
Renaissance of the Plastic Age

Discoverers of Conducting Polymers Honoured with the
Millenium Nobel Prize in Chemistry

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Discovery and development of conducting polymers has opened up new frontiers in materials chemistry and physics. This new generation of polymers combines the mechanical properties and processability of traditional polymers with electrical and optical properties unknown earlier. The enormous technological potential that this rare combination offers, is beginning to be tapped. The Nobel Prize awarded in Chemistry this year, is a grand recognition of the dawn of the new plastic age.

Consider a simple experiment. A small amount of aniline is dissolved in hydrochloric acid taken in a beaker. A pair of electrodes is dipped into this solution; the anode should preferably be transparent, say, a piece of indium tin oxide (ITO) coated glass. A controlled potential is applied using a cell and variable resistor assembly. Depending on the potential applied, a colourless, green, dark blue or purple film forms on the anode within minutes (for details see [1]). If the green film is produced with adequate thickness and good quality by careful control of experimental conditions, it will show an electrical conductivity as high as $1-10 \text{ S cm}^{-1}$. The deposited film is a conducting polymer, the so-called emeraldine salt form of polyaniline. This conducting plastic may be contrasted with the well-known polymer teflon, which has a conductivity of $10^{-16} \text{ S cm}^{-1}$, seventeen orders of magnitude lower. An experiment similar to the one described above, on the anodic oxidation of aniline in sulphuric acid was in fact carried out by H Letheby of the College of London Hospital as early as in 1862. However, it took more than 100 years and great many advances in chemistry and physics as



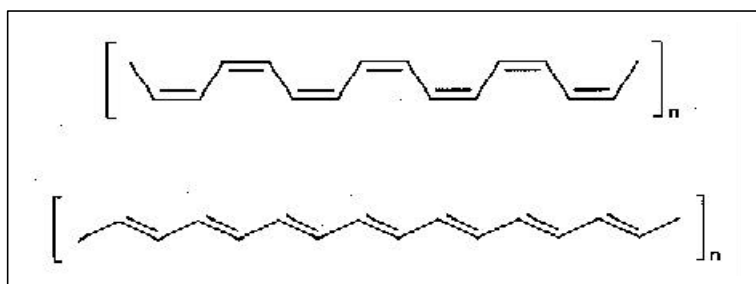


Figure 1. Structure of *cis* and *trans*-polyacetylene.

well as in polymer science, before the gates to the fascinating world of conducting polymers were opened.

In the early 1970's Hideki Shirakawa and coworkers at the University of Tsukuba, Japan, utilised the Ziegler–Natta polymerisation technique to prepare high quality films of polyacetylene. They introduced acetylene gas in controlled amounts over a solution of $\text{Ti}(\text{OBu})_4$ and Et_3Al in toluene at -78°C to produce a copper-coloured film of all-*cis*-polyacetylene. When the reaction was run over a *n*-hexadecane solution of the catalyst at 150°C , silvery all-*trans*-polyacetylene was obtained (Figure 1). Alan Heeger and Alan MacDiarmid at the University of Pennsylvania, USA, (Heeger is now at the University of California at Santa Barbara, USA), fresh from their studies on the famous inorganic polymer $(\text{SN})_x$, turned their attention to the purely organic polymer prepared by Shirakawa. This collaboration led to some remarkable developments that opened up new avenues in materials chemistry and physics. The $(\text{CH})_x$ polymer films prepared by Shirakawa showed poor electrical conductivity; 10^{-10} – 10^{-9} S cm^{-1} and 10^{-5} – 10^{-4} S cm^{-1} , respectively in the *cis* and *trans* forms. Shirakawa also noticed a strong decrease in the infrared transmission of polyacetylene treated with bromine and chlorine, reminiscent of metallic behaviour. MacDiarmid has been studying $(\text{SN})_x$ polymers modified by iodine treatment. The logical step therefore was to study the conductivity of polyacetylene treated with halogens. Measurements in the laboratory of Heeger showed an astounding enhancement of the conductivity of *trans*-polyacetylene on treatment with halogens. The highest conductivity recorded was 38 S cm^{-1} for a silvery-black film having the composition,

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Heeger, MacDiarmid and Shirakawa (this photograph taken at the International Conference on Synthetic Metals, ICSM 2000 was kindly provided by Prof. Heeger).

