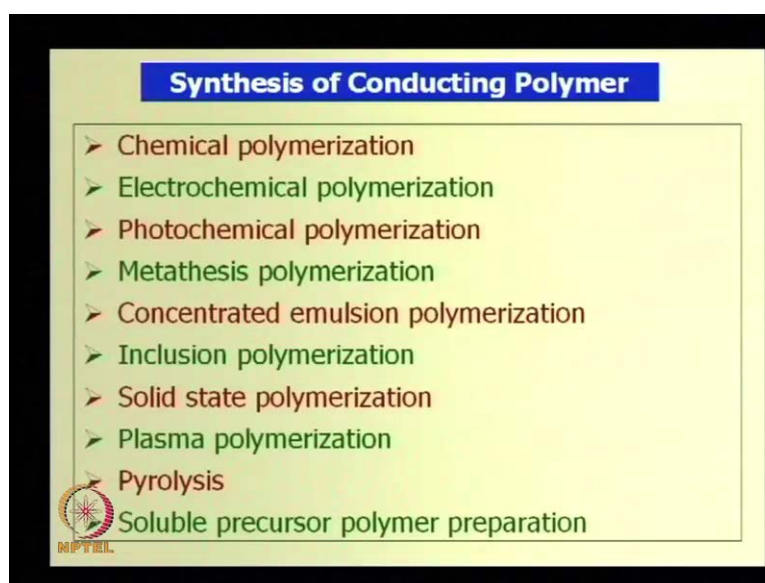


Science and Technology of Polymers
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Lecture - 23
Conducting Polymers (Contd.)

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From this list of different techniques for the synthesis of conducting polymers I mentioned that only few are very important, and many people are following those things, one is chemical synthesis, other is electrochemical synthesis. And the third one is plasma synthesis, so which helps, and this electrochemical synthesis can be done directly on a device on a substrate and there is no need to dissolve the polymer insolvent or heat the polymer to melt it for depositing a thin film on a substrate.

So, for direct deposition electrochemical synthesis is a good method provided a suitable electrode is available, suitable solvent is available of these things and then one can go for direct plasma deposition of the conducting polymer synthesized.

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Synthesis of polyaniline

Dissolve 5.17 g of aniline hydrochloride in 100 ml water

Dissolve 11.42 g of APS in 100 ml water and add to monomer solution drop wise with constant stirring

Stir the resultant solution for 1 h and keep for overnight

Filter, wash with distilled water, 1(M) HCl, DI water, diethyl ether, 1(M) NH_4OH and acetone and dry in vacuum oven at 60°C for 6 h

Keep the polymer in ammonia solution for overnight to get the emeraldine base form of the polymer

And for a typical synthesis of polyaniline as case studies, if you want to synthesize polyaniline by weight chemical method, how it is done? It can be done using this, either aniline monomer, pure aniline monomer or you can take aniline hydrochloride. Now, it is a case of oxidative polymerization, oxidative polymerization, where an oxidant is used, say ammonium persulfate and the polymerization is carried out in acid medium.

And we have found there is an influence of the pH of the polymerization medium on the polymer synthesis on the growth of the polymer molecular weight of the polymer and molecular weight distribution and microstructure of the polymer and molecular order that means crystallinity of these things. And during polymerization it has been observed, that that weight chemical synthesis of polyaniline from aniline in acid medium using ammonium persulfate as oxidant. It is an exothermic reaction. It increases the temperature, so there are some data on the increase of temperature during the course of polymerization of aniline to polyaniline in acid medium.

If you are interested there are some published papers from my laboratories, you can contact me, I can give you those papers. So, you can see there, as well as the concentration of acid, that means, the pH of the medium plays an important role there and the yield of the polymer also depends on the molarity of the acid, which is used during polymerization.

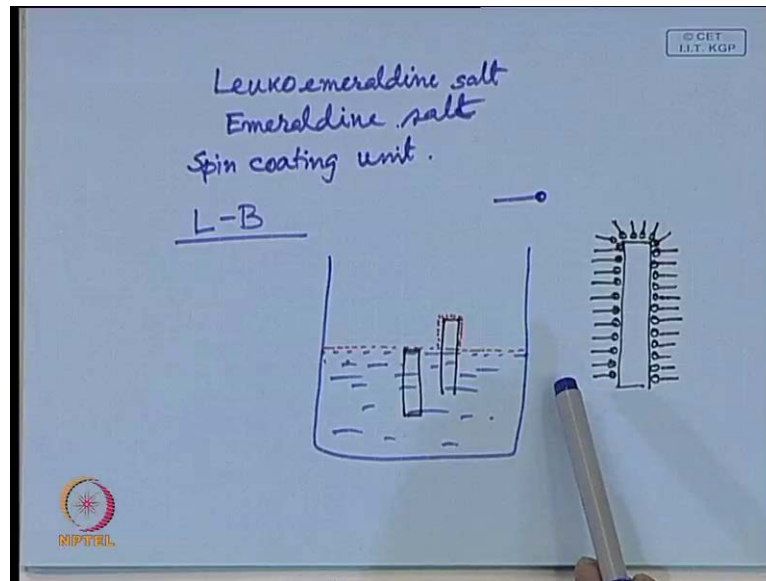
Now, here in a typical synthesis of polyaniline from aniline hydrochloride is 5.17 gram of aniline hydrochloride need to be dissolved in deionized water or pure water, say here it is, for this case 100 milliliter water was taken, then separately ammonium persulphate, APS, aggregated as APS, 11.42 gram of APS is to be dissolved in 100 milliliter water. And then this needs to be added to this aniline hydrochloride solution drop-wise with constant stirring. And since it is aniline hydrochloride it may or may not need to add external acid, hydrochloric acid, because here it contains already hydrochloric acid.

