

Science and Technology of Polymers
Prof. Basudam Adhikari
Materials Science Centre
Indian Institute of Technology, Kharagpur

Lecture - 22
Conducting Polymers

Now, we are going to see how a polymer moves from an electrical insulator to an electrical conductor. These are organic molecules, polymers are organic molecules made of carbon, hydrogen, nitrogen, oxygen like those with covalent bonds. Now, materials with covalent bonds do not suppose to be electrically conducting, because there is no availability of the electrons, so these are not conductors.

What do you think, now this brain or brain these biological molecules made of biological molecules, our neurons they are all biological molecules. But how this neurons transpreting electronic signals and pulses submitting heart, heart; they are you can measure some electrical pulse perform that electric pulse is generated, and that electric pulse is communicated transmitted from one location to the other location. That means, organic molecules can also transmit this electricity or current something like that. Although there is no free electron, that means there is some sort of mechanism are system is available who is can provide this electrical conduction.

Somehow, this concept came in the mind of scientist, in around before say in around see 1960's and say 65 like that, 60's people started this research in research with this conducting polymers or organic conductors or organic semi conductors from 1970s, 70s in last decades your last century.

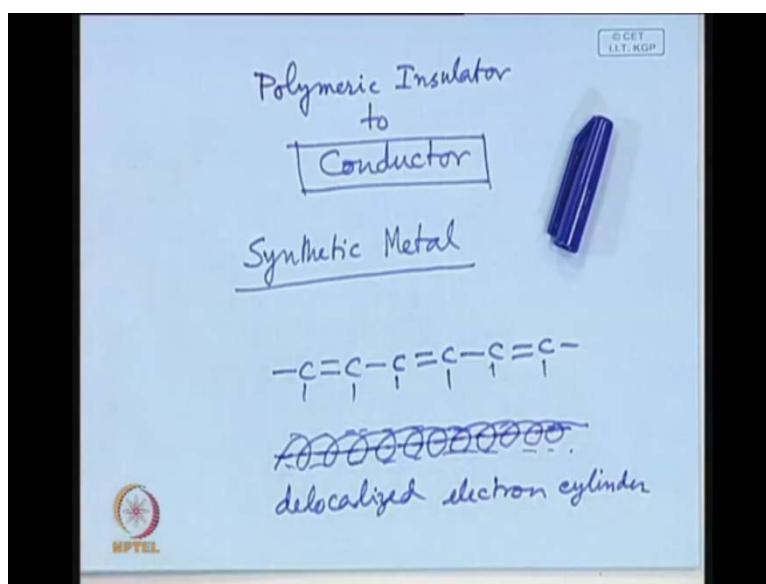
Now you see, if you find some free electron available it is a very fundamental concept in metal. There are free electrons that is why their conducting. So if we can make some electron to remain free electron in polymer molecules it can also conducting electricity. It is suppose to conducting electricity and that we can call as synthetic metal. Organic molecule can be considered as synthetic metal. Organic molecule continent free electron or free electron devises there who which can conducting electricity can be considered as synthetic metal. There is a Jardnel today of course, they synthetic metal they publish publish very fundamental works good works research works synthetic metals.

What is this now we see pi electrons in molecules you know this pi electrons they get delocalized pi electron clouds. Now if this pi electron clouds can be exploited for such conduction then we can get electrical conductivity in conducting polymers. If delocalized or delocalizable pi electron can be exploited in organic molecules, we can make them conducting electricity which can behave as in organic semiconductors we can behave we can make devices like p-n junction electronic devices can make defect-free electronic devices or electronic devices contain some defects.

Because, semiconductors are called defective materials semiconductors they have certain conductivity it puts some defect either you had some donor or acceptor who is taking an electron from the system or donates electrons to the system and that so, and that way it creates certain defects in materials and helps in conducting electricity known as a semiconductor.

