Drug Delivery Principles and Engineering

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Lecture – 05
Polymers Properties

Hello everyone, welcome to another lecture for Drug Delivery Principles in Engineering. Today we are going to continue our discussion that we were having on Polymers. Again, I just want to quickly remind you all that this drug delivery course will involve lots and lots of different interdisciplinary things. So, what I am doing currently is basically bringing you all up to par at what are the different areas and what do they mean for drug delivery.

So, we initially talked about what is drug delivery, how is it is distributed, what is the current methods. So, pharmacokinetics of the drug how the administered and then we talked about pro drugs which are quite a lot present in the market, almost 10 percent of the drugs are pro drugs. We then followed it up with what we would desire the current drug delivery field to go in direction so, that the patients can have a much better quality of life.

And to go further into that I am introducing some concepts of polymers which are a big part of modern drug delivery fields at least in research and more and more products are coming out in the market for that. So, right now what I am doing is I am building up some of the basic concepts of polymers that will be required as we go along in the course. So, probably in the next 3 or 4 classes we are going to go jump into the core of the drug delivery fields and all of this will be required for that.

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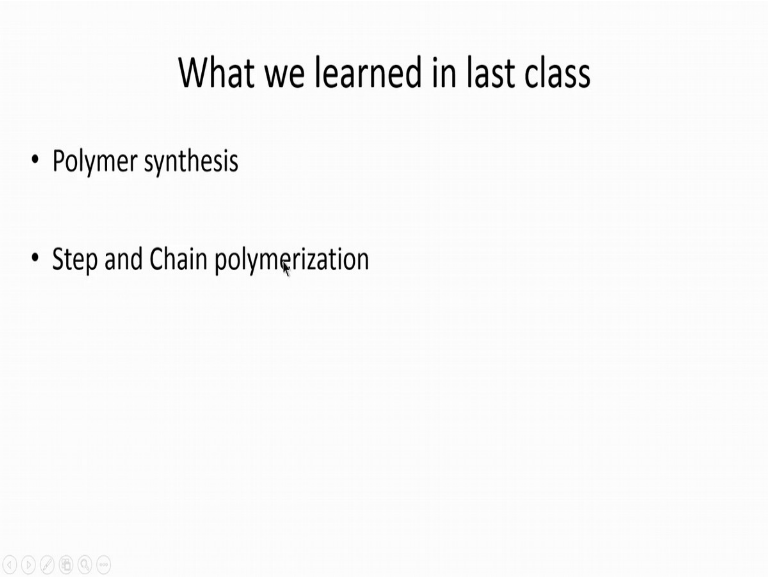

What we learned in last class

- Polymer synthesis
- Step and Chain polymerization

So, let us continue our discussion on polymers. So, what we learned in the last class we talked about the ways for synthesis of the polymers and mainly we discussed about step and chain polymerization, how this is done, what are the advantages and disadvantages and all of that.

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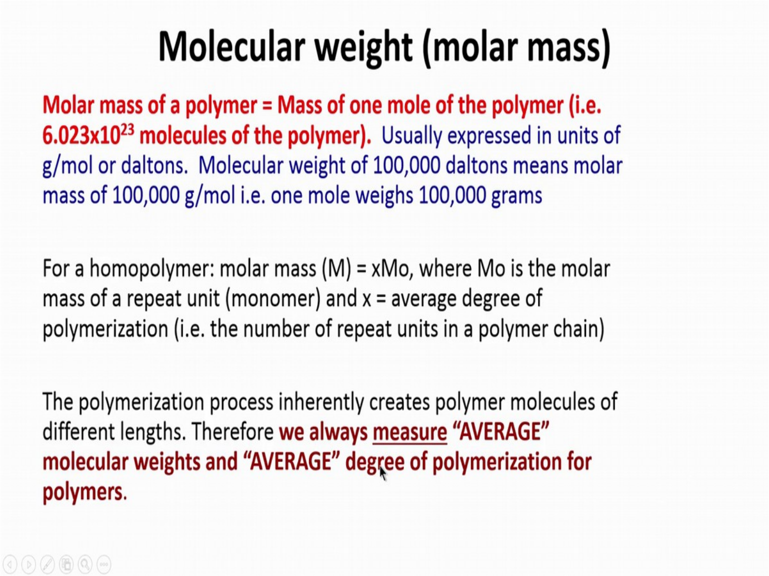

Molecular weight (molar mass)

Molar mass of a polymer = Mass of one mole of the polymer (i.e. 6.023×10^{23} molecules of the polymer). Usually expressed in units of g/mol or daltons. Molecular weight of 100,000 daltons means molar mass of 100,000 g/mol i.e. one mole weighs 100,000 grams

For a homopolymer: molar mass (M) = xMo, where Mo is the molar mass of a repeat unit (monomer) and x = average degree of polymerization (i.e. the number of repeat units in a polymer chain)

The polymerization process inherently creates polymer molecules of different lengths. Therefore **we always measure "AVERAGE" molecular weights and "AVERAGE" degree of polymerization for polymers.**

While we were in the last class this was the slide that we last left it at. So, talking about the molecular weight and as I just said typically in a polymerization you will have an average molecular weight, because the chains will be varying in terms of the molecular weights each of them will have a different molecular weight. So, we quantify this thing called average molecular weights. So, just now we are going to continue this discussion on this molecular weight.

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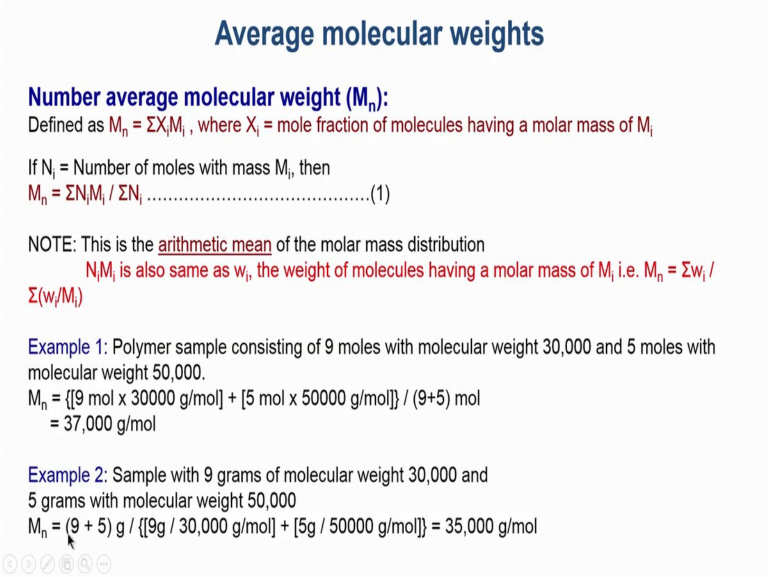

Average molecular weights

Number average molecular weight (M_n):

Defined as $M_n = \Sigma X_i M_i$, where X_i = mole fraction of molecules having a molar mass of M_i

If N_i = Number of moles with mass M_i, then

$M_n = \Sigma N_i M_i / \Sigma N_i$ ....(1)

NOTE: This is the arithmetic mean of the molar mass distribution

$N_i M_i$ is also same as w_i, the weight of molecules having a molar mass of M_i i.e. $M_n = \Sigma w_i / \Sigma(w_i/M_i)$

Example 1: Polymer sample consisting of 9 moles with molecular weight 30,000 and 5 moles with molecular weight 50,000.