Now, as soon as this APS comes in contact with this aniline in this acid medium, immediately dark coloration starts and it becomes green, from green to deep green looking like black color formation, that is due to the growth of the polymer chain from aniline and that polymer, immediately once it forms, say more than dimer or trimer size. It becomes insoluble in the medium and it phases out; it comes out as precipitate. So, this way the reaction has to be allowed, allowed for maturing.

Now, the small oligomeric intermediates, which are found during such polymerization, during such synthesis, that need to be given scope for further growth and for that reason, that mixture is to be allowed to stand for overnight in stirring condition. Say, after 12 hours of stirring this precipitated polymer is to be filtered, washed with distilled water, then with acid in order to remove any unreacted monomer aniline hydrochloride. Then deionized, washed with followed by deionized water followed by diethyl ether and finally, with ammonia solution, then acetone in order to remove water before drying.

So, these are, these are the sequences of purification steps. First, distilled, your distilled water to remove the soluble, unreacted components, then acid, then DI water, then diethyl ether, then 1 molar ammonia solution and acetone and then it needs to be dried in vacuum oven at around 60 degree Celsius for 6 hours or more than 6 hours time. Then what is the, what polymer is obtained there? Now, it gives the polyaniline base, polyaniline base, since finally, it is treated with ammonia.

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So, initially the polymer, which precipitates out from the medium, that is salt, known as leucoemeraldine salt, leucoemeraldine salt, then emeraldine salt, both, both are insoluble in water. When that leucoemeraldine salt is treated with ammonia, that salt converts to base form, that is leuco, that is emeraldine base.

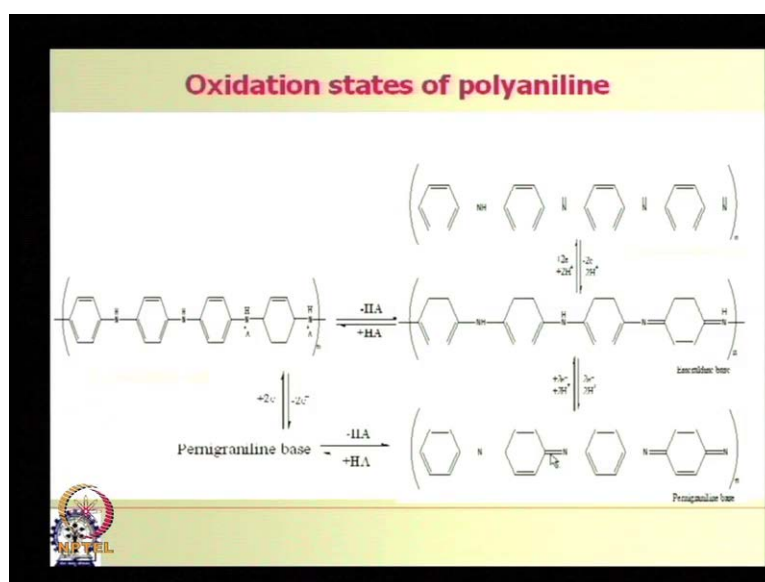
Now, it has been found, that the salt form is conducting in nature, whereas base form is non-conducting. Then what is the necessity of such conversion from salt to base? The reason is, salt is insoluble in solvents, that means, neither it is soluble in a suitable solvent or common solvents, nor it is fusible. So, how can you process? You can make it a pallet from there, you can make, you can measure the conductivity and rather electrical properties, but you have to have a device from this polymer. You have to dissolve the polymer or you have to melt it to make a film or a thin film or a coating on a substrate on a (()), that is not possible with emeraldine salt if you go through this weight chemical synthesis, as the method is shown over here, alright.

But if it is converted to base by treating with ammonia, now they, that base form is soluble in organic solvents like MF, dimethyl formamide, dimethyl acetamide, highly polar solvent can dissolve that base ball, ok. After dissolving, then you can make a thin film, we can cast a film by film, one of the various techniques of film casting on a substrate, then we have to make it again conducting by doping process. We expose that base form to ammonia vapor, sorry, to acid vapor, again it will convert to salt form and

by that time already you have fabricated it, we have processed it, that means, we have got a film over a substrate, do you understand.

So, the tactic is you make a solid polymer precipitate of salt, emeraldine salt, convert it to base, dissolve in an organic solvent, cast a film, then expose that film to some acid again it will be converted to salt form. That means, that is, you can say, that is, acid doped polyaniline or you can dope with other dopant species, dopant agent, doping agents, which can make it conducting. So, keep, for storing the polymer, keep the polymer in ammonia solution for overnight to get the emeraldine base form of the polymer.

