Polymer Chemistry
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Lecture - 34
Structural Analysis of Polymers by Spectroscopic Methods

Welcome back to this course on polymer chemistry. In the last lecture we were discussing about gel permeation chromatography, and then about mass spectroscopy for determining polymer molecular weights. And with that we came to end of the discussion of how to determine polymer molecular weight. Today we will move to a different topic, which is Structural Analysis of Polymers by Spectroscopic Method.

Now, we have in the beginning of this lecture series, we knew or we found out how to synthesize polymers by different process. And then and next set of lectures we found how to characterize the polymers in solution, including the how to determine the molecular weight of the polymers.

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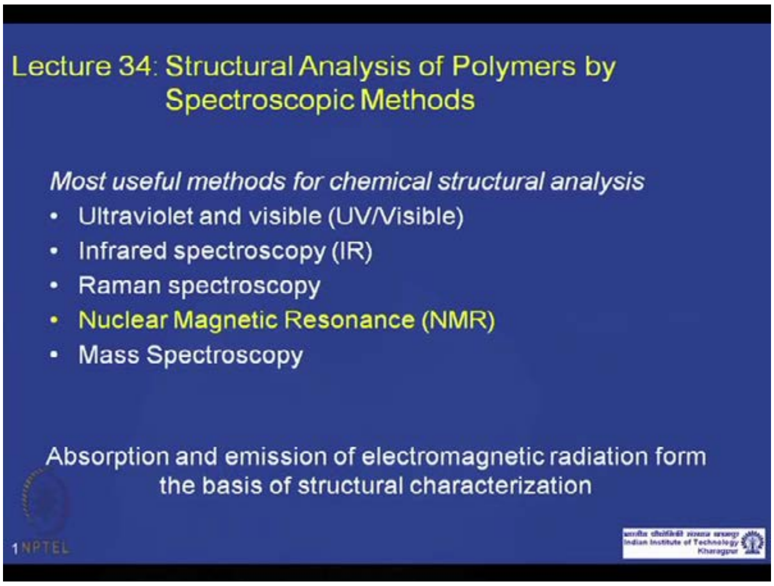

Lecture 34: Structural Analysis of Polymers by Spectroscopic Methods

Most useful methods for chemical structural analysis

- Ultraviolet and visible (UV/Visible)
- Infrared spectroscopy (IR)
- Raman spectroscopy
- Nuclear Magnetic Resonance (NMR)
- Mass Spectroscopy

Absorption and emission of electromagnetic radiation form the basis of structural characterization

Now, we will know whether the polymer, what is the polymers we have made, so in this chemical structure analysis we will be basically discussing, mainly this spectroscopic techniques, by which we will be analyzing the chemical structures including the microstructures of polymer molecules. And out of this listed spectroscopic method, we will mainly discuss the NMR techniques to use up the NMR techniques mainly and we will briefly mention about UV visible, and IR spectroscopy, and we have discussed mass spectroscopy in the last class.

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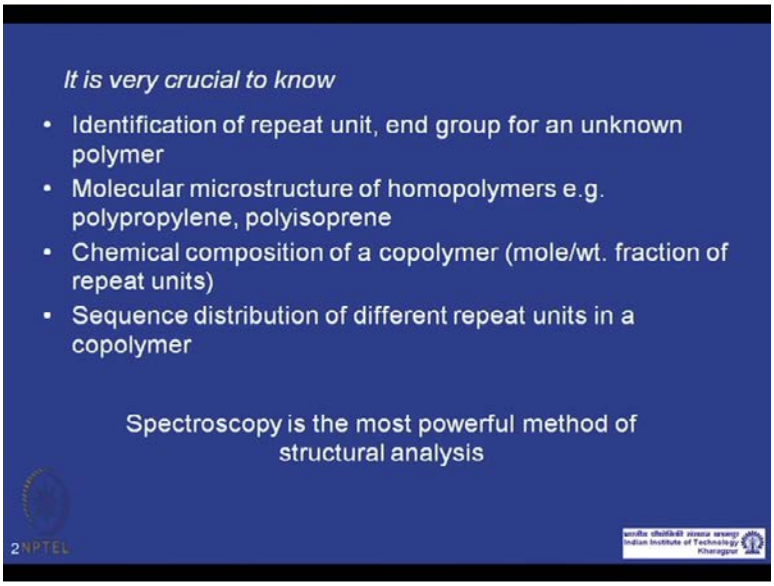

It is very crucial to know

- Identification of repeat unit, end group for an unknown polymer
- Molecular microstructure of homopolymers e.g. polypropylene, polyisoprene
- Chemical composition of a copolymer (mole/wt. fraction of repeat units)
- Sequence distribution of different repeat units in a copolymer

Spectroscopy is the most powerful method of structural analysis

So, it is very critical when we make that, we now we know how to make this polymers, and what is the molecular weight of the polymers we made. Now, obviously we need to know whether, we have made the right polymer, you know we may be have something particular in mind, in terms of chemical structures, in terms of end groups of the polymer and if you are making copolymer. Then the microstructures of copolymers, the composition, the series, the sequence of the monomers by which the copolymer is made, so the all these are important.

So, we must know before going to further, to do know the property or to determine the property of these polymers which we made, you must know what is actually the chemical structure of the polymers. So, it is very important crucial to know you know the repeat units, we may have used a particular monomer, whether that monomer exist in the same form as repeat unit we need to find out; what is the end group of that polymer, what is the molecular microstructure in terms of homopolymer?

For example, the tacticity whether it is seen that syndiotactic, atactic or isotactic, and then chemically compositions of the of a copolymer, the mole fraction of the repeat unit, the sequence of the different repeat units in a copolymer. And spectroscopy is a most powerful method, which we can utilize to get this structure analysis done.

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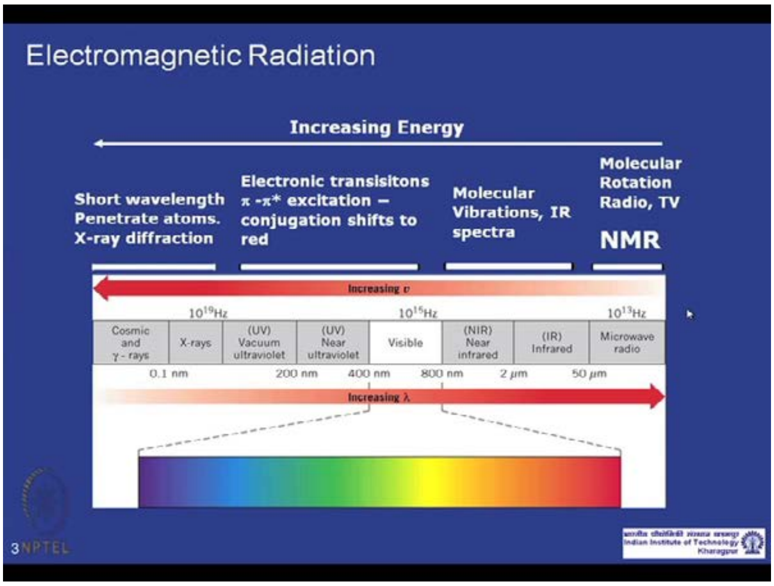

Electromagnetic Radiation

Increasing Energy

Short wavelength
Penetrate atoms.
X-ray diffraction

Electronic transisitons
π -π^* excitation –
conjugation shifts to
red

Molecular
Vibrations, IR
spectra

Molecular
Rotation
Radio, TV

NMR

Now, what will do with in this lecture, we briefly talk about the interaction of the electromagnetic radiation, the basis of spectroscopy, interaction of electromagnetic radiation with maters in this case polymers. This is you all of us know, the electromagnetic radiation, and this is the increasing wavelength, so this is left hand side is increasing frequency, which makes this increasing energy, and this is a short wavelength it can penetrate atom, so we can study extra refraction using x-rays here.

Next is a little higher wavelength or little less energy is the UV visible, UV visible spectrum, where we mainly mainly mainly prove the electronic transitions of a molecules. And then using IR, impetrate spectra we can prove the molecular vibration and finally, with radio frequency radiation, we can use this radio frequency in NMR technique to know the chemical structure of the polymer molecules.

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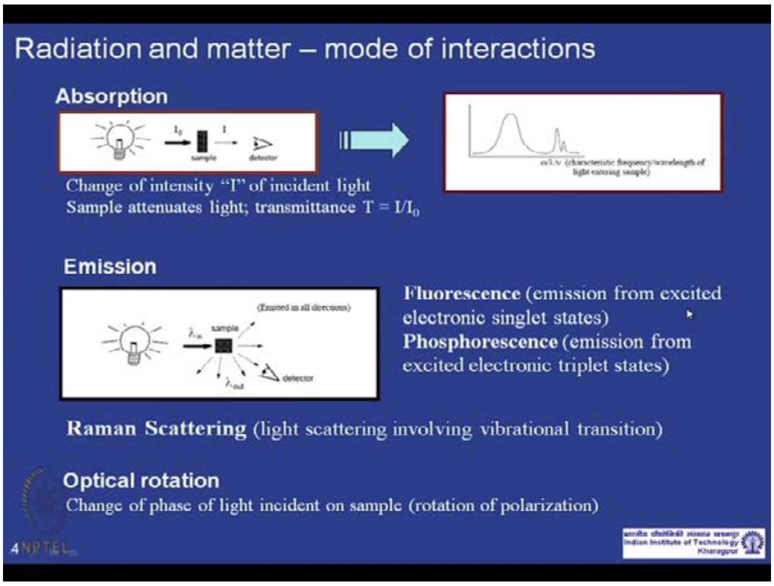

Radiation and matter – mode of interactions

Absorption

Change of intensity "I" of incident light
Sample attenuates light; transmittance $T = I/I_0$

Emission

Fluorescence (emission from excited electronic singlet states)
Phosphorescence (emission from excited electronic triplet states)

Raman Scattering (light scattering involving vibrational transition)

Optical rotation
Change of phase of light incident on sample (rotation of polarization)

So, basically matter can interact two three ways, with the radiation it can absorb, and intensity when it absorb, intensity can change from I 0 to o I, so you can plot transmission or the absorbance versus wavelength, and to find out we at which wavelength it is absorbing maximum, and what is criteria and so on. (( )) emission spectra light it when we sign a light in a sample, it can absorb and then it can emit emit, may be in the same wavelength or different wavelength, and with the help of detector we can get a get the intensity of this emitted radiation.