M_n = {[9 mol x 30000 g/mol] + [5 mol x 50000 g/mol]} / (9+5) mol

= 37,000 g/mol

Example 2: Sample with 9 grams of molecular weight 30,000 and 5 grams with molecular weight 50,000

M_n = (9 + 5) g / {[9g / 30,000 g/mol] + [5g / 50000 g/mol]} = 35,000 g/mol

So, the average molecular weights in the traditional fields have been defined in several ways, unfortunately this is the case with most of the drug delivery areas where you will find that literature has several different ways to define somewhat the same information that is being given.

So, we need to know all this because when you read papers, when you talk when you read different literature on these you will find different terms being used. So, now, I am going to explain what are the most common terms being used. So, one of them is the number average molecular weight and this is defined as the sum of the mole fractions of the molecule with different molecular weights.

So, if let us say I have 3 different types of chains with 3 different molecular weights in different fractions. So, all I have to do is just multiply the fraction with the molecular weight of these 3 chains and then add them up. So, essentially further let us say this can be changed as if Ni represents the number of moles with mass Mi then the total average molecular weight will be

$$M_n = \Sigma N_i M_i / \Sigma N_i$$

So, note this is the arthmetic mean of the molar mass distribution NiMi is also same as Wi which is essentially nothing, but the weight of the polymer having the mass Mi. So, we can also write the Mn, the number average molecular weight as nothing,

$M_n = \Sigma w_i / \Sigma(w_i/M_i)$

So, just an example so, let us says if I have a polymer sample containing 9 moles with the molecular weight of 30,000 Daltons and 5 moles with a molecular weight of 50,000 Daltons.

Then in this case what will be the number average molecular weight.

$M_n = \{[9 \text{ mol} \times 30000 \text{ g/mol}] + [5 \text{ mol} \times 50000 \text{ g/mol}]\} / (9+5) \text{ mol} = 37{,}000 \text{ g/mol}$

So, essentially we are using this formula so, mole here is nothing, but numbers. So, this is here and then essentially you are dividing by the summation of the total moles which is 9 plus 5, which will give you an average of one number average molecular weight of 37,000.

Let us say in a second example we have a sample of 9 grams of molecular weight of 30,000 and 5 grams of molecular weight of 50,000 in that case we will have essentially we will use the bottom formula which is essentially derived from the first formula

$M_n = (9 + 5) \text{ g} / \{[9\text{g} / 30{,}000 \text{ g/mol}] + [5\text{g} / 50000 \text{ g/mol}]\} = 35{,}000 \text{ g/mol}$

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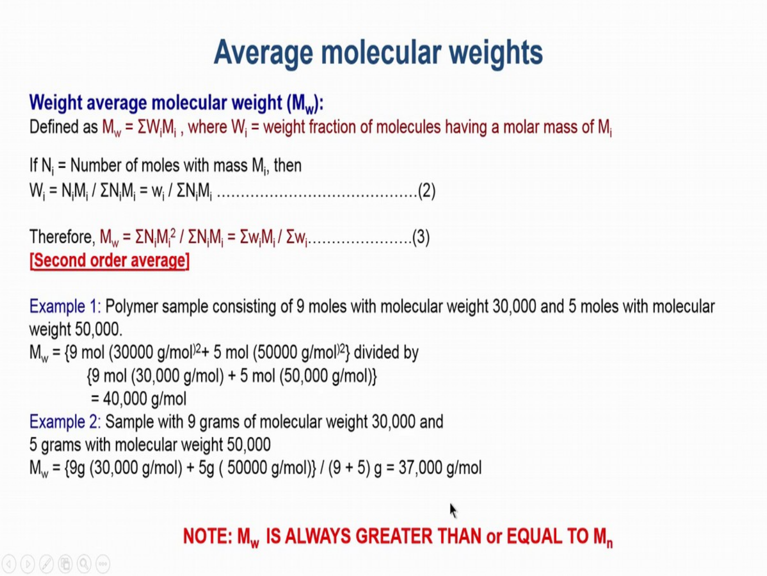

Average molecular weights

Weight average molecular weight (M_w):

Defined as $M_w = \Sigma W_i M_i$, where W_i = weight fraction of molecules having a molar mass of M_i

If N_i = Number of moles with mass M_i, then

$W_i = N_i M_i / \Sigma N_i M_i = w_i / \Sigma N_i M_i$ ....(2)

Therefore, $M_w = \Sigma N_i M_i^2 / \Sigma N_i M_i = \Sigma w_i M_i / \Sigma w_i$.....................(3)

[Second order average]

Example 1: Polymer sample consisting of 9 moles with molecular weight 30,000 and 5 moles with molecular weight 50,000.

M_w = {9 mol (30000 g/mol)^2+ 5 mol (50000 g/mol)^2} divided by

{9 mol (30,000 g/mol) + 5 mol (50,000 g/mol)}

= 40,000 g/mol

Example 2: Sample with 9 grams of molecular weight 30,000 and

5 grams with molecular weight 50,000

M_w = {9g (30,000 g/mol) + 5g (50000 g/mol)} / (9 + 5) g = 37,000 g/mol

NOTE: M_w IS ALWAYS GREATER THAN or EQUAL TO M_n

Another one that is used is a weight average molecular weight and this is different from the number average. This is defined as Mw is the summation of individual weights multiplied by their total mass.

$M_w = \Sigma W_i M_i$

So, molar mass represents a weight fraction and these are the formulas given here this is nothing, but a second order average of the total distribution. So, another example. very similar example to what we had done last time, but this time we want to compute what is the weight average molecular weight. So, we have 9 moles with molecular weight of 30,000 and 5 moles in the molecular weight of 50,000. In that case, all we have to do is multiply the 9 mole with 30,000 square.

And then apply this formula and we will get 40,000, note this is very different from what you got last time where you got close to about 37,000. So, it kinds of highlights that the weight average molecular weight is different from the number average molecular weight and again this can be represented in grams directly this is going to make the calculation much simpler if you have grams there. So, essentially in this case you have to just multiply the grams with the molecular weight and add them up and you get about 37,000. So, as we said note that the Mw is typically always either greater or equal to Mn.

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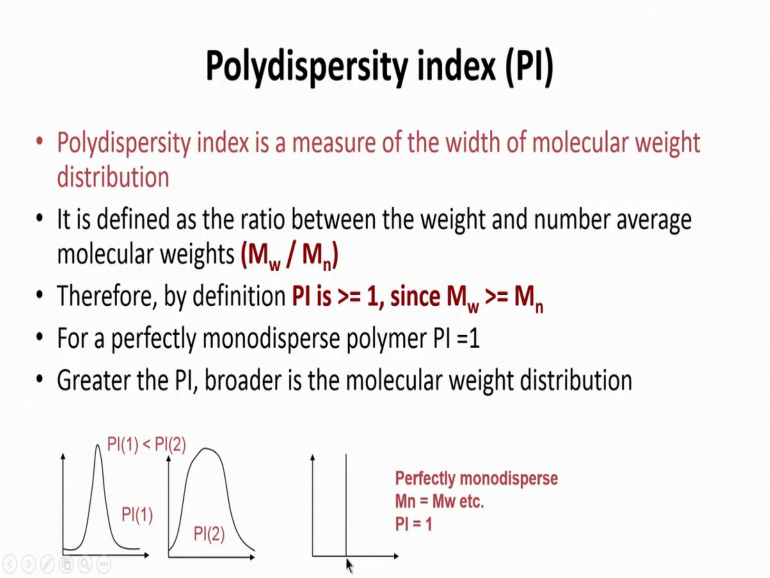

Polydispersity index (PI)

- Polydispersity index is a measure of the width of molecular weight distribution
- It is defined as the ratio between the weight and number average molecular weights **(M_w / M_n)**
- Therefore, by definition **PI is >= 1, since M_w >= M_n**
- For a perfectly monodisperse polymer PI =1
- Greater the PI, broader is the molecular weight distribution

Perfectly monodisperse
Mn = Mw etc.
PI = 1

And this brings us to the polydispersity index which is a measure of the width of the molecular weight distribution in a polymer sample. So, it is defined as a ratio between the weight average molecular weight divided by the number average molecular weight.