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Look at the structure of the polymer; look at the structure of the polymer. Here, we see, this is leucoemeraldine base, sorry, leucoemeraldine, leucoemeraldine base formula of the leucoemeraldine base. You see, there is no conjugation in the structure. Why, if I ask you the question, why this leucoemeraldine base or emeraldine base is not conducting in nature?

For getting the conductivity from this polymer what we need? We need a conjugated double bond system, but here we see double bond, single bond, single bond, double bond. So, conjugation is effected here. So, there is no conjugation, but if there is some double bond in between this nitrogen and carbon or this nitrogen and carbon and there is shifting of double bond and then you can get, you see this structure here, you see the

double bond, single bond, single bond. So, these also not, but here in this structure double bond, single bond, double bond, single bond, double bond, single bond, double bond, like this.

So, this emeraldine base, after protonation, after protonation it can show little bit of conductivity. Then again it can be converted to emeraldine salt. This emeraldine salt, it is actually a color of this font, is not visible or may not be visible from there. This is emeraldine salt here, you see this double bond is there. So, this is the salt, N plus A minus NH plus N minus, actually this is known as imine form, m, i, m, i, n, e; imine form, imine form, imine form. That means, you have to have this kind of structure.

So, this is the original polymer; this is the original polymer. Here, you see this, a bond is there, here is also bond, it is, I do not know why it is not visible, but a bond is there. So, a benzene ring, these are all benzene rings, all benzene rings. So, there is, since there is no conjugation, since there is no conjugation you cannot get this conductivity from this structure. So, in order to get the conductivity of such type of structure you have to convert it to salt form by doping with acid or other agents. So, which will convert this structure to this imine structure, this imine structure, this is imine structure and this is actually a partly granulin base.

These structures are available in books, you can say books or in papers published in journals, like synthetic metals or sensors and actuators (()), you can see those journals, you can get there. So, this is the structure, you see single bond, double bond, single bond, double bond, so there is long extended conjugation. So, this, yes...

Student: So, the conjugation is only inside the ring no. So, how current propagate flow from one end of the polymers to the other end of the polymers?

You see, not only inside the ring, you see, it is the nitrogen connected three double bond here, then single bond, double bond, like this. So, here you see, from, in this structure single bond, double bond, single bond, double bond, single bond, double bond. So, this way the path may be like this or this or path may be like this. So, again it is like this. So, it provides a delocalized system of electrons, electron cloud, delocalized electron cloud.

Student: Sir, delocalization due to the lone-pair of the nitrogen (())

It will be due to the pi bond because here, here lone pair is here also, but it is not conducting and that lone-pair is helping the doping process.

Look at this structure, here lone-pair is available, but how you can get the conjugation here? You cannot get conjugation here, you have to, you have to get the conjugation by this salt formation or that means, if you, if you donate the electron or accept electrons from this structure, then you can get, that this kind of structure, this kind of structure electron donation or electron acceptor. So, that is the role of dopants and this is true for all conducting polymers.

Now, there may be some intrinsic conductivity that is different. Intrinsic conductivity is different, but for these extrinsic properties with the help of dopants, that can either provide electron to the polymer or that can accept electron from the polymer. So, that affects the electronic configuration within the polymer chain, polymer backbone, polymer molecule and that makes the polymer conducting in nature.

Now, in order to get that, you have to have a very good molecular order there. As I mentioned earlier, molecular order, if it is amorphous, then there will be, there will be conduction, electronic conduction or electrical conduction will be far more complicated and there will be scattering, electron scattering due to randomness or disorder in the molecular structure and conductivity will be less because we have read the semiconductors theory, semiconduction theories, semiconduction mechanism here we can see. Let us discuss, here is something we will understand the conduction mechanism from the subsequent slides.

(Refer Slide Time: 18:50)

Techniques of conducting polymer film fabrication

- Solution casting
- Spin casting
- Vacuum deposition
- Langmuir – Blodgett (LB) film fabrication

Nature of dopants and doping

The conductivity of a polymer can be increased several fold by doping it with an oxidation/ reductive substituents or by donor/ acceptor radicals.

NPTEL

And techniques of conducting polymer film fabrication, as I mentioned, it is done by solution casting. Dissolve the polymer in a solvent, make a solution, cast on a substrate, smooth, clean and smooth surface with the help of doctor's blade or by adjusting the viscosity of the polymer solution. So, we can get a thin coating over the substrate after evaporation of the solvent. It will give you a thin to thick films and that film can be sometimes face tending film provided the molecular weight of the polymer is sufficient, that means, you can peel off the film from the surface of the substrate on which you have cast the film.

Say, for example, you take a microscopic slide, which is flat or a flat based Petrie's, petri-dish over which you pour the solution, then evaporate the solution in controlled, at post solution, the polymer degradation oxidation does not happen there. So, after evaporation of the solvent, the polymer present in the solution, that will form a film. You can remove the film by peeling off and that film, if it is made from a reasonably high molecular weight polymer that will be mechanically stable, mechanically strong, so that you can handle it. That means, during such handling it does not tear out, so it is reasonably mechanically strong, so that you can handle it, you can make a device with that film.