Now that concept as will be extended with polymer materials also. Today these polymeric semiconductors are making the revolution in electronic industries in microelectronic devices. So we can have some exposure to these conducting polymers or semiconductor organic semiconductors. He was he knew molecule you know ethylene molecule you know there is a pi electron, there is a pi bond. Now if we think that that ethylene molecule is used to synthesize polyethylene now, once you react this ethylene molecule it forms a macromolecule polyethylene that pi electron cloud is consumed in polyethylene there is no pi electron cloud but, if you can make a polymer from ethylene.

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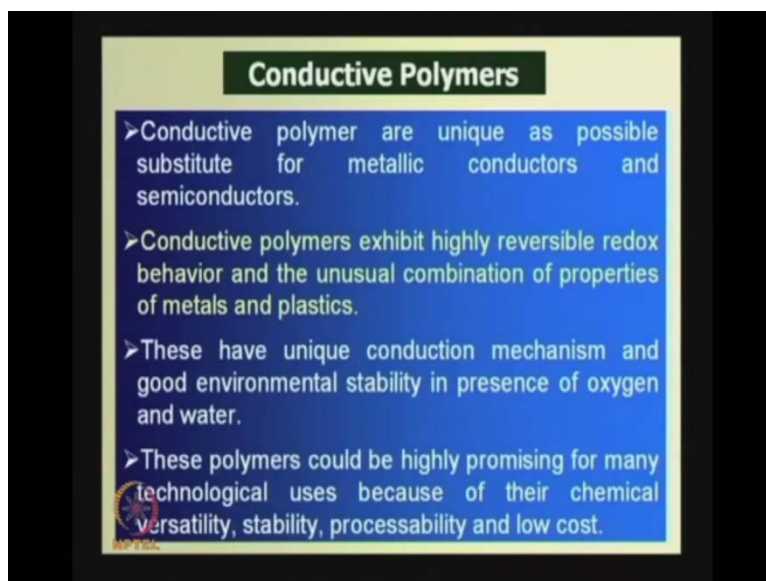


If you can make a polymer of ethillin like this, hypothetically would not know what is that molecule. So if this pi bond repeats like this, theoretically one can think you see, we do not know, from where we are make it. But at least I can draw on a piece of paper that, if you can make a design of such a molecule, then we find there is a alternate single bond, double bond, single bond, double bond that means conjugated pi electron device pi electron molecules that means, if you have a skeleton carbon skeleton like this; over this carbon skeleton, over this carbon skeleton, if you can develop like this that means delocalized system of electron over this central skeleton molecule. Then it can help in electric conduction. If there is they are such conjugated system of pi electron that means it can provide a cylinder of delocalized elect your electron cylinder or cylinder of localized electrons or delocalized electron cylinder or ideally ideally at least we can think. In reality, we have to see how far we can achieve that is different think, but ideally we can think that we can have a pi electron cloud over a skeleton carbon chain. That can be an ideal conducting polymer or semi conductor or organic semi conductor molecule.

Who told you acetylene? I do not know, what is acetylene? Do not jump on that. My point is today you have some prior information you could say acetylene poly acetylene. When these concepts came to the mind of scientist for which people got Nobel price, that time people did not know, actually I am telling you the Jenesis, he can have your key idea like this. You can think of a new molecule, over which if you can design is pi electron cloud or electron cylinder then...

Now actually this type of your write this type of system these represent polyasetaline because asetalin as got one sigma 2 by wants but, it difficult to polymerize is cyclogis is cyclogis to form bangin ok. But If sufficient and your adequate and appropriate conditions are ahh supplied then it can form a polymer polyasetilin of high molecular wait of polyasetilin of high molecular Wight zinc good conductor ok,

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Now let us see here, see conductive polymer unique as possible substitute for metallic conductor and semiconductors. Conducting polymers exhibit highly reversible redox behavior and the unusual combination of properties of metals and plastics. See redox behavior you see is very important redox behavior for which the mechanism of conductivity is dependent, the way how did becomes conducting. That means, it is the donor and acceptor system a substitute is there to the substrate something is donated some such cloud is donated. Some such carrier is donated or it is removed from substrate either it is donated to the substitute or it is removed from the substrate. In both the cases the system become unstable or starts flowing electron and we get the conductivity.

