Polymer Chemistry
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Lecture - 33
Determination of Molecular Weight of Polymers (Contd.)

Welcome back to this course on polymer chemistry. In today's lecture, we will continue our discussion which we started on determination of polymer molecular weight.

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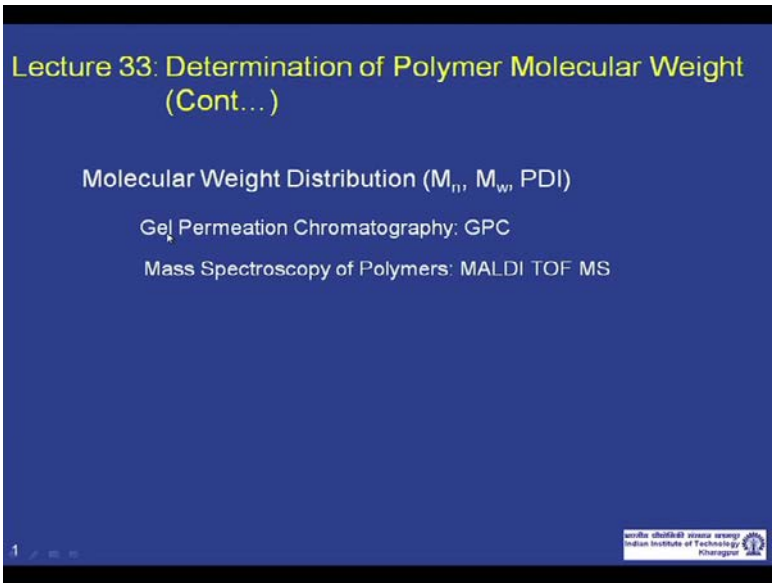

And today basically, we will continue our discussion; we had started on gel permeation chromatography or size exclusion chromatography and then briefly discussed mass spectroscopy of polymers in particularly MALDI TOF MS.

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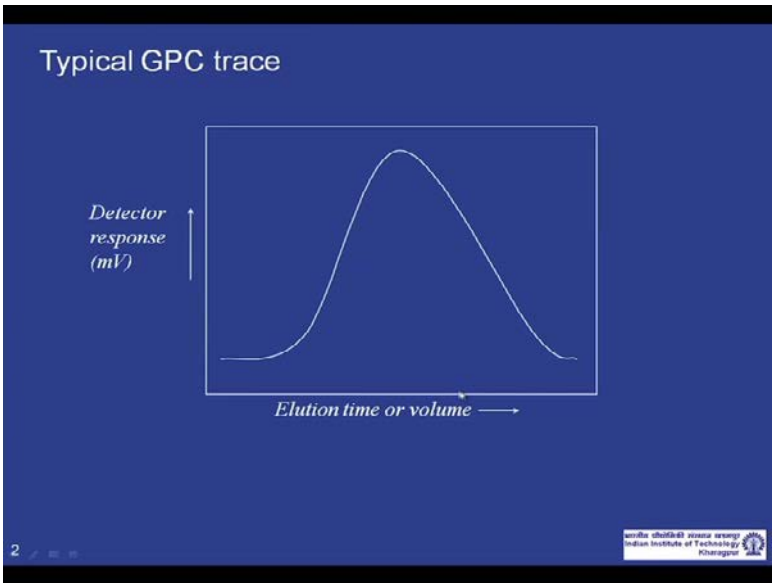

Now, this is the last slide we had stopped in last lecture. Now, this is the typical GPC trace where in the y axis you have detector response and in x axis typically you have elution time, and which can easily become what is in to elution volume. Now, if you want to convert elution time to elution volume, there should be the pump, which are getting used in the GPC equipment should be pulse free and it should be able to maintain a steady flow typically around 1 ml per minute.

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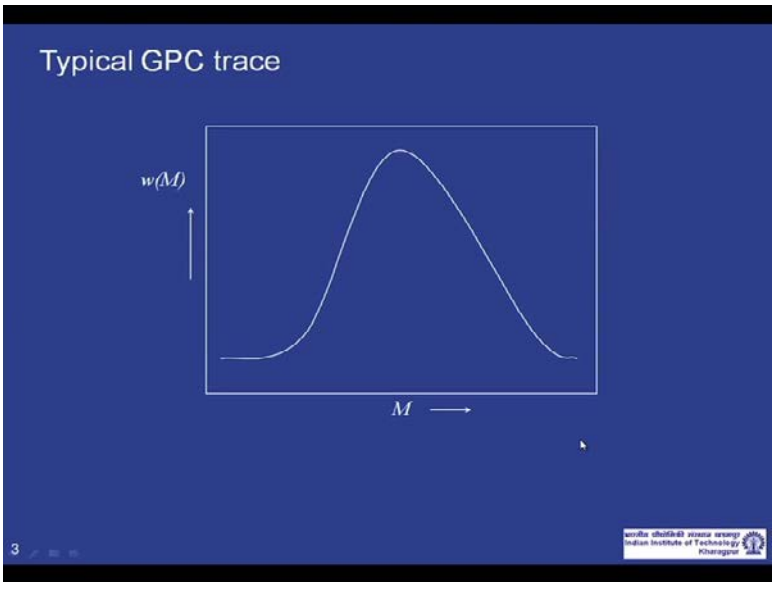

Now, from this raw data we must transform this data as a weight fraction molecular weight distribution which is a plot of weight fraction versus molecular weight.

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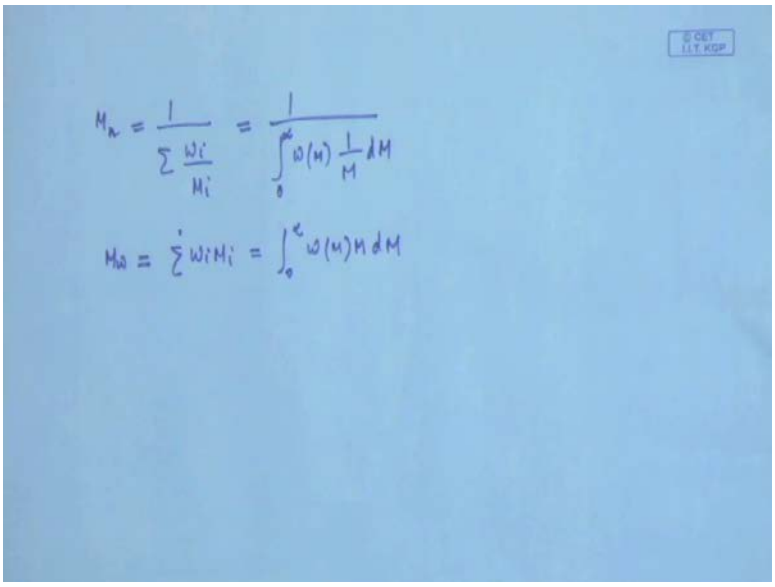

The requirement for this type of transformation is this, because we know the definition of M n is given by where w is the weight fraction of a polymer chain having molar mass of M i and we can express this in terms of an integral form like this. So, basically we need to plot this weight fraction distribution against molecular weight to integrate this which will give us M n.

Similarly, M w weight average molecular weight can be obtained from the formula. So, basically this is example of M n and M w expressed in integral form; this shows why we require the raw data to be transformed in this type of weight fraction molecular distribution with plot of weight fraction versus molecular weight. Now, to do that, let us first look at the principle of the separation in gel permeation chromatography.

