

# Conducting Polymers

From a Laboratory Curiosity to the Market Place

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Polymers that exhibit high electrical conductivity have successfully been synthesized in the last few decades. The early problems associated with the stability and solubility of such conducting polymers have largely been overcome using chemical intuition and experimentation. A fairly wide range of interesting applications based on these polymers is emerging; some of these are highlighted in this article.

## Introduction

Polymers, by virtue of their light weight and greater ease of fabrication, have replaced and are continuing to replace metals in several areas of applications; as often remarked – ‘from buckets to rockets’. Polymers have traditionally been considered good electrical insulators and a variety of their applications have relied on this insulating property. However, for more than a decade now, researchers have shown that certain class of polymers which are conjugated (those that possess an extended  $\pi$ -conjugation along the polymer backbone), exhibit semiconducting behavior. The discovery of doping<sup>1</sup> led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as  $10^5$  S/cm (compare copper  $\sigma_{rt} = 10^6$  S/cm)<sup>2</sup>.

<sup>1</sup> Doping is a process by which the polymer is either oxidized or reduced to create charge carriers.

<sup>2</sup> S/cm stands for Siemens/centimeter, a unit of conductivity. Other units such as mho/cm is also often used, where mho stands for  $\Omega^{-1}$ ;  $\Omega$  (ohm) being the unit of resistance.

The chemical origins of such a remarkable difference in the material properties between various types of polymers can be readily rationalized. Traditional polymers, such as polyethylene or polypropylene, are made up of essentially  $\sigma$ -bonds and hence a charge once created on any given atom on the polymer chain is not mobile. The presence of an extended  $\pi$ -conjugation



tion in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting. One problem is that, due to the presence of this extended conjugation along the polymer backbone, the chains are rigid and possess strong interchain interactions resulting in insoluble and infusible materials. These conjugated polymers, hence, lacked one of the most important and useful properties of polymers, namely their ease of processability. More recently, however, it was demonstrated that when lateral substituents were introduced, even conjugated polymers can be made soluble (hence, processable) without significant loss in their conductivity. One other problem that plagued this field from its inception, is the inherent instability of these polymers (especially, in the doped form) to ambient conditions. Today, conducting polymers that are stable even in the doped form have been prepared. We shall highlight some specific examples of such systems and discuss some of their potential applications.

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### Examples of Conducting Polymers

Polyacetylene, in view of possessing the simplest molecular framework, has attracted the most attention, especially of physicists, with an emphasis on understanding the mechanism of conduction (see *Box 1*). However, its insolubility, infusibility and poor environmental stability has rendered it rather unattractive for technological applications. The technologically relevant front runners belong to essentially four families: polyaniline (PAn), polypyrroles (PPy), polythiophenes (PT) and polyphenylene vinylenes (PPV). Polyaniline is rather unique as it is the only polymer that can be doped by a protic acid and can exist in different forms depending upon the pH of the medium. (see *Box 2*). While polyaniline is soluble in the neutral emeraldine form in highly polar aprotic solvents like N-methyl pyrrolidone (NMP), all other polymers are insoluble. However, as mentioned earlier, laterally substituted deriva-



**Box 1. The first observation of the shiny lustrous polyacetylene film.**

The search for conducting polymers, incidentally, goes back to the days of Natta (of the Ziegler-Natta catalysts fame), who polymerized acetylene gas using his newly developed catalyst, that revolutionized the plastics industry by providing a route to polypropylene. (Ziegler and Natta jointly won the Nobel Prize in chemistry in 1963 for their discovery.) What he obtained from his acetylene polymerization, however, was a black powder which looked much like charcoal. With the anticipation that such conjugated structures would exhibit electronic conductivity, their conductivities (of compressed pellets) were indeed measured by others, and were found to be fairly low; they were at best semiconducting (in the  $10^{-7}$  S/cm range). The finding in the mid seventies, by Shirakawa and his colleagues in Japan (believed to be serendipitous), that polyacetylene can be prepared as shiny metallic films (these films, in fact, look almost exactly like aluminium foil) when a thin film of 'soluble' Ziegler-Natta catalyst solution (as it drained along the reactor vessel at  $-78^{\circ}\text{C}$ ) was allowed to come in contact with acetylene gas, spurred some activity in this area after a lean period of about two decades. The major resurgence of research activity, of course, had to wait another couple of years for a trans-pacific collaboration between Shirakawa and MacDiarmid (from the USA), when it was discovered that the conductivity of these polyacetylene films can be increased by almost 10 orders of magnitude from  $10^{-7}$  to  $10^3$  S/cm by a process they termed as 'doping', paralleling the terminology used in semiconductor physics. One among the many ways that scientific discoveries are made.