And the different type of emission spectra we can use fluorescence, emission from excited electronic single states, phosphorescence, emissions from excited electronic triplet states. The other type of interaction is scattering, and optical rotation, the sample might change the rotational rotation or polarization of the sample causing change in optical rotation of the light.

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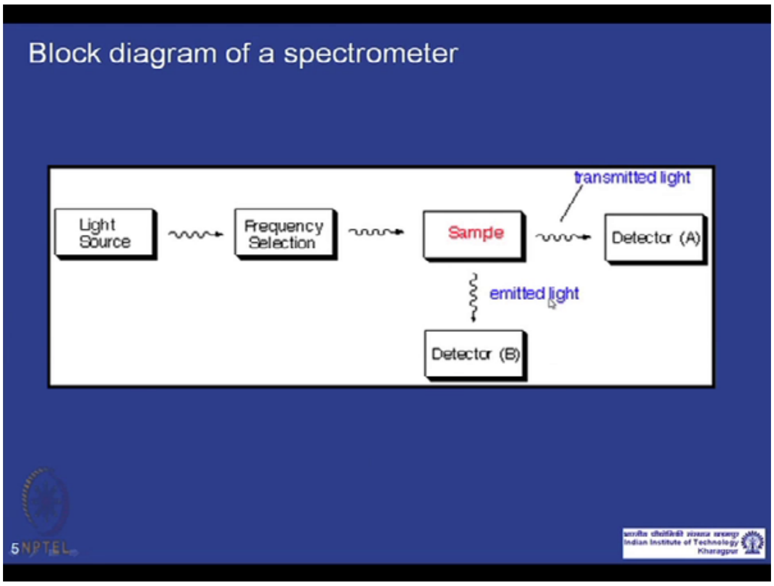

Block diagram of a spectrometer

In in a basically, very same manner how this equipments are done, light sources there is a light source, and there is a frequency selector, which basically select a single frequency or you can have the entire light in that particular region of interest pass through this. And it is the sample, and then you can detect the transmission transmitted light of the emitted light using detectors, and then you get the information about the sample from absorption spectra, emission spectra or a scattering like Raman scattering.

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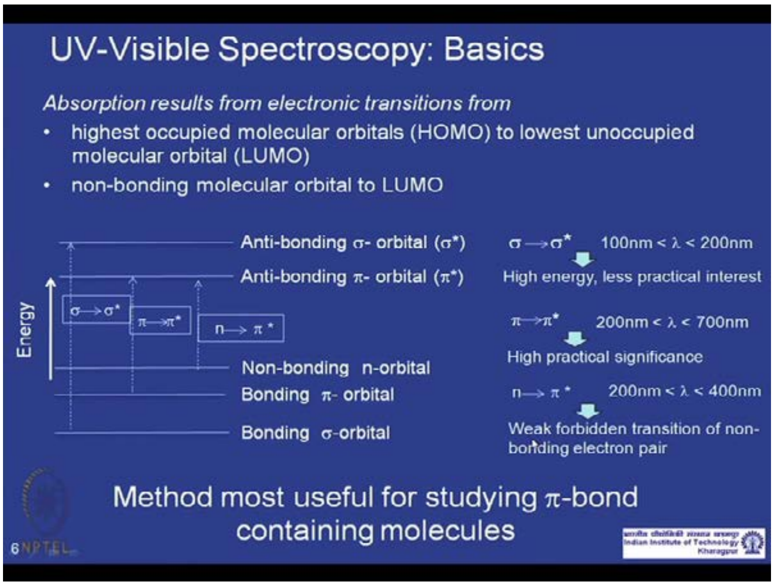

UV-Visible Spectroscopy: Basics

Absorption results from electronic transitions from

- highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbital (LUMO)
- non-bonding molecular orbital to LUMO

$\sigma \rightarrow \sigma^*$ $100nm < \lambda < 200nm$

High energy, less practical interest

$\pi \rightarrow \pi^*$ $200nm < \lambda < 700nm$

High practical significance

$n \rightarrow \pi^*$ $200nm < \lambda < 400nm$

Weak forbidden transition of non-bonding electron pair

Method most useful for studying π-bond containing molecules

Now, come to UV-visible spectroscopy or just talk about in this course, we are not going into details about this spectroscopic techniques, because these are very basic techniques; what I will just mention basic few basic like points, and then tell you what is the application of this particular spectroscopy in terms of polymer characterization. So, in terms UV-visible, basics of UV-visible spectra, it is basically electronic transitions from the highest occupied molecular orbital to the lowest unoccupied molecular orbital, homo and LUMO.

Then nonbonding electrons, molecular orbital sometimes if the nonbonding molecular weight are the highest orbitals, occupied (()) then the electronic transition may happen from nonbonding molecular orbital to lowest unoccupied molecular orbital. So, for molecules which have only sigma orbital, mainly sigma orbital, then homo LUMO transition happens between sigma and sigma star, which is of quite high energy and not having very practical interest.

If there is a pi bond in the compound or a molecule and specially, if the pi bond there are many pi bonds which are pi orbitals or pi bonds which are conjugated, then the pi pi transitions, transitions are of like UV-visible range, and the mole conjugation, mole it goes to visible range, and higher wavelength. And this is having great practical significance which helps us to find out the group, functional groups or the conjugation present in the molecule. And non-bonding end to, and non-bonding pi star are very weak very weak absorption, which happens in this region 200 nanometer to 400 nanometer, which, so basically implies presence of nonbonding electron in the compound.

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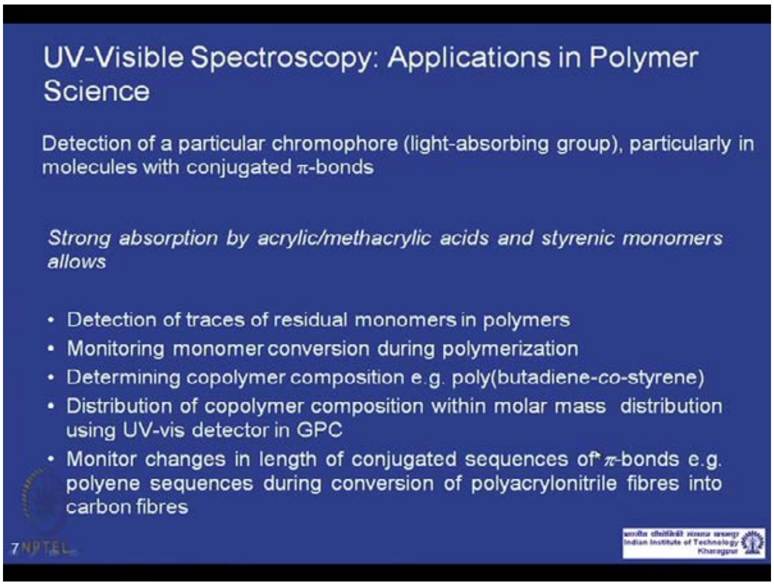

UV-Visible Spectroscopy: Applications in Polymer Science

Detection of a particular chromophore (light-absorbing group), particularly in molecules with conjugated π-bonds

Strong absorption by acrylic/methacrylic acids and styrenic monomers allows

- Detection of traces of residual monomers in polymers
- Monitoring monomer conversion during polymerization
- Determining copolymer composition e.g. poly(butadiene-*co*-styrene)
- Distribution of copolymer composition within molar mass distribution using UV-vis detector in GPC
- Monitor changes in length of conjugated sequences of π-bonds e.g. polyene sequences during conversion of polyacrylonitrile fibres into carbon fibres

So, how this UV spectroscopy is applied in polymer science, in characterization of polymers basically, it is like the how the UV spectroscopy is applied to in for the small molecules for example, it helps in detection of particular homophobes, which been light absorbing group present in a molecules. And if we have groups like, acrylic acids, methacrylic acids or styrenic, which have a strong absorption, then this this this type of polymers actually help us in detecting the trace amount of residual monomers; if the monomers are present, then it will give us from UV signal, UV-visible absorption signal for that monomers.

And obviously, here that the UV visible absorption spectra for the monomers, and for the peaks of the monomers and the polymers will be different, so we can follow the monomer peaks, and to find out the conversion during the polymerization. If one the, in the copolymer, if one of the polymers you know the two monomers they have a different UV spectra, UV-visible spectra, then we can follow their, we can isolate their polymer after the polymerization is over from the polymerization medium, then we can get the composition simply by studying the UV spectra, UV-visible spectra of the polymers.

For that of course, we need to know the absorption behavior of the individual homopolymer, like in this case called polybutadiene, and the polystyrene. If we know the individual UV visible spectra, absorption spectra for polybutadiene, and polystyrene homopolymer, then from there we can easily get the composition of polybutadiene-co-styrene. We can use as we discussed in the case of GPC technique, we can use UV visible detector to find out the molar mass distribution, and we can get (( )) spectra, we can detector we can get the GPC, molar mass distribution **(( ))**.

