

# **BUILDING LIGHT EMITTING DEVICES BASED on POLYMERIC SUBSTANCES**

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## **Abstract**

This paper discusses the properties of light emitting polymers (LEPs) and the physics behind their workings. It also some of the process of constructing these devices and introduces the reader to various apparatus operated during the building process. Since my line of work mostly consisted of building already existing designs, this document does not contain large amounts of data, plots or calculations that one would expect to find in an ordinary physics publishing.

## Introduction

Light Emitting Polymers (LEPs) are semi-conducting devices that exhibit electroluminescent characteristics. The phenomenon known as electroluminescence (EL) is caused by the emission of light generated from the recombination of electrons and holes electrically injected into a semi-conductor. So far conventional and marketable electroluminescent devices (EDs) have always been inorganic semi-conductors but recent developments in the late 1990s are opening the doors for organic materials.

Obtaining organic materials with electroluminescent properties was first achieved in the 1960s on anthracene crystals by Pope et al. at New York University. However these early devices had high operating voltages and very low quantum efficiency thus they did not attract much attention for two decades. In 1987 a breakthrough was made by Tang and VanSlyke at Eastman Kodak who, by using multilayers of sublimated organic molecules, succeeded in reducing the operating voltage dramatically and increasing the quantum efficiency significantly. Another important discovery was made in 1990 by Burroughes et al. at Cambridge University who detected electroluminescence from diodes based on luminescent conjugated polymers.

Polymer means “many parts”, polymers are very large organic molecules formed by thousands of repeating units linked together. One can view these heavy organic molecules (molecular weight between 5,000 and 150,000) as very long chains mostly made of C-C, C-O and C-N bonds. Polymer technology has existed for decades. Use of natural rubber and common plastics such as *polythene* dates back to as early as 1820s. However finding polymers with intrinsic properties of semi-conductors is very recent. In 1967, electrically conducting polymers from pyrrole, thiophene and furan were

characterized and the electrical conductivity of *poly(anilines)* noted. The report in 1977 about doping *polyacetylene* to achieve conductivity opened up important vistas for chemistry and physics.

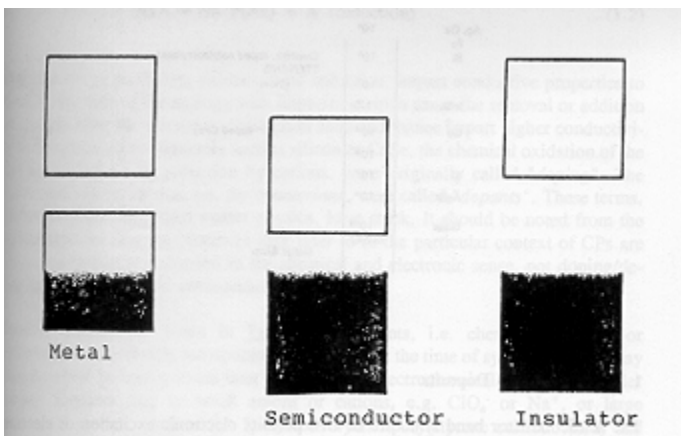


**Figure 1:** Two commonly used polymers, note the repeating structures

Polymer based light-emitting diodes (LEDs) were discovered in 1990 by Friend et al. The first polymer LEDs used *poly(phenylene vinylene)* (PPV) as the emitting layer. Since 1990 many different polymers have been shown to emit light under the application of an electric field (EL). PPV and its derivatives are still the most commonly used materials, but *polythiophenes*, *polypyridines* and *polyphenylenes* are now being tested for higher efficiency, longer lifetime and lower power requirements.

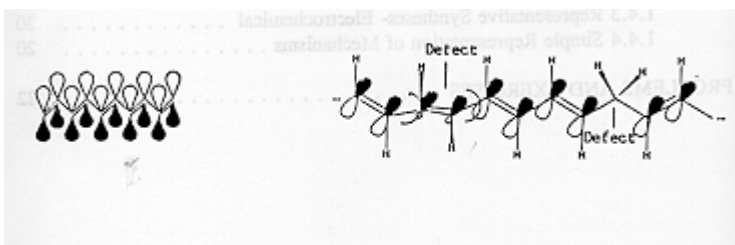
### Conducting Polymers (CPs)

What makes a material insulating or semi-conducting is the size of the *bandgap* between the *valence band* and the *conduction band*. For insulators the size of the gap is at least 10 eV or larger. If the gap is small, e.g. 1 eV, the electrons can easily be excited into the conduction band by means such as thermal excitation, vibrational excitation or photoexcitation and a semi-conductor results. Conductors do not have a similar problem of jumping over such large gaps because their valence bands are not filled (See figure 2 below). As an example of an intrinsic polymeric semiconductor, consider *poly(phenylene vinylene)* (PPV) with a bandgap of 2.2 eV.