We as the conductivity and by virtue of such properties, we can exploit that material for various applications assenting electronic nose, electronic tongue ,actuator artificial muscles. Those can be made from these things, huu by such electron pushing or electron withdrawing that means, it happens through redox behavior either oxidation reduction in simple oxidation and reduction. What happens, either electron is withdrawn taken out or electronic given, so it becomes either positive or negatively charged that is a redox behavior alright.

Now that this redox behavior oxidation reaction this is not a new thing. That is old thing that is old concept was we thought 200 years back. Now it took such a long time to think of some organic molecules, were it also can be exploited, it was actually meant for only

metals. If not that only metals can show such type of behavior such type of characteristics, which can accept electron, or remove electron give away electron ahh. So by virtue of that it changes it is your charges positively charge or negatively charge like that monovalent valent like that this also possible polymer.

Now, the content of charge depends on the depends on the extent of this oxidation or reduction process. So these have in the conduction mechanism and good immortality stability in production of oxygen and water. Again you try to correlate with this, if there are many things you see, it takes few hours or if in more than few courses to discuss on this conducting polymers polymeric semi conductors all these things. I am not going to that side is that can be done.

I am not going to that side the thing I want to tell you that this ahh metals by virtue of their oxidation reduction characteristics they are not go electro chemical combination, that means stability stability of metals are stake. Is not stabilize of metals are stake. Today we are trying to protect metal from their electro chemical degradation etc. by covering with something else, which is non electrolyte non electrolytic. So we try to cover metals with non electrolytic metal material to protect the materials metals that means they are unstable we are try to the metals by by putting some coating.

We take aluminum aluminum is good good metal we take aluminum all why because aluminum was such a metal it oxidized eventually repeatedly from some alumina Al_2O_3 thin film over aluminum metal which passivates the aluminum there is an advantage so we try to use aluminum with other metal so that presence of aluminum helps in passivation through a thin alumina aluminum oxide formation.

So we think of various techniques and devices to stabilize metal now from there you try to understand the problem the problem with metals is their reactivity is their redox characteristics. so we are asking for redox characteristics in polymer forgetting conductivity. so there is a failure in case of metals now if we develop such type of reactivity in polymer for getting conductivity again where avoiding that failure situations what we what we should do we should think of some polymer which will provide redox characteristics but, you should be stable.

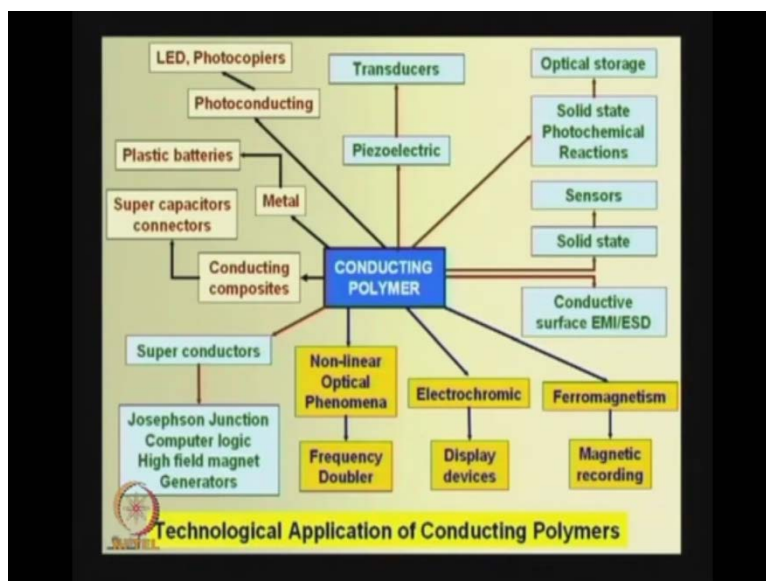
I tell you about the polyacetylene because; for which it provides you the conductivity that becomes the reason for its instability once again is a chemical process chemical reaction

chemical interaction is... We need free electron for conductivity if there is free electron ahh it will not remain sitting ideal it will try to form bond with its with some of the radiant in the monument means it is becoming unstable for these things should be kept in mind while thinking about this conducting polymer development device making all this thinks.