Now, that is not, that is possible with this polyaniline, that is possible with polypyrrole, that is possible with polythiophene. I have seen it, yes, it is done, it happens, that

depends on how you have synthesized the polymer, to what extent you have grown the polymer, that means, what is molecular weight. And by virtue of that film casting, what happens? If it is a thin film one, then by applying adequate, adequate and suitable conditions of, during evaporation of the solvent, the polymer molecules can organize themselves in the film form to get better crystalline order. If you can achieve that, then you can increase the, you can get increased or higher conductivity rather than from in amorphous film. Do you understand? So, that is solution casting.

Then, there is another technique, spin casting, for getting a very thin film. Now, there are spin coating units available in the market, spin coating unit is nothing but a disk attached to a motor with the help of a shaft, horizontal disk. Over the disk, over the disk you put a dilute solution, a drop of a dilute solution of the polymer, then you rotate the motor at high speed, what will happen? By virtue of the centrifugal force, that will spread over the surface. Means, it is a, it is a flat platform over which you have put your substrate, say silicon on which you have added a drop of polymer solution, then you rotate the spin coating unit. So, that will rotate at high speed by virtue of the centrifugal force. So, it will be spread over the substrate and a very thin film coating can be available by that spin casting, that is called spin casting or spin coating of polymer film, that is, and the unit is known as, instrument is known as spin coating unit.

Or you can do vacuum deposition, say if in polyaniline, say in your laboratory you do not have this electrochemical synthesis setup. Do not worry, you go for this weight synthesis, as I described, get a pure and dry polymer powder, polyaniline powder, take a small quantity of polyaniline powder and in a small ampule, glass ampule or say, quartz ampule, it is better quartz ampule, keeping one end of the one side of the ampule open, now we place that ampule with the polymer in a vacuum deposition unit. Means, a cavity a container, which is connected to a high vacuum pump, say diffusion pump. Then you apply vacuum and you have to have a heating system over the, surrounding the ampule.

Suppose this is your ampule, small ampule, small ampoule. You can, you must have some heating element surrounding this ampule and that heating element with the ampule is placed in the vacuum unit, that container, then apply vacuum and simultaneously, you go on increasing the temperature by, through electrical heating, what will happen? That will increase the temperature of this ampule along with the polymer.

So, under such high vacuum, under such, say 10^{-6} or 10^{-7} () like that, under such high vacuum what will happen? And that, at the temperature this polymer will sublime or evaporate, alright. Over the ampule, open surface of the ampule, inside the ampule there is polymer and that is heating arrangement there that is getting heated. And the entire system is placed in a vacuum and over that ampule you have kept, placed a small substrate over the ampule keeping some space free, say 1 centimeter or 2 centimeter away from the open mouth of the ampule, alright. Then you continue this process of heating as well as vacuum application. Slowly, what will happen?

This polyaniline will evaporate and since this substrate is placed over this ampule, which is at, the temperature of which is not very high, cold, it is cold and this ampule is hot. So, when it is, the vapor is coming up, so when it gets the contact of this cold surface of your substrate, it will be deposited over there and you will get very thin film deposition of this polyaniline on the substrate. So, this is the technique, vacuum deposition.

Or else, you can go by, go for LB technique, Langmuir-Blodgett technique. You know what is Langmuir- Isotherm? There is a journal in the name Langmuir, those who works in physics, chemistry of physics they publish their research papers in the journal Langmuir. This is high standard journal. And what is LB technique, Langmuir-Blodgett technique?

Now, in order to get a monolayer deposition of a material on a substrate you have to do monolayer or a bilayer or a triple layer, all are organized layer. For example, you want to deposit stearic acid molecules, lipid molecules on a subsurface. What are this lipid molecules? Say, if you consider schematic of acid, stearic acid, lipid like, this having polar head, hydrophilic head, polar head, say carboxyl group, stearic acid and the tail is hydrocarbon chain, hydrophobic. So, a stearic acid molecule looks like this.

So, you take the solution of stearic acid in chloroform or some organic solvent, which is immiscible with water; chloroform is immiscible with water. So, you take a solution of stearic acid in chloroform, then if you put a drop of this chloroform solution of stearic acid on water, say if you take water in a beaker, you place a drop of stearic acid solution in chloroform, we will find that chloroform containing the stearic acid will spread over the entire surface. And you have seen, if you put a drop of kerosene oil or mustard oil or any oil on water what happens? Immediately it spreads over surface for a very thin layer

of that oil by virtue of the surface tension of the water and surface tension of this oil. So, by virtue of that property, this stearic acid in chloroform will spread over this water. So, it will remain, a very thin layer is remained.

And LB technique is nothing, say, suppose where is the interface? Just imagine here is a beaker or container. water is there like this. This is level, water level, upper meniscus and here is water molecules and over this, suppose you have a thin layer of stearic acid solution in chloroform. Then you take a substrate, you take a substrate (()), a substrate like this and you have to have a mechanism, so that you can lift it upwards, you can move it upwards. So, what will happen? By moving it upward this layer will be deposited on this surface like this. What will happen if you want to make a coating on a substrate with this stearic acid molecule? It may look like this.

