

Conducting polymers: Nobel Prize in Chemistry, 2000

The Nobel Prize in Chemistry¹, 2000 has been awarded to Alan J. Heeger² (University of California at Santa Barbara, USA), Alan G. MacDiarmid³ (University of Pennsylvania, USA) and Hideki Shirakawa⁴ (University of Tsukuba, Japan). The citation for the reward – ‘for the discovery and development of electrically conductive polymers’. Moreover, The Royal Swedish Academy of Sciences¹ pointed out that the award is being motivated by the ‘important scientific position that the field has achieved and the consequences in terms of practical applications, and of interdisciplinary development between chemistry and physics’.

The conventional wisdom suggests that polymers (plastics, rubbers, etc. used in everyday life) offer substantial resistance to the flow of electricity; and being widely used for electrical insulation purposes. In usual carbon-based polymers, the sp^3 carbons form sigma-bonds, as a result the electrons are in bound state. Due to this, there hardly exist any free charge carriers to assist the flow of electric current in common polymers. Hence, the term ‘conducting polymer’ was considered as an oxymoron till late 1970s. Moreover, before the advent of organic conductors⁵ in early 1970s, the prevalent view was such that electrical conduction mainly occurs in inorganic systems like Cu, Si, etc. (with the exception of graphite) due to the presence of delocalized electron sea; whereas, in organic and biological systems the electrons are localized by covalent bonding, hence not really conducive for electrical transport due to the lack of free/delocalized charge carriers, low mobility of carriers, etc.

From the early works of Pople and Walmsley⁶, Salem⁷ and Little⁸, it is known that in a linear chain of sp^2 carbon atoms, consisting of alternating single and double bonds, the delocalized p -electron cloud can attribute special features to the electrical and optical properties in organic systems. For example, **b**-carotene, the orange pigment in carrots, consists of nine repeated alternating single-double bond units (conjugated bonds). The delocalized p -electrons in these single-double bond units induce a blue-shifted absorption, hence gives the orange colour to carrots. Since the p -electrons are less bound to the carbon nuclei, they require less energy to go to the excited states. This type of strong absorption of light in the visible region is one of the special features of molecules containing conjugated repeat units.

The simplest example of a polyconjugated system consisting of several repeat units of (CH_2) is polyacetylene $[CH_x]$, as shown in Figure 1. After the discovery of Ziegler–Natta catalysts,

Natta and coworkers⁹ attempted to synthesize CH_x by bubbling acetylene gas through a titanium/trialkyl catalyst solution, in the year 1958. The main product of the reaction was a black, semicrystalline powder; and it was completely insoluble, infusible, and unstable in presence of air and water. In 1971, Shirakawa and Ikeda¹⁰ found that $Ti(Obu)_4/AlEt_3$ yields CH_x exclusively, in the form of polycrystalline/flexible film. This work revolutionized the field of polyacetylene chemistry and physics, also this opened up the field of conducting polymers. Shirakawa and coworkers¹¹ further optimized the synthesis of CH_x by using higher concentration of catalyst to produce dense and tough free-standing films.

In a typical CH_x synthesis¹¹, $Ti(Obu)_4$ was added to a Schlenk flask with 20 ml of toluene followed by the addition of 4 equivalents of $AlEt_3$ in an inert atmosphere. The catalyst was aged for 30 min at room temperature. The catalyst solution was degassed at $-78^\circ C$ and then slowly rotated to coat the wall of the

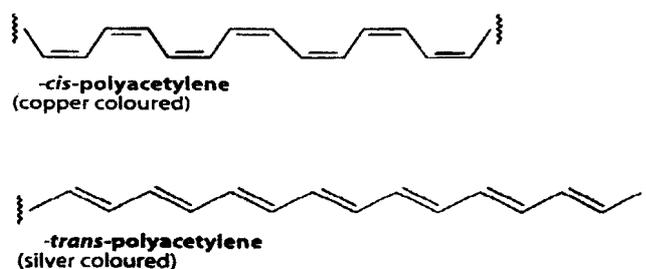


Figure 1. *Cis* and *trans* structure of polyacetylene.