Remember, we have discussed in the last lecture that you have in gel permeation chromatography the polymers are passed through a columns containing beads which have definite pores. So, when polymer samples is injected in to this column then the solvent takes away or carries this polymer molecules to the detector and this pores which are in the column are responsible for the separation it brings about.

Now, what happens? How the separation happens? The flow rate we typically work the GPC's work like in the range of 1 ml per minute. It is has been that the elution volume does not depend up on the flow rate which means that the polymer samples are not carried away or dragged away by this solvent molecules; the polymer molecules basically equilibrate between the pores inside and outside, and the higher molecular bonds are resides most of the times outside the pores whereas the smaller molecular what are more size polymer molecules they partition more inside the pore volume; thus taking longer time to elute.

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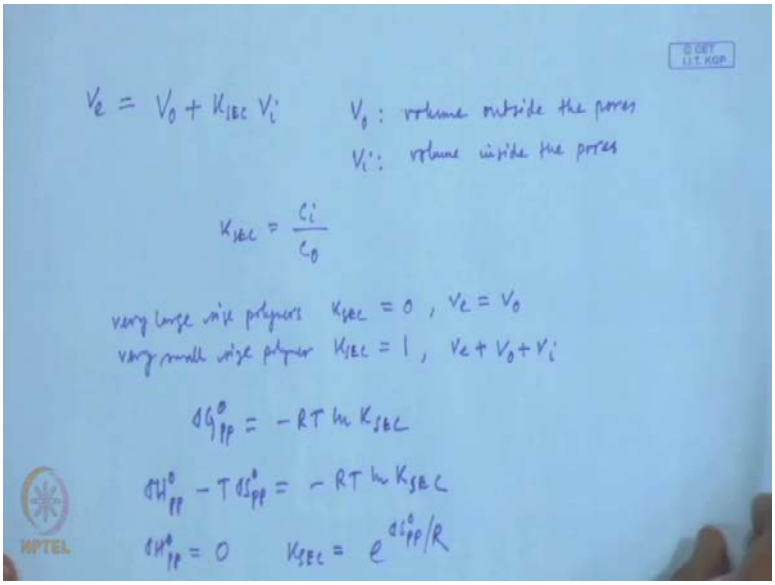

If we express this mathematically little bit and see what is happening. See if we consider the elution volume V e for a particular polymer sample as V 0 plus K s c into V i where V 0 is the volume outside the pores whereas, V i is the total volume inside the pores; and K is K s c is the equilibrium constant which basically is given by the concentration of the polymer sample inside divided by concentration sample outside the pores.

So, for very large size polymer chains which has a larger size does not penetrate in the pore size. So, K s c is 0. So, V e is given by the outside volume and if the polymer is low, the size is very small then almost exclusively they will enter the pores and K s c will be 1 which gives us V e is V 0 plus V i. So, K s c is basically the equilibrium constant between the concentrations or because of the partition of polymer molecules inside the pores and outside the pores.

Now, from our thermo dynamical knowledge we can simply write the delta G 0 p p is for pore penetration is given by RT l n this equilibrium constant and del G can be written as del H 0 p p enthalpy and T delta S 0 p p. Now, as we know that in gel permeation chromatography there is no interaction between the polymer molecules and the pores or the column there is no interaction between them. So, the value of del H for pore penetration must be 0. Hence K s c would be given by e to the power del S 0 p p by R.

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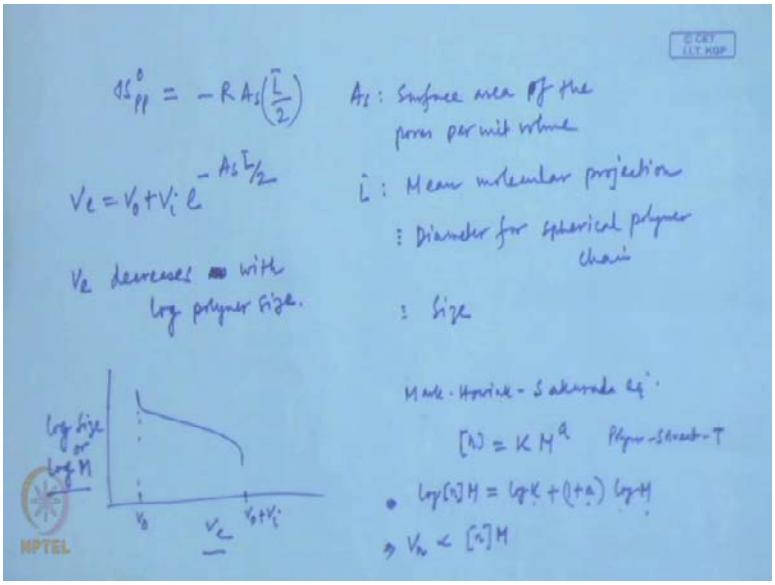

Now, for a flexible chain it can be statistically shown as this entropy for pore penetration given by this expression where A s is surface area of the pores per unit volume and L dash is the mean molecular projection which is basically given in to diameter for spherical polymer chain which is basically related to size of the polymer. Now, as you can think that when a polymer molecule goes inside the pores the conformational entropy of the polymer chain get reduced, because the sum of the conformations which requires the central mass to be very closer to the rigid walls of this pores are forbidden which means the conformational entropy of the polymer molecules reduced or get decreased when a polymer molecule goes inside the pores.

And this reduction of entropy becomes more permanent if you have a large size polymer or if you have a small size pore. So, this entropy of pore penetration is always negative and it becomes more negative if the polymer size grows or the pore size becomes smaller; and that is expressed by this expression where if the pore size becomes smaller

A s goes up; hence the entropy becomes more negative; similarly, if the polymers size goes up this becomes higher and this entropy becomes lower.

So, if you look at this expression here and we know K s c is this and ESR is this. So, we can simply write from these two, V is V 0 plus V i e to the power minus A s L dash by 2. So, this is the expression we can write and which shows that V e decreases as decreases with log of polymer size; log of L hence polymer size. So, this expression tells us that V e decreases linearly with the polymer size goes up V will go down.

So, you can expect a linear relationship. So, if we plot log of size against V e you can expect that to be a linear graph. Now, from Mark Houink and Sakurada equation we know that intrinsic viscosity given by K M to the power a where K and a are constant for a particular polymer solvent temperature combination. So, I can write log eta M is log K plus 1 plus a log M.

Now, remember from our discussion in solution behavior of polymer molecules a polymer size which is basically hydrodynamic volume V h proportional to eta M. We have seen this relations before; hence we can expect from this and this relation, and whatever we have seen here that log has if the K and a remains constant, log M should linearly decrease with elution volume or V e.

So, we expect that instead of log size if we plot molecular weight we can get linear relationship between V e where elution with the size log M goes up, V e decreases. Now, this two regions are the exclusion limit and they are the cut off for the two regions where the size goes up beyond this molecular weight then none of the polymer chains can go in. So, they will have elution volume of V 0 and if polymer size becomes lower and lower, and becomes such a low that all of them can penetrate equally in the pores then all will come at the same time, and this become V 0 plus V i.

So, this is the linear region where the polymers get separated. So, basically from this discussion we can understand that a plot of log M versus elution volume should give a linear relationship and V e should decrease with increase in the log M. This is what is found in practice when you inject different molecular weight or sample in the GPC column we do actually see that the elution volumes becomes decreases linearly with log M.