PI = $\mathbf{M_w / M_n}$

So, therefore, by definition if the polydispersity index has to be greater than or equal to 1 since we know that the Mw is always greater than or equal to the number average molecular weight.

But if it is a perfectly monodispersed polymer only then you will have the Mw equal to Mn and in that case the polydispersity index will be 1. So, greater the PI, broader is the distribution of the weights. So, typically we want any polymers, we would like these distribution to be narrow because that will help us identify what are the different properties and how the polymers will behave. Higher the PI it is difficult to predict how it is going to behave in terms of it is different properties.

So, as we can see here, in this case we see a fairly monodispersed polymer with a very narrow distribution; however, the other case we see it quite a bit distribution. So, in this case we can say that; obviously, the polydispersity for the 2 is much greater than polydispersity for the 1 and it is of course, absolutely perfect we get a polydispersity of 1 which is a straight line in terms of the curves.

Where do you typically get this? So, typically in all synthetic reactions it is very difficult to get this. But; however, biology systems are very good, typically the proteins that are synthesized by the body are all extremely monodispersed. So, if you quantify any proteins present in the cell in terms of their molecular weight you will get some sort of a distribution which is with the PI of 1 and a straight line in this curve.

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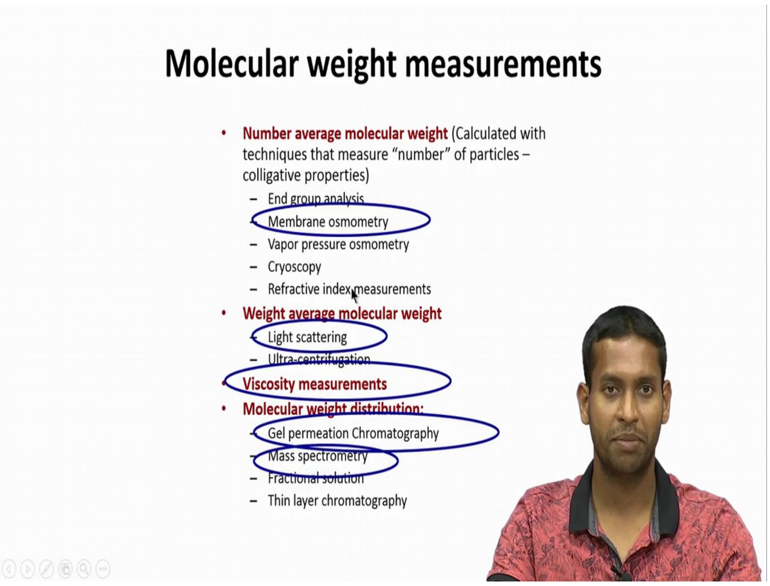

Molecular weight measurements

- **Number average molecular weight** (Calculated with techniques that measure "number" of particles – colligative properties)
  - End group analysis
  - Membrane osmometry
  - Vapor pressure osmometry
  - Cryoscopy
  - Refractive index measurements
- **Weight average molecular weight**
  - Light scattering
  - Ultra-centrifugation
- **Viscosity measurements**
- **Molecular weight distribution:**
  - Gel permeation Chromatography
  - Mass spectrometry
  - Fractional solution
  - Thin layer chromatography

So, how do we measure these molecular weights, I mean; obviously, these were all theoretical values, but how do we know what is the molecular weight of a sample that we are given with. And so, there are a number of techniques to use this and different techniques gives different results, some techniques may give number average molecular weight, while some will give weight average molecular weight.

So, some of these techniques are listed here we are not going to go through all of them, but some of the common ones that we are going to talk about is membrane osmometry, light scattering, viscosity measurements, as well as GPC and mass-spec.

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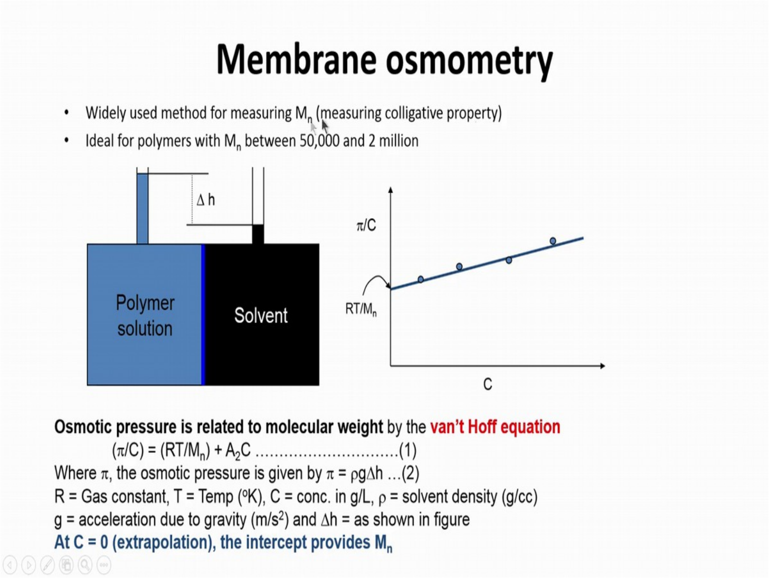

Membrane osmometry

- Widely used method for measuring M_n (measuring colligative property)
- Ideal for polymers with M_n between 50,000 and 2 million

Osmotic pressure is related to molecular weight by the **van't Hoff equation**

$(\pi/C) = (RT/M_n) + A_2C$ ....(1)

Where π, the osmotic pressure is given by $\pi = \rho g \Delta h$ ...(2)

R = Gas constant, T = Temp (°K), C = conc. in g/L, ρ = solvent density (g/cc)

g = acceleration due to gravity (m/s^2) and Δh = as shown in figure

At C = 0 (extrapolation), the intercept provides M_n

So, let us talk about membrane osmometry, this is a very widely used and this gives a measure of the number average molecular weight. So, essentially it is a colligative property and it is typically ideal for polymers in a wide polymer range wide molecular weight range. So, from starting from all the way from 50,000 to millions of a molecular weight. It is fairly simple here, all you do is you have 2 compartments which is separated by a semi permeable membrane that will allow the solvents to move through but will prevent polymer to move through and you can measure the height difference because what will happen due to the osmotic pressure, the solvent will try to reach into the polymer solution to essentially make sure that the osmotic pressure is not there; however, as it further goes in here this is also a height difference so, that creates a reverse pressure as well. So, at some point it stabilizes and you can fit it in the equation from van't Hoff equation we are not going to go into the derivation, but you can use the van't Hoff equation to essentially get a relationship between the height difference here and the concentration of the polymer here.