If the surface is polar, if the surface is polar what will happen? You will get a layer of stearic acid coating on the substrate, it looks like this. So, a single layer of stearic acid is deposited on the surface. Now, this technique by which such monolayer is deposited, monolayer coating is done on a substrate, is known as LB technique or a double layer coating is done or organized layer coating is done on a substrate is known as LB technique, Langmuir-Blodgett technique.

Now, there is some technique epitaxial growth. Those we have read the semiconductor technology subject, epitaxial growth, what is epitaxial growth? Very thin layer of crystal, monolayer crystal is deposited on a substrate is called epitaxial growth that is, high organized. Now, for these organic molecules you can follow this LB technique. So, here if you have a conducting polymer, if you can find out a suitable solvent in which you can dissolve the conducting polymer, then if you have one LB unit in your lab, then with the help of that LB unit you can deposit a monolayer or a double layer. That means a thin film on a substrate.

Now, in our center we have one Langmuir-Blodgett film deposition unit. If you are interested you can see that unit, you can do in your lab class also, you can do some experiment there, we have one unit in our lab in our center. So, this is called LB deposition, Langmuir-Blodgett film fabrication, a deposition.

Then, let us see the nature of dopants and doping. The conductivity of a polymer can be increased several fold, several fold by doping it with an oxidation or oxidative or

reductive substituent's or by donor acceptor radicals, donor acceptor species, that is the basic concept. Now, abruptly you see, you cannot select any agent as dopant on a polymer. You have to see what is the structure of the polymer? Whether it can accept electron or it can donate electron. You have to look into the polymer structure. If you can judge that, then you find out some chemical agent, which can either provide electron to the polymer film or which can accept electron from the polymer and by doing so it can alter the conductivity of the polymer and accordingly, you can get a device, you can prepare a device with that polymer for certain applications. Say, in sensor technology these polymers are used by such, from that concept, using that concept.

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Electrical conductivity of polymers, although primarily depends on doping, are influenced by many factors, viz.,

- synthesis method resulting in different structures
- processing of polymers
- degree of crystallinity
- temperature

Stability and Processability

Conducting polymers exhibit

- Poor thermal and environmental stability
- Insoluble and infusible (due to extended chain conjugation)
- Hence their processability is poor

Due to the delocalization of electrons in the extended chain structure (conjugation) probably higher intermolecular cohesion occurs. This restricts the solubility in suitable solvent and causes degradation of polymers before melting.

Electrical conductivity of polymers, although primarily depends on doping, are influenced by many factors, namely synthesis method resulting in different structure. I mentioned that it can be branched, it can be low molecular weight, it can be high molecular weight or it may or may not be extended by electronic conjugation. This is a major requirement in conducting polymer extended by electron conjugation. If there is no extended by electronic conjugation we cannot, get conductivity, have conductivity from that polymer, so those are affected.

Then, processing of polymers, how is it processed, means, how you are depositing a thin film? Are you getting an organized molecule in the film or not? If it is organized you can expect better conductivity; if the molecules are not organized conductivity will be lower

and your device performance will be affected by that way degree of crystallinity and the temperature, then stability and processability conducting polymers exhibit.

Poor thermal and environmental stability; insoluble and infusible due to extended chain conjugation, yes, why it is infusible? Why it is insoluble? Now, you have seen, if two units combine together forming aggregates by virtue of their electronic interactions through secondary forces, etcetera, anything, then it becomes bigger in size and such species are difficult to dissolve in a solvent. Similarly, that means, it is, energy aspect is there, that is, salvation energy of the solvent is not sufficient enough to break those intermolecular, inter-unit species, your physical bonds or say thermal energy is also, may not be sufficient to break those bonds because the total quantity of such intermolecular force will be higher than the bond energy.

So, instead of breaking that, those intermolecular forces, what will happen? It will break the primary bonds and the stability of the polymer will be low. So, by, by heating or by putting in solvent that is not possible, so there conductivity or thermal properties are poor and environmental stability. And if this electron is responsible for such, free electrons are responsible for conductivity that cannot be environmentally stable, is not it, that will interact with, with oxygen, that mean, that will be oxidized by atmospheric oxygen or ozone or any other things present in the atmosphere. You do not know what is there in the atmosphere, so that means, they will be less environmentally stable than insoluble solvents and infusible by heat due to extended, that chain conjugation.

So, if I ask you why polyaniline is insoluble, because of this lone-pair of electron they form association, they form clusters. So, immediately after trimer or tetramer formation, they form clusters with inter-unit clusters and that form an, form aggregates and phase out. If it phases out, then that cannot grow to bigger molecular size because it should remain in (()) because this hetero phase reaction cannot occur. I do not know if some phase transfer catalyst is used, I do not know whether people have tried or not, phase transfer catalyst can, may solve such problem.

I, somewhere, I remember I told one of my student to try with this phase transfer catalyst, but he was impatient. He said no sir, it is not happening. But I believe, I believe from my concept and knowledge that this problem of insolubility of this polyaniline synthesized during weight polymer synthesis, weight polymerization, keeps a suitable

phase transfer catalyst can be found out that can help preventing the speciation of the polymer from the soluble solution phase to insoluble face. So, based on these considerations we can say, their processability is poor, processability of these conducting polymers are poor.