So these have unique conduction mechanism and good environmental stability in presence of oxygen and water. These polymers could be highly promising for many technological uses because of their chemical versatility, stability, process ability and low cost. If you think of inorganic semi conductor, you want to make some device you have to you have to go that crystal which needs very sophisticated arrangements sophisticated instruments well in the laboratory for research purposes it is ok. But, for commercial development of some semi conductor devise huu it cannot be economically possible very high this same devise cannot be reach the common people at cheap cost at cheaper price.

Today you see we get we are getting these electronic gadgets all most free of cost you can say as compare to 15 years back 15 20 years back isn't. today we are getting mobile a mobile set with in 1000 rupees can you imagine the situation certainties 5 years back that means cost is involved that means it contain some devices chips if its really expensive for his making that is not possible but, today these are possible only because of this organic semi conductor which is easy to prepare easy to prose's so the cost is less stable so and these of astatine so these polymers could be highly promising for many technological uses because of their chemical versatility, stability, process ability and low cost.

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If I show you the application, sorry look at these conducting polymer, how many different application today, although this is old, this is not today's, say 2, 3 years back I get it from somewhere. So there are further additions to these least different types of applications, you can find from these conducting polymers.

What not today? Because, of its because of its flexibility to prepare, because of its good procesability, easy procesability, because of its stability etcetera. And unique properties on usual properties which is not always found with in organic semi conductors.

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Comparative picture of conductivities of some materials

Materials	Conductivity	Sp. Gr.
Ag	10^8	10.5
Cu	6×10^6	8.9
Al	4×10^6	2.7
Polyacetylene ---CH=CH---	1.5×10^4 (doped)	1.0
Polythiophene ---S---	10^4 (doped) 200 (undoped)	1.0
Polypyrrole ---N---	600	1.35
	10^4	13.5

NPTEL

Now let us see this one you see just compare you just compare the conductivity properties conductivity on specific gravity of metals and organic molecules, see here silver silver conductivity by 6 copper 6 into 10⁵ alumina 4 into 10⁵ poly acetylene in dope condition almost it is achieve the mettles conductivity.

You see it is achieve the metallic conductivity polyacetylene huu and platinum so in between this you are polyacetylene polythiophene the place of ahh platinum is in between these 2 10⁴ to 4 doped 200 undoped conductivity ,and look at these specific gravity specific gravity has come down. so the device become liter cheaper stem and highly conducting and easy to make it.

But, we have to do how to do because, there is problem whenever you are going to make this conducting polymer device it we keep in mind. that the ahh other characteristic of polymers are achieved .That means there is variables difference variables of stability molecular weight molecular alignment crystallinity and these what is that called oxidation state of the polymer ahh and carrier concentration there mobility correct all these things those semi conductor properties those things you keep in mind then polypyrroie.

You see 600 now we had you see this is polacetylene this conjugated system of pai electron so conjugated system of pai electrons then here also polythiophene single bond double bond single bond double bond again another in the next double bond is there so these way ahh conjugated system of pai electron is there, now polyacetylene shown like these but, actually polyacetylene have two like these you can place the double bond here here like this this is says says from and transform. you practice at home.

Conductivity of marcury 10⁴ and see carbon fiber organic material or dis carbon fiber that is gratified carbon that is graphitic form that means it contains s v 2 carbons so there is level electron so that helps in conduction. so you can have a thin graphite film very thin graphite film graphite thin film today carbon nano tubes dancing carbon nano tubes single walled and multi walled somebody as tellet multiwall somebody is telling multi walled either multiwall or multi wall up to you ok .