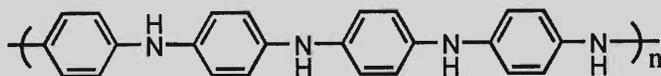
tives of the remaining three classes are soluble in pristine form and are solution processable. A typical example of a laterally substituted conjugated polymer which has been extensively investigated is poly(3-hexyl thiophene) (P3-HT) (see *Box 3*).

PAn, PPy and PT can be prepared either by chemical or electrochemical oxidation, the latter approach being often preferred as they result in polymeric films deposited on the anode surface, which can be removed to give free-standing films. The electrochemical method, in addition, may also be well suited for fabrication of microelectronic devices in which polymer films are directly deposited on to metal contacts. Although chemical oxidation yields powders, the reaction when done in the presence of surfactants, in some cases, permits the preparation of emulsions, which upon drying form coherent films. In the case of the substituted derivatives, however, the chemical method is often preferred, as the resulting polymers are soluble, and hence can be purified and solution processed. (*Box 4 ex-*



**Box 2. The Special Case of Polyaniline.**

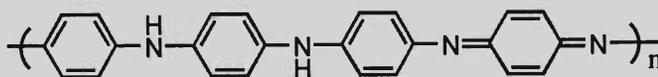
Polyaniline has a rather unique structure, containing an alternating arrangement of benzene rings and nitrogen atoms. The nitrogen atoms can exist either as an imine (in an  $sp^2$  hybridized state) or an amine ( $sp^3$  hybridized). Depending on the relative composition of these two states of nitrogen, and further on whether they are in their quaternized state or not, various forms of polyaniline can result. The structures of these forms can be best represented by choosing a minimum of four repeat units, as shown below.



Leucoemeraldine

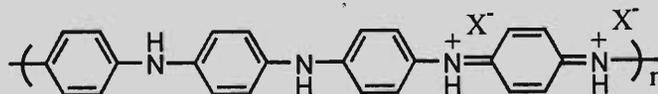
Attributes

Pale brown, insulating



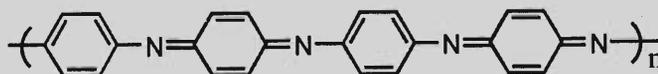
Emeraldine

Blue, insulating



Protonated Emeraldine

Green, partially oxidized conducting form



Pernigraniline

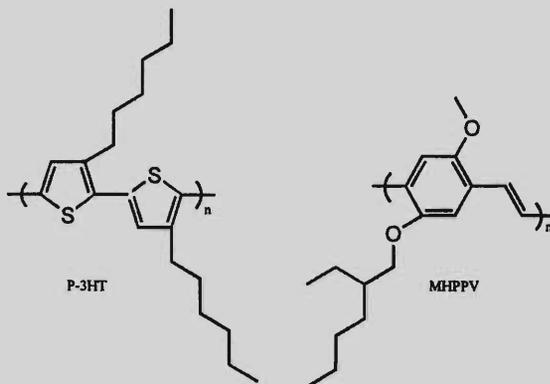
Black, insulating

The only form that is conducting, among the four, is the green protonated emeraldine form, which has both the oxidized iminium and reduced amine nitrogens, in equal amounts (i.e., it is half oxidized). Thus, the blue insulating emeraldine form can be transformed into the conducting form by lowering the pH of the medium and vice-versa. Another interesting feature of polyaniline is that, by use of an organic counterion ( $X^-$ ), for instance, by using camphor sulfonic acid as the dopant acid, polyaniline can be retained in solution even in the doped conducting form, further enhancing its versatility. The transport of charge in these systems can be understood in a simple fashion, by causing the imine and amine nitrogens to exchange places along the polymer backbone (in protonated emeraldine). Try and push arrows to cause this change and observe that this process effectively causes the charges to move along the polymer backbone!