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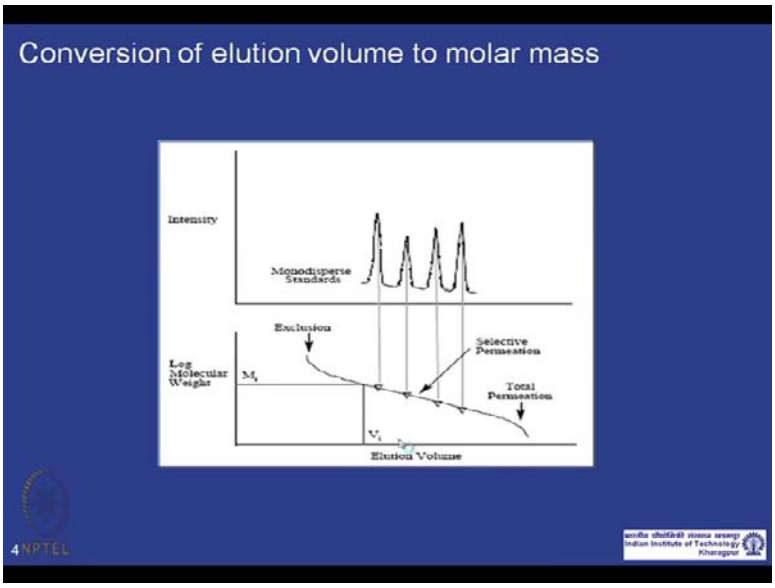

And this has been taken advantage to make a calibration curve where known standard very mono dispersed polymers sample which are very low poly dispersity like in this case four samples are shown here.

So, they are injected and their elution volumes are recorded and likewise calibration curve is constructed by injecting many mono dispersed polymer sample. So, from this calibration curve we can easily convert this elution volume to log molecular weight data. So, this is the way calibration is done for a GPC; several mono dispersed polymer sample with known molecular weight are injected in the column and their elution volumes are plotted against log of molecular weight, and such as linear plot is constructed.

So, we can remember what the purpose we were trying to convert this raw data to distribution plotting weight fraction versus molecular weight. Now, from the calibration curve we can convert the elution volume to the molecular weight.

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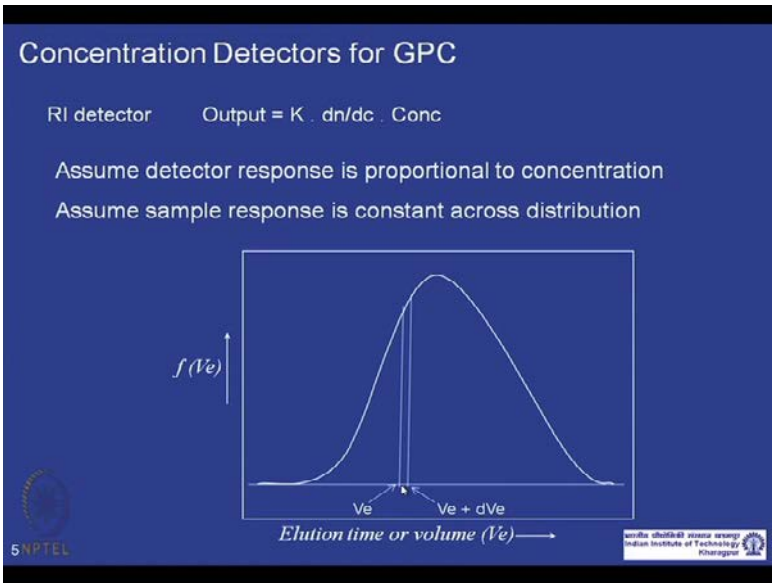

Now, what about the detected signal? Now, for example, if we take a RI detector then this output of this detection signal is proportional to the concentration.

Typically, we use concentration detector. So, the output signal in this detector is proportional to the concentration and if we assume that detector response is proportional to the concentration in the range we are working, and also this response does not depend on molecular weight. The output will be similar for a given concentration of different molecular weight. So, if we assume that the output does not depend on the concentration, not on the polymer molecular weight; this is the detector signal and this is the elution volume V e.

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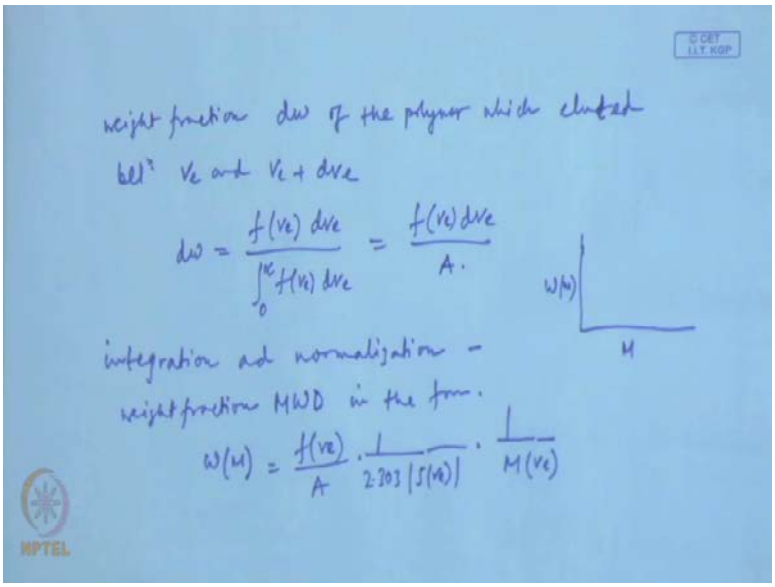

So, we can simply write the weight fraction d w of the polymer which eluted between V e and V e plus d V e; we can consider the sample this slice which is very infinitesimal slice. So, that weight fraction which eluted the polymer between this V e and V e plus d V e. So, this is again let me repeat this d w is the weight fraction of the polymer chains which eluted between V e and V e plus d V e.

So, this is the weight fraction between the polymer which eluted and they can be written like this where a is the area under this curve; and if we do interrogation and followed by normalization we can get this weight fraction molecular weight distribution in the form. So, this is mathematically we can do and this wet fraction distribution can be expressed by this formula where this is the detector signal at V e, and this is molecular weight which we got from the calibration curve for this particular V e, and S V e is the magnitude of the slope for this log M versus elution curve plot for that particular point V e.

Now, we do not have to do ourselves; now a days fortunately software's are available which can take this and give us this output of this type of output they can give and from which using the formula which we used at the beginning. So, these are the formulas for M w and M n, we have seen in the beginning of this lecture. So, now, we know what is w M? How the weight fraction distribution varies with molecular weight? So, once we know that with the help of the software this things can be easily calculated.

So, we know that from the raw data of GPC trace we can get the number of distribution and weight average molecular weight, and weight molecular rate, and we can also get the other M z, and from the values of K and we can get K v also.