And this essentially you can then extrapolate to find molecular weight. This intercept here, if you put it in the equation is nothing, but RT divided by the number average molecular weight and since you know R you know T at what temperature the experiment was performed and this line you have experimentally plotted you can get the value of Mn through this intercept value.

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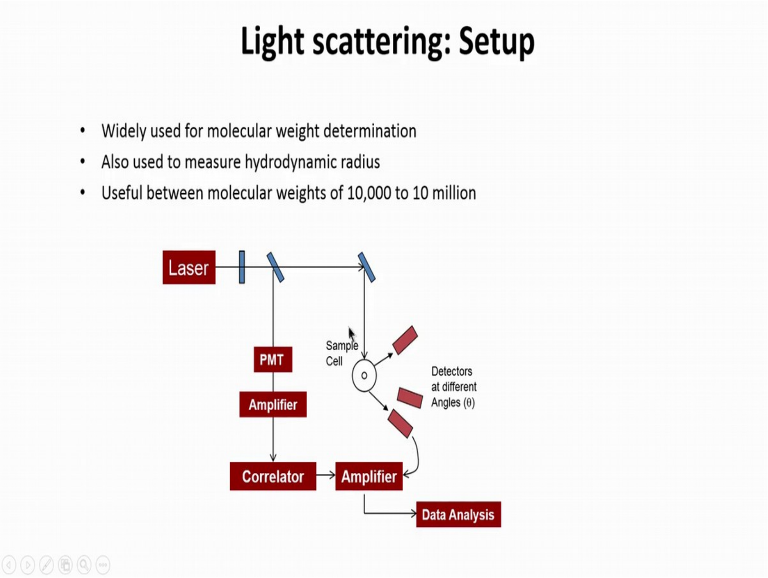

Light scattering: Setup

- Widely used for molecular weight determination
- Also used to measure hydrodynamic radius
- Useful between molecular weights of 10,000 to 10 million

Then there are light scattering-based methods these are representative of the molecular weight determination again these are number average molecular weight and what they typically give you is also an hydrodynamic radius.

So, how big these polymer chains are and not in terms of the molecular weight itself, but in terms of the actual diameter or hydrodynamic radius of them. Typically these techniques work again between wide ranges from all the way from 10,000 to millions of the molecular weight and again we are not go into the details of the electronics here.

But essentially, a sample is put in a laser it is hit on the sample at different angles and the scattered signal is then used to amplify and see how much the polymer sample is scattering and then once these equations are fitted and gives you an estimate of what is the molecular weight that is being present in your initial tube.

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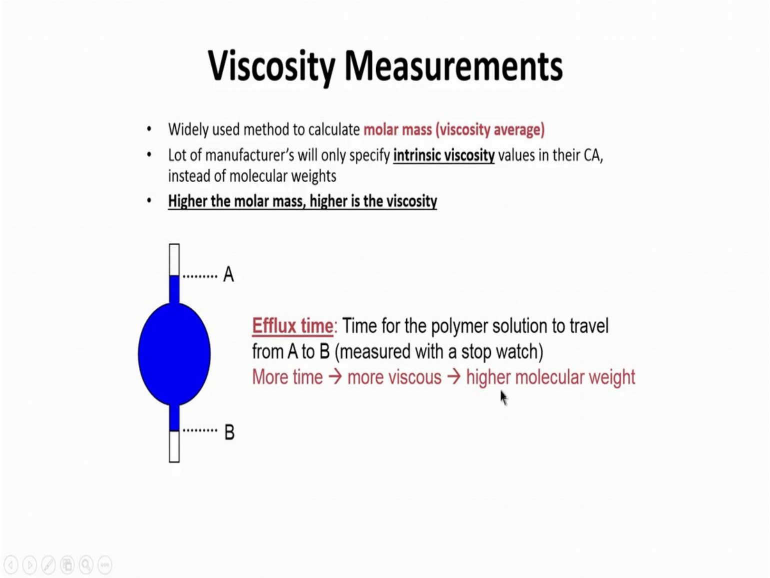

Viscosity Measurements

- Widely used method to calculate **molar mass (viscosity average)**
- Lot of manufacturer's will only specify **intrinsic viscosity** values in their CA, instead of molecular weights
- **Higher the molar mass, higher is the viscosity**

Efflux time: Time for the polymer solution to travel from A to B (measured with a stop watch)
More time → more viscous → higher molecular weight

We can also have viscosity measurements again these are widely used as well. This also represents molar mass. Lot of manufactures will only actually specify intrinsic viscosity and not the molecular weights and generally the relation here is the higher is the molar mass, the higher is the viscosity. Here is a very simple experiment. You fill in solution containing your polymer and you basically time it as to how long it takes from the level to go from A to B and this a efflux time will basically can be used to then measure what is the viscosity. So, more time it takes; that means, it is more viscous which essentially also means that it has a higher molecular weight.

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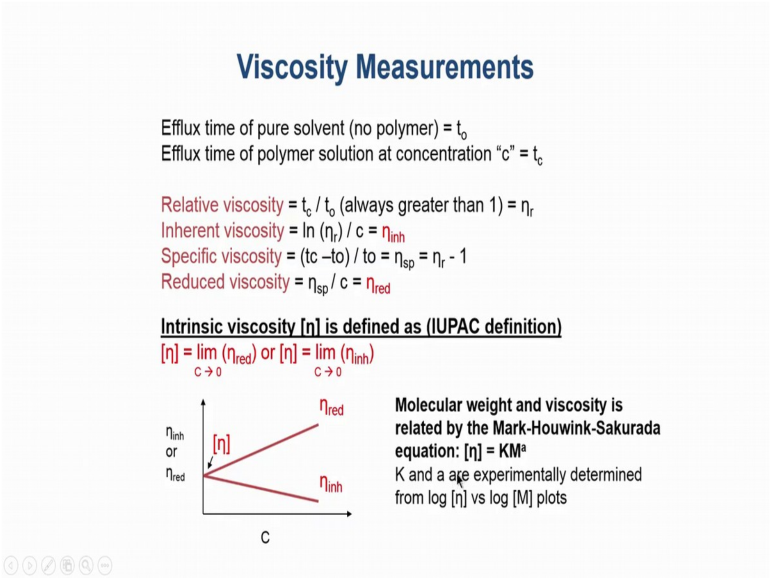

Viscosity Measurements

Efflux time of pure solvent (no polymer) = t_o
Efflux time of polymer solution at concentration "c" = t_c

Relative viscosity = t_c / t_o (always greater than 1) = η_r
Inherent viscosity = $\ln(\eta_r) / c = \eta_{inh}$
Specific viscosity = $(tc - to) / to = \eta_{sp} = \eta_r - 1$
Reduced viscosity = $\eta_{sp} / c = \eta_{red}$

Intrinsic viscosity [η] is defined as (IUPAC definition)

$[\eta] = \lim_{c \to 0} (\eta_{red})$ or $[\eta] = \lim_{c \to 0} (\eta_{inh})$

Molecular weight and viscosity is related by the Mark-Houwink-Sakurada equation: $[\eta] = KM^a$
K and a are experimentally determined from log [η] vs log [M] plots