And of course, as the pi bonds you know, the conjugation pi bonds, the more the conjugation the higher is the absorption, so I following the conjugate sequence of pi bonds, we can follow the conversion of polyacrylonitrile fiber into carbon fibers. So, these are some of the examples of UV visible spectroscopy in polymers.

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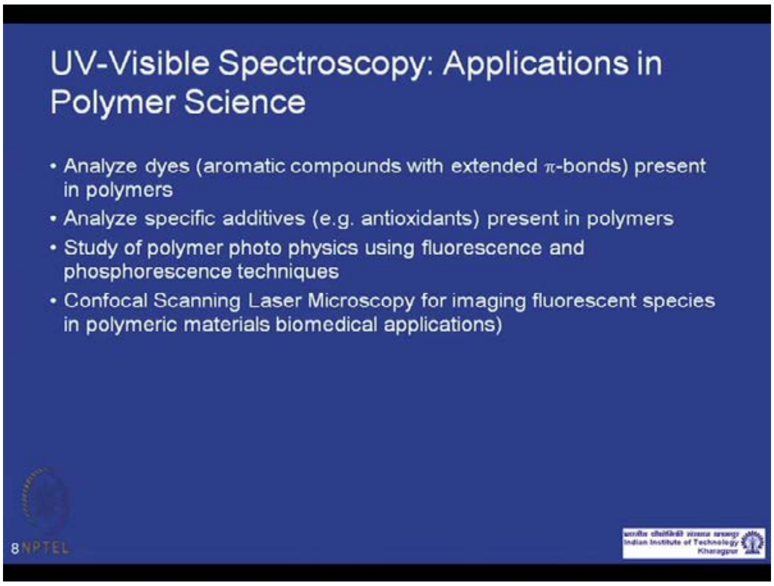

UV-Visible Spectroscopy: Applications in Polymer Science

- Analyze dyes (aromatic compounds with extended π-bonds) present in polymers
- Analyze specific additives (e.g. antioxidants) present in polymers
- Study of polymer photo physics using fluorescence and phosphorescence techniques
- Confocal Scanning Laser Microscopy for imaging fluorescent species in polymeric materials biomedical applications)

And next, we will move there are few more examples like dyes, sometimes we use dyes in a polymers for carbonation. So, we can analyze the amount of dyes present, we can also analyze specialized additives which are, where the additives are UV visible active. So, basically, we can use this sort of, we can use UV visible spectroscopy for this sort of use in polymer science.

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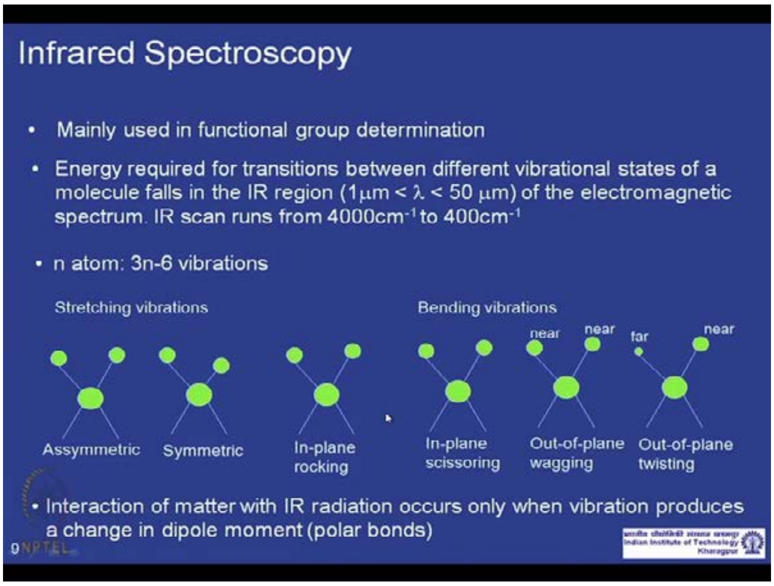

Infrared Spectroscopy

- Mainly used in functional group determination
- Energy required for transitions between different vibrational states of a molecule falls in the IR region ($1 \mu m < \lambda < 50 \mu m$) of the electromagnetic spectrum. IR scan runs from 4000cm^{-1} to 400cm^{-1}
- n atom: 3n-6 vibrations

- Interaction of matter with IR radiation occurs only when vibration produces a change in dipole moment (polar bonds)

So, next move to the IR spectroscopy, and as I mentioned, we will just mention the basic things about the spectroscopy, and then move to the application polymer science. Now, as we all know that IR spectroscopy are mainly used in functional group determination, and it is basically, a transition between in different fiber, vibration states of a molecules. And this energy gap between the vibrational states such that, that it it resonate with the electromagnetic radiation about, having wavelength of 1 micron to 15 micron.

So, typically we run IR spectra from say 4000 centimeter inverse to 400 centimeter inverse, and for a non-linear molecules there are n atomic, if the molecule have n atom, the numbers vibrations is 3 n minus 6, so you can imagine for a polymer molecules which have large number of atoms. So, many numbers of vibrations are possible, and each have a individual individual absorption in that higher region, so the higher spectra of polymers have lot of this absorption bands, and it is impossible very difficult to assign for a particular reason, or particular vibration, for all the absorption peaks in IR spectra for a polymer.

But, obviously, that does not restrict us to use highest technique to polymer characterization, because the functional groups present in a in a molecule, it may be in the polymer as well, they do not change the absorption the absorption in IR whether, it is present in a small molecule or a large polymer molecule. So, what happen if we found those particular vibration bands or IR peaks, then we know the, we can assure the presence of those particular functional groups in the polymer, which help us to characterize the polymer molecules.

So, as we know that there are a different types of vibrations possible like stretching and bending, and this is important that interaction of matter with IR radiation offers only when this vibrations produces a change in hyper movement. So, it happens, so the higher spectra, higher absorption happen only for the vibrations or bending vibrations for polar bonds.

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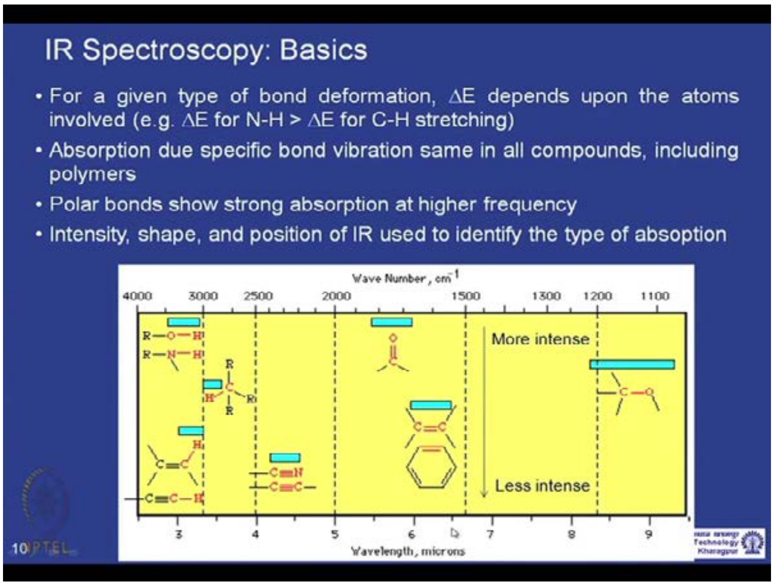

IR Spectroscopy: Basics

- For a given type of bond deformation, ΔE depends upon the atoms involved (e.g. ΔE for N-H > ΔE for C-H stretching)
- Absorption due specific bond vibration same in all compounds, including polymers
- Polar bonds show strong absorption at higher frequency
- Intensity, shape, and position of IR used to identify the type of absoption

And this is the chart or carton gives, typically the range where this IR absorption happen for a particular bond vibrations, like range, N H, (( )) in this range, see triple bond in then comes this say C over double bonds comes around here. So, this is basically a guideline for where the peaks come for a corresponding to functional group, polar bonds show strong absorption that IR frequency generally, and intensity shape and the position of this IR bands are typically used to identify the type of absorption.

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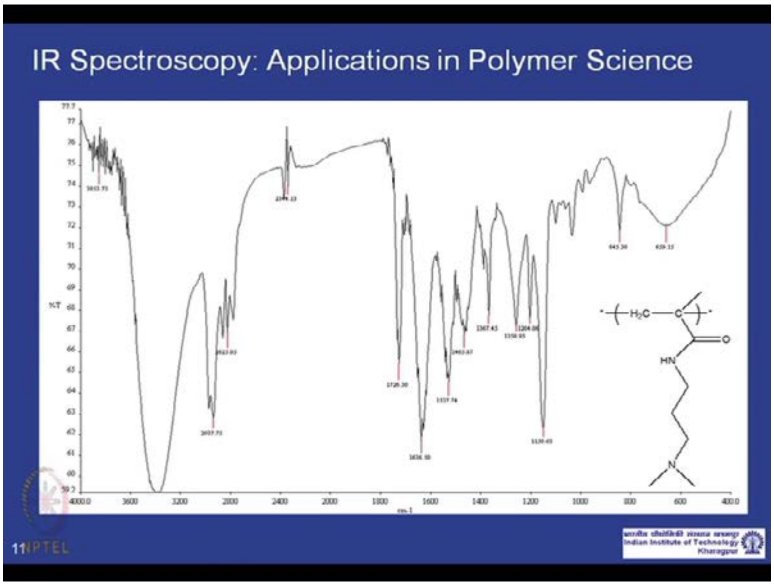

IR Spectroscopy: Applications in Polymer Science

This is example of H 2 I x spectra for this particular polymer, and this is like this is a particular bond for NH 3, NH stretching, this is for CH stretching and so on. So, this the IR spectra, for it is not very special in the sense, that it is same as the that the use of IR in detecting the chemical chemical structure of polymer molecules is similar to the application of IR for small organic molecules. It basically, help us to determine the presence of functional groups in polymer molecules.