For that reason you see, that remarkable discovering leading to this Nobel prize winning took so many years, more than 15 years of time in order to make it in processable form, although that was, that was accidental discovery. I heard a lecture from Shirakawa who is, who is one of the Nobel laureates, Nobel laureates in this group, Shirakawa, MacDiarmid and Heeger, this is three persons were jointly awarded this Nobel prize in 2000, in the year 2000 due to their discovery success in 1987. They started this work in 1970. See, after such a long time they could show, that yes, very high molecular weight of polyacetylene can be developed, high molecular weight polyacetylene and that was accidental discovery by that group.

Due to the delocalization of electrons in the extended chains structure, probably higher intermolecular collision occurs. This restricts the solubility in suitable solvent and causes degradation of polymers before melting due to thermal energy.

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Doping techniques

- ❖ Gaseous doping
- ❖ Solution doping
- ❖ Electrochemical doping
- ❖ Self doping
- ❖ Radiation induced doping
- ❖ Ion exchange doping

Doping agents or dopants are either strong reducing agent or strong oxidizing agents. They may be neutral molecules and compounds or inorganic salt forming ions, organic dopants or polymeric dopants.

Now, let us come to the doping technique. Doping technique means, that means, either you want to incorporate some foreign agent, say you can say them as impurity; foreign agent as impurity. Those are, impurities are chemical compounds, how to incorporate

those impurities as dopant in the polymer chain, which is insoluble or infusible, that is a difficult task. So, people tried in many ways, various ways and these ways are your general roots, are mentioned over here: gaseous doping, solution doping, electrochemical doping, self doping, radiation induced doping, ion exchange doping.

Self doping, you see, that polyaniline synthesis from aniline hydrochloride leading to emeraldine salt, salt for the polymer obtained. That means this emeraldine salt is a self-doped polymer. Self-doped means, (()) polymer that is called self doping or in-situ doping, in-situ doping, alright, otherwise if you want to dope with other foreign agents, then either you have to take a solution of that dopant in suitable solvent. And we have to have a polymer solution in the same solvent or other solvent, which is miscible with the solvent of the dopant. Then we mixed these two, then cast a film, you can get dope polymer film solution, that is called solution doping or gaseous doping.

Say, if you want to dope iodine in polyaniline or polypyrrole or polythiophene, how you, do you know iodine sublimates? That means, it directly goes from, solid to, solid to vapors, say without, through any liquid phase vapor to as, your solid to vapor phase, then if that vapor can be condensed, then you can get solid once again without going through messy liquid phase. So, you take this polymer in a chamber, close chamber. There you keep this polymer and this small amount of iodine there, supply heat. So, heat the chamber slowly, iodine will sublime, vaporize. Now, that vapor, by virtue of their attraction, affinity with the polymer, if there is crunch of electron in the polymer, then iodine will be accepted, that means, if your polymer is electropositive like and this is electronegative like, then there will be attraction, affinity, then it will go into the bulk, from the surface it will diffuse through the surface into the bulk. So, you can dope with iodine that is called gaseous doping.

Similarly, that means, a kind of, you just convert this solid dopant to the vapor stage or gaseous stage, stage exposed to the polymer, then it will slowly diffuse into the bulk of the polymer and your polymer will get doped. Electrochemical doping, during electrochemical synthesis you put the dopant in the electrolyte there, electrolytic solution. So, during deposition of the film, this dopant will also be deposited, co-deposited along with the polymer, alright. Self doping, I have already said.

Radiation induced doping radiation, induced doping means, say, you can take a foreign agent, which is inert in the polymer as dopant, but that inert dopant can break. If you expose this thing to some high energy radiation, will forming free radicals or some ionic species, free radicals are ionic species. Keeping the polymer stable, polymer will not decompose, will not degrade or will not form any free radical, whereas the dopant will form free radical. So, by radiation induced process you can create this active species, which is present inside the polymer before which it is inactive or inert. Do you understand?

So, these are few concepts you can try with ion exchange doping, ion exchange doping. Now, if ion exchange process, you know, it depends on again the affinity of one ion to another ion. Suppose sodium chloride is ionic compound, cation and anion. Now, if this sodium cation, depending on its electropositivity, if it gets more electropositive, electro negative anion, then that anion will be exchanged with this fluoride ion. It is a very simple thing, very simple concept, easy concept. So, you have to see what is the electronegativity and the electropositivity of the polymer and the dopant, vice versa. Then you can find out a suitable dopant. Do not go blindly, apply some, apply your merit, apply your concept, basic concept, fundamental concept, then you can find out, you can select a suitable dopant for this particular polymer ion exchange doping.

The doping agents or dopants are either strong reducing agent or strong oxidizing agents. As I mentioned earlier, they may be neutral molecules even and compounds or inorganic salt, which can form ions or they can be organic dopants, which can create free radicals in presence of the polymer or where it is excited with some energy. When you are making, when you have already made some device, when that is exposed to some energy for the functions of the device to obtain there, it can act as dopant. That means, at, it can act as acceptor or donor or sometimes polymeric dopants can be used.

