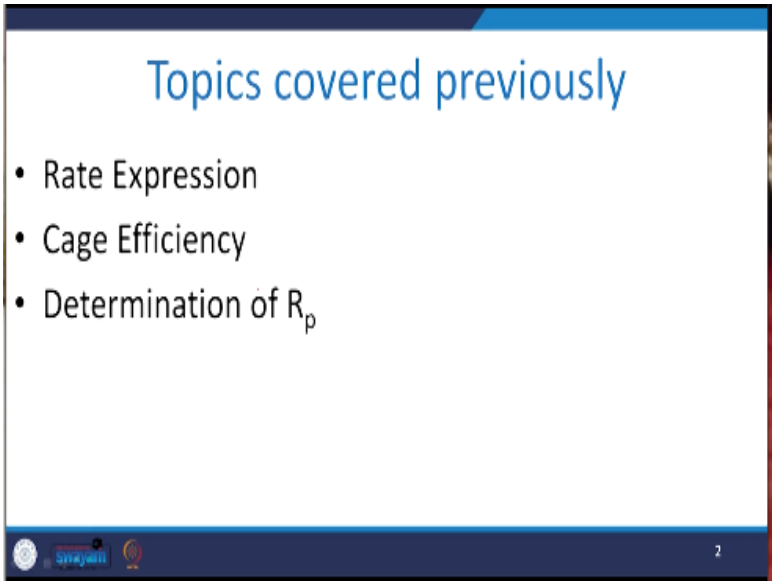
Polymer Reaction Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology – Roorkee

Lecture – 37
Process Analysis – I

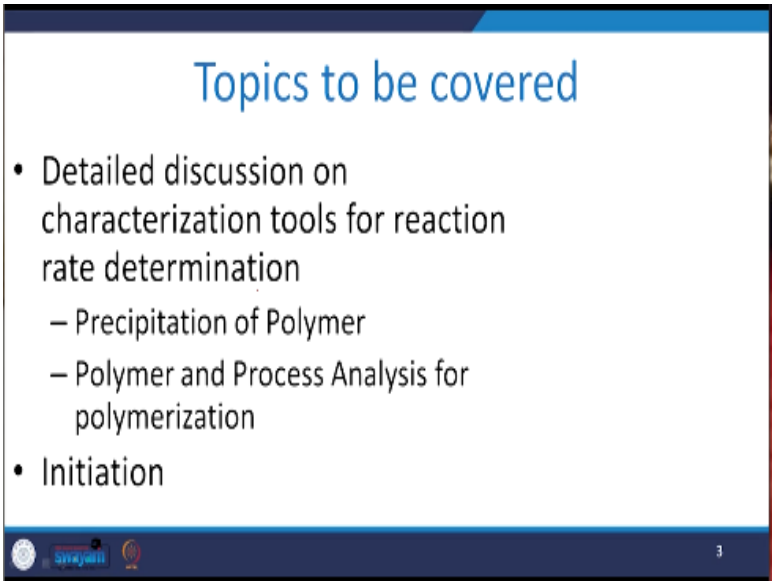
Welcome to the radical chain polymerization. Under this head, we will study about the process analysis and the various parameters, those who are associated with the polymerization process analysis. So, we are going to discuss about this particular concept in this particular lecture. Now, before we go in to deep of this particular process analysis concept, let us have a brief look at what we studied previously.

(Refer Slide Time: 00:54)



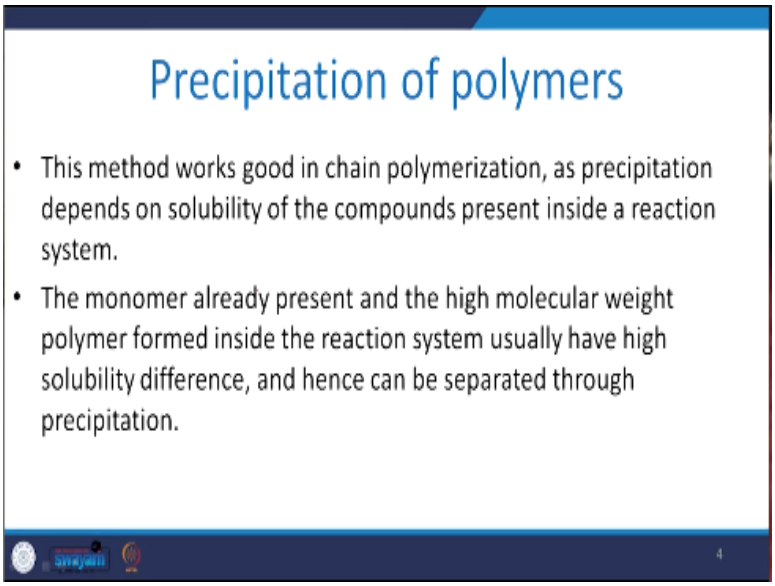
We developed the rate expression equation for radical chain polymerization. We talked about the cage efficiency and its implication and its radical chain polymerization. We developed various mathematical equations related to the rate of propagation steps in the radical chain polymerization. Now, let us have a brief look of what we are going to cover in this particular segment.

(Refer Slide Time: 01:21)



We will discuss about the characterization tool for reaction rate determination under the head of this particular concept. We will discuss about the precipitation of polymer is a very important phenomenon in the radical chain polymerization. Then, we will discuss about the polymer and process analysis for various polymerization steps again under the edges of initiation.

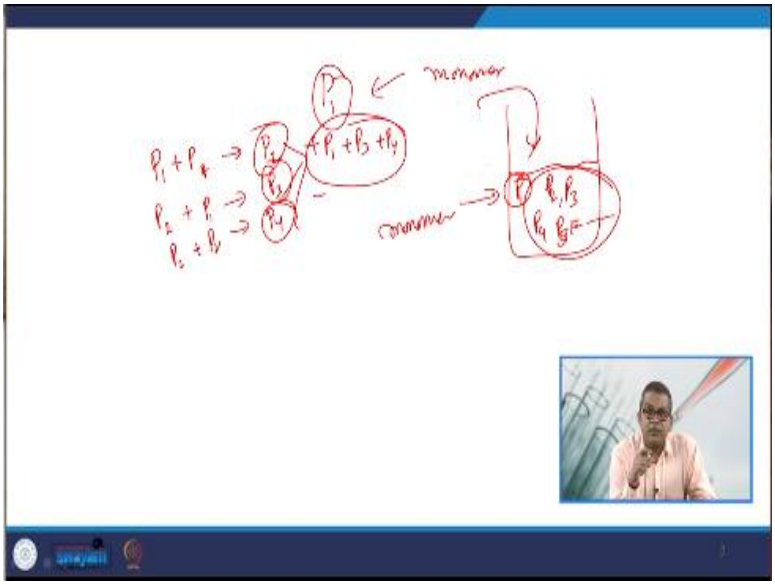
(Refer Slide Time: 01:43)



Now, let us have a look about what is the concept of precipitation of polymer. Now, this method works good in chain polymerization. As precipitation depends on solubility of compounds, those who are present inside a reaction system. Now, usually the monomer those who are already present and the high molecular weight polymer formed within the reaction system usually have high solubility difference. Hence, they can be separated through the precipitation.