Nano tubes is the reactive modified carbon nano tubes there having these graphite exozonal rings with s v t s v 2 have a digestion single free electron. Now, if we can make organized thin film of graft it highly conducting and that conductive is suits are borbers that can be used in sencer that can be used in elides and in many device I do not know my

knowledge is very limited of there in those devices names of those devices functioning of those devices but, I know this material and how to prepare those materials I know at least if I try. I can make people are making carbon nano tube but, it look like particles you see it look like particles. What is the l by d aspect ratio? so more is the l by d, more will be the nano effect more will be the nano effect and if you can make some device with these carbon nano tube in that is semi conducting in nature so carbon fiber and you see in my lab there is carbon fiber you can see that carbon fiber is made from picaser polymer what is that Picasa polymer? p e n poly ectriilo nytrain that is convert into p e n people have made carbon fiber from pinolic igense also, I have seen report that people have make carbon fiber from natural fiber from penolicgrgence.

Carbon black filled poly polyethylene conducting now I told you a grade of carbon black three great I mentioned thermal black fudnis black and channel black channel black is conducting in nature. Conducting in nature means, it may not be high conducting or so called conductivity. Well, why it is conducting? Because, if you look into the manufacturing process of carbon black how it is done it is made from either natural gas or petroleum oil.

In by controlled ahh by heating at high temperature of it may be 1000 to 1400 degree Celsius in controlled supply of air or oxygen. Some time in absence of oxygen that means the case of pyrolysis pyrolysis means carbon hydrogen bond is pyrolized hydro carbon which is hydro carbon if the carbon hydrogen bond is pyrolised sometimes carbon carbon bond is pyrolized. what happens? There are plenty of your your infinite number of few radicals produced.

Now those few radicals combine interact in such way depending on the conditions of that manufacture in process what happens they forms this graphite rings there. Especially, in hydrogen more the graphitic effect more will the conductivity more will be the strength of the carbon fiber, more will be the carbon black particle and if those are used in rubber compound in plastic compound and becomes conducting .

So you if you make some ahh polymer composite. if you want to develop some antistatic properties there than you will add little bit of carbon although you have to sacrifice the color if you add little bit of carbon it will be black it cannot develop any other color other than black, so if you can sacrifice this color carbon black is the best 1 and to protect from

even degradation use little bit of carbon black. that it protect the product from even degradation.

Look at polyethylene it is a perfect conduct insulator you can say conductivity is almost that is in the insulator range minus 8 order 18 order polyethylene 2 3 minus 22 polyethylene is come down to 10 polyacetylene is the best one until now known, you can increase the conductivity of polyacetylene for the fountain that by using the thing is the thing is I was telling you if you consider this diagram this one this diagram electron cloud ok .

So if you can make some device for that either you can pump electron to this system or you can suck electron from this system in both the cases. It will become conducting either pumping in or sucking out that means by donating electron donor effect or by accepting electron acceptor effect is nothing but, doping dopants thus this function donor acceptor.

Polyacetylene some formulas are given along here poly phenylene vinylene, poly p phenylene sulfide, polyisothianaphthene or naphthalene naphthene actually ahh this double bond these double bond these double bond is not there is a mistake only sulfur atom is there sulfur is link to this carbon and this carbon the double bond is not there is a mistake polyisothianaphthene. These are very easy to draw the formula on paper on board but, difficult to say in the size because once this polymers are form it becomes insoluble and infusible how to process.

For example; you take you can try in your lab class in my lab aniline is available in my lab ammonium persulfate is available also you take aniline and few crystal persulfate within a minute. you will find that green to black colored formed that means your successful synthesized polyacetylene filter it wash it we find try to find out the conductivity you will get the conductivity of polyacetylene and doubt. off course you have to take acid bedium asial diasial take aniline in dilute asial add ammonium persulfate you will get polyaniline filter it and then make a palaeen measure.