So, you see, these few words give a vast area of, vast scope of work on this conducting polymer and people are doing work. If you are interested, yes you can do, I am giving you the basic concepts only. It is high interesting, highly interesting.

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Mechanism of doping in polymers

Since dopants are strong oxidizing or reducing agents, on doping positive or negative charge carriers are developed in the polymers

$$\text{Polymer} + \text{Dopant} \xrightarrow{\text{Oxidation}} (\text{Doped polymer})^+ + \text{Dopant}^-$$
$$\text{Polymer} + \text{Dopant} \xrightarrow{\text{Reduction}} (\text{Doped polymer})^- + \text{Dopant}^+$$

In doped polymers charged soliton are formed

Soliton \longrightarrow **Charged defects with no spin**

A reducing, i.e., donor type, dopant introduces an electron to the polymer chain which couples with a neutral defect resulting in a negative soliton with zero spin.

Similarly on oxidizing (acceptor type) dopant abstracts an electron from the polymer chain and a positive spinless soliton is formed.

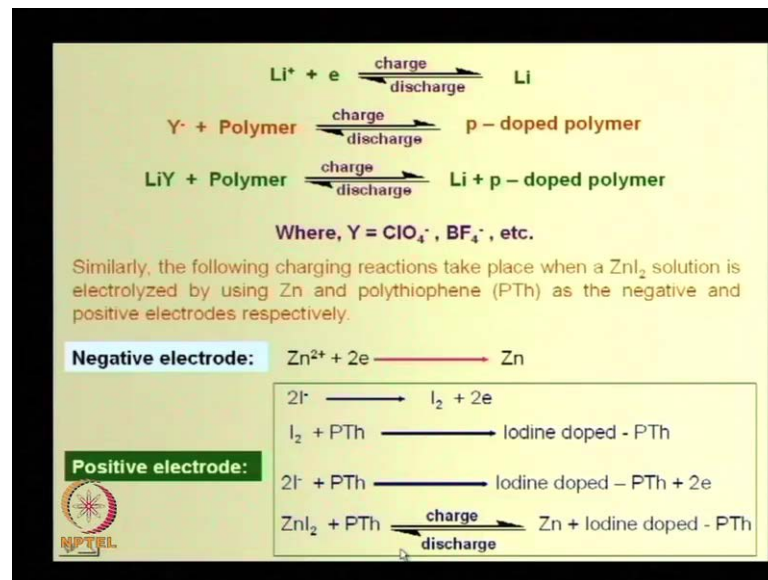
Now, look at the mechanism of doping of polymers. Since dopants are strong oxidizing or reducing agents, on doping positive or negative charge carriers are developed in the polymer. Polymer dopant oxidation, so doped polymer will be positive or doped polymer will be negative and dopant gives accordingly negative or positive.

In doped polymers charged soliton are formed. What is soliton? These are charged defects with no spin, charged defects with no spin, charge defect. Reducing, that is, donor type, dopant introduces an electron to the polymer chain, which couples with a neutral defect resulting in a negative soliton with zero spin. Similarly, on oxidizing, that means, acceptor type dopant abstracts an electron from the polymer chain and the positive spinless soliton is formed.

Student: (())

Discuss later.

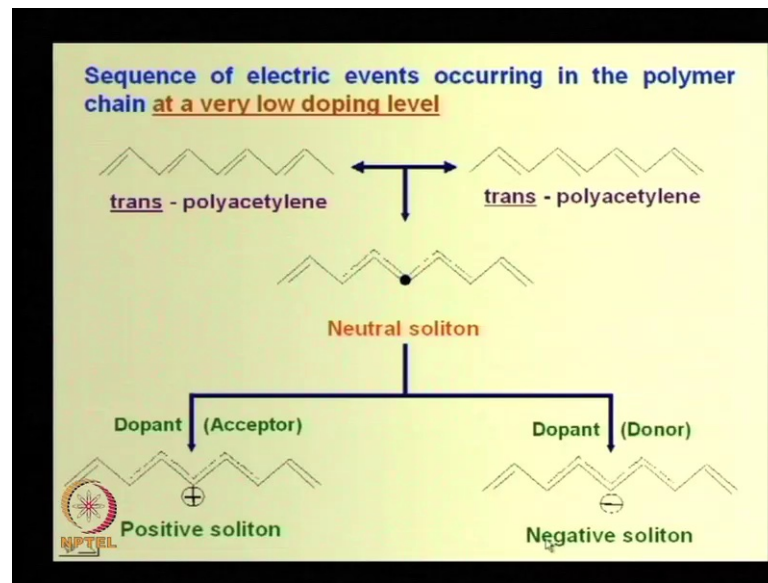
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This lithium ion when adds one electron adds to it, it becomes metallic lithium, neutral lithium. And suppose this is a dopant, anionic dopant, (()), it is a dopant, (()) X, Y, Z, like this Y minus (()), that p doped polymer, that means, electron is here. So, polymer becomes p doped means, it will create hole, it will create hole in the polymer or it will create an excess electron, n dope polymer. So, p dope polymer, n dope polymer provided the dopants are like this chloride or (()) anions are there. You put your thoughts on this thing, simple chemistry, you will understand.