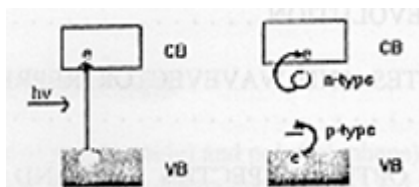
**Figure 2:** The three conductivity classes

For a conduction to take place in conventional, inorganic semiconductors, electrons must generally be excited from the valence to the conduction band. Normally, thermal excitation at room temperature gives rise to some conductivity in many inorganic semiconductors. However, unlike the widespread inorganic compounds, doped polymers are semiconductors as a result of their unique, extended  $\pi$ -conjugation. Indeed the extended-overlap  $\pi$ -bands become the valence band and the  $\pi^*$  bands become the conduction band in conducting polymers (CPs). The  $\pi$ -conjugated system is formed by the overlap of carbon  $p_z$  orbitals and alternating carbon-carbon bond lengths and is the common electronic feature of pristine (undoped) conducting polymers. The semi-conducting behavior of polymers originates from these delocalized  $\pi$ -orbitals formed in carbon-containing compounds.



**Figure 3:** Schematic representation of  $\pi$ -conjugation in the CP poly(acetylene)

The conductive properties of pristine electronic polymers are attained through simple chemical or electrochemical oxidation, or in some cases reduction, by a number of simple anionic or cationic species called “dopants” The entire process of transformation from insulator to conductor is called “doping” with conductivity increasing as the doping level increases. Conjugated polymers can be easily oxidized or reduced. When oxidized, electrons are removed from conjugated polymers and counter ions (anions) are introduced into the system such that the local charge neutrality is preserved, causing *p*-doping (e.g., I<sub>2</sub>, PF<sub>6</sub><sup>-</sup>, Cl<sup>-</sup>, AsF<sub>6</sub><sup>-</sup>). On the other hand, when reduced, electrons are added to the polymer chains. Counter ions (cations) are also introduced to the polymer system to preserve the charge neutrality, yielding *n*-doping (e.g., Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>). In short, *p*-type doping is electron accepting where as *n*-type is electron donating. Compared to the intrinsic semiconducting polymers, the conductivity of doped conjugated polymers increases by several orders of magnitude and approaches that of metallic conductors.



**Figure 4:** Photoexcitation and doping

Another unique property of conjugated polymers is the reversible doping capability through electrochemical process. Certain conjugated polymers can be doped reversibly to *p*- or *n*- type. The doping procedures are usually carried out by exposing polymer films or powders to vapors or solutions of the dopant. Most doped CPs have conductivities ranging from 10<sup>-2</sup> to 10<sup>4</sup> S/cm, some nearly as high as copper’s (5 × 10<sup>5</sup> S/cm). Conducting and semiconducting polymers continue to generate much interest and

remain at the forefront in many new areas of development such as batteries, light emitting diodes (LEDs), sensors, corrosion protection, electro-optics, microwave-based technologies, electrochromic devices, photovoltaics and drug/chemical delivery.

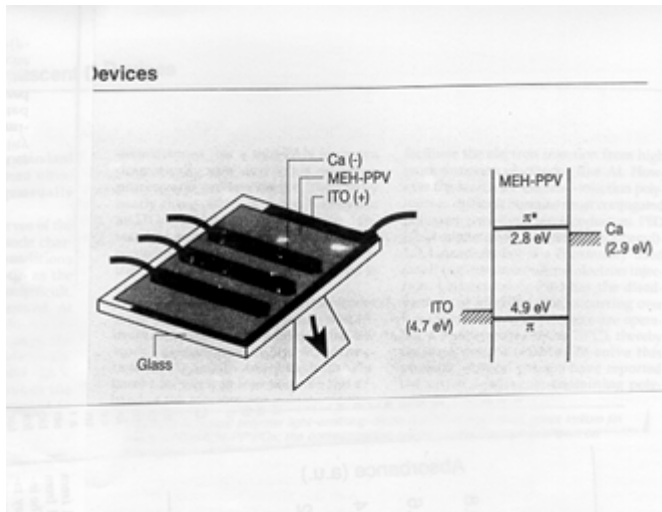
### **Light Emitting Diodes (LEDs)**

One of the most exciting developments in the field of CPs in the early 1990s was the discovery of Cambridge, England group that CPs such as PPVs could be used as the emissive layer in LEDs. The motivation for this renewed interest was straightforward; high-efficiency surface emission across the whole visible spectral range could be obtained easily. In other words, researchers were able to achieve the emission of many different colors of light using these devices. Since that time, however, this excitement has somewhat been tempered with the realization that practical and commercial implementation still has a number of difficulties to be overcome before LEDs can begin to take on more established technologies in flat panel displays for computer and electronics uses.