The conductivity you will find the conductivity you have got into a minus 4 order conductivity can assume from there huu but, how to make a device if you have to make a device either you have to dissolve the polymer in a suitable solvent it to prepare a solution so that take from that solution you can cast a thin film over a substrate or by heating you can melt on melting you can form a thin film or coating or a substrate but, does not melt

does not dissolve normally the polyaniline which is formed in acid medium it is a salt known as salt that salt is in solid.

Now you put that polyaniline salt here since it is synthesized in acid it will form a salt here had had you see this nitrogen bonded to hydrogen form like hydrogen salt by also of that formation. It actually does the protonation that means this nitrogen will be protonated this nitrogen will be protonated once this nitrogen is protonated that means that has influence on this conjugated electrons that helps in conductivity ok.

Then you take that emeraldine salt put in some base means ammonia solution. So it will be converted to base form means HCl is removed from there now that base form is soluble in organic solvent but, base form is not conducting base form is not conducting so that will form that base form of polyaniline is soluble in say dimethylacetamide, soluble in dimethyl carbonate, dimethyl sulphide is soluble depending on the molecular form of the polymer alright.

So after dissolving the base form take the solution cast a film on a substance then you reexpose that film to some acid or immerse in acid solution and what will happen it will be again converted to salt. That means in other way, you are converting that polyaniline base film to polyaniline salt by doping of asiline now there you do not have to take hydrochloric acid you can take other acid other organic acid, paratonic sulphuric acid, camphor sulphuric acid, chlorosulphuric acid, can take sulphuric acid you can take different acids depending on the dissociation constant of those acids you will get different doping effect alright.

Now these processes of synthesis conversion to base formation of film re-doping these are all tricky processes. That means here is the skill of your finger, skill of your mind, skill of your technique, skill of your setup, sophistication of your setup all these things, all those parameters add to the conductivity of the polyaniline somebody is getting a conductivity of 10 or even 22 bar 2 from polyaniline.

How they could prepare a very organized film? Because, you see you think of molecular organization suppose suppose this is a layer of polymer consider an imaginary plane of a single molecular chain like this like this in 1 plane. Then what happens in a solid device. what we are having we are having another plane stacking 1 plane over another plane like this. In a solid device here so in 1 plane there is 1 molecule top of this plane another

molecule top of the molecule another molecule that means you are stacking the molecules 1 over the other 1 over the other.

So this is an imaginary system imaginary stacking ideal system they are what happens. Now if we consider one individual polyaniline molecule or polypyrrole molecule has a conductor. so it has got 2 ends so you can tie this to a ends to a device so that ahh or apply some potential electron flows from 1 end to the other so it can be like a conductor.

Now it it looks like bear conductor instead polyaniline molecule looks like a bear conductor. Now over 2 bear conductor you are adding another bear conductor it is like that of a that of an wire have been multistrand, means 30 thin ,30 thin wires, 30 numbers of thin wires in a bundle bundle of thin wires. For passing high current isinted so depending on the diameter of the wire . You see diameter of the wire affects the conductivity current flow resistance all these things. Now the concept of resistance resistivity all these things are coming. That means, if there is scattering of the carrier if there is scattering of the carrier during mo your mobile or during mobility. what happens, we actually sacrifice the conductivity of the material. So, what should we do.

Now in electric fan electric motors what do you see there are 2 quails are bycher coils and feel quails and the efficiency of a fan how fast it can rotated with higher at low consumption energy? The depends on the length of the wire are are the capacity of a motor depends on the length of the wire which is included that means number of trans number of trans if number of trans with more then it becomes high capacity. So that depend the length of the wire.