Similarly, the following charging reactions take place when zinc iodide solution is electrolyzed by using zinc and polythiophene as the negative and positive electrodes respectively. So, these are the sequences of steps, this is zinc, zinc, form zinc, metallic zinc after accepting electron; zinc cation after accepting electron, it forms metallic zinc. Iodide ion can form molecular iodine releasing two electrons. So, by this concept, by this concept, either you can get iodine doped polythiopheneah, which releases electron or which creates hole in the polymer chain. So, using this zinc iodide you can get iodine doped polythiophene and metallic zinc in the polymer system.

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It needs a little knowledge in physics to understand this doping mechanism, conduction mechanism after doping, you see. Sequences of electric events occurring in polymer chain at a very low doping level, say this is the schematic formula of trans-polyacetylene conjugated system of double bond. Now, this trans-polyacetylene can have structure like this or structure like this and from this you can have some neutral soliton. That means, you are asking for what is a charge defect? This is a charge defect that means, in the system if somebody enters there, that, that takes a quantum of electron from there, some defect site is created. That means, there will be a pool of electron cloud as bonding electrons in the material.

Suppose, suppose by your, what is this kind of biting by a dog if it takes a portion of your skin or tissue from here? You will feel like instability, pain and bonding, all these things. That mean, some defect is created by this dog bite.

Student: (())

Such defect, so this dopants like dogs or dogs like dopants, if those are incorporated in polymer, that can get some side defect. Yes, you have to have this concept, like this, otherwise you cannot understand. Yes, it is like this.

Suppose you want to, you like eating, suppose you like eating, one of you like eating and you have gone to your friend's room. Tere are some snacks and your plenty of fruits and

something, things are kept over there for his consumption. Now, somehow you have gone to his room and he has gone to bathroom, then what you will do? Hurriedly you will eat those things and somehow you keep your lips close. So, that, and your friend has arrived and somehow you keep, you have kept your lips closed, but you are unable to speak, cannot open your mouth, like that. Now, he will be annoyed, that is, only the amount was kept only for minimizing my hunger or, and you are eating it, then how can I, how can I live. You are not supposed to eat. These are like dopants, you understand.

So, creating some instability in your friend by you, you are the dopant your friend is the polymer, conducting polymer, alright. So, this way neutrals, this is called neutral soliton, called neutral soliton with no spin, charge defect with no spin is neutral soliton. Then donor, acceptor or donor, acceptor, if this acceptor takes some quantity of, quantum of electron from the polymer, some positive center will be created or some donor is there. It does not like these electrons, is little excess, is having problem with this electro-excess electron. So, it will try to remove it. So, if it gets some suitable acceptor, so that will release.

Student: (())

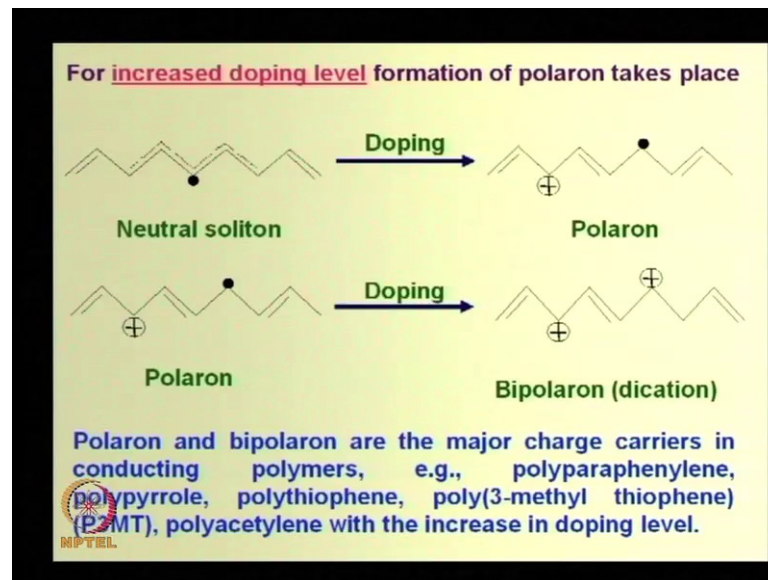
Positive charge, concept sense, positive sense, negative sense, it is there negative sense excess, negative sense deficiency, positive sense like this or vice versa, whatever you like, that, that is your convention. Excess you call it negative here or deficiency positive

Student: (())

Charge defect, charge defect with no spin, actually this definition has been given by physicists, not by me.

Now, take the previous thing, you see, if you take very small quantity of dopant, either donor or acceptor, so that will create small concentration of the charge defect sites. Now, if the dopant concentration is high what will happen? The sites will be more.

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Now, if there are, this is neutral, no charge. This polaron, polaron positive and neutral polaron, this is also polaron and this is bipolaron, 2 positive sites are there. See, now we know a cation always remains close, at the closer vicinity to an anion or anion and cation, vice versa, they always try to remain very close to each other. If there is some positive center, there must be a negative center, otherwise neutrality cannot be maintained. But here you see only positive centre, that means, to that friend's room, your friend's room if two, three friends enter and he will eat away all the snacks, everything, all foods, that means, your, that host will have no food, that means, it is full of deficiency there.

Student: (())

Thank you.