymerization. The x-axis is Degree of Polymerization and the y-axis is Melting Temperature. The curve shows a sharp increase in melting temperature that levels off at high degrees of polymerization.

Now there is a 3rd concept, which I already told you earlier that is the Degree of polymerisation. How do we quantify it? Well if the average, number average of the molecular weight that is \bar{M}_n and if you know the unit molecular weight m , then dividing that by \bar{M}_n , you are going to get the degree of polymerisation DP. One example suppose, you consider Polyvinyl chloride okay.

This is a typical maneuver of polyvinyl chloride as you can see that it is just like Methane unit CH_4 or C_2H_4 and then 1 hydrogen is actually replaced here by Chlorine, so that gives us the polyvinyl chloride. And the molecular weight of it if you find it out corresponding to use no carbon, hydrogen and chlorine, we will get it as 62 g per mole is the each unit molecular weight.

Now suppose the species is we are talking about has number average molecular weight of 21,150g per mole. So by dividing this \bar{M}_n by this 62 gram per mole, we are going to get the DP, which means on an average you can expect this n to be close to 341 on an average, there can be some which are higher, some which are lower, but an average sense about 340 of such bars or unit are actually merging together to form the particular polymer in this particular case.

Now molecular weight plays a very significant role in terms of at least few things. One is as you can see here in terms of the strength, as the molecular weight increases, you are getting better strength, of course it saturates at a point. As the molecular weight increases, the

viscosity also increases tremendously. In fact, in the electrorheological fluid or magnetorheological fluid, that is the technique that is tried to actually control that.

So the viscosity increases as the molecular weight increases and then the melting temperature also if you look at it, the melting temperature that also increases as the molecular weight increases. So the improvement in molecule weight is good from the strength point of view, from the viscosity point of view and also from the temperature point of view that we have to keep in our mind.

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Polydispersity Index

Polydispersity index, $PI = \frac{M_w}{M_n}$

- The larger the polydispersity index, the broader the molecular weight.
- Monodisperse polymer, where all the chain lengths are equal (such as a protein) has an $PI = 1$.
- Step polymerization reactions typically yield values of $PI \approx 2.0$
- Chain polymerization reactions yield values between $PI = 1.5 - 20$.

Number-average, \bar{M}_n

Weight-average, \bar{M}_w

Amount of polymer

Molecular weight

Distribution of molecular weights for a typical polymer

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Reference: W.D. Callister, J Ed.

The next important point once both M_w and M_n is actually the Polydispersity index okay. We call it PI, the Polydispersity index, which is nothing but the ratio of M_w to M_n so that is what it is. So the larger is this Polydispersity index, the broader will be the molecular weight of the sample. For example, I mean monodisperse polymer, you have only one species of the molecular weight, so all chain lengths are equal.

So that means, M_w and M_n will have no difference because you have only one type of a chain, so than the Polydispersity index is unity. If you have Step polymerisation if you remember, what is Step polymerisation? Suppose we have in this container we have monomers and then the polymerisation is happening, it is happening at many places simultaneously that is what Step polymerisation is.

So in that case, each one of the individual species will not grow unnecessarily very long because the process of chain making is happening in many places simultaneously. As a result,

the M_w and M_n will not be different much and hence it can be typically something like 2 or so, so it is not much dispersed, less dispersed kind of a thing if there is step polymerisation.

On the other hand, if there is chain polymerisation then how does it happen? It starts with only one active side and then in this polymer gradually these active sides grow. So as it is growing, you are going to get very large chain lengths, (10:03) very small chain length monomers, which are actually waiting to be concatenated with this neck. So as a result, you get a much larger number of the Polydispersity index.

So if suppose the 1st of all, the M_n the number average or M_n , that is very high in comparison to the M_w and of suppose your M_n is here and M_w is somewhere here, you may say that the difference is so high that it is actually chain polymerisation that is happening in the system. On the other hand, if they are very close then you may say that it is like a step polymerisation that is happening in the system.