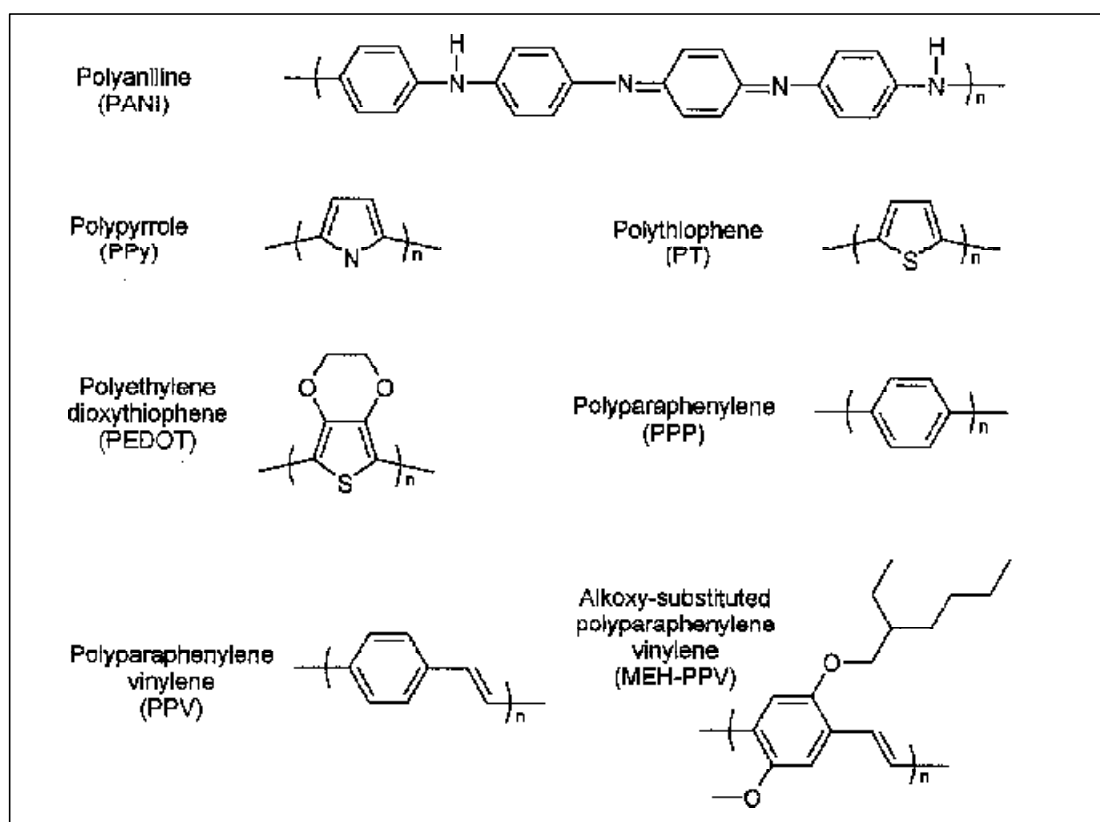


$(\text{CHI}_{0.22})_x$, an enhancement of more than six orders of magnitude with respect to pristine $(\text{CH})_x$. This remarkable discovery was published in 1977. The rapid and multi-faceted developments that followed in the field of conducting polymers have now gained further momentum with the award of the Nobel Prize to these pioneers in the year 2000. The ‘plastic age’ has truly entered the renaissance period.

Articles in previous issues of *Resonance* have addressed several aspects of conducting polymers ([3], [4]); readers are referred to these articles for details on the types of conducting polymers and their applications. An overview of the area of molecular materials is also provided in the series article. Following the discovery of conduction in polyacetylene, a whole class of conducting polymers has been developed. This includes polyaniline, polypyrrole, polythiophene, polyparaphenylene and polyphenylenevinylene (*Figure 2*). Polyaniline is used in transparent conducting electrodes and for electromagnetic shielding of electronic circuits. It is also used extensively as a corrosion inhibitor. The electrochromic property (recall the experiment described above) makes it useful in ‘smart windows’ that absorb sunlight in summer. Polypyrroles have been tested as microwave-absorbing radar-invisible screen coatings and as active thin layers in sensing devices. Polythiophene derivatives are used as field-effect transistors, anti-static coating material and as hole injecting electrode material in polymer light-emitting devices. One of the prime candidates for the active layer in light-emitting devices is polyphenylenevinylene and its derivatives. The field of electroluminescent polymers is burgeoning into a

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major scientific and commercial enterprise. Significant advances have been made over the years in the solution processing of semiconducting polymers, thin film formation via precursor routes, counter ion induced processing of the metallic form of polymers such as polyaniline and template synthesis of colloidal dispersions of conducting polymers.

Figure 2. Structure of some conducting polymers.