So, again going further into details here so, let us say if you use a pure solvent the efflux time is t0, once you have the solvent containing a certain concentration c, let us say the efflux time is tc. Then there are several types of viscosity that are mentioned, you can go through these the one that is very widely used is the intrinsic viscosity which can then be computed through this particular method by extrapolating it to the concentration 0 and from the Mark-Houwink-Sakurada equation we know that the intrinsic viscosity is related with M as intrinsic is equal to K multiplied by M to the power of a, where K and a are again experimentally determined through several experiments.

$$[\eta] = KM^a$$

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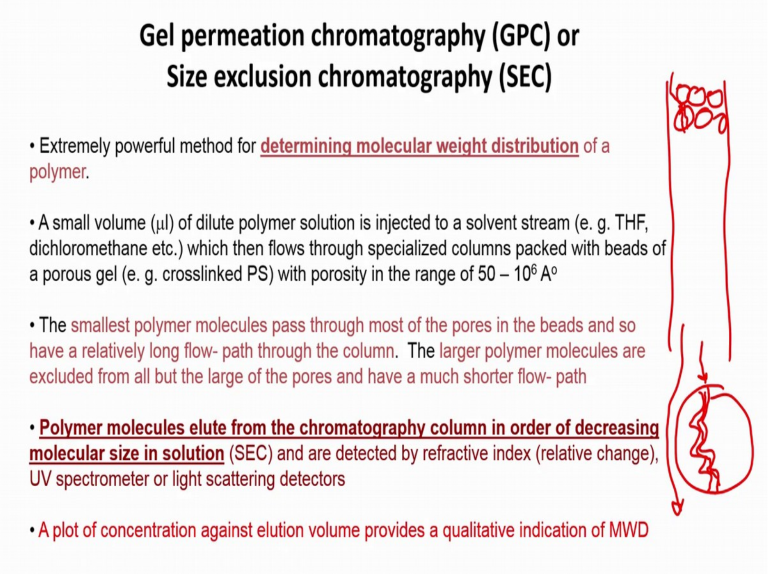

Gel permeation chromatography (GPC) or Size exclusion chromatography (SEC)

- Extremely powerful method for **determining molecular weight distribution** of a polymer.
- A small volume (μl) of dilute polymer solution is injected to a solvent stream (e. g. THF, dichloromethane etc.) which then flows through specialized columns packed with beads of a porous gel (e. g. crosslinked PS) with porosity in the range of 50 – 10^6 A°
- The smallest polymer molecules pass through most of the pores in the beads and so have a relatively long flow- path through the column. The larger polymer molecules are excluded from all but the large of the pores and have a much shorter flow- path
- **Polymer molecules elute from the chromatography column in order of decreasing molecular size in solution** (SEC) and are detected by refractive index (relative change), UV spectrometer or light scattering detectors
- A plot of concentration against elution volume provides a qualitative indication of MWD

And then another very widely used, a very powerful method is the gel permeation chromatography also called size exclusion chromatography and what it is you take small volume of your dilute polymer solution and you inject it into a column that is packed with beads. These are porous gels typically with the diameter in ranges of angstrom and what happens here is, you have a column which is packed with beads, which are porous. So, these beads have small pores going through them. So, if the polymer is small enough to enter these pores the polymer then goes through it. If I zoom into a bead, you have these pores going through these beads and if the polymer is small enough it goes and interacts into these channels and it has to traverse all the way down through these pores. So, whereas, the big polymers will essentially just come and go right through from the outside because they cannot enter these pores. So, what essentially happens is the larger polymer molecules will start coming out first whereas, the smaller polymer molecules will take lot more time because they have a lot more path to cover through these beads.

So, that essentially results in separation of these polymers. So, the first one to elute is the largest molecular weight and then as time goes on smaller molecular weights come out. So, you can then plot concentration against the elution volume, which will give you also a qualitative indication of what is the distribution of these and not only that you can actually then separate them out into different fractions to make sure that you can get different molecular weight fractions. And then that will also result in narrowing of your particular polymer distribution ok.

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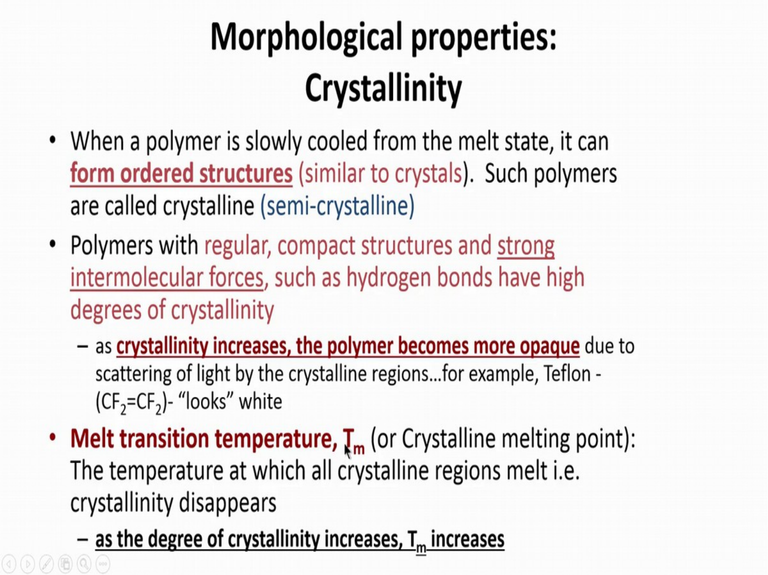

Morphological properties: Crystallinity

- When a polymer is slowly cooled from the melt state, it can **form ordered structures** (similar to crystals). Such polymers are called crystalline (semi-crystalline)
- Polymers with regular, compact structures and strong intermolecular forces, such as hydrogen bonds have high degrees of crystallinity
  - as **crystallinity increases, the polymer becomes more opaque** due to scattering of light by the crystalline regions…for example, Teflon -(CF$_2$=CF$_2$)- "looks" white
- **Melt transition temperature, T_m** (or Crystalline melting point): The temperature at which all crystalline regions melt i.e. crystallinity disappears
  - **as the degree of crystallinity increases, T_m increases**

So, that is in terms the techniques for measuring the molecular weight, next we are going to talk about the crystallinity which is again a very important property when we talk about drug delivery.

So, when a polymer is slowly cooled from a melt state, it typically forms an ordered structure, these are similar to crystals such polymers are called crystalline or they can be semi crystalline. And polymers with the regular, compact structures and strong intermolecular forces like hydrogen bonds or ionic interactions have a very high degree of crystallinity. And essentially what it means is, as the polymer chains are getting attracting more and mor they are coming closer and closer and packing very well and that results in the polymer being highly crystalline.

So, as crystallinity increases the polymer becomes opaque, because the chains are very close now and it does not allow the light to pass through, it causes scattering of the light so, something like Teflon will look white because of this reason. And if you heat this polymer up, what will happen is more and more heat energy will go into this polymer sample and there will be temperature Tm which is called a melt transition temperature, at which all the crystalline regions are melted and the crystallinity disappears.

So, as the degree of crystallinity increases so, if you have more and more intermolecular interactions between the chain, the melt transition temperature also increases.