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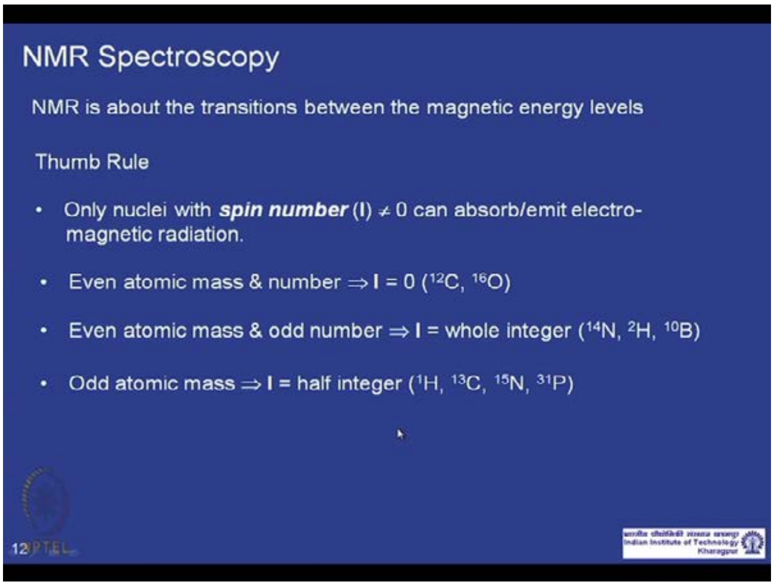

NMR Spectroscopy

NMR is about the transitions between the magnetic energy levels

Thumb Rule

- Only nuclei with ***spin number*** **(I)** ≠ 0 can absorb/emit electro-magnetic radiation.
- Even atomic mass & number ⇒ **I** = 0 (^{12}C, ^{16}O)
- Even atomic mass & odd number ⇒ **I** = whole integer (^{14}N, ^{2}H, ^{10}B)
- Odd atomic mass ⇒ **I** = half integer (^{1}H, ^{13}C, ^{15}N, ^{31}P)

So, what we will do, we will go next to NMR mass spectroscopy, and now as this all of you may be knowing that NMR is about transition between magnetic energy levels, so few thumb rules like, if the molecules is NMR or a nuclear is NMR active, if the spin number I is not equal to 0, if it is 0 then it is a it is not a NMR active. And there few general thumb rules, if the atomic mass if the atomic number are both given then I is 0, so they are NMR inactive the atomic mass is given, atomic number is odd, then it is I s whole integer, and all nuclei having odd atomic mass, they have a half integers, so like proton, carbon 13 they all have I value of half.

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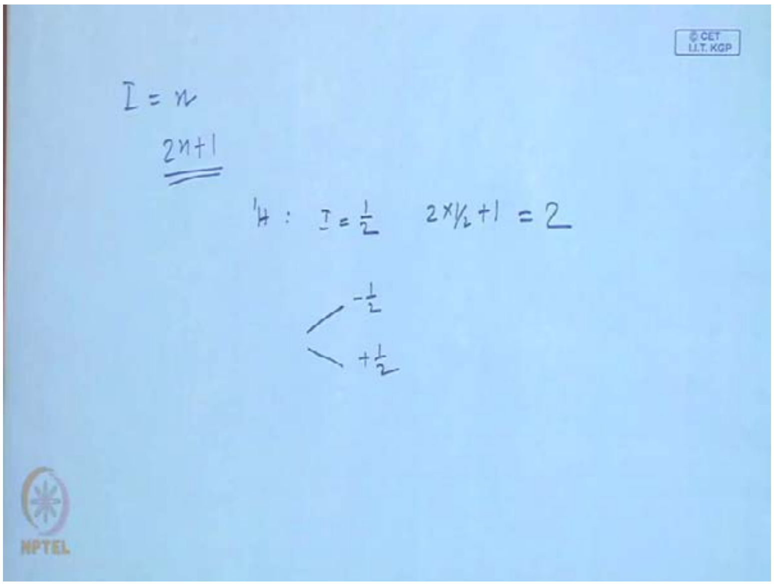

Now, they can they can in general term rule of thumb is that, if the I is I has some value than 2 n plus 1 is the numbers of states, they can basically, they have the number of states levels, energy levels, magnetic energy levels. So, if for a proton I is half, so it can have 2 into half plus 1, which makes it two different energy levels, which is basically we call this is minus half and plus half.

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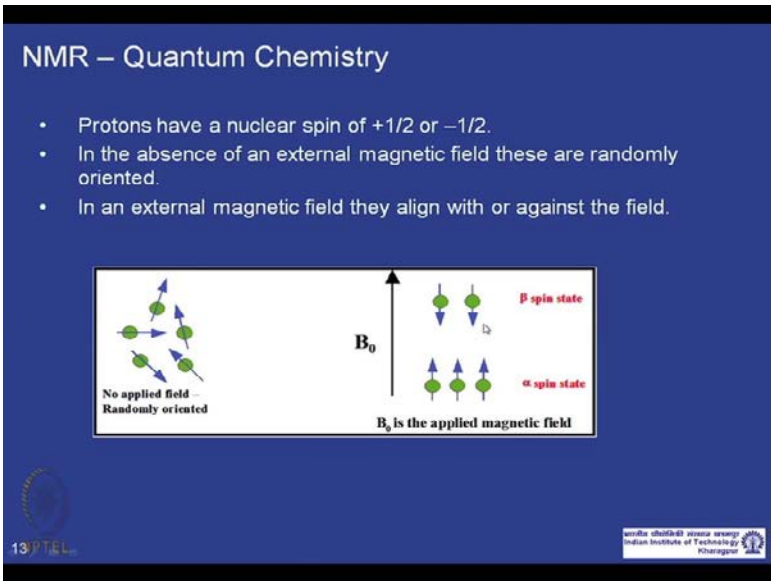

NMR – Quantum Chemistry

- Protons have a nuclear spin of +1/2 or –1/2.
- In the absence of an external magnetic field these are randomly oriented.
- In an external magnetic field they align with or against the field.

So, what happened, in terms of pictorial representation and this for a proton molecule, this pins are randomly oriented, when there is no external magnetic field, now in the absence of any external magnetic field, these are randomly oriented. Now, if there is external magnetic field applied to the molecule, then they can align in two different way, they can align with the external magnetic field or they can align against the magnetic field; now there is two states or energy different where this is having higher energy, then this, so this lower energy and this is half energy, less than higher energy.

So, in presence of external magnetic field, the nuclei can have two different energy state and now if we apply a nuclear magnetic radiation, whose energy is in this in this gap, in this range. Then sum of the spin, some of the nuclei from this lower energy level, can move to the higher energy level by absorbing the nuclei magnetic radiation.

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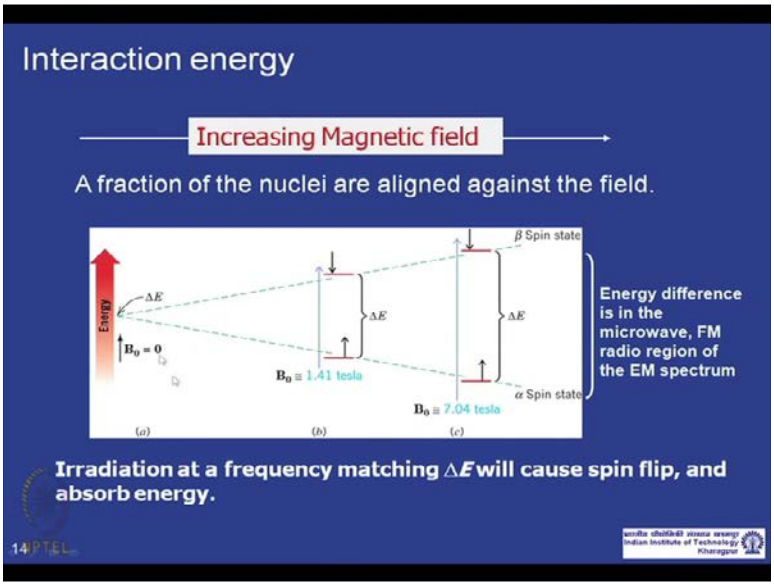

Interaction energy

Increasing Magnetic field

A fraction of the nuclei are aligned against the field.

Energy difference is in the microwave, FM radio region of the EM spectrum

Irradiation at a frequency matching ΔE will cause spin flip, and absorb energy.

With increasing external energy, external magnetic field, the energy between the two state increases, and with increasing in the difference between the two energy states, the population is in the lower state which is ground state, becomes more and more compared to the higher states. So, if we have higher magnetic field, there will be more number of molecules or nuclei in the lower state, then higher state, so when you have a nuclear magnetic radiation coming, the more number of nuclei can move to the higher higher state causing absorption. So, with increasing in external field, the intensity of absorption always go up, and the sensitivity of the instrument, of the of the measurements goes up.