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Example

| No. of molecules (N_i) | Mass of each molecule (M_i) (g/mol) | Total mass of each type of molecule, ($N_i M_i$) in g/mol | $M_i^2 N_i$ |
|----------------------------|---|---|--|
| 1 | 800,000 | 800,000 | 6.4×10^{11} |
| 3 | 750,000 | 2250,000 | 16.8×10^{11} |
| 5 | 700,000 | 3500,000 | 24.5×10^{11} |
| 8 | 650,000 | 5200,000 | 33.8×10^{11} |
| 10 | 600,000 | 6000,000 | 36×10^{11} |
| 13 | 550,000 | 7150,000 | 39.3×10^{11} |
| 20 | 500,000 | 10,000,000 | 50×10^{11} |
| 13 | 450,000 | 5850,000 | 26.3×10^{11} |
| 10 | 400,000 | 4000,000 | 16×10^{11} |
| 8 | 350,000 | 2800,000 | 98×10^{11} |
| 5 | 300,000 | 1500,000 | 4.5×10^{11} |
| 3 | 250,000 | 750,000 | 18.75×10^{11} |
| 1 | 200,000 | 200,000 | 0.4×10^{11} |
| $\sum N_i = 100$ | | $\sum M_i N_i = 50,000,000$ (Total mass) | $\sum M_i^2 N_i = 370.75 \times 10^{11}$ |

Number average molecular weight, $\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i}$
 $= \frac{50,000,000}{100} = 500,000$ g/mol

Weighted average molecular weight, $\bar{M}_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$
 $= \frac{370.75 \times 10^{11}}{50,000,000} = 741,500$ g/mol

Polydispersity index, $PI = \frac{M_w}{M_n} = 1.48$

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So there is a small example here, let us try to do it so that we will get an idea that how to find out the Number average molecular weight and the Weighted average molecular weight. So suppose we have here a total number of samples which are like 100 if you actually add up all of them $\sum N_i$, you will get it as 100. For each one of them, you have the mass of each molecule available with you.

Suppose the 1st one you take, it is with only one sample so what is $M_i N_i$ and you also know what is $M_i^2 N_i$. Similar thing I can do for 3 and we get it, we can do it for 10 and we

get it, we can do it for 20 and we get this. Like that if I complete the table, I am going to get 2 things, one is $\Sigma M_i N_i$ and another is $\Sigma M_i^2 N_i$.

So once I get this and also I know ΣN_i , so I can find out what is $\Sigma M_i N_i$ by ΣN_i and that gives me \bar{M}_n , which is like 500,000 for this grams per mole for this artificial polymer. And for \bar{M}_w , I got it as 741,500 gram per mole. If I find out the Polydispersity index, it will be something like 1.48, what it means is that this is a case of a Step polymerisation okay because the PI is not very high. So this is a typically sample, which shows you how to calculate the average molecular weight, the number average as well as the weighted average molecular weight. Now we will talk about chemistry of the polymer molecules.

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Chemistry of Polymer molecules

- When all the mers are the same, the molecule is called a **Homo-polymer**.
 - Diagram of a homo-polymer chain: $\text{---}[\text{CH}_2\text{---}(\text{CH}(\text{Cl}))\text{---}]_n\text{---}$
- When there is more than one type of mer present, the molecule is a **Co-polymer**.
 - Block Copolymer: $\text{---}[\text{A}]_m\text{---}[\text{B}]_n\text{---}$
 - Random Copolymer: $\text{---}[\text{A}]\text{---}[\text{B}]\text{---}[\text{A}]\text{---}[\text{B}]\text{---}$
 - Alternate Copolymer: $\text{---}[\text{A}]\text{---}[\text{B}]\text{---}[\text{A}]\text{---}[\text{B}]\text{---}$
- Mer units that have **2 active bonds** to connect with **other mers** are called **bi-functional**.
 - Chemical structure of Polyethylene: $\text{---}[\text{C}(\text{H})_2\text{---}(\text{C}(\text{H})_2)]_n\text{---}$
- Mer units that have **3 active bonds** to connect with other mers are called **tri-functional**. They form 3-D molecular network structures.
 - Chemical structure of Phenol-formaldehyde (Bakelite): $\text{---}[\text{C}_6\text{H}_3(\text{OH})(\text{Cl})_2]\text{---}$

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When all the mers are the same that means all the units are the same, then we call that kind of polymer to be a Homo-polymer. So the similar examples here as you can see of Homo-polymers like polyvinyl chloride okay, all units are of Vinyl Chloride. When there is more than one type of mer, then it is a Co-polymer. Again for co-polymers, there are 3 or 4 various varieties of it.