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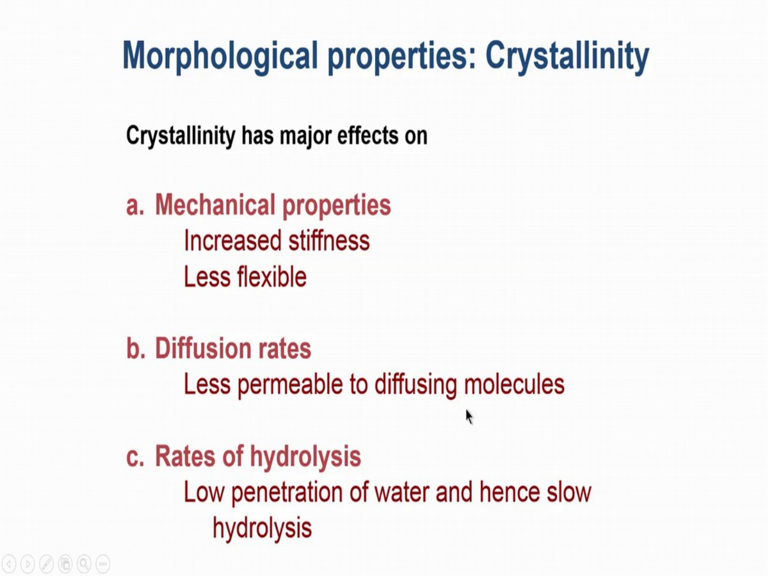

Morphological properties: Crystallinity

Crystallinity has major effects on

a. Mechanical properties
    Increased stiffness
    Less flexible

b. Diffusion rates
    Less permeable to diffusing molecules

c. Rates of hydrolysis
    Low penetration of water and hence slow hydrolysis

So, the crystallinity can have major effects on several properties, it will change the mechanical properties because more crystalline it is the more compact these chains are. So, increased stiffness and it will become less flexible. The diffusion rates will change, because now these chains are very tightly packed. So, because they are so, tightly packed it will be less permeable to allow diffusion of molecules through it.

The rate of hydrolysis will change, because now even the water will find it hard to go in and break these interactions apart. So, the rate of hydrolysis will also become slower.

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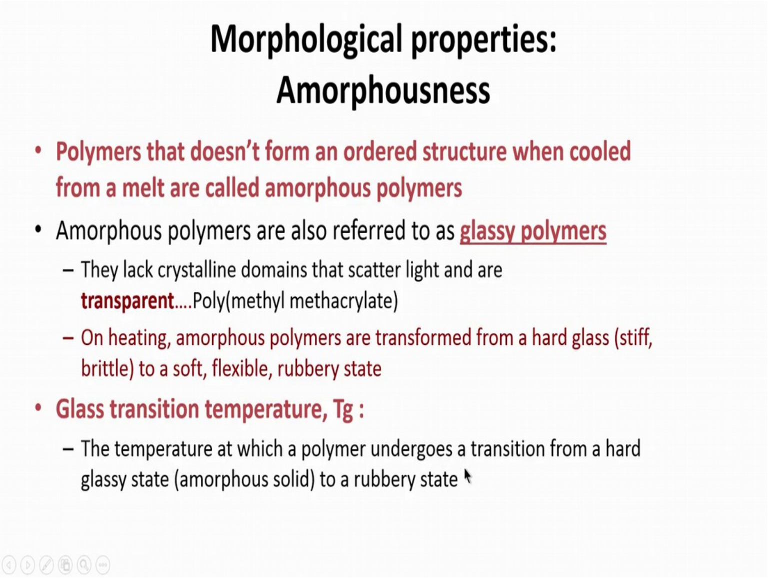

Morphological properties: Amorphousness

- Polymers that doesn't form an ordered structure when cooled from a melt are called amorphous polymers
- Amorphous polymers are also referred to as glassy polymers
  - They lack crystalline domains that scatter light and are **transparent**....Poly(methyl methacrylate)
  - On heating, amorphous polymers are transformed from a hard glass (stiff, brittle) to a soft, flexible, rubbery state
- Glass transition temperature, Tg :
  - The temperature at which a polymer undergoes a transition from a hard glassy state (amorphous solid) to a rubbery state

And then like crystallinity, there is also amorphousness and not all polymers exhibit crystallinity. So, they are polymers that are amorphous so, some polymers does not really form any order structure, even though you can cool them down from melt state and these polymers are called amorphous polymers.

And they sometimes are also referred to as glassy polymers and they essentially lack any kind of crystalline domains and that scatter light so, they are typically transparent. On heating, amorphous polymers are transformed from a very hard glass which is a transparent to a very soft, flexible, rubbery state which is just molten chains flowing around.

And loss of this amorphous structure to more a rubbery flexible state is called glass transition temperature. So, at this temperature it will go from hard glassy state to a much more rubbery state. So, very similar to Tm, but this is more defined for amorphousness.

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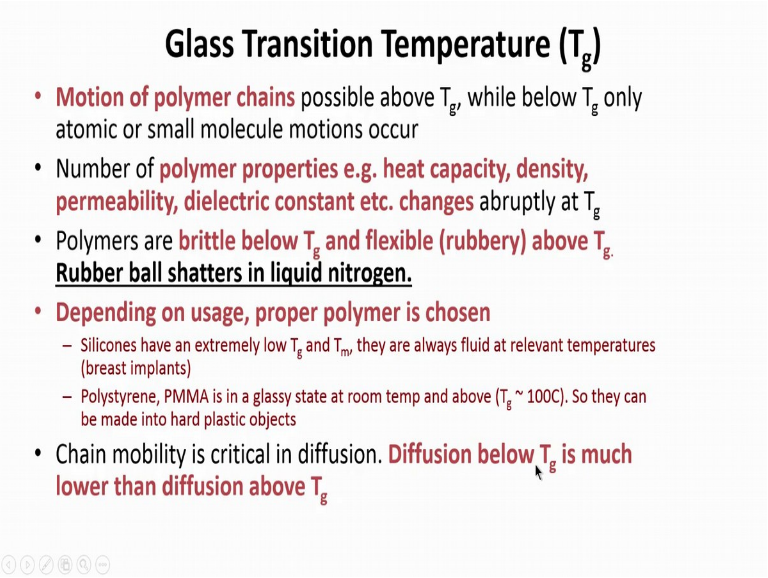

Glass Transition Temperature (T_g)

- **Motion of polymer chains** possible above T_g, while below T_g only atomic or small molecule motions occur
- Number of **polymer properties e.g. heat capacity, density, permeability, dielectric constant etc. changes** abruptly at T_g
- Polymers are **brittle below T_g and flexible (rubbery) above T_g.** **Rubber ball shatters in liquid nitrogen.**
- **Depending on usage, proper polymer is chosen**
  - Silicones have an extremely low T_g and T_m, they are always fluid at relevant temperatures (breast implants)
  - Polystyrene, PMMA is in a glassy state at room temp and above (T_g ~ 100C). So they can be made into hard plastic objects
- Chain mobility is critical in diffusion. **Diffusion below T_g is much lower than diffusion above T_g**

So, again how does this glass transition temperature affects properties. So, since the motion of polymer chains will increase above Tg, because it is now become rubbery above the glass transition temperature, you will have lot more motion lot more diffusion through it. It will change lot of properties like heat capacity, density, permeability, dielectric constants, they all chain very abruptly at Tg.

Polymers are typically brittle below Tg. So, good example is a rubber ball if you cool it down with let us say with liquid nitrogen and try to throw it with the impact it will just completely shatter where as, otherwise if it is above the Tg which is at room temperature even if you throw the rubber ball down it is fairly elastic and it will not break.