Now, I like to give you an example about this particular concept, because of the significant amount of molecular weight and molecular weight distribution. Let us have a look about this particular aspect.

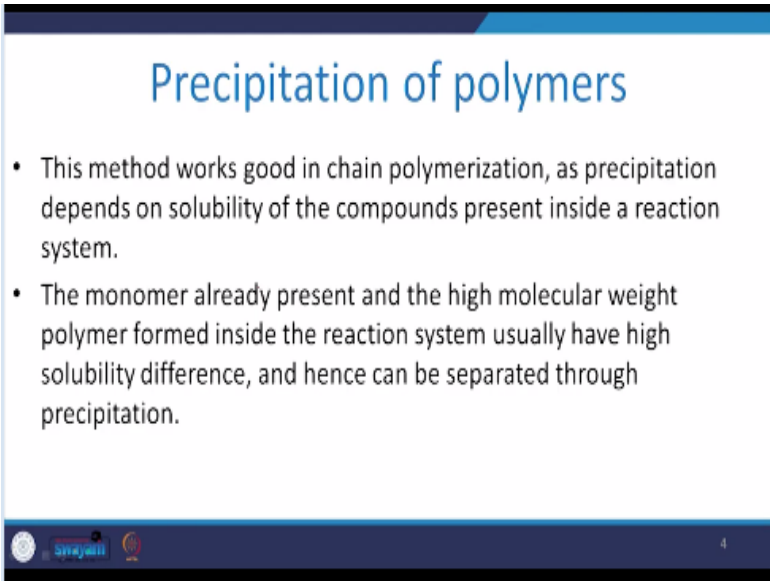
(Refer Slide Time: 02:36)



Now, here initially, you are having P_1 this is your monomer. Now, if you start your polymerization process then again $P_1 + P_2$, it may combine $P_1 + P_1$, they may give you P_2. Now, this P_2 may react with P_1 and this P_2 may react with P_2, so, this may give you P_3 and P_4. Similarly, all these 3 polymer chains may have other options or different options, it may get combined with either P_1 may combined with P_3 may combine with P_4 and so on.

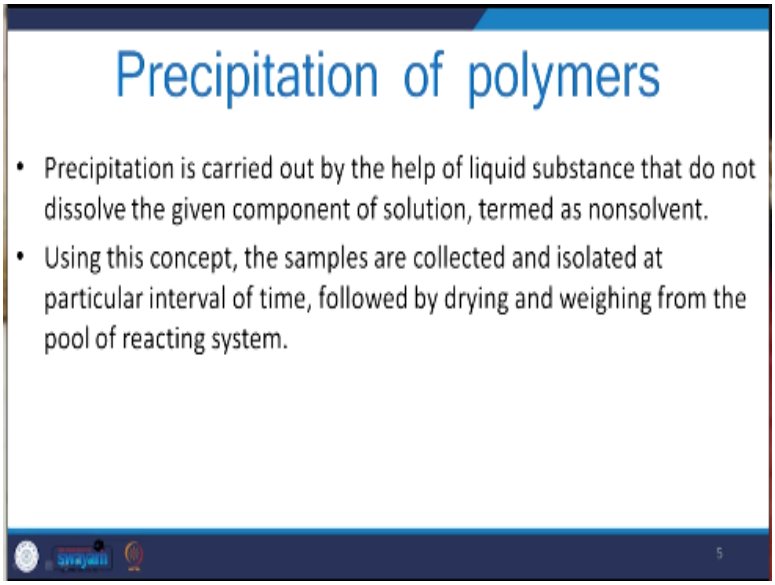
So, significantly the molecular weight of these chains will go on increasing. Therefore, whenever you consider the reaction mass, where you find that it may be the P_1 that is your original monomer, it may consist of P_2, it may consist of P_3, it may consist of P_4, it may consist of P_5 and so on, the higher chain molecules polymer molecules. Now, this particular concept or this particular thing gives you an opportunity to separate the different polymer chain, those who are having higher molecular rate.

(Refer Slide Time: 04:02)



And that is why this particular line says that, it offers a very good candidature for the separation or precipitation of polymer. So, in general you see that this particular thing gives you an opportunity for the ease of precipitation.

(Refer Slide Time: 04:19)



Now, usually precipitation is carried out by the help of a liquid substance that do not dissolve the given component of a solution, they are termed as non-solvent. Now, whenever you use this particular concept, the samples, those who are collected isolated at different interval of time followed by drying, weighing from the pool of reacting system. So, you see that usual chemical engineering operations, they do prevail and they do offer very good services for the precipitation of polymers, whatever you generated in due course of time.

Now, however, during the precipitation concept, the continuous monitoring of reaction system and collection of samples at different intervals. It is very essential. Because it develops a lot of human error as well as it is a tedious jobs. Therefore, it is important that you must have a continuous monitoring to the entire reaction system. Now, therefore, this method is usually not preferred in the commercial level because whenever you go for this particular approach, definitely it may invite a certain economic burden to the organisation.

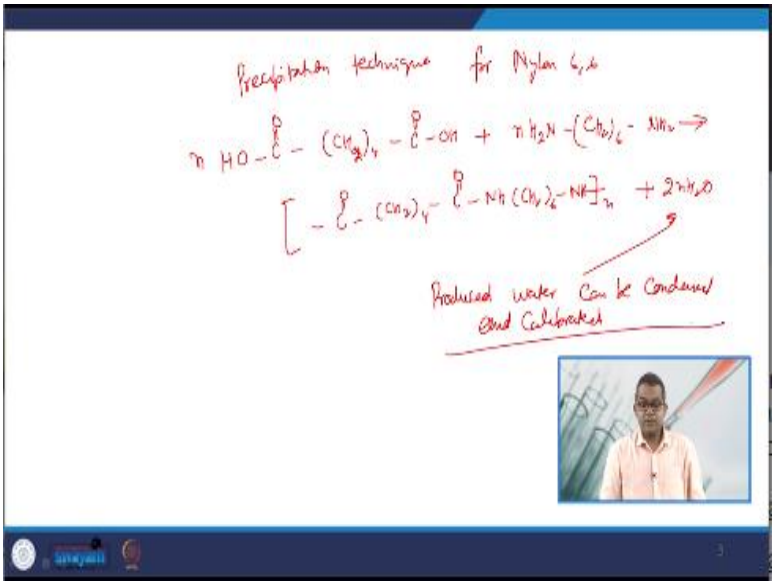
Now, whenever we talk about the laboratory testing or if you see about the pilot plant is study, this method is very much attractive. Now, this because of and also it offers the good attention, because due to the requirement of less sophisticated instruments and less engineer level. So, you can see that by this way both the things are supplement or both the things are all together 180 degree different.

So, commercial level you may face difficulty, but as far as the laboratory level, because of the less requirement of any kind of a sophisticated instrument. It is preferred one. Now, in the case of step polymerization, usually this method is not preferred. The reason is that a lot of monomer and intermediates or intermediate compounds with a different solubility, those were involved in the step polymerization from very beginning of the reaction. Therefore, it is not being preferred in due course of time.