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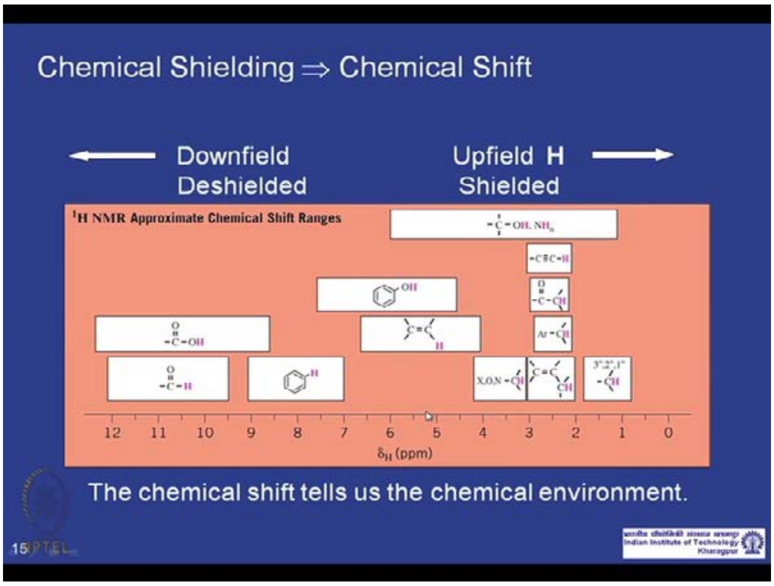

Chemical Shielding ⇒ Chemical Shift

Downfield
Deshielded

Upfield H
Shielded

The chemical shift tells us the chemical environment.

Now, this is we know that in a molecule, in a molecule not every nuclei experience same amount of field basically, in surrounding a nucleus there is there are electron clouds, which basically seals some of the external magnetic field applied. And the more the shielding, more is the effective; less is the effective external magnetic field the nuclei experience. So, with the change in the chemical environment around nuclei, the effective magnetic field the nuclei experience will change, and hence the radiation the lambda at which it absorbs.

So, if you compare in a in a standard different groups, in case of in case we are talking about hydrogen atom proton, now this protons will have chemical environment, so they will have experience of a different magnetic field; so the resonance resonance energy will be different. Now, by though they are very small they can resolved, and so they can be put in a scale, so from the enormous spectra we can get idea about the chemical environment of the of the proton here. So, the more shielded it has higher delta, lower delta H value, and if it is deshielded, then it is a higher delta H value, now this probably (()) known to you, so I am not spending too much time on this.

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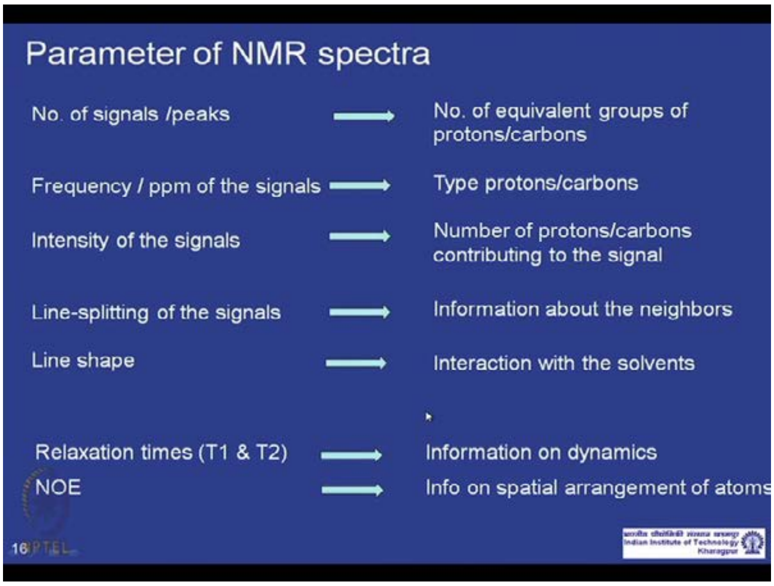

Parameter of NMR spectra

No. of signals /peaks → No. of equivalent groups of protons/carbons

Frequency / ppm of the signals → Type protons/carbons

Intensity of the signals → Number of protons/carbons contributing to the signal

Line-splitting of the signals → Information about the neighbors

Line shape → Interaction with the solvents

Relaxation times (T1 & T2) → Information on dynamics

NOE → Info on spatial arrangement of atom

There are, this may be also known, but let me complete when you observe a NMR spectra, what does it mean the number of signals or peaks we see in NMR spectra, it means that is the number of equivalent groups of protons or carbon, if you are talking about carbon. So, then spectra NMR spectra, then we are talking about that many number of that many number of equivalent groups of protons present in the molecules; the chemical shift of the delta H value will give the idea, what type of idea, what type of chemical environment, so what type of group.

So, what type of proton or carbon they are, intensity of the signals will be proportional to the number of protons or carbons contributing to a signal, so obviously, the signal from two protons will be double than the signal from one proton. The signals can have splitting which gives the idea about the neighbors, and the line shape whether it is a sharp, or it is broad it gives idea about the interaction of the solvent. More sophisticated NMR techniques like, relaxation time in a way, they give idea or information about dynamics of a molecule. So, in case of polymers, we apply lectures in time, if we get the relaxation time, then we can get the information about polymer dynamics, and we gets information about pressure went off atoms.

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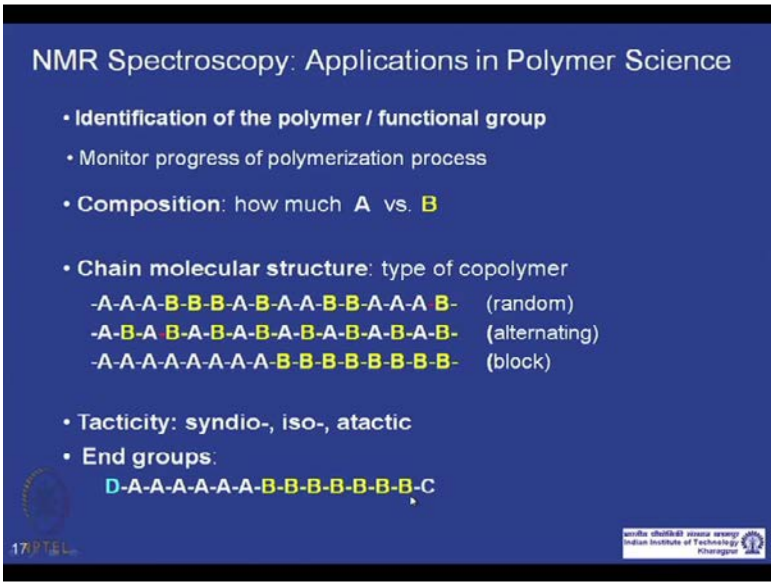

NMR Spectroscopy: Applications in Polymer Science

- **Identification of the polymer / functional group**
  - Monitor progress of polymerization process
- **Composition**: how much **A** vs. **B**
- **Chain molecular structure**: type of copolymer

-A-A-A-B-B-B-A-B-A-A-B-B-A-A-A B- (random)
-A-B-A B-A-B-A-B-A-B-A-B-A-B-A-B- (alternating)
-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B- (block)

- **Tacticity: syndio-, iso-, atactic**
- **End groups**:

D-A-A-A-A-A-A-B-B-B-B-B-B-B-C

Now, this is interesting in terms of how we apply NMR spectroscopy for polymer science, the discussion about, last few minutes about NMR spectroscopy is about general, which applied to any organic chemistry or any other science NMR, any other course. But this is specific to polymer science or polymer chemistry where we apply NMR for identifying the chemical structure, composition and microstructure; obviously, the first one is the identification of polymers, and functional group, and this is same as the way we identify the organic molecules from NMR spectra and functional groups, so this is this is not made from the chemicals shift.

And the intensity, and the coupling values we can get information about the polymer, and the functional groups. Obviously, we know which are the monomers we have used for making the polymers, so we have a priory some idea about the NMR spectra, so basically, this confirms that the polymerization has taken place. Obviously, the NMR spectra for the monomer will be different, then it specially different than the polymers for example, if you have vinyl, any vinyl molecules. So, with polymerization the double bond will be absent, so with progress, with falling intensity of the double bonds and protons in that C C double bond, we can follow the polymerization process.

We will just give a example in a minute to elaborate more on that, composition if you are talking about say copolymer between A and B, we will be able to find out using NMR how much A, and how much B, in the final polymer what is type of chain structure, whether it is random or it is alternating or it is a block. Nature of copolymer; that is able to we will be able to find out using NMR spectra for a homopolymer, we can get idea about the tacticity, and also if we apply some chemical reaction or if we can find out the end group; we can get information about the end group present in the polymer.

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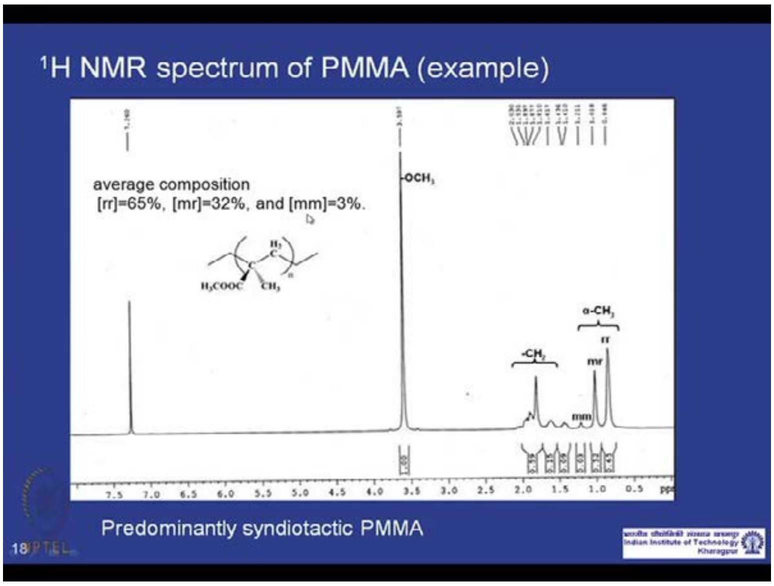

^{1}H NMR spectrum of PMMA (example)

average composition
[rr]=65%, [mr]=32%, and [mm]=3%.