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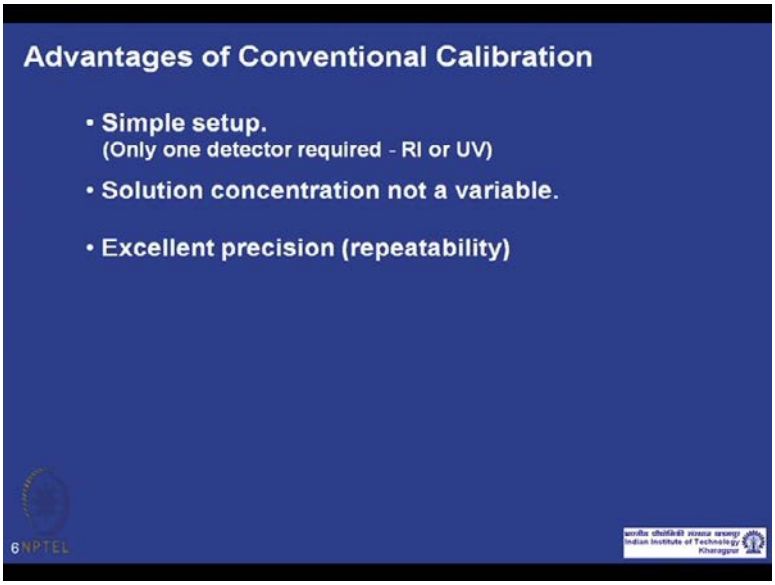

So, let us go back and talk more about the calibration. Remember, we did calibration in we have taken mono dispersed standard; standard means half molecular weight and standards, and then injected, and according to their elution volume, and then for the calibration cut we have plotted log M versus V e elution volume.

There are few advantages like this is a simple setup, only one detector is required whether it is a refractive index detector or only one concentration detector and we can do this calibration without knowing exact concentration; concentration can be variable little bit without no problem and this calibration is very precise and repeatable.

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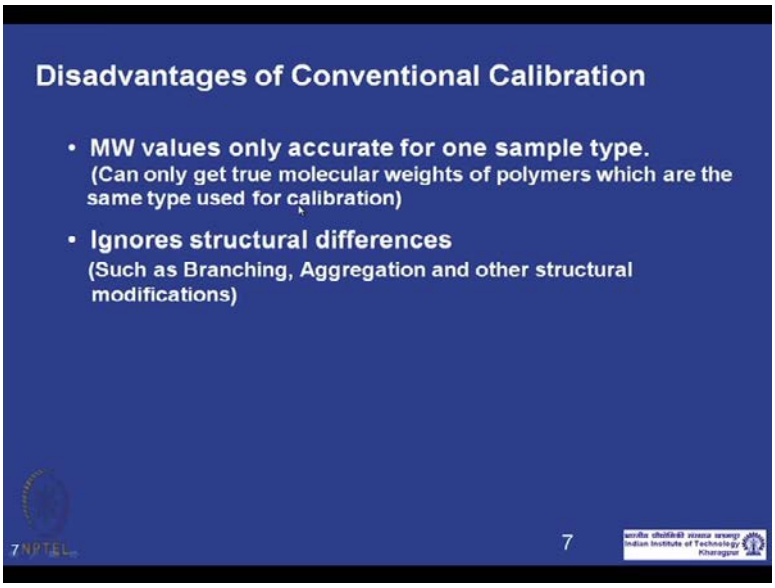

However, there are many disadvantages for this conventional calibration. For example, if we go back and look at this formula remember, we said that as long as this K and a are constant we can write log m instead of log size to construct this calibration curve.

So, if the value of K and a changes, and that will change for a different polymer even if we keep the solvent same and temperature same; if we change the polymers the value of K and a will change; value of K and hence the intrinsic viscosity will change. So, we will get different curve for a different polymer. So, these calibration curve between log m log of molecular weight and this elution volume is applicable only for a particular polymer whose K and a are constant.

Whenever we change K and a for a different polymer; obviously, we get a new set of calibration. So, this calibration can be obtained used to get a true molecular for weight of polymer. So, this calibration can be used to get true molecular. So, the polymer which are same type used and calibration. So, for example, calibration is done for polystyrene then using this calibration curve we can determine the molecular weight of polystyrene sample only, because the K and a value will remain same for polystyrene only.

Instead of polystyrene, if we change it to polycarbonate then K and a value will change. So, we cannot use this calibration curve, but most of the times we may we use one set of calibration curve for lot of other polymers which gives us error may be 0 to 30 percent error in terms of the molecular weight. The reason that we cannot get the calibration

curve made for all the polymers, because we cannot get narrow dispersed polymer for all types of polymers; specially, for coordination polymers, for polycarbonate polyesters, polyamides that is very difficult to synthesize narrow dispersed polymers which SPI is 1.1 or less than that it is very difficult; and unless we have a narrow dispersed or mono dispersed samples which can be retry standards we cannot use this for calibration. Hence, this calibration is mostly done with a mono dispersed synthesized with a precise mono dispersed molecular weight like living anionic polymerization.

Typically, this polystyrene, polymethylmethaacrolate they are used as standards for organic solvents, organic soluble polymers and the molecular weights for other polymers are reported agility to polystyrene or polymethylmethaacrolate and for aqua soluble or water soluble polymers; the standards typically used are say polyethylene oxides which also can be synthesized at very narrow or mono dispersed standards. So, typically the water soluble monomers are reported relative to polyethylene oxides standards. Second disadvantage is that if the polymers are different in branching like different shapes like branching or other structural modification we cannot also get that difference captured in the calibration.

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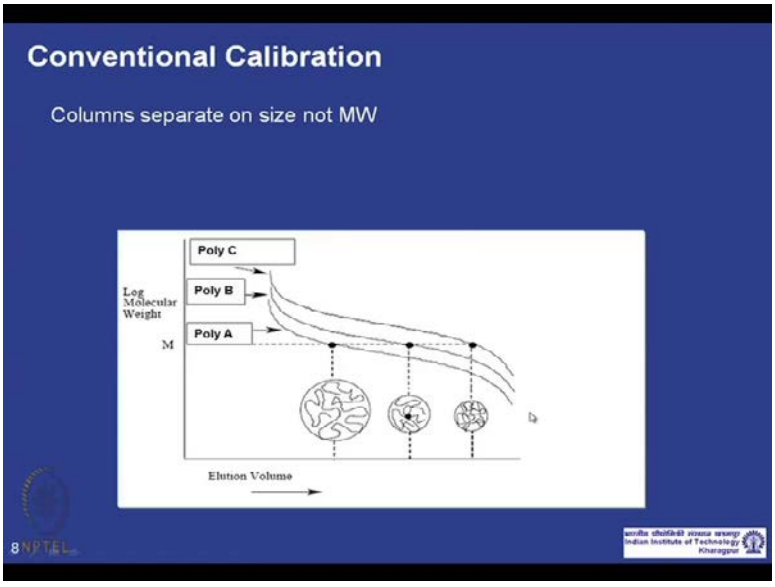

Let us go back and explain with those graphs like if you have repolymers as I explaining for a given molecular weight their sizes could be different depending up on the value of K and a intrinsic viscosity, and they can form a different calibration curve. So, if you use

a calibration curve which is constructed for polymer A and use the same calibration curve for polymer B then these error will be erratic; that is what we are explaining till now.

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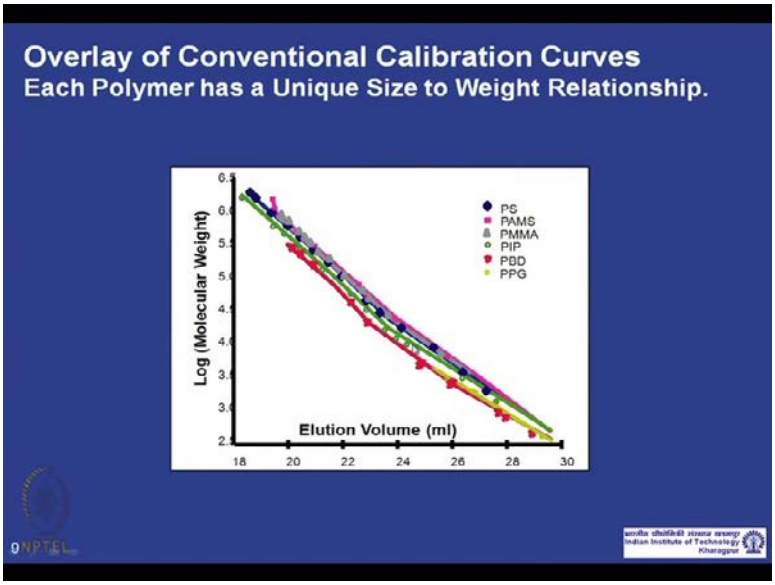

This is the real example where several polymers are plotted and you can see this each polymer has a different caliber has a unique size to weight relationship. So, if we use one calibration for the other sample there will be error.