Now, the selection of non-solvent does become very difficult for the step polymerization and that we need to pay several attentions for this particular step. Now, there are similar technique is used for understanding, there are some steps related to the step polymerization processes. Now, where if a particular by-product like sometimes water, if you recall that when we discussed the nylon synthesis, the water may be a by-product.

This can be separated out using some conventional techniques like condensation, etcetera or those chemical engineering approaches. Therefore, the volume of condensed by-product, it can be measured and it can be calibrated for obtaining the desired result. Now, again go back to your previous example of a polymerization of nylon 6,6 using adipic acid and hexamethylenediamine. Let us have a look about that what the important things we are going to discuss.

(Refer Slide Time: 08:01)



Now, in the precipitation technique, let us have example of nylon 6,6.

Precipitation technique for Nylon 6,6

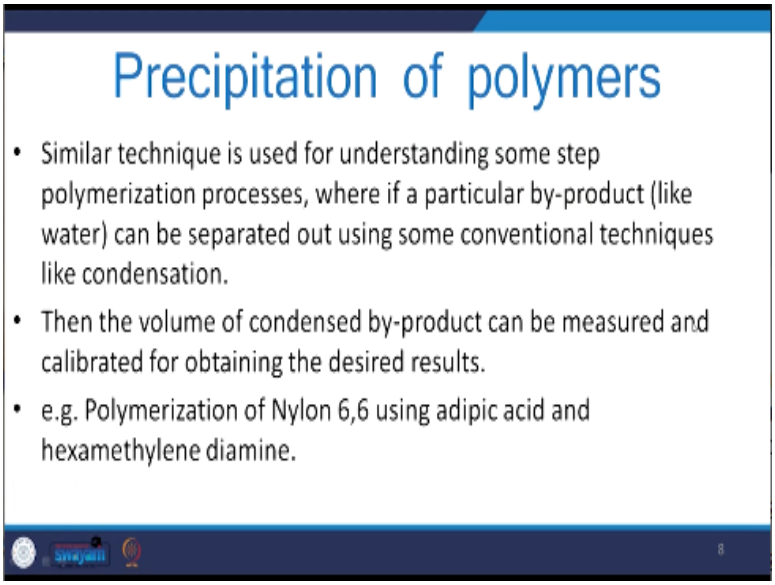
$$n\ HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\ H_2N-(CH_2)_6-NH_2 \rightarrow$$

$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH\right]_n + 2nH_2O$$

Produced water can be Condensed and Calibrated

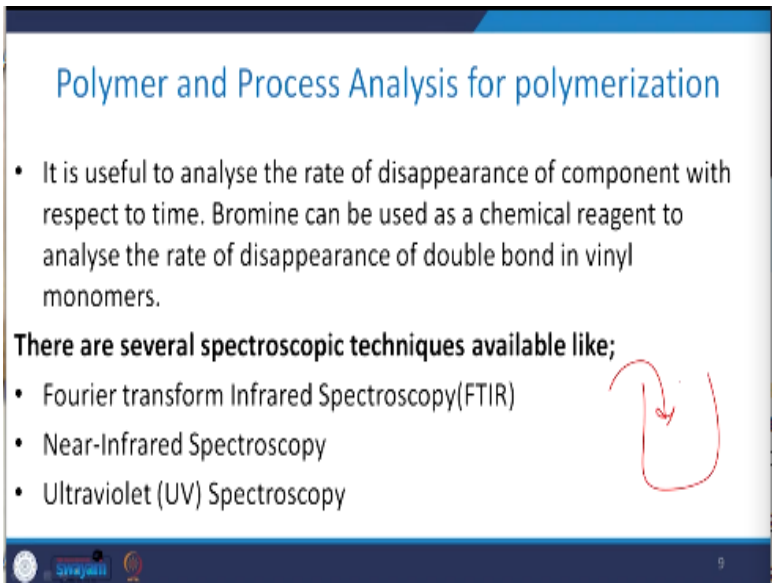
The produced water can be condensed and calibrated. So, this is the basic theme of precipitation technique.

(Refer Slide Time: 09:29)



And we explained with the help of this polymerization of nylon 6,6 with adipic acid and hexamethylenediamine. Now, when we talk about the polymer and process analysis for polymerization, now, it is useful to analyse the rate of disappearance of component with respect to time. Sometimes bromine can be used as a chemical reagent to analyse the rate of disappearance of double bond in vinyl monomer.

(Refer Slide Time: 10:08)



This is just for the sake of an example, because see in reaction mass, whenever you are having the monomer which is being converted into the different polymeric chain. In that case, your point of attention must be that how much your raw material that is monomer in this case is converting into the desired product or different chains. So, in that case, you need to find out that how much your monomer is disappeared during the course of a reaction.

So, this is a very useful technique and with the help of this example, like when you are polymerizing vinyl monomer, then bromine you can utilise to find out that how much vinyl monomer is being disappeared or consumed during the course of reaction. Now, apart from this, there are several spectroscopic techniques available as on date to give you any idea about the process analysis concept of polymerization.

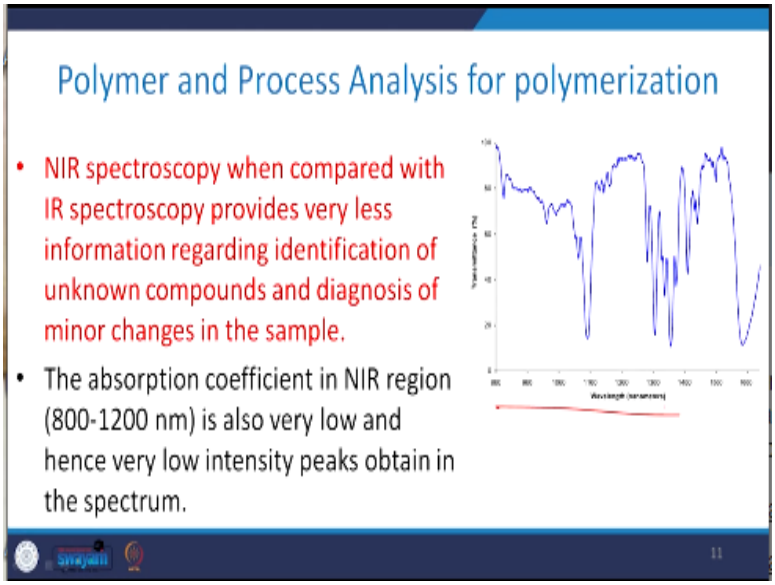
One in this category is Fourier transform infrared spectroscopy, very popular one that is FTIR, then infrared spectroscopy, then ultraviolet spectroscopy. So, these are some of the spectroscopic techniques being used to find out or give the concept of a process analysis. Apart from this, the nuclear magnetic resonance spectroscopy plays a very vital role in determining the analytical aspect and Raman spectroscopy, XRD etcetera.