Predominantly syndiotactic PMMA

Now, let us discuss few examples, now this is a NMR spectra, proton NMR spectra form PMMA, this is one example, one PMMA not every PMMA in the lab or plant should look like this; but it is one example, one PMMA made in the lab, this is the proton spectra of that particular PMMA sample. Now, this obviously, this shows that the, this is for O methoxy group O methoxy group, and this peaks up for alpha methyl group this one and these two protons are given by here, Now, this alpha, the protons from alpha methyl groups they will have different chemical shift, depending upon the special arrangement of the next carbon for example, if the next carbon here this particular one, if we draw this in explain little bit here.

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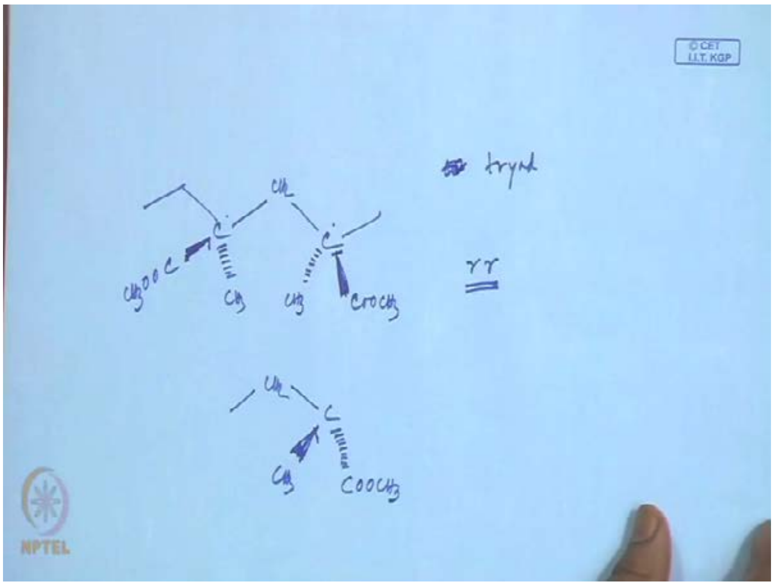

Now, here it can have two special arrangements, one it can have like CH 3, and so in this case we as we discussed in terms of copolymerization. This is one arrangement and you can have same here, and now this is a arrangement which is alternating here, and this is two carbon have alternating stereochemistry, so this is a tryad, this is a t over tryad, and their arrangement is r r, racemic.

And this case, it is if I talk about this thing, they will be different, so all these three arrangement r r, m r and m n they will have different chemical shift. And from this particular sample it is seen that it is seen that, if you go back and look at that NMR spectra in the computer screen, this this r r is the maximum compared to the other two other two signal. So, if you compare under this curve which is nothing but the intensity of those signal it comes out approximately 65 percent, and this is 32 percent, and this is 3 percent, which shows that this synthesize PMMA is predominantly a syndiotactic

PMMA, if you have this m n groups maximum, then you would have isotactic PMMA maximum (Refer Slide Time: 33:51).

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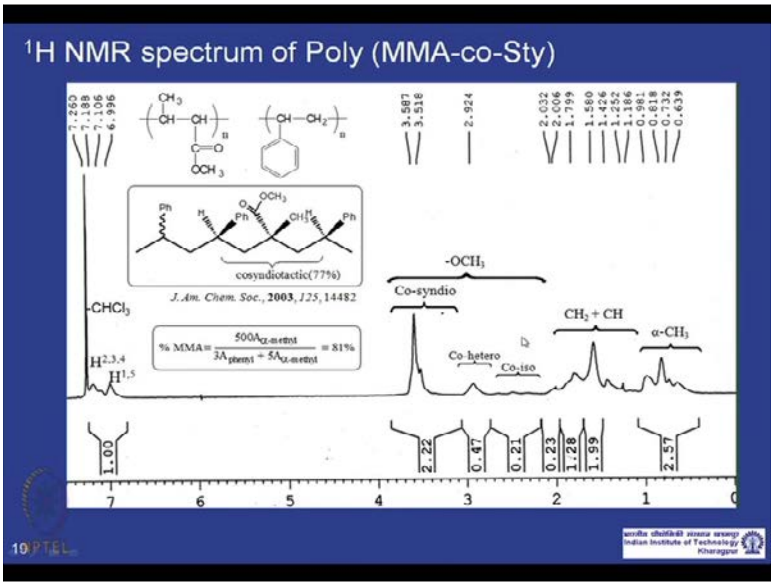

^{1}H NMR spectrum of Poly (MMA-co-Sty)

J. Am. Chem. Soc., 2003, 125, 14482

$$\% \text{ MMA} = \frac{500A_{\alpha\text{-methyl}}}{3A_{\text{phenyl}} + 5A_{\alpha\text{-methyl}}} = 81\%$$

Now, let us this is a spectrum for a copolymer of MMA and styrene, so this is a copolymer of copolymer of styrene and MMA, Methyl methacrylate.

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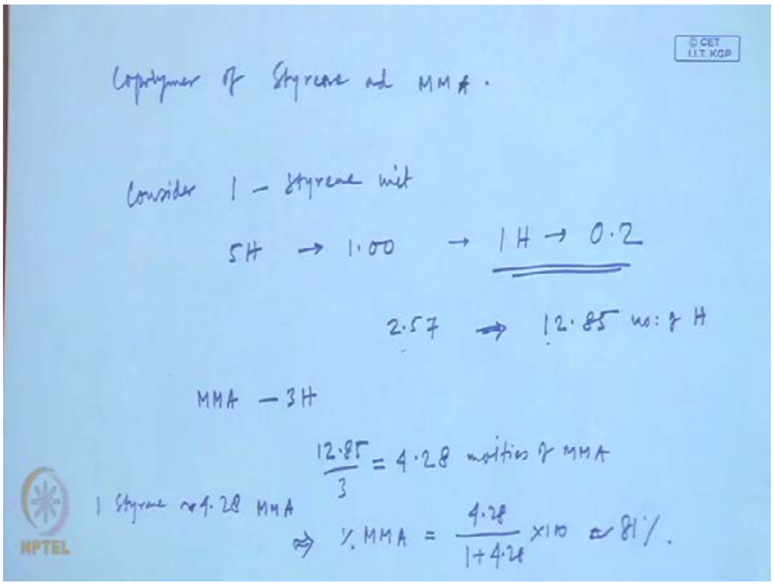

Copolymer of Styrene and MMA.

Consider 1 – styrene unit

5H → 1.00 → 1H → 0.2

2.57 ⇒ 12.85 no: of H

MMA – 3H

$\frac{12.85}{3} = 4.28$ moieties of MMA

1 styrene ~ 4.28 MMA

⇒ $\% \text{ MMA} = \frac{4.28}{1+4.28} \times 100 \approx 81\%$.

Now, if you look at this sub NMR of this particular compound, this three proton peaks are for the 5 hydrometric hydrogen of the styrene, (( )) is so this 1, 2, 3, 4, 5 this, they are 5 hydrogen, for this 5 hydrogen automatic. These 3 peaks, 1, 2, 3 for this O methoxy protons, for this O methoxy group, and they also not same depending upon whether, they are syndiotatctic or hydrostatic or a isotactic, they are chemical shift value will defer. This is for your alpha CH 3 of the PMMA group, and these peaks are these 3 carbon atom from polystyrene backbone, and this took hydrogen from the PMMA background.

So, what does this spectra help us, this spectra can give us the idea about the composition, for example, if we talk about this 5 hydrogen see, if I consider just consider that you have one styrene molecule, one styrene one styrenic unit rather in the polymer background, so it have 5 hydrogen now the integration corresponded to this is 1.00, so this is 1.00 for 5 hydrogen. So, 1 hydrogen give me, this means 1 hydrogen corresponds to 0.2 integration, so if you consider now this alpha CH 3 this is from 3 proton for the NMR it is, now the integration for this 2.5457. So, if 1 hydrogen corresponds to 0.22, 0.57 integration will corresponds to 12.85 multiplied this by 5 you will get 12.85, so this is the number of protons.

Now, each MMA (( )) each MMA munity will have 3 hydrogen, so how many MMA munity, if you divided if you divide 12.85 by 3 which is 4 2 8 around 4.28 munity of MMA. So, in this spectra corresponds to 1 styrenic munity, and 4 point may be about 4.28 MMA munity, which means the composition percentage of MMA is 4.28 1 plus 4.28 into 100, which gives around 81. So, from this is one example that using the proton NMR spectra, you can actually get the information about this, the composition of the copolymer.

Now, obviously, to do this exercise you have to identify peaks, which are correspondence to particularly 1 munity for example, this one we had for the styrene munity this one for this PMMA munity. And also we need to very careful about that we have to run as many as can in the NMR as possible, this spectra more quantitative the lesser, the number of scam the error the more will be error in the in the composition. So, from this example where we can find out the composition of the copolymer, and what is the copolymer in this case it is, it can be seen it is more of course, syndiotacttic copolymer.