We will confine our current discussion to a brief look into the mechanism of conduction in conjugated polymers and an appraisal of their status as high performance materials. Polyacetylene, the polymer with the highest conductivity measured to date can be chosen as the prototype. Let us consider polyacetylene to be a linear chain of carbon atoms. We focus attention on the π -electrons, which are delocalised over the carbon framework. The simplest description of the π -electronic structure would be that based on a free-electron molecular

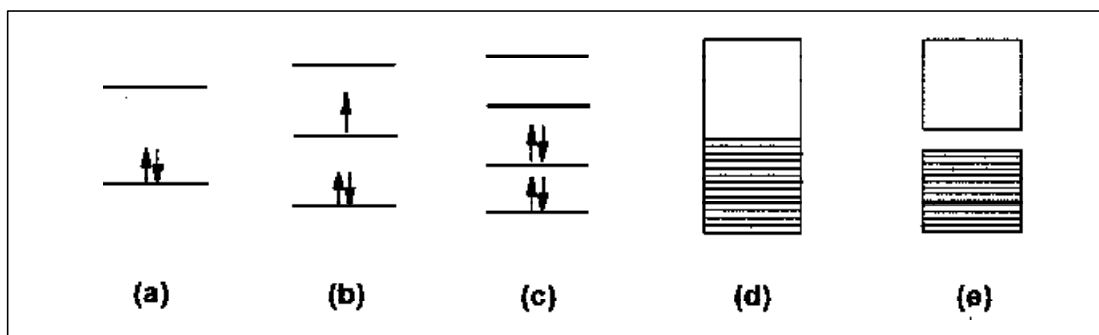


Figure 3. Schematic representation of *p*-electronic energy levels and electron occupation of these levels in a) ethylene, b) allyl radical, c) butadiene, d) regular trans-polyacetylene and e) dimerised trans-polyacetylene. In d) and e) the electron filling is indicated using hatched lines.

orbital model. Extending the picture from ethylene to allyl radical, to butadiene and so on, the polyacetylene chain consisting of N atoms (N being very large) will have a continuum of energy levels or a band (Figures 3a-3d). Since the band can accommodate $2N$ electrons and there are only N π -electrons available, this will be a half-filled band. Such a simple band description would predict polyacetylene to be a metal. However, as we have seen above, pristine polyacetylene is at best a poor semiconductor.

The simple band picture assumed a regular arrangement of carbon atoms in the polyacetylene chain with equal carbon-carbon bond lengths throughout. However in polyacetylene, the bond lengths have a distinct alternation with every second bond having a double-bond character; the structure shown in Figure 1 is a realistic description. The reason for this can be understood from the argument put forward by Rudolf Peierls in the 1930's who showed that a hypothetical chain of equidistantly placed sodium atoms is unstable to a distortion which would make the interatomic spacing alternately long and short and lead to a metal-insulator transition. This instability is similar to the famous Jahn-Teller distortion of molecules with degenerate electronic states. In polyacetylene, the bond alternation leads to a band gap opening up at the middle of the band (Figure 3e). The resulting electronic energy stabilisation, more than compensates for the energy required for the bond rearrangement and turns polyacetylene into a semiconductor (more details on Peierl's instability can be found in Part 2 of [4]).



The critical role of the halogen treatment described above will now be obvious. Oxidation by strong electron acceptors such as halogens (or reduction by donors such as alkali metals) generates a variety of charge carriers on the carbon spine. Different types of charge carriers are formed in the various conducting polymers depending on whether the two possible bond alternation patterns are energetically degenerate as in polyacetylene or non-degenerate as in polymers like polythiophene, PPP and PPV. We use the polyacetylene skeleton to illustrate the different cases. A typical scenario on iodine treatment is illustrated in *Figure 4*. The cation radical produced called a polaron, though mobile, is localised typically within the space of a few carbon atoms, since the counter ion I_3^- is immobile. However, when the extent of oxidation is increased, sufficient density of polarons are produced which move freely in the field provided by the high concentration of counterions and the conductivity is enhanced. New charge carriers called bipolarons are also being formed (*Figure 5a*) contributing to the conductivity. Another important class of charge carriers is the solitons, which are neutral when formed during *cis-trans* isomerisation (*Figure 5b*) or charged when created through doping (*Figure 5c*). Work by the Nobel Laureates as well as several others have led to