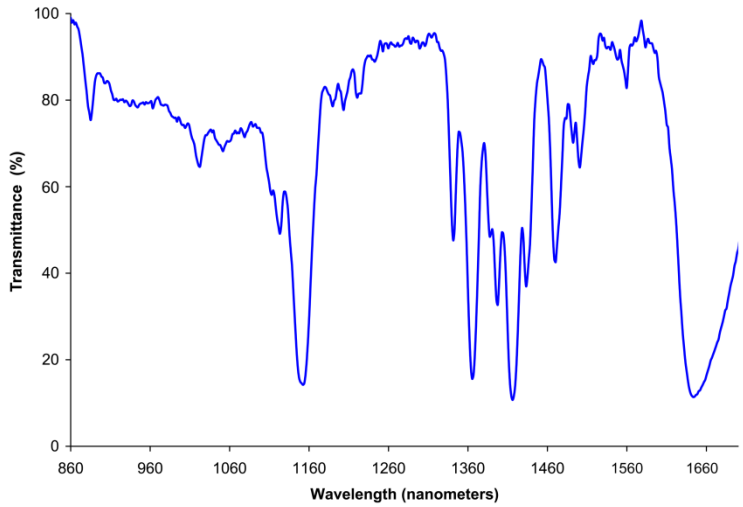
These are the some of the instrumental techniques which are being used to find out the various segments of the polymerization steps. Now, these techniques, you can also utilise, to perform the analysis related to the rate of disappearance of monomer or appearance of polymer. So, these 2 things are again very important. In-situ, there is disappearance of monomer and simultaneously, you may have a different polymer chains having different molecules rate in the reaction mass.

So, these particular things are extremely useful to carry out this particular approach. Now, let us have a brief discussion about these instrumental techniques. Although large segment in the literature can be devoted to this particular approach. Now, near infrared spectroscopy is utilised when it is compared with the infrared spectroscopy provided a very less information regarding the identification of unknown compounds and diagnosis of minor changes in the sample.

And sometimes it is very useful when you are performing the speciality polymerization process, maybe you are grafting, maybe you are performing with the help of co-polymerization steps, etcetera.

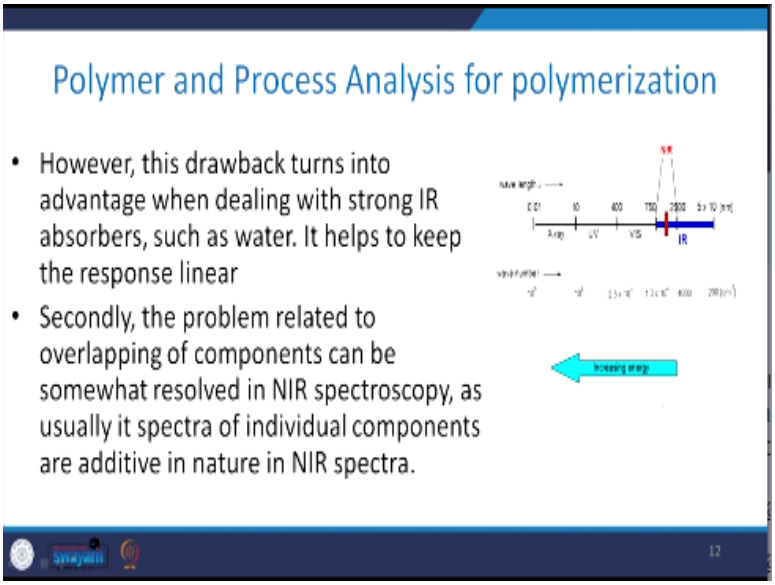
(Refer Slide Time: 13:07)

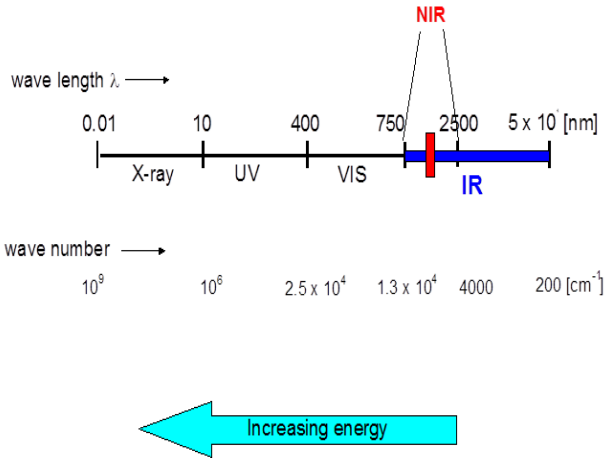




Now, the absorption coefficient in the range of NIR range of 800 to 1200 is very low. And there is the very low intensity peaks, you may obtain in that particular spectrum as it is visible in this particular plot. However, this drawback because, it is sometimes, people feel that this is a drawback. So, when we talk about this thing, then this drawback turns into advantage when you are dealing with strong infrared absorbers such as water.

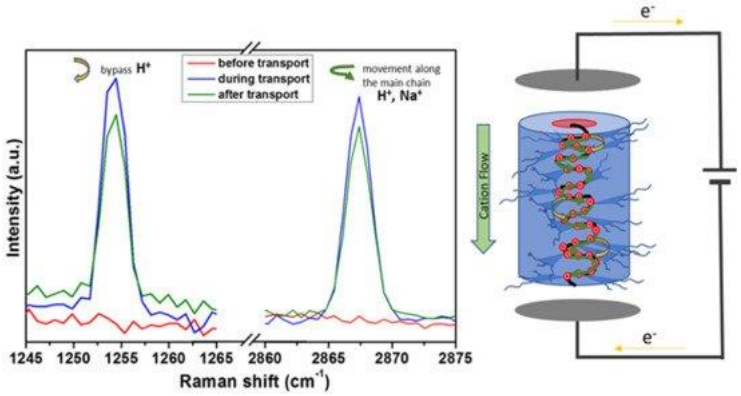
(Refer Slide Time: 13:42)





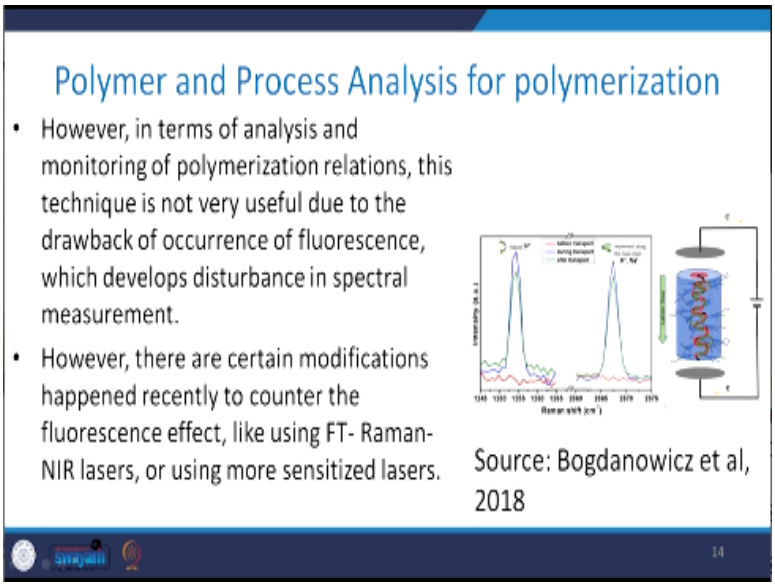
Usually, to keep the response in a linear range, as quite visible in this particular figure. Now, secondly, the problems related to overlapping of component, it can be some somewhere resolved in these types of infrared spectroscopy things. As these a spectra of individual component, they are sometimes additive in nature when we talk about the domain of near infrared. So, this is again a good aspect related to the NIR thing.