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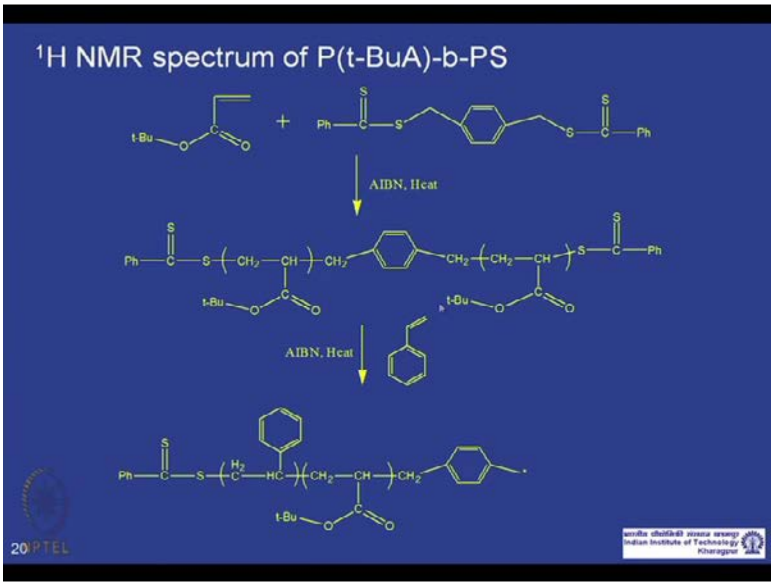

^{1}H NMR spectrum of P(t-BuA)-b-PS

Next example is, this is we are tying to we made a block copolymer of poly tertiary butylacrolate, and polystyrene using living radical polymerization raft, so this is the monomer. First this is the reaction scheme this is the monomer tertiary, (( )) and it was reacted with this, it is underground radical polymerization by AIBN in range of heat, in presence of this gel transformation, and you have this first (( )) or first block.

So, this is a block of tertiary, butyl, acolyte there should be two ends here to represent this is unit, now from this what we can do, we can get the molecular weight of the first block, and then when we react with a another monomer this case styrene, then we can make a block copolymer, this is also present in this side. So, we have this is the way we synthesized a block copolymer of this (( )) and polystyrene, so from this the NMR structure of this we can get the molecular weight of the first block, and from the NMR of the proton NMR of this second we can get the composition of polystyrene and poly tertiary applied, and obviously, from that we can get, the length block length of the second block as well, how?

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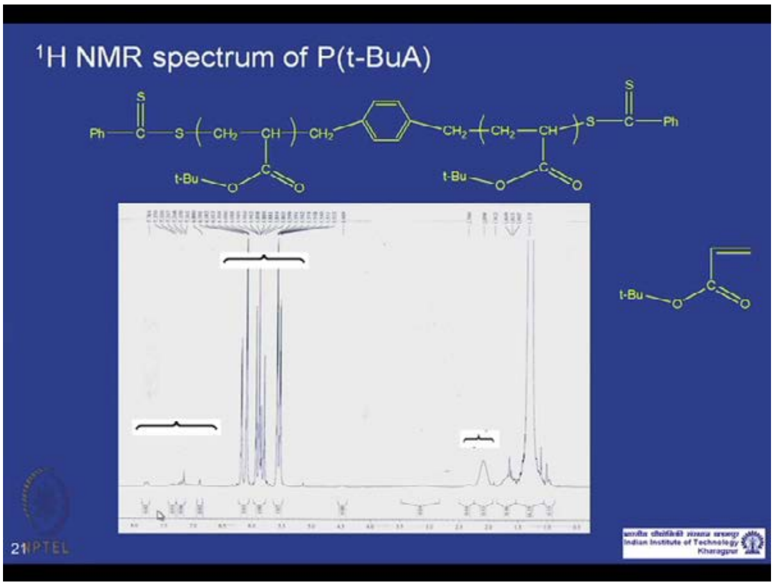

^{1}H NMR spectrum of P(t-BuA)

This is the example, the spectra for the first block, which is the tertiary block, the block of tertiary butylacrolate; now this this peaks corresponding to this 4 aromatic protons, so you cannot see properly.

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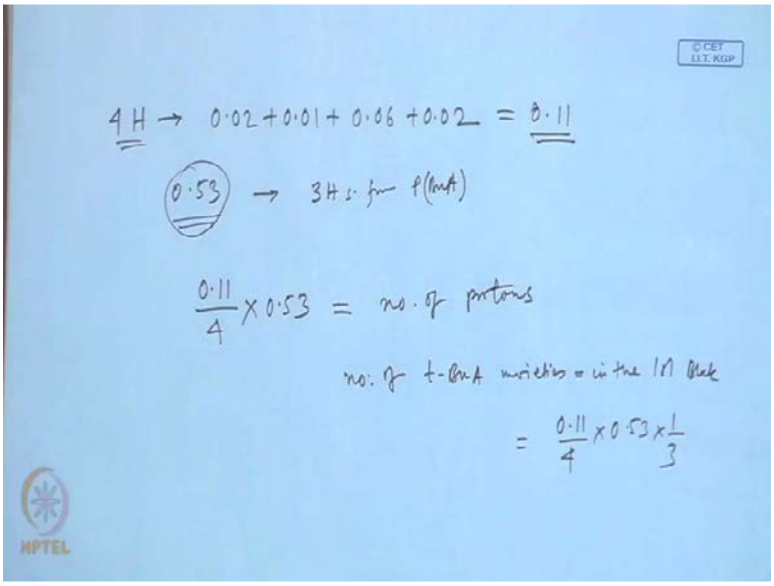

$\underline{\underline{4H}} \rightarrow 0{\cdot}02 + 0{\cdot}01 + 0{\cdot}06 + 0{\cdot}02 = \underline{\underline{0{\cdot}11}}$

$\boxed{\underline{\underline{0{\cdot}53}}} \rightarrow$ 3Hs. from P(tBuA)

$\frac{0{\cdot}11}{4} \times 0{\cdot}53 =$ no. of prtons

no. of t-BuA moieties in the 1st Block

$= \frac{0{\cdot}11}{4} \times 0{\cdot}53 \times \frac{1}{3}$

But, it comes around total 4 hydrogen comes around 1 1, so this corresponds to 4 hydrogen of 4 aromatic protons. Now, this 0.53 this 0.53, this 0.53 is from the 3 hydrogen, this 3 hydrogen of the polymer, poly butylacrolate blocks that corresponds to 3 hydrogen hydrogens from poly butylacrolate block. Now, if 4 hydrogen corresponds to

1 1, then how many hydrogen it should correspond to 0.11 divided by 4 multiplied by 0.53, so this is the number of protons, for that particular signal. So, that the number of tertiary, butylacrolate munities in the first block in the first block is by 4 divided by divide by 3, 4 hydrogen corresponds to 1, so 1 hydrogen corresponds to there may be a mistake I am making here, so this could be fine.

So, what I may be, the calculation may be something may be little different, but what you understand what you know that, if you consider this R from, this four aromatic protons, and this form this three protons from tertiary, butylacrolate munities, then obviously, you can find out from the intensity ratios. How many protons are there, and from that how many tertiary, butylacrolate groups, and from that you can get the molecular weight of the first block simple.

And look at these peaks, this are for the these 3 hydrogen present here in the monomer 1, 2, 3 and 1, 2, 3, 3 peaks for the polymer 3 olefinic hydrogen present in the monomer. So, if you had the ratio from the ratio of the peaks of this corresponds to 3 protons for the monomer and this correspondence, and this corresponds to the 3 protons of the polymer, so from this ratio, you can find out what is the conversion of monomer into polymer.

So, obviously, with more and more time the reaction goes, this will come down and this will go up as the molecular weight also goes up, so this means that not only using proton proton NMR spectra we can get the molecular weight of the first polymer, but also we can monitor the this is a spectra from fluid sample. So, we can monitor the amount of conversion of monomer into polymer with time, so basically we can do a kinetic study of kinetic study of the polymerization process.

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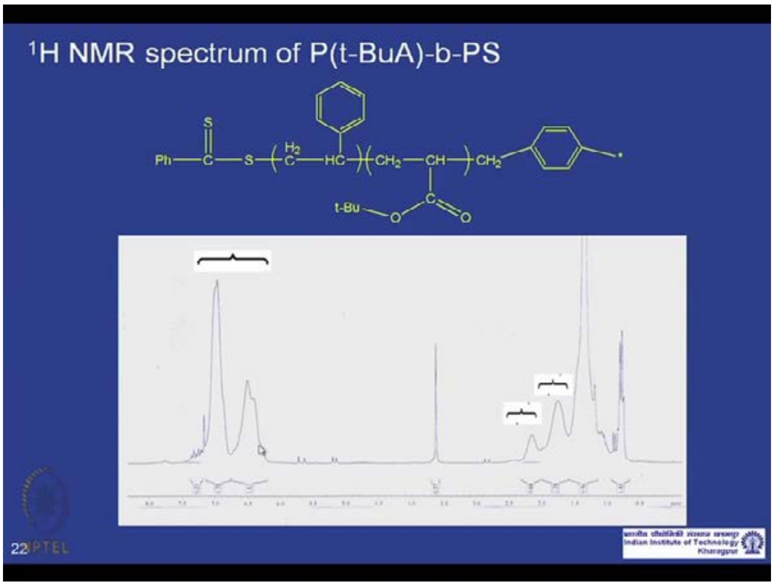

¹H NMR spectrum of P(t-BuA)-b-PS

Now, once you isolate the pure monomer first block, and then add to the, and then reacted with the styrene molecule we get this block copolymer; obviously, from the ratio. Now, this if you this is a longer longer chain, so obviously, you can ignore this four aromatic compounds compare to the number of aromatic protons present in the styrene. So, you can assume that all the aromatic protons peaks are from this 5 styrenic munities, whereas, this particular peaks are from the 3 hydrogen’s from tertiary butylacrolate munity, and for styrenic munity.

So, from the ratio of these two, you can now find out what is the moral ratio of the styrenic munity and the tertiary butylacrolate munity, and you already know the molecular rate of the tertiary butyl munity, so obviously, now you can find out the molecular weight of the styrene munity or styrene block as well. So, with this is the example where we showed that using proton NMR, you get the molecular weight, and obviously, you need a end group type, which is specific pick for end group it was the styrenic peak, which were available to determination.