reaction flask with the catalyst solution. Then, acetylene gas at 600 torr was introduced at -78°C , and immediately the wall of the flask turned deep red, indicating the formation of *cis*- CH_x film (see Figure 1). The thickness of the film can be controlled by varying the acetylene gas pressure, reaction time and catalyst concentration. The rate-determining step of the polymerization reaction is the diffusion of the acetylene gas through the initial thickness of the polymer film that gets coated on the substrate. The proposed mechanism for acetylene polymerization is the typical Ziegler–Natta insertion-type mechanism with a *cis* approach of the monomer leading to a *cis*-polymer. In order to obtain a high quality dense film a higher concentration of the catalyst is required. As the film thickness increases, the initial red colour changes to dull copper-colour.

This so-called Shirakawa polyacetylene¹¹ (*S*- CH_x) is completely insoluble in any solvent, though the hydrogenated sample (that is linear polyethylene) is fully soluble in hot tetralin. By using this modified polyethylene route, the number-average molecular weight of pristine CH_x was estimated to be around 6000 g/mol, with a polydispersity index of ~ 2.4 . With the Shirakawa method either *cis* or *trans* can be synthesized. At a polymerization temperature of -78°C , *cis*- CH_x is formed exclusively. Whereas, a higher percentage of *trans*- CH_x is formed with increasing temperature, and at 150°C *trans*- CH_x is formed exclusively. Also, the *cis*- CH_x can be isomerized to *trans*- CH_x by heating or by chemical doping of the sample, since the *trans*- CH_x is thermodynamically more stable.

The *S*- CH_x has a complex, semicrystalline fibrillar morphology, depending on the polymerization conditions¹². The electron micrographs show that the diameter of the fibrils varies from 30 Å to 1 μm . *S*- CH_x has a strong *p*-*p** transition, with $I_{\text{max}} = 594 \text{ nm}$ for the all *cis*- CH_x and $I_{\text{max}} = 700 \text{ nm}$ for the all *trans*- CH_x . The band gaps of *cis*- CH_x and *trans*- CH_x are 1.8 and 1.5 eV, respectively. The conductivity of undoped *cis*- CH_x and *trans*- CH_x is 10^{-9} and 10^{-6} S/cm , respectively. Hence, the undoped *cis*- CH_x and *trans*- CH_x are insulator and semiconductor, respectively. This is mainly due to the fact that the *p*-electron delocalization is higher in

trans- CH_x with respect to *cis*- CH_x . After Shirakawa's pioneering work, several modified routes have been attempted to synthesize CH_x , for example Naarman's and Akagi's routes¹². The practical application of CH_x is limited, since the double bonds in CH_x are highly susceptible to oxidation, thus it is not very stable in air.

The seminal work of Shirakawa and coworkers (1971–74) is described in refs 10 and 11. Then, in the year 1975, MacDiarmid met Shirakawa during an International Conference in Japan and invited him to University of Pennsylvania for collaborative work. Shirakawa visited MacDiarmid in 1977, and they worked together and further improved the synthesis of CH_x to obtain higher quality material. At the same time, Heeger (then at University of Pennsylvania, and later moved to University of California at Santa Barbara in 1983) was carrying out detailed physical property studies on organic metal [donor–accepter charge-transfer complex, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)]¹³, and on polymeric metal and superconductor [polysulfur nitride, (SN)_x]¹⁴.

Heeger and MacDiarmid¹⁴ together found out that the intercalative-doping of (SN)_x by iodine/bromine can increase the conductivity of (SN)_x from 10^3 to 10^5 S/cm . They applied the same idea (*in situ*-conductivity measurement while exposing the sample to iodine vapour) to CH_x , and to their surprise they observed a seven orders of magnitude increase in conductivity, from 10^{-4} to 10^3 S/cm . Thus the first metallic organic polymer was discovered in 1977 (ref. 15). The three winners of Nobel Prize in Chemistry, 2000 established that an insulating polymer can be made to be metallic and conduct electricity if alternating single and double bonds link the carbon atoms in a chain, and the electrons are either removed via oxidation (*p*-type doping) or introduced via reduction (*n*-type doping). These extra charge carriers created by doping move along the polymer chain, making them conduct electricity, and metallic¹⁶.