Suppose, you have one mer and then it is another one grafted together, then it is a Block co-polymer. Suppose you have it in such a manner that one then the other in a randomly attached manner samples, then it is a random co-polymer. And suppose it is like our 14 sequences like ATGC, so one unit then the other then the other repetitive type, then it is an alternate co-

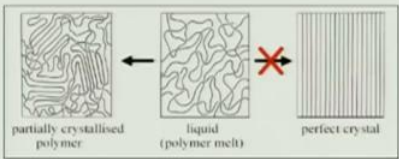
polymer, so we can have 3 types of co-polymers; Block copolymers, Random copolymer or Alternate copolymers.

The other thing is that, if you have only 2 functional sides then it is a bifunctional unit, 2 active bonds. If you have 3 active bonds, then you get a trifunctional unit, so naturally if you have more active bonds, you can actually form more network structures and which is important for network polymers. Now we will talk about the possible physical states for polymeric materials.

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Possible Physical States for Polymer Materials

Traditional classification of physical states (gases, liquids, crystals) is not informative for polymer materials.



Classification of polymer materials:-

- ❖ **Partially crystalline state**
- ❖ **Viscoelastic State** (polymer melt)
- ❖ **Highly elastic state** (e.g. Rubbers)
- ❖ **Glassy state** (e.g. Organic glasses from poly(styrene), poly(methylmethacrylate), poly(vinyl chloride))

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Now in case of metals for example, you have generally, not under random conditions or very extreme conditions you know, when you can have a very cold state or you can have a plasma state if exclude that, generally you get 3 states; the gaseous state, the liquid state and crystalline state. However, the difference between this material and the polymers is that here you get more number of states inside the solid state itself.

You can get the solid state, the partially crystalline solid state, you can get the viscoelastic state, you can get highly elastic state or you can get a highly amorphous state, which is glassy state is actually highly amorphous. So depending on the degree of crystallinity because for polymers having accompanied crystallinity is kind of impossible, so it is generally always partially crystalline.

Now, out of that partial crystallinity, it can be like the polymer is more close to elastic state, then it is highly elastic state, it can be that the polymer is totally amorphous, then it is a glassy state or it can be in between the 2 that means it is like a viscoelastic state. So these are

the various variations and all happens because how the polymeric chains are folded against each other.

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Now, most of the polymers their chain lengths are so long that they do not stretch out fully. Instead, they fold back on themselves after going straight a short distance, somewhat like this okay. So we can like if we in a macro scale if we try to look at it, it can be something like this as you can see that the polymer is not very long and it is actually very nicely folded on each other, so you have folds of each one of them.

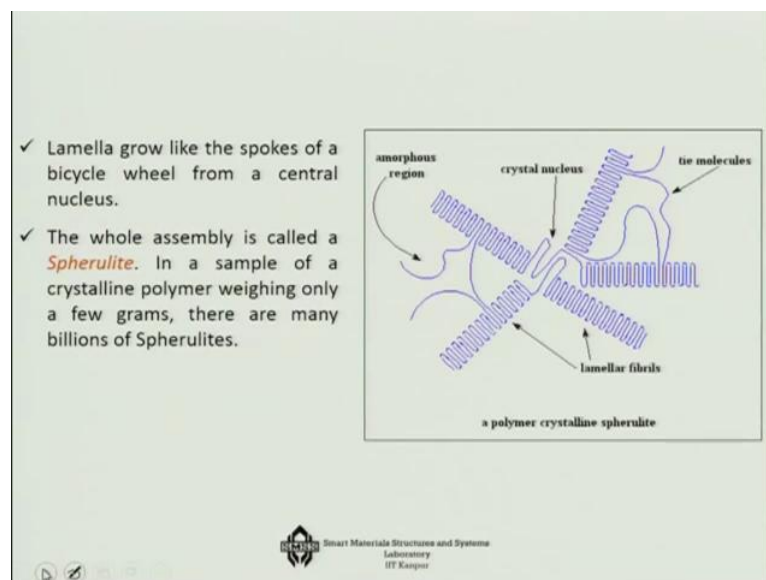
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So this is a regular folding, which means this type of a regular folding can actually generate crystalline structure. What is the other possibility? That is simply that you have something like totally messy, there is no regularity in the folding at all, something like a clumsy hand of nature as if it made all the things together, this is the totally amorphous one. So, you can have in a typical polymer or variation of the 2 that means, some part is messy and is nicely folded.

Depending on if this part is more, then you get more crystalline kind of a polymer, which has much higher better mechanical properties in some sense or you can have totally glassy one, which has different set of mechanical properties altogether. So that is kind of an analogy that this is regular folding and in most of the lamella cases that the regular folding gets lost beyond a certain link and this actually starts the amorphous region.