So, not only we can find out the molecular weight, we can find out the conversion from monomer to polymer, and also if we add the second monomer to form a block, then we can get the information about the composition of the block, as well as the length of the all the molecular weight of individual block. So, this is example where we showed that the proton NMR can be useful to get information about polymer microstructure.

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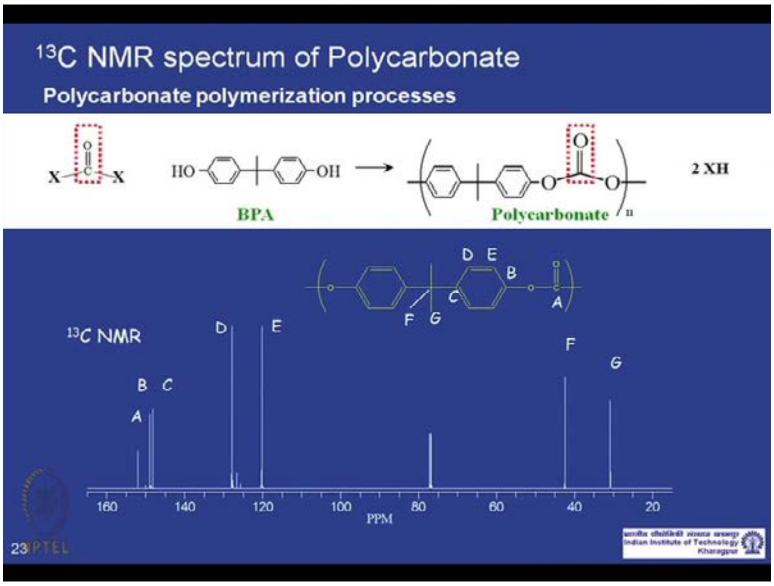

^{13}C NMR spectrum of Polycarbonate

Polycarbonate polymerization processes

Now, let give, let us give few examples where we talk about carbon 13 NMR, can be used to quantify and identify the polymers. Let us take a example of polycarbonate, we know we have seen during our first few lectures, this is the way we make polycarbonate, this final a is reacted with a carbonate source, so this is the structure of polycarbonate. Now, from a carbon 13 NMR spectra, we can assign each individual carbons in this polycarbonate and this is this is the special A, this carbon this carbon from the carbonate peak is special, because with help of this spectra we can find out the composition of a copolymer, which will show as a example in the new next slide.

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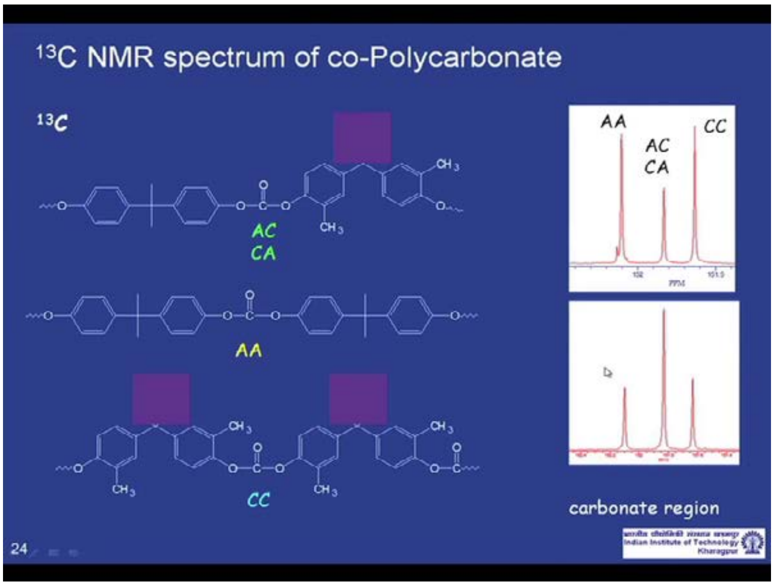

^{13}C NMR spectrum of co-Polycarbonate

So, this is a example of co-polycarbonate which is consist of DPA, and the other compound TNB time, we are talking about, now this carbonate peak we call this A and this A, so this particular is from, if this is if the copolymer have two, this final A group making A carbonate linkage, which we can get information from the disfinal polycarbonate homopolymer. So, we can assign this polymer A from polycarbonate DPA homopolymer, similarly we can make a homopolymer of this particular monomer, there we can know what is the chemical shift for this carbon C 13 peak for this particular carbonate.

So, when you have copolymer from the ratio of the three, these three peaks, the amount of this type of carbonate present in the system, so if you these are the example for this copolymer made from this two processes. So, in case of in case of a, say if you are having a 50:50 mixture of A and C, these are 2 monomer.

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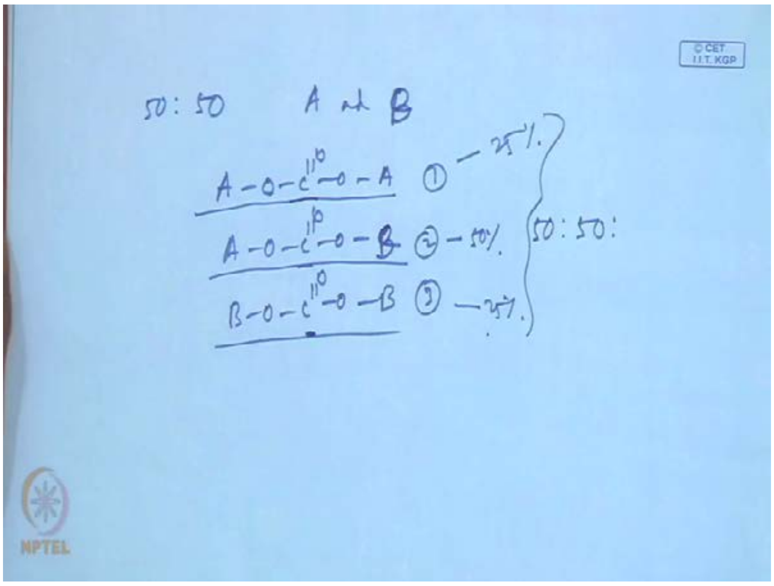

And you can have A C O, you can A C O O C, let us put it B make it, and you can have, so three types of carbonate possible, this one, this three, 1, 2, 3, now this peak we can find out from a homo polycarbonate of A, this one from homo polycarbonate B. So, the third peak would be from this, now from the ratio of the intensity of these three, we can like in this NMR green spectra, we can find out what is the ratio of this particular type of present in the copolymer.

So, if you go back and look at this screen, computer screen, this is the in this process of polycarbonate this peak is correspondence to A A, this block, this carbonate, and this is corresponding to this particular carbonate, and this is for the this particular group. So, which makes that, this is present in double amount corresponding to this individual, so if you start with a 50:50 mixture obviously, if it random it is from a random copolymer, you will get this as a 25 percent, this is 25 percent, and this is 25 percent plus 25 percent 50 percent.

So, if it forming A and B is forming a completely random statistical copolymer, then the percentage of these 3 carbonate peaks would be 25 percent 50 percent, and 20 percent that is exactly this is the example of 50:50 copolymer, this is where exactly happens. So, this is, from this curve this NMR we can say that, in this process we get a statistical random copolymer whereas, in this case you can see that the tendency of formation of A block, A type carbon carbonate and C C type carbonate is much higher than the A C or C A type carbonate, which means the polycarbonate here is more of a block in nature, then this, this is a more random work.

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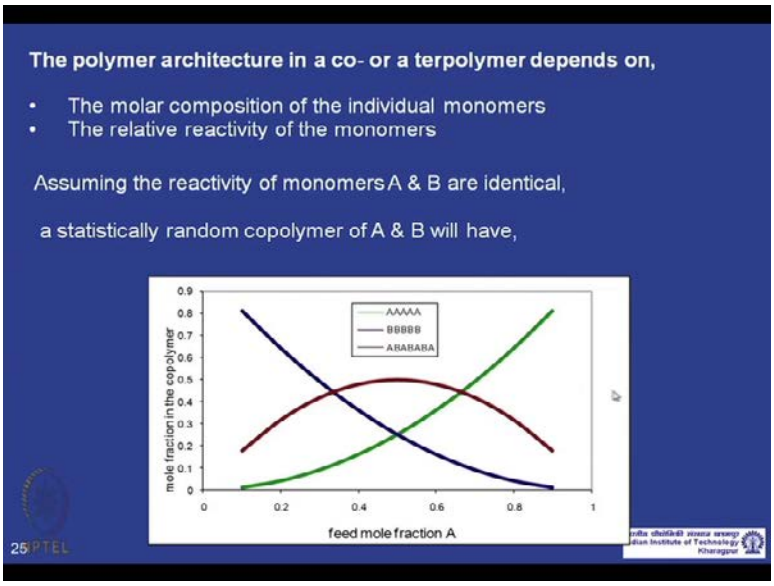

The polymer architecture in a co- or a terpolymer depends on,

- The molar composition of the individual monomers
- The relative reactivity of the monomers

Assuming the reactivity of monomers A & B are identical,

a statistically random copolymer of A & B will have,

So, if at least with this type NMR’s analysis, we can clearly say that whether a copolymer is a random copolymer or a block type copolymer. So, if you from this chart, we can this is a this is a statistical way of presenting the expected value of mole fraction of the type of linkages in the copolymer, with the mole fraction like in this case, if we have a 50:50 composition of A and B, so our composition was mole percent 0.5. Then this a block would be 25 percent, B B block would be 25 percent, and this alternating A B clock will be 50 percent.

So, this is for a purely statistically random copolymer which is the case for in this case, so this is how we can use NMR, we can get the information about the randomness and the blockiness in this. So, with this we stop for this lecture, and we will start the next topic in next lecture.