After the discovery of metallic CH_x , intensive research started by several groups to prepare new types of polyconjugated systems¹⁷. Some of the well-known conducting polymers are shown in Figure 2. The physical and chemical

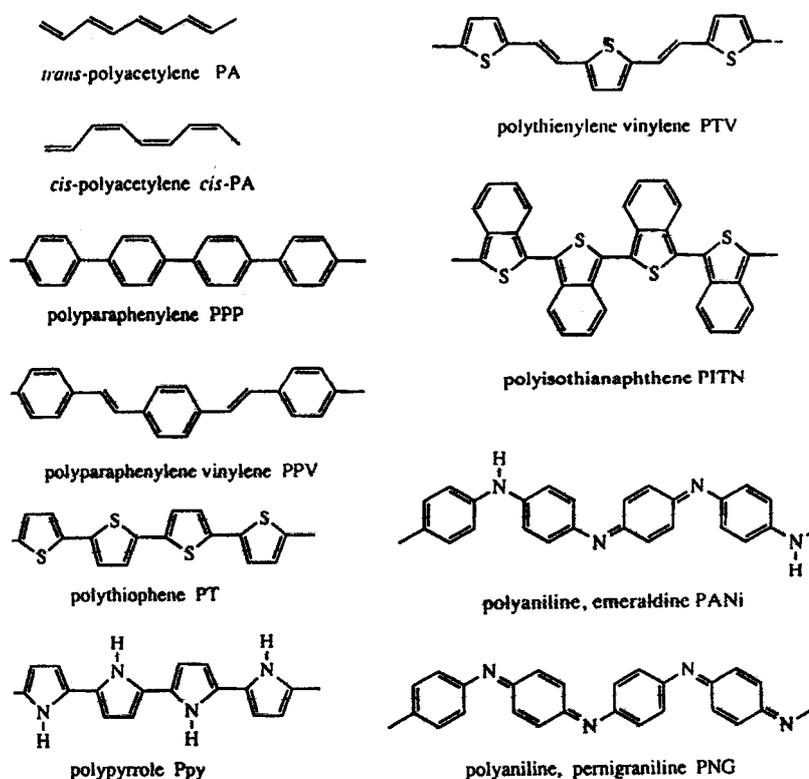


Figure 2. Structure of conducting polymers.

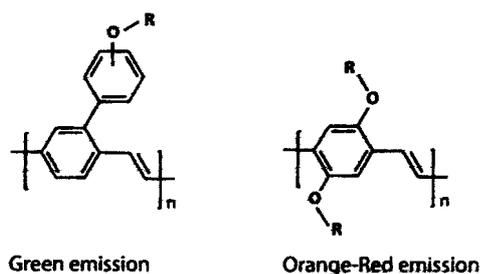


Figure 3. Structure of green and orange-red light emitting PPV derivatives.

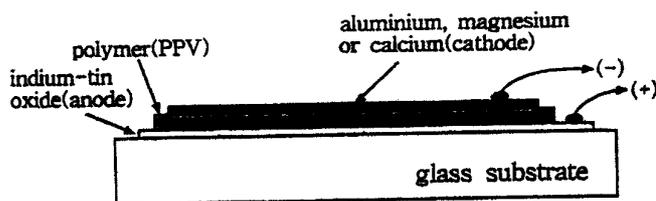


Figure 4. Schematic diagram of a polymer light emitting diode.

properties of polyconjugated systems can be easily tuned by varying the side groups attached to the main chain (for example, to induce solubility), the extent of π -electron delocalization, interchain interactions, structural conformation, morphology, etc. As a typical example, the band gap of polythiophene can be lowered from 2.5 to 1 eV by modifying it to polyisothionaphthene (see Figure 2) (ref. 17). This type of band gap engineering is quite easier in conjugated polymers with respect to other types of semiconducting materials. This is very well illustrated in controlling the emission colour in light-emitting diodes (LEDs) fabricated from poly(paraphenylenevinylene) (PPV) derivatives, by varying the side groups, and that in turn tunes the π -electron delocalization and band gaps. For example, the side group substitutions in PPV backbone, as shown in Figure 3, can yield green and orange-red light emission from PPV-based LEDs¹⁷. By this molecular-scale engineering, it is possible to have all the colours from blue to red in conjugated polymer LEDs.