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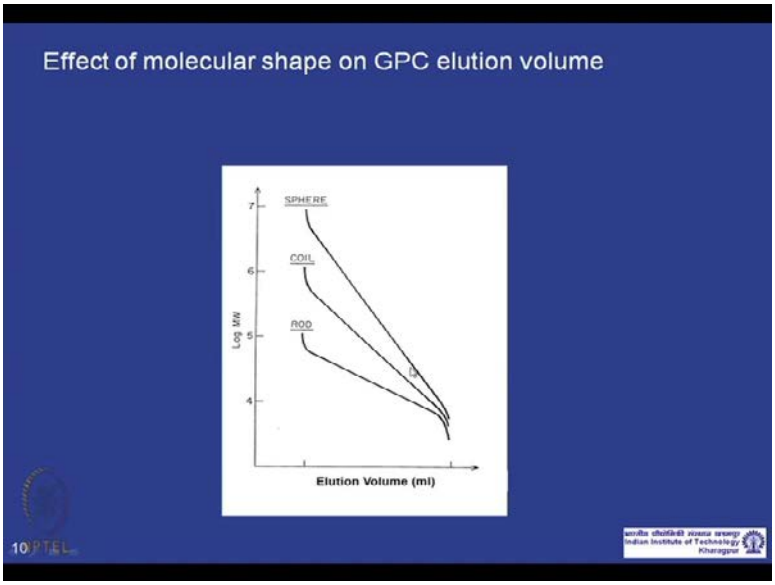

This is what we are talking about the molecular shapes. Now, for a given molecular rate, if you consider one molecular weight here and keep the molecular weight, and change the shapes like from raw to coil to sphere; obviously, this sphere will have lowest size then coil then rod.

So, obviously, the elution volume will defer according to size. For a given molecular weight, the shape of the polymer changes like from rod to sphere to coil then the molecular size changes and the elution volume is related molecular size not molecular weight; hence, the elution volume also changes. So, this calibration if it is done for linear polymer we cannot use that for other shaped polymer like branched polymer which will have different shape.

So, there are two advantages we must remember using this calibration once that this is always reported with some non-standards gather always some error and if the calibration cub is done with linear polymers if we find or determine molecular weights of other shapes using that calibration cub there will be also error.

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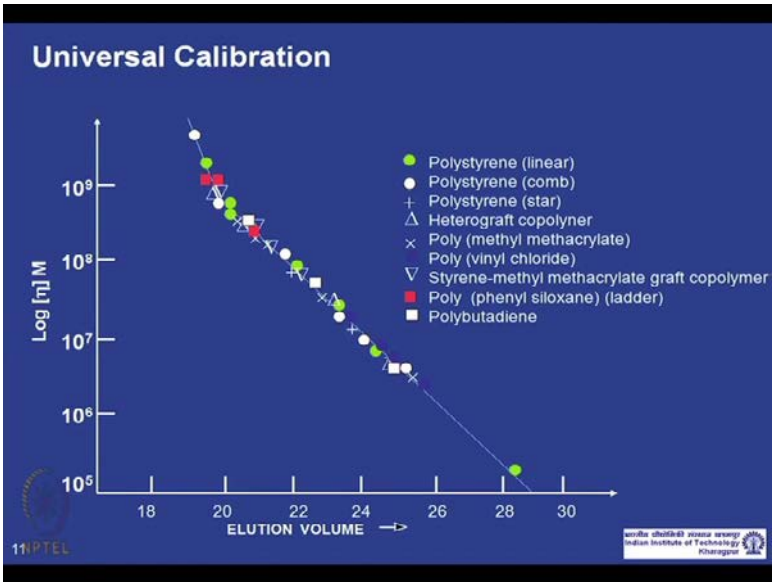

So, what is done? To avoid this remember, we talked about again that V h polymer size is proportional to intrinsic viscosity multiplied by molecular weight. So, if you can find out intrinsic viscosity is a polymer then plot of log eta M, because this gives the polymer size and this elution volume.

So, now this is independent of which polymer you are using as long as we are using log of eta multiplied by molecular weight that gives the size of the polymer whether it is a different shape polymer or different type polymer. So, you get a universal calibration curve. So, if you can construct with one of the polymers say polystyrene then the molecular weight of the other polymer can be also determined using this calibration curve; as long as we know the intrinsic viscosity for the polymers we are using and the elution volume from our GPC curve.

So, as long as we know the intrinsic viscosity of the polymer sample we are using and the elution volume of the sample; using this universal calibration curve we can get the molecular weight which is fairly accurate.

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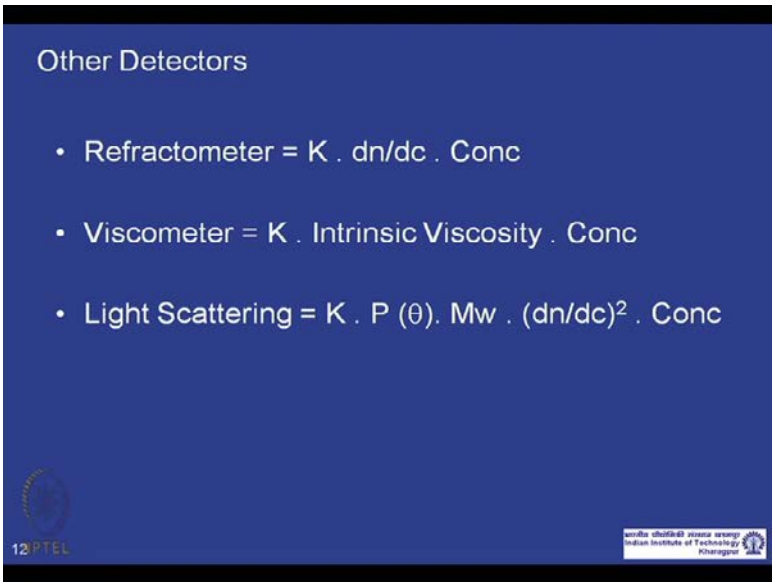

Now, there are other detectors which can be used now a days modern GPC equipment used like viscometer which can detect the intrinsic viscosity on line in a real time and light scattering detector which can determine the weight average molecular weight online, which basically gives us the scope to find out this molecular weight distribution in actual sense.