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So if I actually look at it that you may get something like this that there are these regular folding and there are this amorphous regions. The whole thing together sometimes may look like something like a wheel and you get something if you consider all the things together, you get nothing like a Spherulite, where you have partially crystalline and partly amorphous state together in the sample.

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Crystallinity

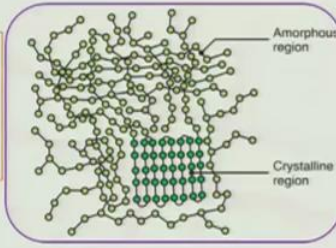
Crystalline region: Orderly arrangement of molecular chains.

✓ High crystallinity means - higher density, more strength, higher resistance to both dissolution and softening by heating.

Degree of crystallinity in Polymers

- Ranges from completely amorphous to about 95% crystalline.
- Metal specimens are almost always entirely crystalline.
- Ceramics are either totally crystalline or totally non-crystalline.

For same material & molecular weight
 $\rho_{\text{crystalline polymer}} > \rho_{\text{amorphous polymer}}$
(due to close packing)



Amorphous region

Crystalline region

Remember: No polymer is 100% crystalline

Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

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Now, what is the implication of it? Why I am talking so much about crystallinity? Actually, higher crystallinity signifies that you have higher density of the polymer, you have more strength, you have higher resistance to dissolution and softening by heating. So in short, many of the mechanical properties actually improve if the crystallinity is high, if you get more of this orderly folded region, the crystalline region.

But remember that no polymer is 100% crystalline; there will be some amorphous part in it. If you look at the degree of crystallinity, completely amorphous is one stage and about 95% crystallinity is another extreme, not 100%, but 95%. In comparison to that, metal specimens are almost always entirely crystalline and in comparison to that, ceramics are either totally crystalline or totally non-crystalline.

Now metals I told you that in today's contexts you can actually make metals to be glassy also, but that means the cooling is to be done so fast that the metal would not get any chance to form the crystalline structure and I told you that that is what we call it as bulk metallic glass, which is like mostly amorphous in terms of the structure. So apart from this extreme case, metals are generally completely crystalline.

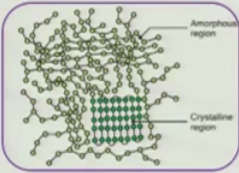
For the same material and the molecular weight due to close packing naturally the packing if it is more better, so you get the density better, so density of crystalline polymers is higher than the density of the amorphous polymer. Now the degree of crystallinity, how do we change it? Of course, one most important point is what is the rate of cooling?

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Crystallinity dependence

Degree of crystallinity is affected by:-

- ✓ **Rate of cooling during solidification**
 - More the rapid cooling – lesser the time for alignment – poorer the crystallinity.
- ✓ **Chain configuration**
 - More the side branching & cross linking - more the restriction to prevent the chain alignment – lesser the crystallinity .
 - Thus, linear polymer have high degree of crystallinity.
 - Most network and crosslinked polymers are almost totally amorphous.



The diagram shows a network of polymer chains. A central portion is highlighted with a green grid, labeled 'Crystalline region'. The surrounding area consists of disordered, tangled chains, labeled 'Amorphous region'.

Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

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If the cooling is rapid, then you get lesser time for alignment, you get more amorphous region, poorer is the crystallinity. The other point is, what is the chain configuration? Do you have side branch or cross-linking? If there is side branch or cross-linking, it will be more difficult to fold it. So the more the restriction to folding in the chain alignment, lesser will be the crystallinity that is why we always see whether the polymers is a linear polymer or not because linear polymers have high degree of crystallinity.

Most network and cross-linked polymers are almost totally amorphous as you can see here that network or cross-linked polymers since it is very difficult to fold them or give any regular structure, so they are generally totally amorphous. So that sense we can say that Thermosets are actually more amorphous than the thermoplastics in general okay. Now one last thing that we want to touch today is the tacticity in the polymers.

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Tacticity in Polymers

- ✓ Different atomic configurations for the same composition.
- ✓ Tacticity is the way pendant groups are arranged along the backbone chain of a polymer.
- ✓ Isotactic & Syndiotactic – **regular geometry facilitates** fitting of adjacent chain, thus **more crystalline**.
- ✓ **Atactic** – Poorly Crystalline due to **irregularity of side group**.
- ✓ Also, larger the side-bonded groups of atoms - the less is the tendency for crystallization.