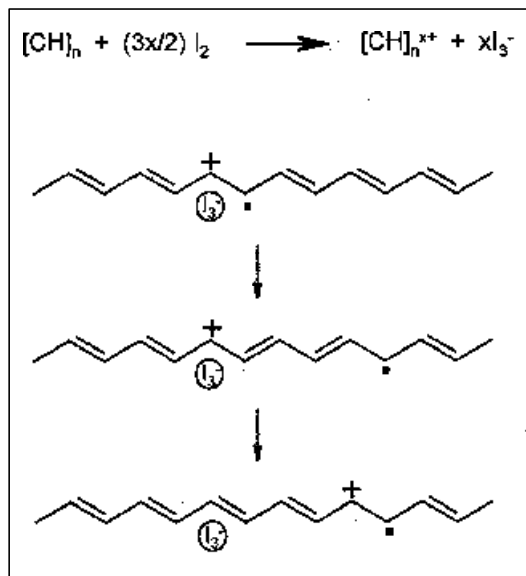
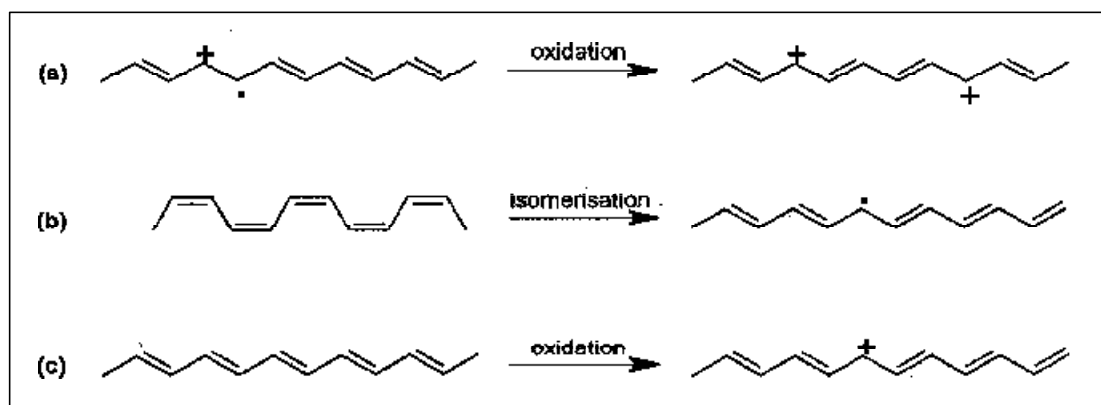


Figure 4. Oxidative doping of polyacetylene by iodine and a schematic representation of the delocalisation of the resulting polaron.

Figure 5. Formation of a) bipolaron, b) neutral soliton and c) positive soliton in polyacetylene.



the development of a variety of doping techniques for conducting polymers including chemical and electrochemical procedures.

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Electrical conductivity of metals and semiconductors show opposite temperature dependence – the former growing and the latter falling as the temperature decreases. Conducting polymers generally show decreasing conductivity with lowering temperature indicating an activated charge carrier transport. In 1990 Alan Heeger raised a fundamental question about the metallicity of conducting polymers – “can we expect polymers with conductivity greater than copper and strength greater than steel?” (see [5]). Excessive doping is generally detrimental to conductivity due to the increased scattering of electrons by the resulting charged impurities. Therefore it may appear that the high doping levels required to achieve good conductivity in conjugated polymers may itself frustrate the development of truly metallic conducting polymers. However, conducting polymers are self-organising systems wherein the stiff conjugated chains force the dopant counter ions into channels or planes within the structure. Indeed, this is reminiscent of the quantum well heterostructures in artificially layered semiconductors (interestingly two of the Nobel Prizes in Physics this year went to Zhores Alferov and Herbert Kroemer for their pioneering work in this area). Therefore, the high doping levels need not be a point of concern in conducting polymers. Based on a simple analysis of the mean free path of charge carriers, Heeger has divided conducting polymers into two classes. (1) ‘Dirty’ conductors are formed with just a moderately high density of charge carriers; the charge carriers possess mean free paths comparable to the lattice spacings and the charge transport appears like a hopping of localised carriers leading to a conductivity of the order of 10 S cm^{-1} or less. (2) Truly metallic polymers with charge carrier mean free paths of several lattice spacing will support electrical transport limited only by true phonon scattering rather than impurities and defects in the chain; conductivities will be in excess of several hundreds of S cm^{-1} . Heeger’s



analysis showed that if conducting polymers can be prepared with high molecular weight, good chain alignment and interchain order, it should be possible to achieve room temperature conductivities higher than 10^6 S cm^{-1} in *trans*-polyacetylene; this would indeed beat the conductivity of copper. Further, the conductivity of these systems would grow exponentially with lowering temperature; a rough estimate of the exponent, $h\nu_0/k_B T \sim 4 - 5$ suggests an increase of 50 – 100 times in the conductivity at 150 K. Though conductivities as high as 10^5 S cm^{-1} have been realised in specially fabricated polyacetylene, the strong temperature dependence expected has not been observed indicating that further improvement in material processing is called for. Adding to the woes is the instability of polyacetylene in the presence of air and moisture. This has catalysed the development of less conducting, but stable polymers such as polyaniline, polypyrrole and polythiophene.