So how it is that how this den actually it is insulated by enameling think coating of insulator polymers insulating polymers are your covered on that codectered. so those are not bear conductors so it is coated so in case of conducting polymer. you cannot do that. If we can, if wan can marvelous think that means cod means codectings there is a sell covering that conductor which can function life insolated ideal situation, think of core is conductor covering is insulated then is kind of seen problem menodaker .

So but, when we are making a film fa where doing where in a thin phin. We are looking about thin phin what is the thickness sir thickness is 500 micron is that thin film sir 100 micron is that thin film now.

If it is of the water of say 10 to 215 manometers. we can say it is thin film how to deposit the thin film how to cast that thin film From a solution is not to be a simple thing is thinking process very thinking process so if you can do that than this tacking effect this tacking effect are the problem arising out of tacking effect can be minimized because what happens during such fill formation 1 manicure from the lower plane can pass through the upper plane.

This way that is a random that is call a alignment that proper alignment is not there although if the there are three imaginary planes if you can make that way in such way that all the molecules in the fast planes a lying with fast plane itself. Than all the molecules' in the second plane along with the second plane itself all the molecules in the third plane like in the third plane itself that no molecules from the first plane when it is to the medium plane to the middle plane to the top plane. If that can be prevented than we can get high conductivity excellent privities' that means molecular and that means it is related to crystalinity molecular order isn't. it others there will be short circuit theoretically telling that electron a cloud is delocalized that means; it is in the direction but, you do not bother to thing in the other direction also conduct in the other direction.

These discussion may not get books is a basic fundamentals that you have to think, looking at the final effects final properties apply some insulator covers with an insulater covers with an insulated. say super conduct they put a lot of efforts to develop super conductors means 0 registers today in colagote thermal power station is there in cola gaint power station is there power is generated there and high voltage is required for transmission of power from that placeto other places from cola gnat board technicians above 30,000 holder are there 40,000 board there is heavy for loss energy loss by discussing transplanting power lose could be minimize.

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Polymer	Doping materials	Conductivity (s/cm)
Polyacetylene	I ₂ , Br, Li, Na, AsF ₅	10 ⁴
Polypyrrole	BF ₄ ⁻ , ClO ₄ ⁻ , Tosylate	500-7.5x10 ³
Polythiophene	BF ₄ ⁻ , ClO ₄ ⁻ , tosylate, FeCl ₄ ⁻	10 ³
Poly (3-alkylthiophene)	BF ₄ ⁻ , ClO ₄ ⁻ , FeCl ₄ ⁻	10 ³ - 10 ⁴
Polyphenylenesulfide	AsF ₅	500
Polyphenylene-vinylene	AsF ₅	10 ⁴
Polyphenylene	AsF ₅ , Li, K	10 ³
Polyisothianaphthalene	BF ₄ ⁻ , ClO ₄ ⁻	50
Polyaniline	HCL	200

You can said money if the power loss is there is no resistance seen there is resistance than we are getting this power at getting power of this lobar days at transpire from there charge high voltage otherwise cannot get. Think of a form suppose he have a reserver in this building now if you want to carry water from this reserver to material center you have to have a pipeline and you have to have a efficient pump which will pump water from this building to the building in this material sand center and you need a pipe line and if the inner wall of the pipe line is rough there will be dredge is far drag that needs high presser to you have to pump this water from a high presser high voltage high presser high voltage that on then only you can get adequate their same thing in the case of the electrical conductivity.