**Box 3. Soluble Conducting Polymers.**

Conjugated polymers, which are generally insoluble and infusible, can be made soluble by lateral substitution. A few examples of such conjugated polymers are shown below.

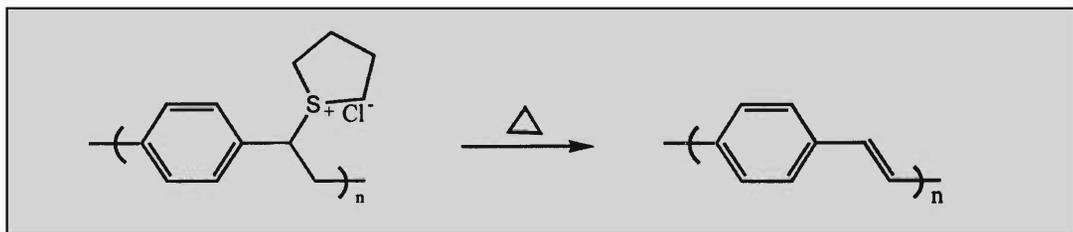


The presence of the long alkyl chains destroys the symmetry and prevents the crystallization of the conjugated polymers in the above two cases, thereby making them more readily soluble in common organic solvents. In poly[2-methoxy-5-(2-ethylhexyloxy)phenylene vinylene], (MHPPV), the asymmetry is even greater due to the presence of two kinds of substituents, one that is selected to be a branched alkyl chain to magnify the effect even further.

plains the use of the chemical approach to prepare conducting composites).

PPV has also attracted a lot of attention in recent years, due to the availability of a synthetic route that gives a water soluble polyelectrolyte precursor, which upon heating to about 200°C under vacuum gives the wholly conjugated polymer (*Scheme 1*). By virtue of this soluble precursor

**Scheme 1.**



**Box 4. Conducting Fabric.**

The chemical oxidation of pyrrole is often carried out by using ferric chloride,  $\text{FeCl}_3$ . It has been shown that the growth of the polymer can be made to occur even at a liquid-liquid interface, such as one of water and an organic solvent. Thus, in an unstirred system, when aqueous  $\text{FeCl}_3$  and chloroform solution of pyrrole are brought into contact, it leads to the formation of a polypyrrole film at the interface. More interestingly, when a fabric that is impregnated with an aqueous catalyst solution is brought into contact with pyrrole vapour, a thin coating of polypyrrole is formed in the surface of the fibre - leading to the formation of a conducting fabric. The unique electromagnetic shielding and microwave absorbing properties of such a fabric are expected to find many interesting applications. Similarly, other materials such as paper, microporous membranes etc., have also been coated with a conducting polymer using this chemical oxidation route. It should be noted here that the oxidation potential of the monomer would be less than that of the dimer, which would in turn be less than that of the polymer. Hence, the polymer generated by this oxidative polymerization approach will be in the oxidized (doped) conducting form, which is also generally true in the case of all oxidative polymerization approaches (both chemical and electrochemical) for the preparation of conjugated polymers.

route, PPV films and fibres for a variety of applications are accessible.

*Table 1* shows the structures and characteristics of some of the above mentioned conducting polymers.

## Applications

Although several conducting polymers have been prepared, it was soon realized that they cannot compete with metals in traditional electrical applications, like wiring, transmission cables etc. Researchers have, therefore, focussed on other applications that exploit the existence of extended conjugation in these polymers. A few interesting possibilities are mentioned below. See *Box 5* for a novel biomedical application.