So, depending on the usage, proper polymers can be chosen. So, let us say if you are looking for breast implants you want those to be more rubbery, more elastic. So, silicones are used which have extremely low Tg and Tm and so, they are always fluid at the body temperature with 37 degree Celsius. And similarly polystyrene PMMA these are glassy state at room temperature and so, they are hard if you heat them up above 100 degree Celsius, they are essentially much more fluidic.

So, chain mobility is again very critical for diffusion. So, below Tg the diffusion is much much slower compared to above Tg.

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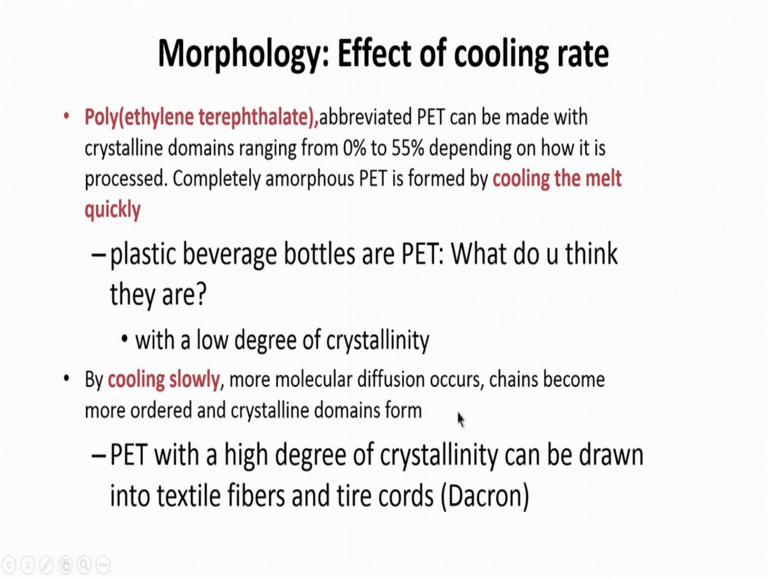

Morphology: Effect of cooling rate

- **Poly(ethylene terephthalate),**abbreviated PET can be made with crystalline domains ranging from 0% to 55% depending on how it is processed. Completely amorphous PET is formed by **cooling the melt quickly**
  - plastic beverage bottles are PET: What do u think they are?
    - with a low degree of crystallinity
- By **cooling slowly**, more molecular diffusion occurs, chains become more ordered and crystalline domains form
  - PET with a high degree of crystallinity can be drawn into textile fibers and tire cords (Dacron)

These are ideal circumstances typically in the nature you would not find polymers which are completely crystalline or completely amorphous, they typically exhibit both to a certain extent. So, an example here is the polyethylene terephthalate, which essentially is abbreviated as PET, and this has several crystalline domains depending on how it is cooled.

So, you can have as much as from 0 percent to 55 percent crystallinity depending on how this is being formed. So, if you cool it very quickly it will result in very amorphous structure, if you give it some time in cooling, very slow cooling let us say half a degree Celsius per hour or something like that. The chains will have enough time to come in contact with each other, interact from strong interactions and result in crystalline structure all the way up to 55 percent.

So, plastic beverage bottles are PET, so, do you what do you think are they crystalline or are they amorphous? So, remember what did I tell you earlier regarding what happens to the light scattering, in general how elastic and soft it becomes. So, yes since we know that these plastic bottles are transparent they cannot be crystalline because crystalline structures scatter light and do not let the light to pass through so, they will be more opaque.

So, the plastic bottles as we know are transparent made of PET so, it has to be amorphous, with a low degree of crystallinity. So, by cooling slowly you can get more ordered crystalline domains. So, the same PET you can get with a high degree of crystallinity which is then used in textile fibers and tire cords and the same one can also be used in plastic bottles, the only difference is how fast they are cooled.

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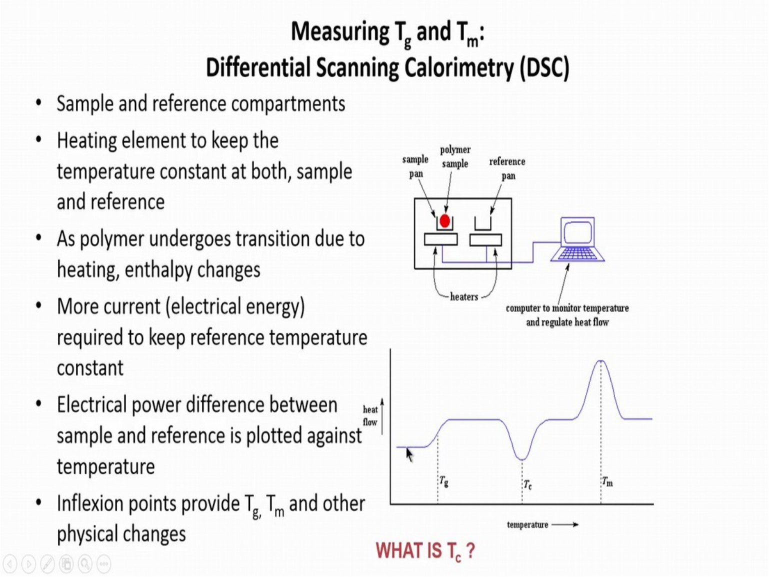

Measuring T_g and T_m: Differential Scanning Calorimetry (DSC)

- Sample and reference compartments
- Heating element to keep the temperature constant at both, sample and reference
- As polymer undergoes transition due to heating, enthalpy changes
- More current (electrical energy) required to keep reference temperature constant
- Electrical power difference between sample and reference is plotted against temperature
- Inflexion points provide $T_{g,}$ T_m and other physical changes

WHAT IS T_c ?

And then finally, how do you measure what is the Tg and Tm of a polymer sample that you are given. So, this is regularly done using differential scanning calorimetry. And so, what is done is, you have a reference pan and you have a sample pan with the polymer and you measure how much heat is being given to each of those and figure out the Tg and Tm on the basis of that.

So, as polymer undergoes transition due to heating so, essentially what will happen is, the heat is flowing the temperature is increasing as more and more heat is flowing, at the Tg, it will cause a lot more absorption of heat to essentially melt these chains. The heat flow increases then it becomes constant again and then when it is close to Tm you need further induction of heat so, that the polymer chains can then be separated from the intermolecular forces, so it goes further up.

So, these transition points you can then determine for all the samples that you have and that will give you an idea of Tg and Tm. A quick note here is what do you think is Tc?. So, this we already discussed, but what is Tc? So, Tc is nothing, but because you are slowly heating it up from the transition from here to here, this is a point where more and more intermolecular chains are coming in contact. Here, the sample was cold and so, these molecular chains had no interactions because they were solid, but at this point these molecular chains can now move around, they become glassy and these can then interact and essentially form crystalline structure which when further heat is given, then breaks apart and essentially leads to the Tm temperature being reached. So, I am going to explain this curve further this is not a trivial curve.