Therefore, this is usually an ideal approach for polymer process analysis for nearly all polymerization reactions. In-situ sometimes, In-Situ, Raman spectroscopy is again a different phenomena which is based upon inelastic scattering of light. This is again a very important concept related to the analysis of polymerization. Now, this technique has several advantages over both IR infrared spectroscopy as well as NIR spectroscopy. Like, it does not detect peak for water. Therefore, it nullifies this particular approach.



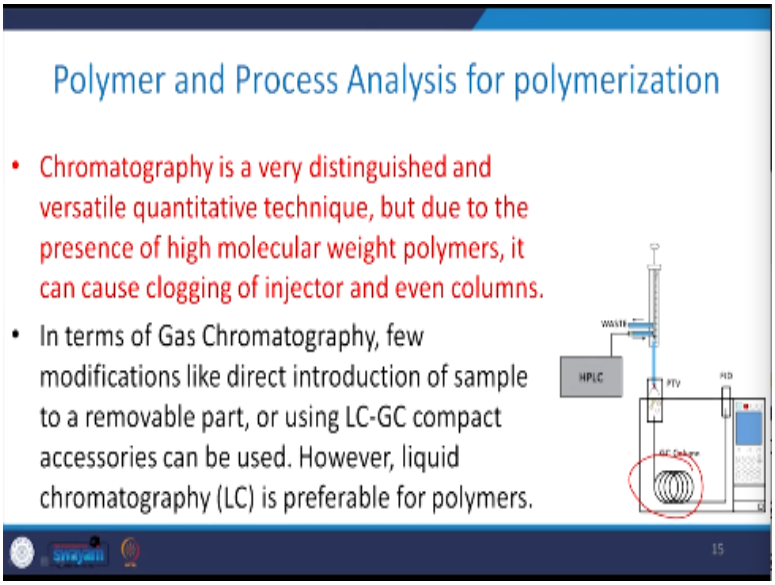
Now, it has sensitivity with the good linearity and it has the bigger spectral resolution when copied with the near infrared spectroscopy. So, this is having some sort of an advantage over this IR and NIR. Now, when talk about the analysis and monitoring of a polymerization reaction, this particular technique is not very useful just because of the fact that occurrence of fluorescence which develops the disturbance in the spectral measurement.

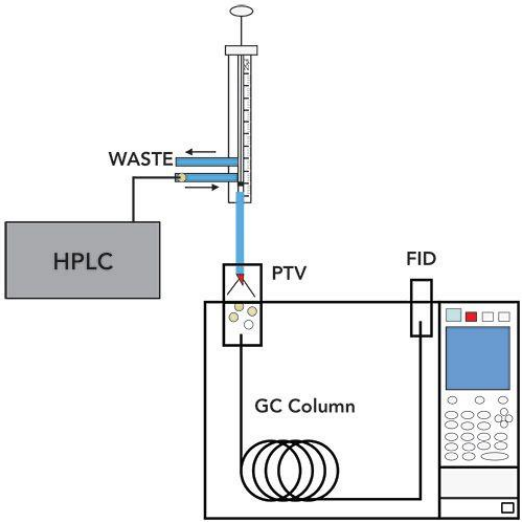
(Refer Slide Time: 15:42)



Somewhat, there are certain modifications happened recently to counter the fluorescence effect, sometimes using the Fourier transformer Raman NIR lasers or using some more sensitized laser, etcetera. So, people attempted and recently in this particular literature, they found that these techniques are useful related to this to overcome this particular drawback.

(Refer Slide Time: 16:13)





Now, when we talk about the chromatographic techniques, it is a very distinguished and versatile quantitative technique, but due to the presence of some high molecular weight polymer, it can also clog the injector or even columns. See, just I am giving you a brief about this particular chromatographic technique. As you see in this particular thing, there are very small openings or very small diameter columns.

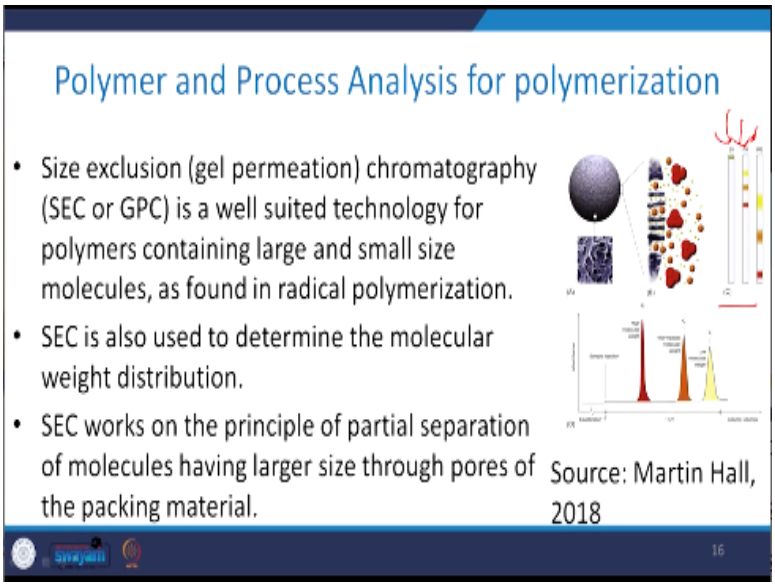
And if you are having the higher molecular weight or high molecular weight chain or high lengthy the chain in your polymeric system, so, sometimes they may have a tendency to clog this column. And sometimes it may have a tendency to clog the injector, because of the highly viscous and a high higher molecular weight polymer chain present in the reaction mass. So, therefore, this is again difficult aspect in while we use either HPLC or gas chromatograph, etcetera.

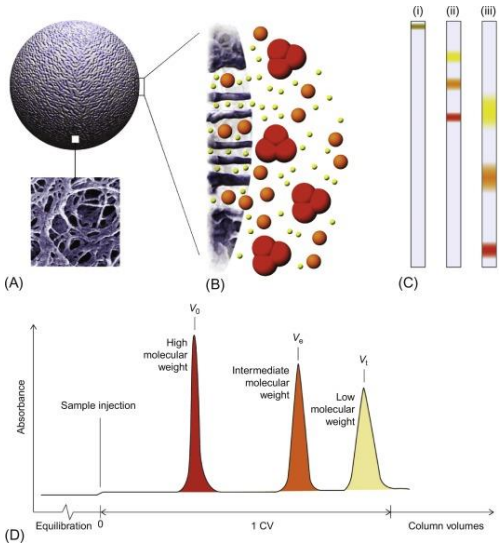
Now, when we talk about the modification aspect in those chromatographic techniques. So, people have suggested certain modification like direct introduction of sample to a removable part or using LCGC compact accessories. LC stands for liquid chromatography. So, therefore, LC or liquid chromatography is preferred for different polymers.