### Polymeric Batteries

One of the first applications of conducting polymers, that was the focus of attention world-wide, was that of light-weight

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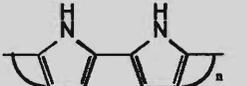
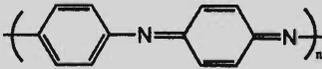
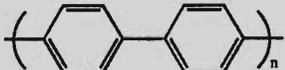
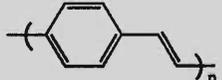
	Structure	Maximum conductivity S/cm	Stability	Processability
Polyacetylene		$1.5 \times 10^5$	Reacts with air	Film not soluble or fusible
Polypyrrole		2000	Reasonably stable	Insoluble and infusible
Polythiophene		100	Stable	Insoluble and infusible
Polyaniline		10	Stable	Soluble in neutral form
Polyphenylene		1000	Stable	Insoluble and infusible
Polyphenylene-vinylene		1000	Stable undoped form	Soluble precursor route available

Table 1.

batteries. While a lot of the conjugated polymers were tried most of them failed to exhibit the desired properties, specifically with respect to stability. However, batteries made using either polypyrrole or polyaniline as the positive electrode (cathode) and lithium–aluminum alloy as the negative electrode (anode) exhibited much more respectable properties. The electrolyte in these cases were either  $\text{LiClO}_4$  or  $\text{LiBF}_4$  in propylene carbonate (a highly polar aprotic solvent, which is also fairly resistant to oxidation). During the battery discharge, electrons move from the lithium alloy (which gets oxidized) to the polyaniline cathode (which gets reduced), as  $\text{Li}^+$  from the anode and  $\text{BF}_4^-$  from the cathode enter the electrolyte.

One major drawback of this battery is that the energy density or energy storage capacity is low and its recyclability (charging–discharging cycles) is relatively poor. More recently, however, some composites of an alkali metal alloy

and polyphenylene have been very effectively used as anode materials in batteries that exhibit much higher energy densities, of around 65mWH/g (compare with standard nickel-cadmium batteries which have about 39mWH/g). In these cases, the conducting polymer serves as a binder for the alkali metal alloy, forming a multiply connected electronically and ionically conductive network within which the alloy particles are held. The mixed ionic and electronic conductivity of the conducting polymer binder allows the alloy particles to continue the electronic and ionic processes associated with the charge-discharge cycles, consequently extending the battery cycle life. Thus, the prospect of a polymeric battery is still alive and is awaiting further technological refinement.<sup>3</sup>

<sup>3</sup> For a detailed article describing the desirable characteristics of batteries, see A K Shukla and P Vishnu Kamath in Suggested Reading.

## Electrochromic Displays

Electrochromic display is another interesting application which utilizes the electrochemical doping and undoping of conducting polymers. The basic idea, in such devices, is to effect a significant change in the colour (both the wavelength of absorption and its intensity) upon application of an electric potential. Depending on the conducting polymer chosen, either the doped or undoped state can be essentially colourless or intensely coloured. In general, the absorption of the doped state is dramatically red-shifted (moves to longer wavelength) from that of the undoped state. Because of their very high absorption coefficients (ca.  $10^5 \text{ cm}^{-1}$ ) in the visible range of the electromagnetic spectrum, only very thin films are required to provide display devices with high contrast and a very broad viewing angle. Polyaniline, polypyrrole, polythiophene and their derivatives have been successfully used to prepare prototypes of such display devices. However, for successful commercial utilization of these materials in display devices, one important aspect is again the cycle life, which should be  $> 10^7$ . A maximum of about  $10^6$  cycles has been achieved using 50



Emission of light upon irradiation is termed as photoluminescence, while the emission on application of a voltage is termed as electroluminescence.

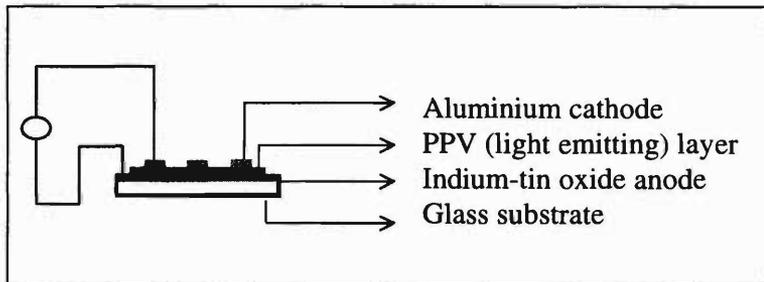
nm thick polyaniline films, wherein the switching occurs between transparent yellow and green in less than 100ms. Thus, while these materials are yet to achieve the set target (in terms of their life cycle) for use as electrochromic displays, other interesting and innovative applications, such as electrochromic windows and other applications in the automotive industry are being actively pursued. Electrochromic windows, for instance, are windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential.