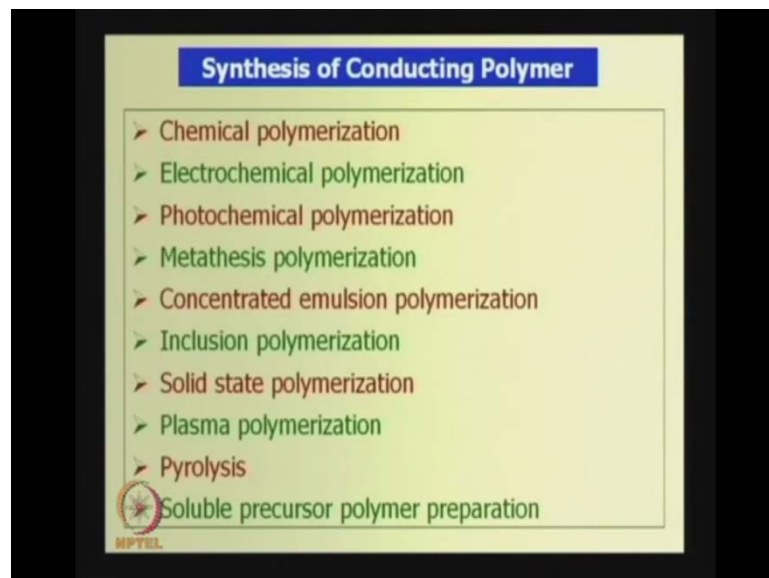
Super conductivity of lot of conductive but, could not achieve it. At the amend temperature people could achieve save 125 or one 50 Kelvin and that to highly expensive it is not effective. Today we get highly scared for our domestic vary after construction of a house for vary we try to investigate how much cost it will incur.

Sometimes we where we do not go for censed wiring we say no, no it will income more cost. So, if you have scared out that cost and how can we aport this for conductor price but, there is a scope to develop conductor which can give you no room temperature conductivity high conductivity 0 resistance, then that will be really remarkable achievement. For that huge power station is not necessary and in case of conducting

polymers that will look in to conducting polymer tracture we can think you can think rite on people but, you have to know, you have to find out, you have to discover that process technology.

How we can make organized molecules organized conductor show that we can get very good conductivity. for these with different materials that means these are all disturbing elements these are all disturbing elements like prospers and silicon bromine, lithium, sodium, arsenic, perasfaric salt, these things chloride, aspens the the photon all these things these are doping materials for different polymers. People had tried and you see they range of conductivity order of conductivity is good achieve. Today billions of people are working in this conducting polymer area.

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How to synthesis there various techniques the following out of which these techniques are very good and very important. 1 is chemical polymerization, chemical syntheses the other is electrochemical polymerization,, plasma polymerization plasma deposition and chemical those are needs sophisticated your working very eases caller to working with somebody in his lab the civil facilities is not there cavity facility are expensive.

Today if there is the civic facilities ferment do the search on conducting polymer yes you can do. you have go through other techniques of conducting polymer synthesis in our department on offer m.tech student your senior they developed small unit plasma unit in which the fabricated..These fabricated the plasma unit and It was run plasma was

generated using some monomer and benign also he got full fill the measure the conductivity that we need in the M Tech lab in our M Tech lab.

We can see so if you do not have even a plasma unit we can fabricate what is plasma unit we can have electric plasma chemical plasma unit that means you have to get some announce fradicle activated spaces take a material suppose you can take it in plasma state that means you have to energies these material to such a level so that it is bonds it is bonds ruptured in such way that smallest unit separated from the they are very much activated.

If you can take it to that activity stage then if there is a suitable substrate on that substrate those activated spaces can be deposited. That is a plasma deposited film of this material, so if you starting with a monomer if you start with aniline if you start with pylon. If you start with hyphen we can get polyaniline, polythiophene, polypyrrole, etc on a substrate. If you take a silicon or if you keep that silicon or in that plasma chamber and that monomer are taken. At force, is very low concentration plasma in activated that plasma condition activity species in the form of radicals and anions then they will interact with each other of inorganic they form from solid material and formed and then they will interact with each other.

After interacting they form solid material and that solid material deposited on the substrate so you can get a plasma deposited thin film of that polymer and chemical synthesis. I have told and electro chemical synthesis is to take a cell suitable electrons take the monomer on one of the electrodes polymer will be deposited on the other electrode polymer provided they have redox potential otherwise the electrochemical polymerization cannot be successful ok, so these techniques for synthesis of conducting polymers today let us human hear.

Thank you so much.

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