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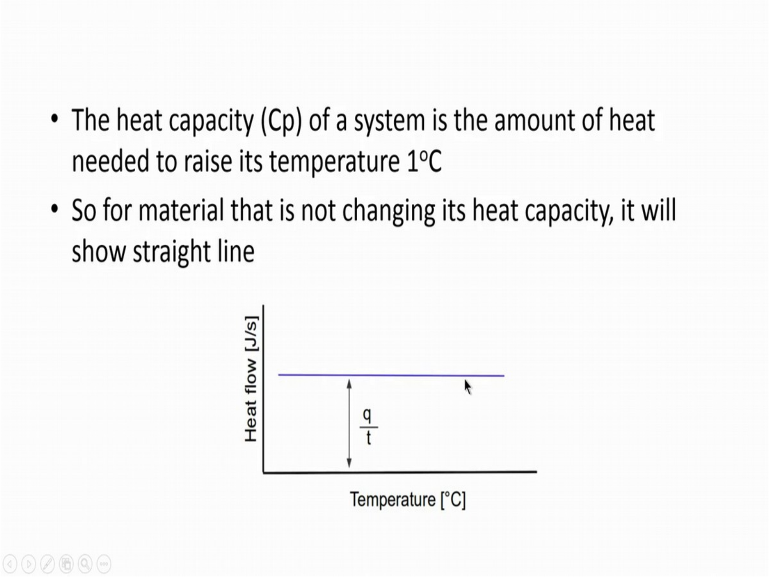

- The heat capacity (Cp) of a system is the amount of heat needed to raise its temperature 1°C
- So for material that is not changing its heat capacity, it will show straight line

So, let us see. So, the heat capacity of a system is the amount of heat needed to raise it is temperature by 1 degree Celsius. So, if the material is not changing heat capacity this curve will look like a straight line right, because you are giving constant energy per second and then the temperature will continue to increase by 1 degree Celsius at it is particularly heat capacity. So, in an ideal circumstances, you should have a straight line like this, typically metals show this.

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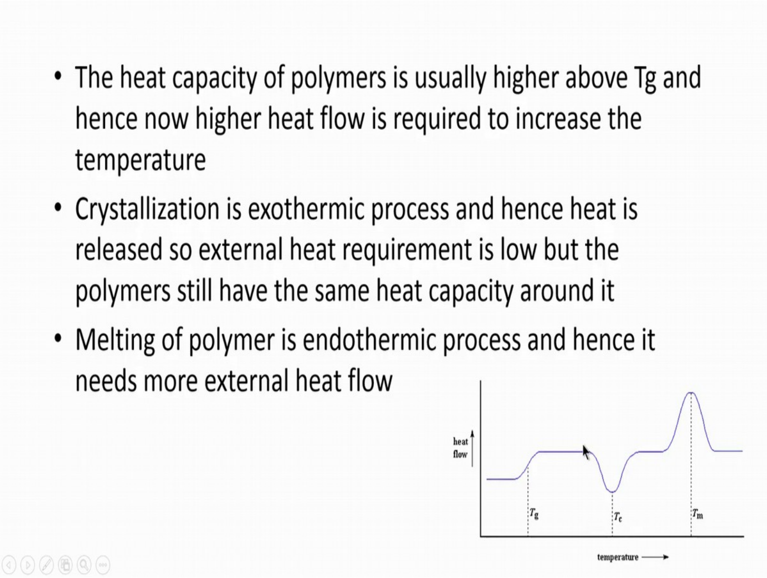

- The heat capacity of polymers is usually higher above Tg and hence now higher heat flow is required to increase the temperature
- Crystallization is exothermic process and hence heat is released so external heat requirement is low but the polymers still have the same heat capacity around it
- Melting of polymer is endothermic process and hence it needs more external heat flow

However, we know that the heat capacity of the polymers is usually higher above the Tg and so, that is why you see that initially it is a straight line. At Tg more heat is required, so, it takes up more to basically melts it and then the resulting polymer is above Tg and so, it has a higher heat capacity. So, that is why you need more this differential that you get is because, now the temperature has changed its property, it is heat capacity as well.

And then the crystallization is an exothermic process so, now these chains are coming in contact with each other and forming bonds it could be Van der Waal, it could be a hydrogen bonds and this releases heat and because it releases heat it does not need any external heat flow that we are giving. So, the external heat flow requirement comes down, but once the chains have formed it goes back up. So, if we are still talking about the same polymer with the same heat capacity so, it is still at the same level.

And now as you go along the melting of the polymer chains to break them apart you need to give further energy, because earlier they had released energy now to give the further energy to break them apart. Hence so, this needs to go up and by this time it becomes completely mobile and you have constant heat flow required to raise the temperature. So, I hope this is now clear as to how this works.

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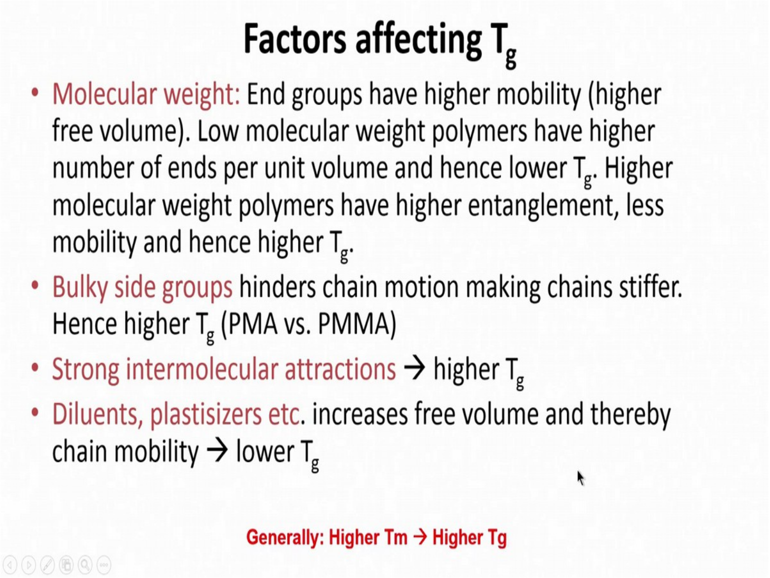

Factors affecting T_g

- Molecular weight: End groups have higher mobility (higher free volume). Low molecular weight polymers have higher number of ends per unit volume and hence lower T_g. Higher molecular weight polymers have higher entanglement, less mobility and hence higher T_g.
- Bulky side groups hinders chain motion making chains stiffer. Hence higher T_g (PMA vs. PMMA)
- Strong intermolecular attractions → higher T_g
- Diluents, plastisizers etc. increases free volume and thereby chain mobility → lower T_g

Generally: Higher Tm → Higher Tg

So, what are the different factors that affect Tg. So, molecular weight is one of the major factors because in a polymer chain the end groups are the ones that are highly mobile and see if you have low molecular weight for the same amount of polymer, you have lot more polymer chains and so, they have lot more energy to move around and so, you will have a lower Tg. But if you have a higher molecular weight these chains can entangle and that will result in a higher Tg.

If you have bulky side groups that will hinder chain motion, if it hinders change motion it will increase the Tg. So, if you have PMA what is this PMMA, PMMA is nothing, but an extra methyl that is present on the PMA chains. So, which one of this will have the higher Tg? It will be PMMA, because it is now having another CH3 that will hinder the motion of this chain.

If you have a strong molecular attraction between them you will have a higher Tg, because now they will tend to interact with each other and will essentially decrease the motion. If you add diluents and plasticizer at the time of these polymer heating, this increases free volume and thereby the chain mobility will increase. So, this is one of the ways that you can lower the glass transition temperature of a particular polymer.

And generally if it is higher Tm, it basically means that that polymer will also have higher Tg.

So, we will end right here and we will now in the future classes we will go more into biomedical polymers. So, this is a general discussion we gave on what polymers are, now we are going to specify into what is the properties for the biomedical polymers, bio engineering polymers that we will use for drug delivery. So, see you next time.

Thank you.