Isotactic Syndiotactic Atactic

Stereoisomers

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So here what happens, the molecular weight even though remains the same, but in the side chains as you can see in a polymeric chain, this is the main chain main carbon chain and then you have the side chains. The side chains which are often quite heavy sometimes will be in only one side of the main chain, we call it to be Isotactic. Sometimes the side chains will be actually one in this side and another in the other side like that it will happen and we call this to be Syndiotactic.

Sometimes it can happen that it is completely random, one here, one here, then two here one here, this is totally random; we call it to be Atactic. So for this type of polymers, which is Isotactic the crystalline it is very high because it is a it is the heavy side chains are only in one side. Syndiotactic also folding is possible. Atactic holding is very difficult as a result, these are poorly crystalline.

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Some Highly Crystalline Polymers:

- ✓ Polypropylene
- ✓ Syndiotactic polystyrene
- ✓ Nylon
- ✓ Kevlar and Nomex

Some Highly Amorphous Polymers

- ✓ Poly(methyl-methacrylate), PMMA
- ✓ Atactic polystyrene
- ✓ Polycarbonate
- ✓ Polyisoprene

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These are poorly crystalline and Isotactics are highly crystalline that is the tacticity in the polymers. So some highly crystalline polymers are like polypropylene, Syndiotactic polystyrene, nylon, Kevlar and Nomex. Many of them like Kevlar or Nomex, they are used for bullet-proof jackets, so they are already very much known for their high strength.

And in the highly amorphous category there is PMMA acrylics, Atactic polystyrene, polycarbonate, poly isoprene, et cetera. These are some of the variations of the highly crystalline and highly amorphous polymers. How do we define the crystallinity?

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% Crystallinity

$$\% \text{ Crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

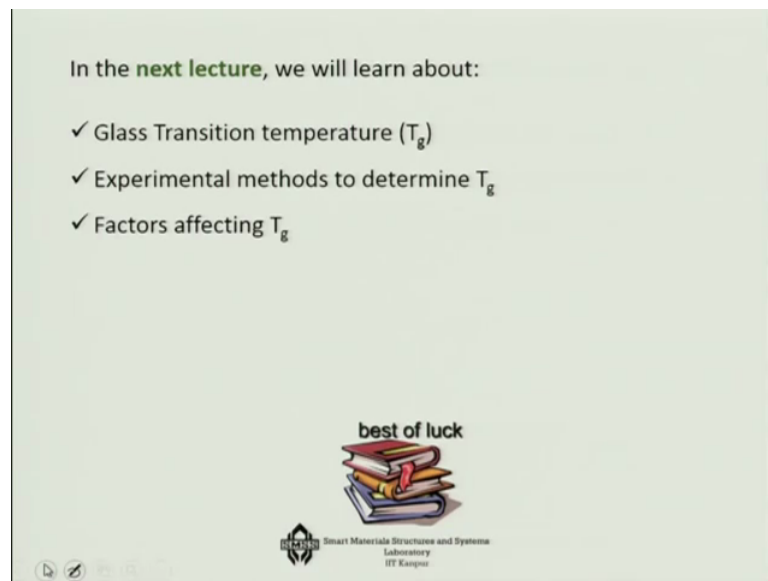
where, ρ_s : Density of specimen
 ρ_a : Density of the totally amorphous polymer,
 ρ_c : Density of the perfectly crystalline polymer

The values of ρ_s , ρ_a and ρ_c are measured by experimental means.

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Well, for that you need to know 3 things, one is the density of the specimen we are talking about, the density of the totally amorphous form of that polymers and density of the perfectly crystalline form of the same polymer. So then by using this particular equation, where you find out what is the density difference in the 2 cases and ρ_c and ρ_s , you can find out what is the degree of crystallinity of a particular polymer.


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In the **next lecture**, we will learn about:

- ✓ Glass Transition temperature (T_g)
- ✓ Experimental methods to determine T_g
- ✓ Factors affecting T_g

best of luck

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The slide features a light green background with a black border. It contains a list of topics for the next lecture, a 'best of luck' message with a stack of books icon, and the logo of the Smart Materials Structure and Systems Laboratory at IIT Kanpur.

This is where we will put an end, in the next lecture we will learn about glass transition temperature, experimental methods to determine T_g and the factors that affect the glass transition temperature, thank you.