### Light Emitting Diodes

Other exciting phenomena, that have caught the imagination of both scientists and technologists alike, are the phenomena of photoluminescence and electroluminescence in conjugated polymers. Emission of light upon irradiation is termed as photoluminescence, while the emission on application of a voltage is termed electroluminescence. Light emitting diode is an example of utilization of the latter phenomenon. It was recently demonstrated that PPV films can be used as the emissive layer in electroluminescent devices. Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e. after thermal elimination of the precursor) (*Scheme 2*). Electrode materials are chosen with a low work function<sup>4</sup> for use as negative, electron-injecting contact, and with a high work function as the positive hole-injecting contact. At least one of these layers must be semi-transparent for light emission normal to the plane of the device. Both indium-tin oxide and thin aluminium films (7-15 nm) have been used as the transparent electrode. For polymer films, of about 100 nm, the forward voltages were as low as 10 V. Further improvements, using soluble PPV derivatives such as

<sup>4</sup> Work function of a metal may be defined as the minimum energy required to eject an electron from it. In chemical terminology, this is similar (although not the same) to the oxidation potential of the metal.





**Scheme 2. A typical LED device construction.**

2,5-dialkoxy PPV's and lower work function metals, particularly calcium, as the electron-injecting contact layer, have resulted in a further drop in forward voltage to about 5 V, and an increase in the efficiency to about 1% (photons per electron injected). These devices are believed to operate by double charge injection of electrons and holes from the negative and positive

#### Box 5. Biosensors

Conducting polymers have also touched the arena of biomedical applications. One such application is the fabrication of a glucose biosensor. Such a device can not only sense the presence of glucose but can also estimate its concentration. The principle involves immobilization of an enzyme and a suitable mediator on a conducting polymer matrix, that is coated on to a suitable sensor chip. Polypyrrole and polyaniline based sensors have been fabricated, both of which are of the amperometric type (based on the measurement of the steady state current at a fixed applied potential). One such sensor, is based upon electrochemically polymerized polypyrrole on an electrode from a solution which contains both glucose oxidase (a flavin-containing enzyme that oxidizes glucose) and ferrocene monocarboxylic acid (which is the electron transfer mediator that shuttles electrons from the redox center of the enzyme to the surface of the sensing electrode). In such a device, the amount of charge transferred (i.e., the current passed) is proportional to the concentration of glucose present in the solution. The specificity of the enzyme (which oxidizes only glucose) imparts to the device a very important characteristic, namely its ability to sense glucose even in the presence of several other components (as would be the case in, say, blood or urine). Prototypes of such microamperometric glucose and galactose biosensors based on a silicon chip employing polypyrrole have in fact been developed by several companies. These types of sensors are likely to soon find their way into analytical clinical laboratories for glucose estimation, for on-line supervision of diabetic patients etc.

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electrodes, respectively. These singly charged excitations combine to form excitons which can then decay by photoemission. Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap. Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to lead to improved devices of greater technological relevance.

### Conclusions

Conducting polymers have, thus, come a long way from purely laboratory curiosity to a class of materials that can find end use in a wide variety of commercial products, ranging from batteries to biosensors. Such a development is a classic example that serves to illustrate the wide range of expertise, starting from chemists, physicists, biologists and technologists, that is required to take some invention in the laboratory to the market place.

### Suggested Reading

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- ◆ WR Salaneck, DT Clark and EJ Samuelsen. *Science and Applications of Conducting Polymers*. Published by Adam Hilger. Bristol, 1991.
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CERF's Comments on Modern Science

- If it's incomprehensible, it's mathematics.
- If it doesn't make sense, it's either economics or psychology.