In a span of two decades of research in conjugated polymers, several interesting applications of these materials have been developed by various research groups^{17,18}. A brief list is as follows: light emitting diodes, solar cells,

transistors, diodes, holographic storage, chemical and biological sensors, capacitors, batteries, antistatic coatings, electromagnetic interference shieldings, anticorrosive coatings, gas and liquid separation membranes, artificial muscles, lithography and metallization, photoelectrochromic devices, xerographic photoreceptors, all-polymer electronic circuits, etc. Several companies are on the verge of commercializing conjugated polymer based devices (for e.g. Pioneer, Dupont, Cambridge display, Infineon, Kodak, Sanyo, Philips, TDK, etc.).

Some typical examples of conjugated polymer devices are described below^{17,18}. In LED fabrication a thin film (few hundreds of Å) of the semiconducting polymer is spin coated on optically transparent indium tin oxide electrode (hole-injecting). On top of it, a thin film of aluminium or calcium (electron-injecting) is deposited by evaporation. Electrons and holes are injected to the semiconducting polymer by applying proper bias (~ 5 V) across the electrodes, and the emission of light is due to the radiative charge carrier recombination in the polymer film. A schematic diagram of the LED is shown in Figure 4. The typical polymer LEDs (with PPV derivative as active material) have a luminance around 300 cd m^{-2} (nearly same as that of the brightness of a tele-

vision screen) with a half-life of over 10,000 h. These LEDs have an external quantum efficiency of nearly 3% with a luminous efficiency of over 20 lmW . The turn-on voltages in these LEDs are usually below 5 V, and the typical current densities are around 1 mA/cm^{-2} . The performance of these LEDs is quite satisfactory for various display applications. Smart pixels consisting of a molecular/polymer thin-film field-effect transistor (FET) monolithically integrated with a polymer LED have been fabricated by several groups^{19,20}. The FET-LED device represents a step toward all-polymer optoelectronic integrated circuits such as active-matrix polymer LED displays, etc. Moreover, the steps towards developing a full-colour large display by patterning the red, green and blue pixels have been achieved by low-cost ink-jet printing techniques²¹.

In photovoltaic diodes, the incoming light photogenerate charge carriers in a sensitized semiconducting polymer film, which in turn builds up an open-circuit voltage^{17,18}. In these devices, the external energy conversion efficiency is around 3% for a standard solar spectrum; having a maximum energy-conversion (in green light) around 7% and the maximum quantum efficiency (charges collected per incident photon) is nearly 28%. The efficiency of these devices can be further improved if the exciton-splitting process that occurs at the conjugated polymer-electrode (or at the junction of two polymers with different electron affinities) can be made more effective, and also by reducing the trapping of the diffusing excitons by defects and impurities. Moreover, detailed studies are essential to improve the efficiency and stability of organic photovoltaics for practical applications.

Recently, several groups have fabricated all-polymer integrated circuits²²⁻²⁴. A major application of polymeric integrated circuits is in the low-end high-volume microelectronics such as smart cards, identification and product tagging, etc. In these items, the excellent performance of the silicon-based devices is not really required; in addition to that, the cost of production is quite prohibitive and to have mechanical flexibility is difficult. While taking these factors into account, the fabrication of low-cost and large-area integrated circuits with organic FETs and

TFTs on flexible plastic substrates by printing techniques is a simple alternative to the conventional expensive semiconductor technology. Large area and low cost all molecular/polymer integrated circuits (up to 864 transitions per circuit with operating speeds ~ 1 kHz) have been fabricated on flexible plastic substrates, and its performance is quite acceptable for several applications.

In conclusion, the pioneering work by the Nobel Prize Winners in Chemistry-2000 paved the way for conjugated organic materials towards electronics and photonics applications. This has led to the possibility of making electronic circuits in single/array of organic molecules/polymers. The conjugated polymers are expected to play crucial role in the fabrication of molecular electronic circuits. This can reduce the dimensions of the electronic circuits from 200 nm (current minimum pattern dimensions in advanced integrated circuits on silicon wafers) to 1 nm. This shrinkage in circuit size can increase the speed and dynamic memory of computers by several orders of magnitude ($\sim 10^6$).

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