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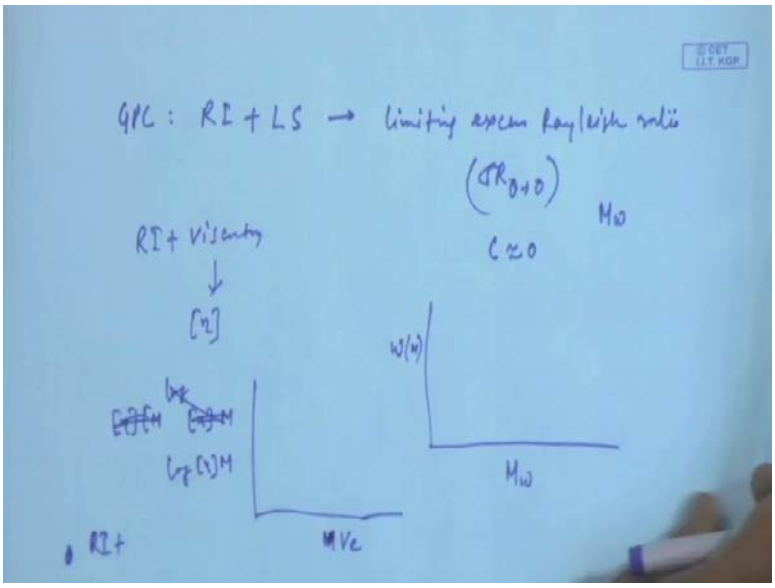

For example, if we have GPC with RI plus light scattering detector, the light scattering gives us the limiting excess Rayleigh ratio delta R theta is equal to 0 and if you are working a very dilute solution we can consider concentration c is equal to 0. So, from this two, we can get as the samples elute; we can get the molecular weight data in real time and from RI detection detector we can get the wet fraction automatically. So, we do not need a calibration curve if we have an absolute molecular weight detector like the light scattering detector. So, that we can get a molecular distribution; similarly, if we have RI plus viscosity then viscosity real time gives the eta value and then we can use the inverse of calibration curve to find out this molecular weight distribution.

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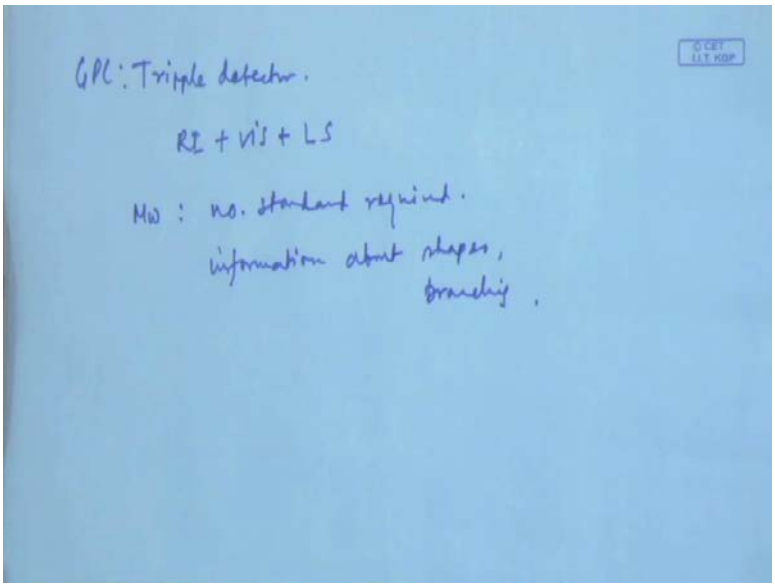

So, GPC with Tripple detector RI plus viscosity plus LS light scattering, we get molecular weight no standard require you can get absolute molecular weight. And we also get information about say shapes of the polymer branching etcetera also can be obtained from these detectors. These are the modern detectors available in the market.

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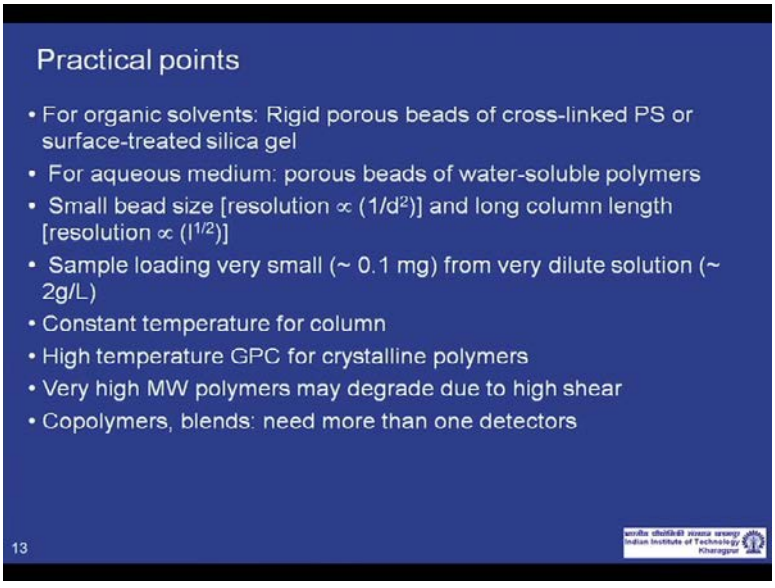

So, with this we come to the end of discussion on gel permeation chromatography. Before that let us go through few practical points and for example, for organic solvent

the beads are typically used as cross linked polystyrene or surface-treated silica gel and for aqueous medium porous beads of cross linked water soluble polymers are used.

The peak resolution is proportional to 1 over d square. So, basically the bead size grows up the resolution becomes inferior. So, it is always preferable to get a smaller width size; for example, nowadays it is 5 micrometer or 10 micrometer at largest we use in actually to get a better resolution. The resolution also depends on the length of the column, but not as much as the size diameter of the beads; it is depends on length l to the power half. So, if you increase the length of the column the resolution goes up. So, preferably we use longer column; typically in normal sense, we actually use few column in series and some cases to make the process faster; we mix bed type columns are used where you have the columns are made with different pore size and you can use two such or three such mix bed columns in series or a single different pore size columns also in series.

Obviously, as you have seen this temperature plays a more important. So, it is preferable that the column is kept in a constant temperature; obviously, the sample loading is small from a very dilute solution; specially, when you are using detectors like light scattering and viscosity there we are assumption the solution is very dilute. So, that we can consider the specific viscosity divide by c as an intrinsic viscosity and the molecular obtained by light scattering; there will be less error.

High temperature GPC's are required for crystalline polymer; crystalline polymers are not typically soluble in room temperature. So, they are dissolved at a high temperature and the column and the escaped at a higher temperature, and the separation is performed at that higher temperature. So, we typically use this term high temperature GPC for that; and very high molecular weight polymers typically more than 6; Dalton they are sometimes 6 gram per mole type polymers might get the inside the column, because generation of high shear. So, we should be careful in using very high molecular weight in determining very high molecular weight in GPC. And if you have computed system like copolymers blend, we require more than one detector to fully characterize to fully determine molecular weight of those.

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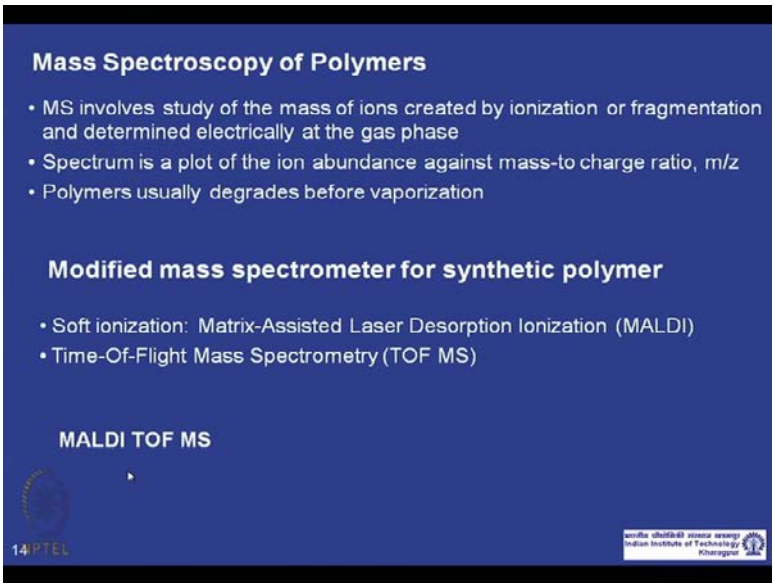

Let us move to the next topic; this is the molecular mass spectroscopy of polymers. Now, we know that in mass spectroscopy which basically involve the study of mass of an ions and created by ionization of fragmentation, and then determine the electrically at the gas phase. For example, a molecule is vaporized and then ionized, and then these ions are taken to the detector, and the molecular weight is obtained. Now, while vaporization the molecules may also get, because it is a high temperature to process the molecules can get degraded also.