There are; again some other the chromatographic techniques like gel permeation chromatography or size exclusion chromatography techniques are much popular nowadays. And they are having, they offer a well suited technology for polymers, those who are containing large and small sized molecule as usually found in radical polymerization. So, size exclusion chromatography is also used to determine the molecular weight distribution.

If you recall that, this is a very important phenomena in the characterization of polymeric process. Now, this size exclusion chromatography, this works on the principle of partial separation as name implicates the partial separation of molecules having larger size through the pores of the packing material.

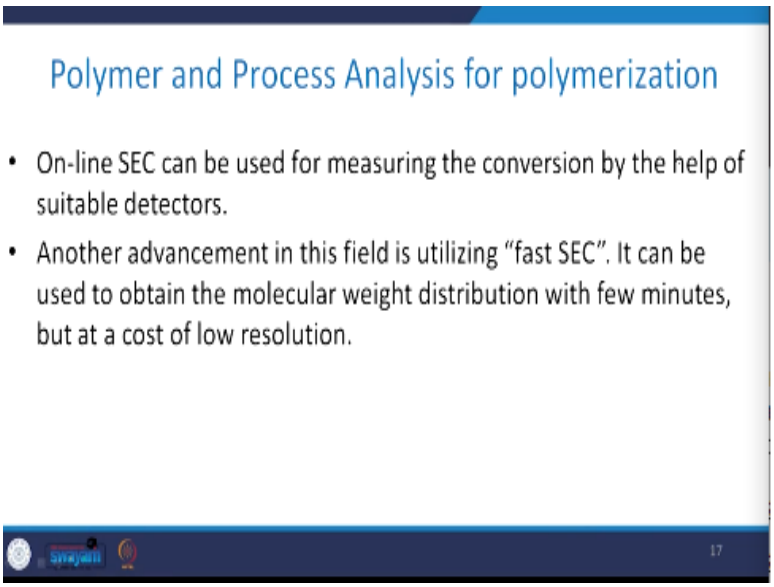
(Refer Slide Time: 19:01)





Now, the people have also carried out the different things. Now, here you see that different type of packing materials and through which you can exclude the particles or you may perform the partial separation of those polymeric segments or polymeric molecules or polymeric chain now, with the help of these pores.

(Refer Slide Time: 19:24)



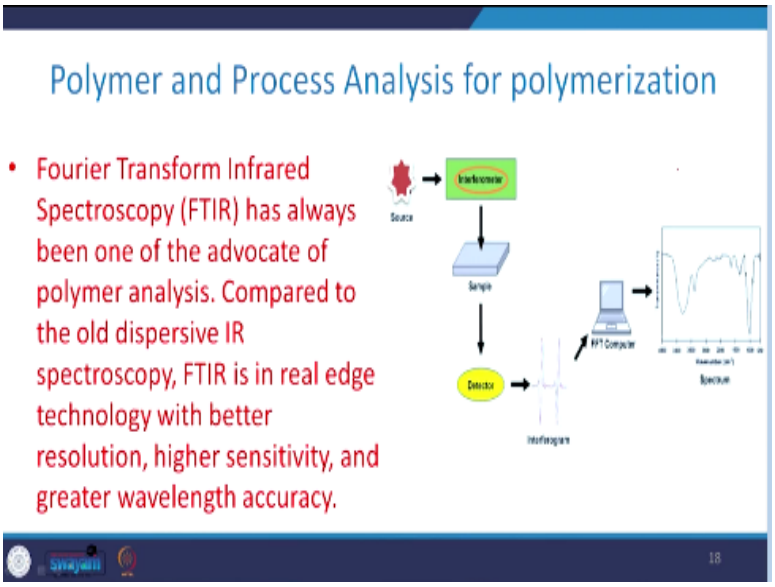
Now, sometimes the online size exclusion chromatography is very popular. And this can be used for the measuring of conversion by the help of suitable detectors. Now, it offers another advantage in the field that is utilising the fast size exclusion chromatography or SEC. Now, it can be used to obtain the molecular weight distribution within a few minutes, but at a cost of very low resolution.

So, one time you are getting at one advantage or some sort of advanced tool and simultaneously, you may experience that there is a loss in the resolution or you may experience the low

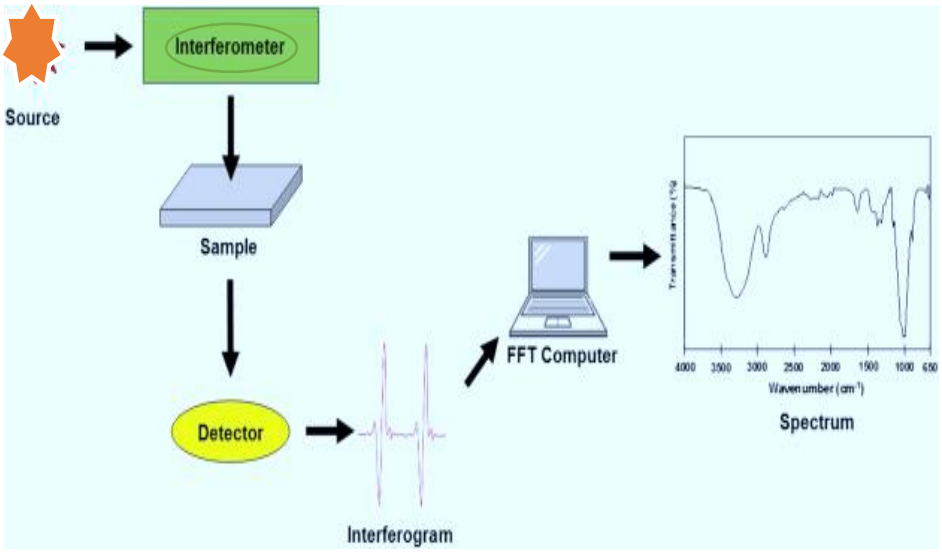
resolution in due course of time. So, these things you need to optimise whenever you are using this particular chromatographic technique. Another very important spectroscopic technique that is the Fourier transform infrared spectroscopy is being used in the polymerization characterization.

Now, it has always been one of the advocates of polymer analysis. Now, if it compared to old dispersed to infrared spectroscopy, the FTIR usually offers a real edge technology with better resolution if you compare with the SEC where you will having the low resolution. Here, you may have some higher resolution; sometimes, higher sensitivity and greater wavelength accuracy.

(Refer Slide Time: 21:12)



Here, a schematic diagram represents the basic concept of FTIR, you are having the interferometer. So, the source may be like this and then it passes through the sample that is infrared. And there is a detector who analyses and by this way, you may get the interferogram and which you can analysed with the help of computer to get this particular spectra.



And with the help of library available or standard samples, you may analyse that what are the different components, what are the different molecular weight polymers they are present in that or what are the different functional groups, they are present in that sample whatever sample you have chosen for. And because and again, it offers a very good services to the radical chain polymerization, because here you may have some radical or a double bond, triple bond etcetera.