The high exponential factor noted above is a consequence of the stiffness of the carbon-carbon bond in polyacetylene. This leads us to the second question that Heeger raised about the level to which the mechanical strength of conducting polymers can be improved. Chain extension and alignment are known to enhance dramatically the strength of polymers. For example, the ordinary polyethylene that pervades our daily life in innumerable ways is a soft material. However, ultra-high molecular weight polyethylene, which is chain-aligned through gel-spinning and subsequent tensile drawing, is one of the strongest materials known; the strength of the stiff carbon-carbon bond is exploited nearly to the full extent in such materials. In conducting polymers possessing high molecular weight, good chain extension and chain alignment, interchain diffusion of charge carriers is expected to be a coherent process, which will give rise to a two-fold benefit. It will help circumvent the problem of localisation inherent in one-dimensional systems leading to improved metallic conductivity and at the same time strengthen interchain bonding minimising the slip of the chains with respect to one another. The latter would enhance considerably,

Suggested Reading

- [1] B C Sherman, W B Euler and R R Forcé, *Polyaniline – A Conducting Polymer*, *J. Chem. Edn.* **4**, A94-A96, 1994.
- [2] H Shirakawa, E J Louis, A G MacDiarmid, C K Chiang and A J Heeger, *Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)_x*, *J. Chem. Soc. Chem. Comm.* **578-580**, 1977.
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- [4] T P Radhakrishnan, *Molecules to Materials (series article)*, *Resonance*, Vol. 3, No. 4, 30-42, 1998, Part 1; No.5, 6-23, 1998, Part 2; No. 7, 8-17, 1998, Part 3; No. 8, 14-24, 1998, Part 4; No.10, 16-25, 1998, Part 5; No. 12, 4-12, 1998 – Part 6.
- [5] A J Heeger in *Lower-dimensional Systems and Molecular Electronics*, (Eds.) R M Metzger, P Day and G C Papavassiliou, NATO ASI Series B Physics, Vol. 248, Plenum, New York, p.293 - 301, 1990.
- [6] A J Heeger, *Semiconducting and Metallic Polymers: The fourth Generation of Polymeric Materials. Nobel Lecture*, Dec.8, 2000.



the chances of exploiting the full strength of the carbon-carbon bond. Mechanical properties characteristic of high performance materials have now been realised in stretched polyacetylene. Further, a close correlation between improved electrical conductivity and mechanical strength has been demonstrated in several conducting polymers (see [6]).

We conclude on an optimistic note that the realisation of a stable conducting polymer with conductivities better than that of copper and strength better than that of steel while still possessing the processing advantages of polymers, is not an impossible dream. When we also note the considerable potential of this new generation of polymers in other applications such as light emitting diodes, photovoltaic cells and thin film transistors, it is clear that the myriad ways in which these novel plastics are going to revolutionise materials technology is just unfolding.

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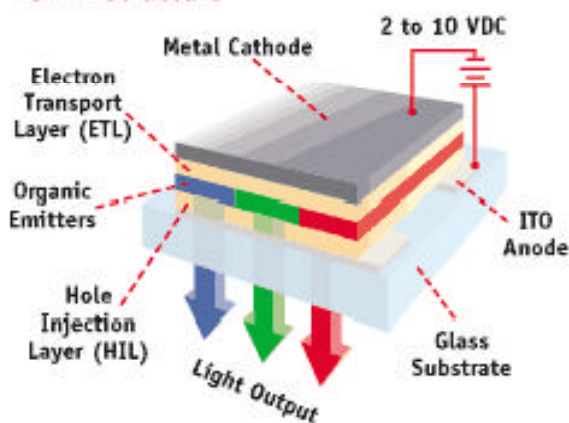
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Organic Light-Emitting Diode (OLED)

A display device consisting of a series of carbon-based thin films sandwiched between two electrodes; one transparent (often glass). OLED technology holds promise because of the ability to tailor the organic molecules to vary color saturation, sensitivity, and other optical properties.

OLED Structure



Source: <http://www.kodak.com/global/en/professional/products/specialproducts/OEL/creating.shtml>