But for small molecules which have all the molecules have same molecular weight fragmentation does not matter, because the highest molecular ion will represents the molecular or will give the molecular weight for the small molecule or the molecules; but in case of polymer, one polymer sample consist of many chains of different lengths or different molecular weight. So, if the polymer while vaporization is gets fragmented or degraded then while we get the molecular ion distribution, we do not know the distribution is because of the fragmentation or degradation of the high polymer chain or because of the actual presence of the low molecular weight chain in the samples. So, that it becomes complicated. So, if you are considering polymer sample this fragmentation of the polymer chain during the vaporization will give you lot of error and that is not acceptable. So, we must have some mechanism whereby which the polymers can be vaporized without having any degradation or fragmentation of polymer chain.

So, what is the modification done to get the mass spectroscopy polymers; one soft ionization mechanism is used where will come in a minute using matrix assisted laser desorption ionization or MALDI by which the polymers are vaporized with the help of a matrix without degradation and we also use the second technique called time of flight mass spectroscopy; and in combination of these two techniques we get MALDI TOF MS matrix assisted laser desorption ionization, time of flight mass spectroscopy which is nowadays very important or very common for polymer samples. So, we will discuss a little bit of MALDI TOF now.

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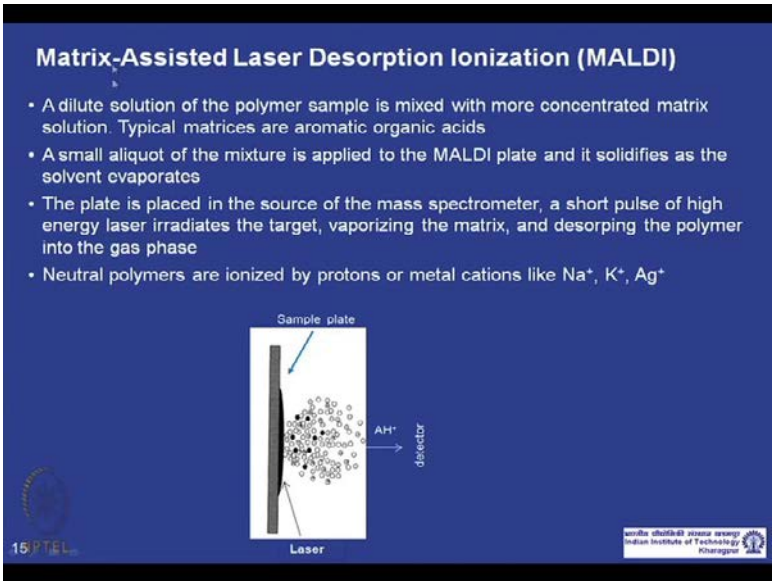

Let us discuss the MALDI matrix assisted laser desorption ionization. In this case a dilute solution of polymer sample is mixed with a concentrated matrix solution and the matrix typically of organic acids. So, basically we make a dilute solution of polymer and they mix with a very concentrated solution of the matrix which are typically organic acids, and a small alicut from this mixture is taken, and applied to the mass spectroscopy plate, and it solidifies as the solvent vaporizes. So, the small alicut is taken from the mixture and applied to MALDI plate and it solidifies as the solvent evaporates.

The plate is placed in a source of mass spectrometer and a short pulse of high energy if this is a must sample plate, and this is your sample along with the matrix; and a short pulse of high energy laser is irradiates the target, vaporizing the matrix when a high energy lasers irradiates with the polymer sample along with the matrix gets vaporized

and in the vapor phase the polymer actually desorbs from the matrix, and if the polymer is ionized already a charged polymer is fine; if it is not charged, it is a neutral polymer then we have to add some salt to cationise this polymers. So, that they can move towards the detector.

So, the neutral polymers are ionized or cationized by protons or metal cations like sodium, Na plus, K plus or say silver plus. So, this the name as the name suggest we take assistance of a matrix to vaporize by help of a laser radiation and in the vaporized states the polymers gets dissolved from the matrix and then get ionized. So, this name MALDI comes from there.

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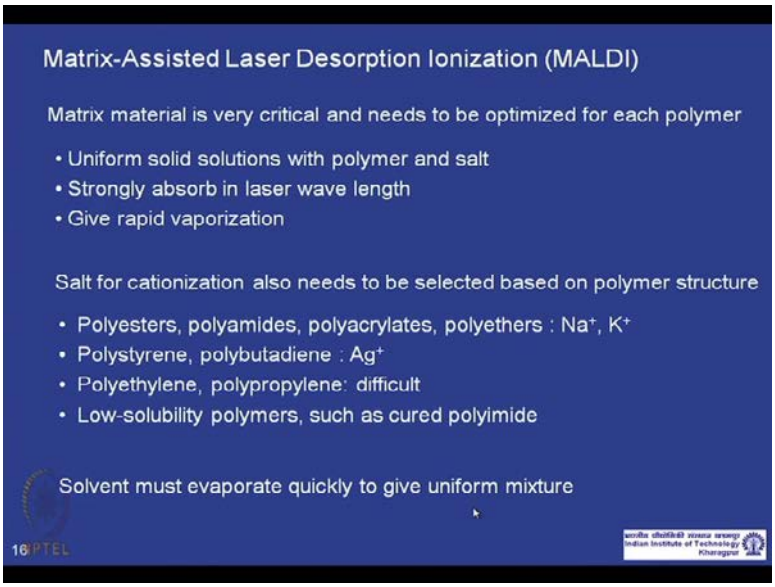

So, in MALDI, choosing of matrix is very critical and it needs to optimize for every polymer samples. It must form uniform solutions with the polymers and the added salt; it must strongly absorb the laser wavelength. So, that the vaporization be taken place and it should give rapid vaporization. The salt you know we said that neutral polymers need that distance from the salt to become cationize and for example, this polyesters, polyamides, polyether's whereas, hetero atom; salts like sodium, potassium, lithium's are used, because these cations are alkyl metal cations can attach with this hetero atom and cationize this polymer.

The polymers having unsaturations, the silver cation can be used; it can actually complex with the pi bond; for example, polystyrene, polybutadiene this polymer cation can be

used. For oliphinic polymers like polyethylene, polypropylene, it is very difficult to find a cation which might complex with these oliphinic polymers; it is very difficult to cationize and then analyze this polymers by MALDI; and water soluble polymers already which does not soluble in a solvent is also very difficult. The solvents must be chosen in such that if you evaporate quickly to give a uniform mixture of the polymer matrix and the salt should quickly evaporate and give the salt.