So, it gives you an edge over the; to find out that how many radicals and how much radicals or how intense radicals are present in that particular sample. So, it offers a very good opportunity to analyse the polymer sample. Now, it offers very good advantages to the other tools available that is the easy sample preparation and then offers the fast analysis. These are the some of the advantages associated with FTIR.

Now, the quantification of overlapped band is quite difficult and sometimes, it leads to an error. So, this particular approach need to be addressed while using any kind of characterization technique. Now, people may ask that what are the causes of error? So, one causes of error that is related to the baseline plot. Now, this can be changed due to the scattering of light from the surface of the sample.

So, this particular approach is extremely crucial in this type. Another limitation that is associated with this includes the non-linearity in absorbance versus concentration curves and the sensitivity of the sample for different absorption band needs also be to be addressed. Now, you may ask the question that what different type of information one can had from the FTIR analysis of polymer sample.

So, let us have a brief discussion about these kinds of information. You may have information pertaining to the chemical composition that may be some presence or absence of a particular functional group as I talked about that we are in the radical chain polymerization. So, it is extremely useful to analyse that what kind of the functional group is present or formed or absent in due course of time, then confirmation of a structure of molecule such sometimes crystalline, amorphous, etcetera.

And it gives you information it may give you information related to the chemical composition of co-polymers. Sometimes, it gives you very useful information which determining the end group in low molecular weight polymers. It also offers services to give you the information

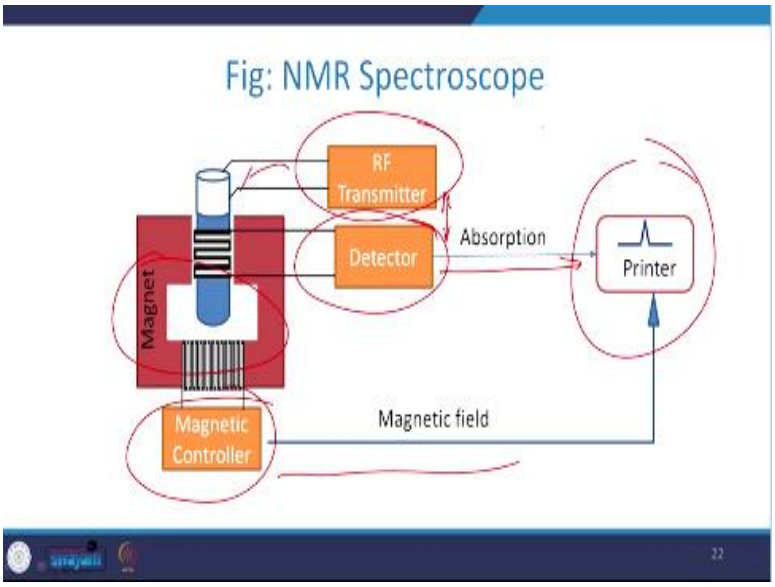
related to the quality of polymers detecting, it may be helpful in detecting the various contamination, various by-products formation, etcetera.

So, it is a very useful technique to give you the information pertaining to the property of polymer. Now, nuclear magnetic resonance spectroscopy is again a very useful tool to obtain the chemical and physical information of the polymer. Now, it is one of the, best tool in our opinion to obtain the highly accurate quantitative information within the range of say 1% of the composition in the polymer. So, it is a very important and a very useful tool.

Now, this NMR can be broadly classified in 2 forms. One is the solution NMR. Another one is the solid state NMR. So, that is why whenever you are having the solution polymer or solid polymer, then you can utilise this NMR. Now, this solution NMR; this provides better resolution of polymer. However, for powder and small particles etcetera, the solid state NMR can be used frequently.

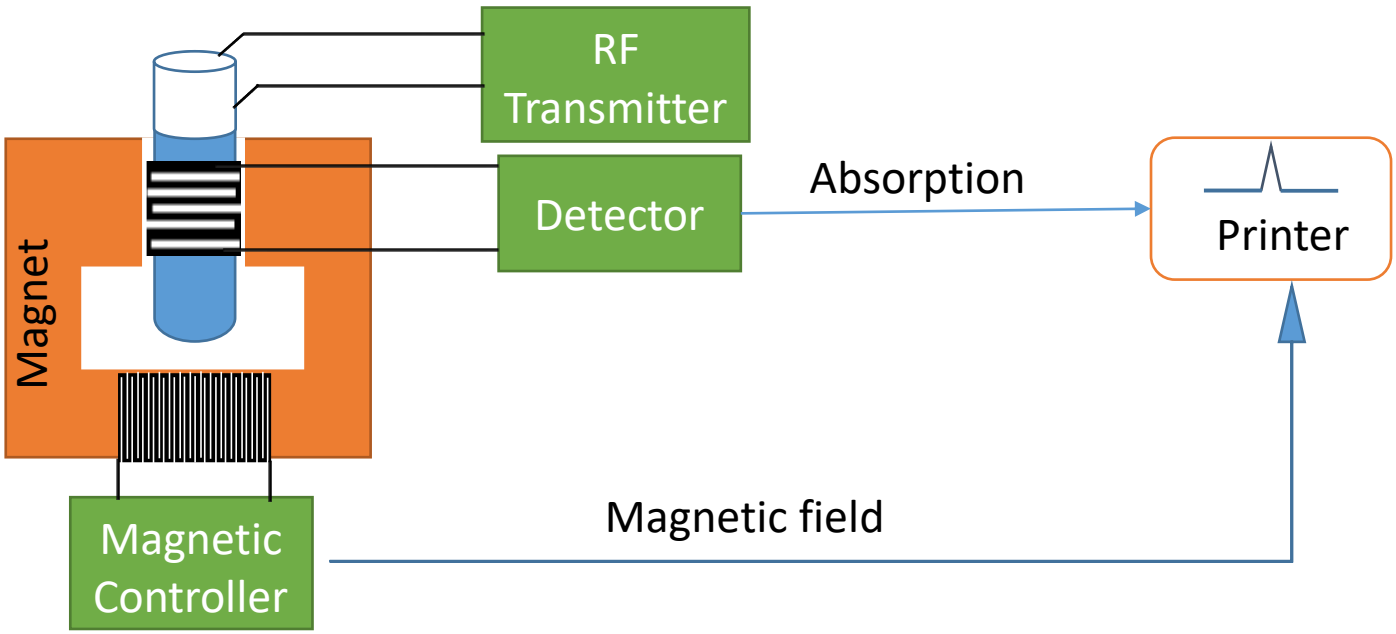
Now, this is a typical diagram of NMR spectroscopy. Here, you are having the magnet, high powered magnet then this is the magnetic controller.