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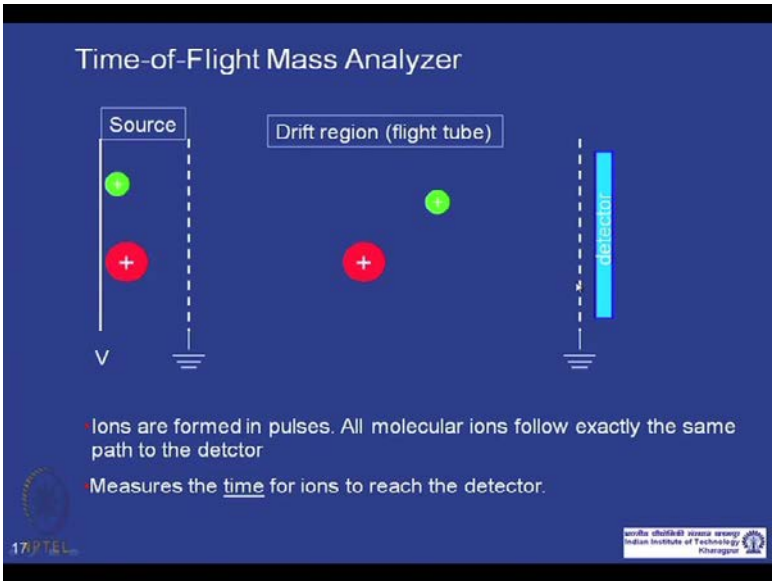

Let us talk about the mass analyzation time of flight mass analyzer which is basically the source for the mass spectrum source where the matrix is vaporized and polymers are ionized, and then they are taken to the detector, and in this case the time of flight mass analyzer; the every cation they actually travel same path all the molecular ions travel same path to a detector and the detector measure the time which the ions take to reach the detector; the heavier ions would take more time to reach the detector where lighter ions; obviously, will take a lower time move faster to the detector.

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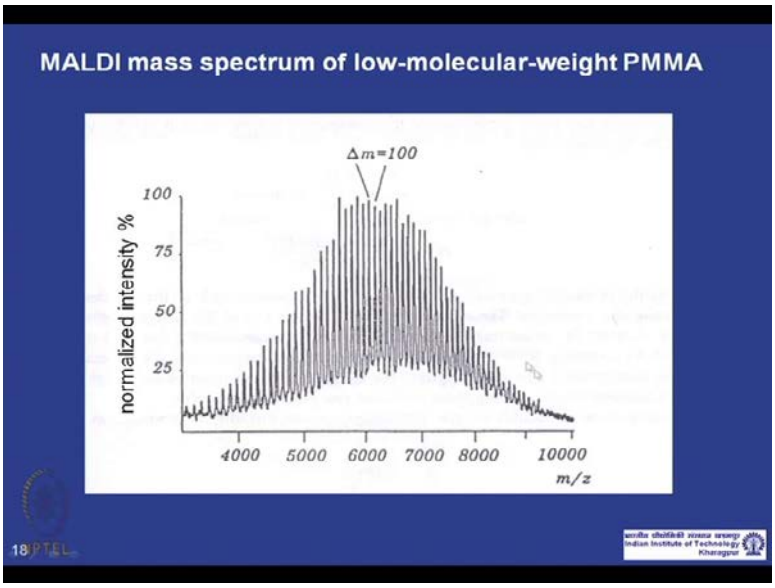

So, this is example of one MALDI from PMMA polymethylmethaacrolate and you can see these are the peaks from different polymer chains. So, this keeps the entire distribution; this is the normalized intensity and if you look at the gaps between the molecular ions you can see the gaps is 100 Dalton which is exactly the mass for a MMA repeating unit. So, here you can exactly get the difference in the signals with a molecular weight of the repeating unit.

And from this distribution the different molecular weight like number average molecular weight, weight average molecular weight and other molecules can be directly obtained. So, this is absolute technique. So, no calibration is required.

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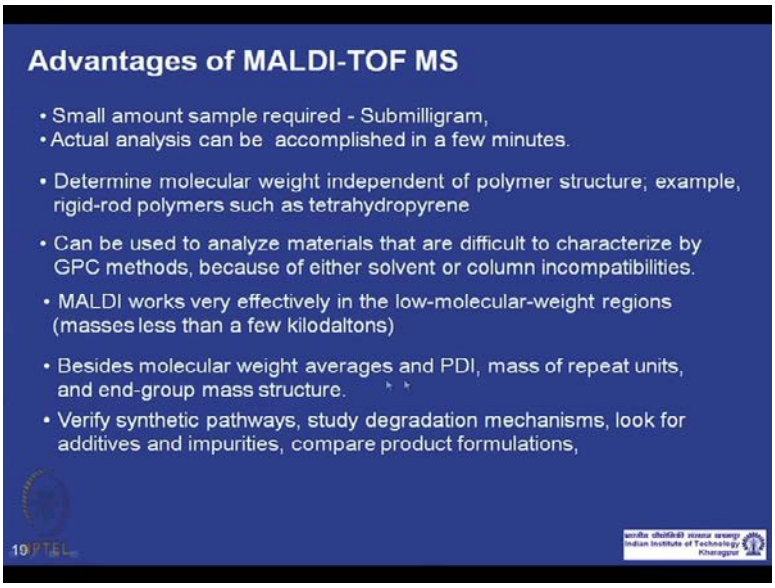

Now, quickly go through advantage of MALDI TOF, it is small amount of sample is required; very sub milligram sample is required and the analysis happens fast within very few minutes compared to the other techniques; it is very efficient. It does not depend whether the polymer structure is a linear structure; for example, for gel permeation chromatography, we typically use the principles and postulates of the Gaussian flexible polymer chain, but in this case we do not need any polymers having any shapes or any structures can be determined; and the MALDI TOF very efficiently for low molecular regions very GPC does not work, and other information besides molecular weight averages and the poly disperisty index, the repeat unit mass, the end group mass this are also can be received.

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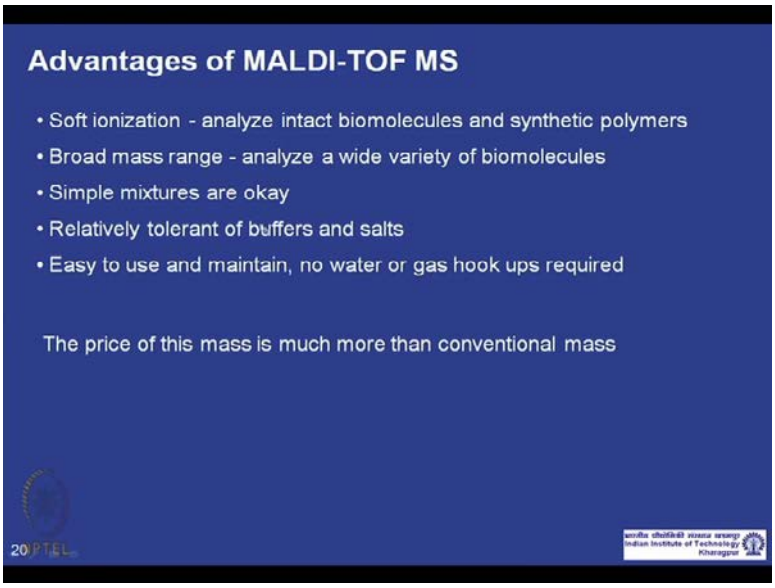

So, just all this benefits, but the only disadvantage is that the price of MALDI TOF is very high. So, it is not very convenient to use the MLADI TOF in every lab. So, with this we stop the discussion of determination of molecular weight and we move to the next topic in next lecture.