(Refer Slide Time: 26:27)

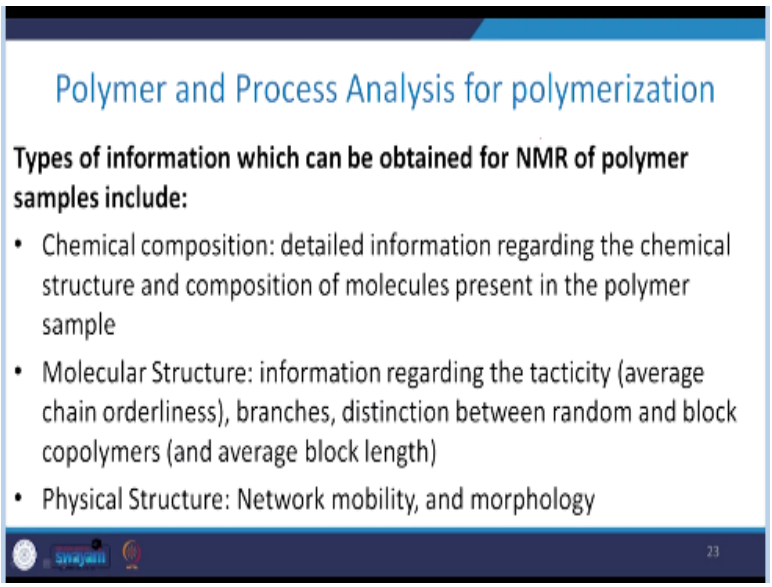


So, this particular range covered the magnetic zone or magnetic field. Now, here, the detector, one detector is having this detects that the changes occur in the polymeric sample, which with the help of absorption phenomena, it analyses the things and gives you the information. Here, one radio frequency transmitter is there just to give you or just to integrate the information

whatever you are getting and all the informations, you can have through the printer. So, it is a very small sketch for the NMR spectroscopy.



(Refer Slide Time: 27:13)



Now, you may ask the question that what kind of information you can obtain from nuclear magnetic resonance spectroscopy of the polymer sample. Again, this is related to the information related to the chemical composition like detailed information about the chemical structure because sometimes, it is crystalline or amorphous. Because, you know that the polymers they are available in the various domains and a different type of, you can say, the isomers are present in that in the case of a polymer.

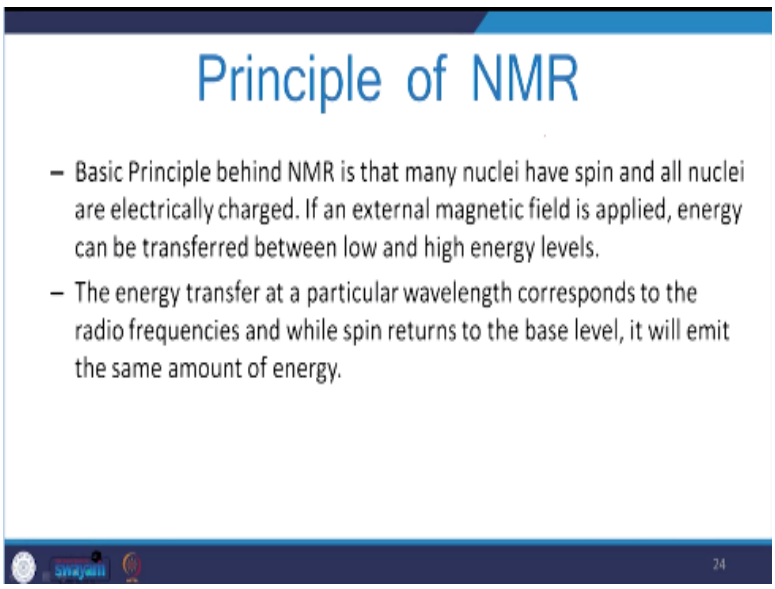
And this may, they may have altogether different properties, what you are anticipating during the polymerization process. So, you are always interested to have information related to the chemical structure. Then composition of a molecule present in the molecule polymers sample. Again, it is a very useful thing, because sometimes, by-products, sometimes, a different type of change may present during the polymerization process or may form during the polymerization process.

So, this type of chemical information related to the chemical composition is extremely important. Then another, information related to the molecular structure that is related to the tacticity average chain orderliness, branches, distinction between the random and a block copolymer, average block length etcetera. So, this type of information is extremely important.

Then you may, interested in to find out the physical structure of the polymer that is related to the either network mobility or surface morphology or internet morphology. So, NMR offers very good services for this to determine the physical structure of those polymer samples, those who are in question. Now, let us have a brief look about the principle of NMR.

The basic principle behind NMR is that many nuclei we have a spin; all nuclei are electrically charged. So, if an external magnetic field is applied as evident from this particular figure.

(Refer Slide Time: 29:42)

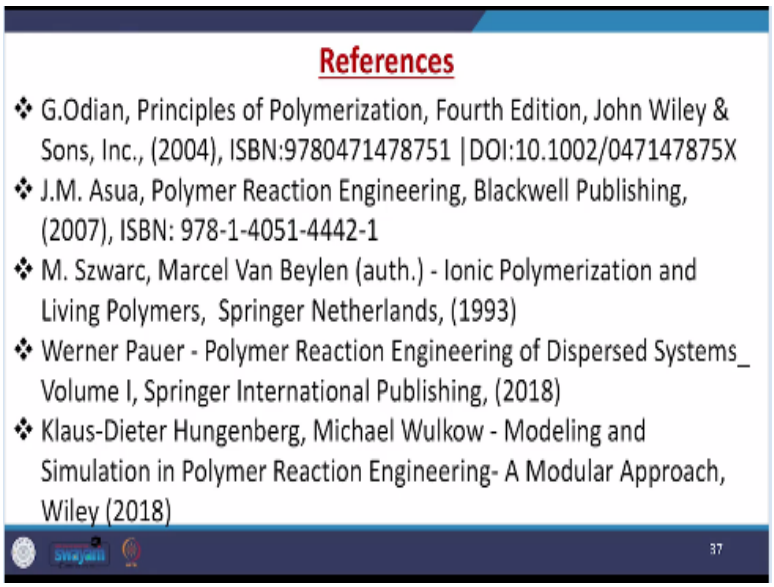


So, if you apply the external magnetic field, the energy can be transferred between low and high energy levels. So, these 2 levels are there. So, it can be transferred between these 2 energy

levels. Now, the energy transforms that particular wavelength it usually corresponds to the radio frequency and wireless spin returns to the base level, it may emit the same amount of energy.

Now, this NMR probes the spin of various atomic nuclei and this field is usually affected by electron shielding, usually, which depends on the different type of chemical environment. So, the effective magnetic field also affected by the orientation of a neighbouring nuclei sometimes neighbouring nuclear plays very vital role. So, they are known as spin-spin coupling.

(Refer Slide Time: 30:37)



Now, in this particular lecture, we discussed about the various analytical tool to determine that properties of polymer, which was developed during the course of radical chain polymerization. We discussed certain instrumental techniques and these techniques are very much useful to determine either the chemical composition, morphological structure, physical structure.

And they too are very important when you apply this particular information to the final product analysis or during sometimes, it gives you an opportunity to change the process parameter in case if you are not getting the desired product as per the mark. Now, in the next lecture, we will discuss or we will continue these particular instrumental techniques along with the initiation in due course of time. Thank you very much.