One of the advantages of polymer LEDs is the easy tuning of emission colors. One strategy of color tuning is through altering the chemical structure of polymers, such as changing side groups or the backbone structure. Another strategy to tune is through the planar microcavity structure. In this approach, the energy of the photons and the photon density of states are distributed such that only certain wavelengths are emitted, which correspond to allowed cavity modes. However, the narrow viewing angle and expensive/complicated device fabrication process remain as crucial issues. The PPV films provide relatively high quantum yield for electroluminescence in the yellow/green

portion of the visible spectrum. Although the  $\pi$ -conjugated polymers provide light from different portions of the spectrum the difficulties in manufacturing and preservation prevent their widespread use in the market.

A typical polymer LED consists of a thin film of a luminescent conjugated polymer sandwiched between an anode and a cathode, on top of a glass substrate. Indium Tin Oxide (ITO) is most frequently used as the anode because it exhibits conductive properties with a relatively high work function. It also is optically transparent, thus allowing the light to propagate through the device. The counter electrode (cathode) is usually a metal with low work function, enabling the electron injection into the conduction band of the polymer medium. Calcium, aluminum, Al/lithium as well as magnesium/silver alloys are generally used. See the figure below for a schematic.



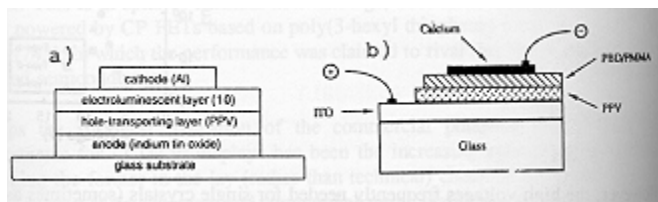
**Figure 5:** A typical LED configuration, the corresponding energy diagram is shown on the right

When a high electric field is applied between the electrodes, electrons are injected from the cathode and holes are injected from the anode into the polymer layer. The injected charges recombine and decay radiatively if the polymer is fluorescent. In the polymer LEDs, the polymer/metal interface determines the charge injection and therefore

plays an important role in operating the devices. A sound method to achieve balanced charge injection is adding appropriate hole- and electron-injection layers between the luminescent conjugated-polymer layer and the electrodes. An electron injection layer serves two other functions: (1) removing the radiative recombination region from near the metal interface and (2) balancing electron and hole injections since the electron-transport layer also functions as a hole-blocking layer that redistributes the electric field inside the polymer film. However this causes the device-operating voltages to increase, which leads to shorter lifetimes for LEDs with an electron-injection layer.

## **Fabrication**

The fabrication of polymers is a lengthy and tedious task with many pitfalls and low success ratio. One of the most harmful substances to the devices is the air we breathe. The oxygen reacts with the polymer and oxidizes it. Ideally, these devices are supposed to be built in glove boxes starting from the very first step of fabrication. However, Dr. Epstein's research group has been experiencing difficulties with the glove boxes in the labs and they have been inaccessible for our use. The surfaces of the ITOs (meaning ITO coated glasses in the expert's language) must to be spotless and free of scratches. Similarly, the polymer coated on the ITO needs to be homogenous and evenly leveled. It is impossible to clean the ITOs without any imperfections. But the cleaner the samples are, the lower the chances are of a glitch inhibiting optical emissions. My research group mostly worked on fabricating the simpler *single-layer devices*, which consist of the polymer sandwiched between a thin layer of metal electrode and the ITO. The various steps of construction are presented below.



**Figure 6:** The single layer design of an LED

### a. Cleaning

Before the cleaning process can be initiated the researches are always checked to see if they are wearing their latex gloves. Wearing this type of protection is emphasized often and it is crucial since human skin contains thousands of different contaminants, which can be passed on to the samples with a slight touch. The ITO substrates undergo rigorous cleaning using different solvents to remove dust particles and contamination on the surface. This is usually done, first, by thoroughly wiping each surface clean by using an alcohol based cleaner, in our case, isopropanol. The wiping procedure is repeated twice for each surface then the samples are placed in a beaker containing an organic solvent. The beaker undergoes ultrasonic shower for approximately 10 minutes. This procedure is done to eliminate microscopic cracks and similar imperfections. Once the ultrasound is over, the substrates are dried using compressed nitrogen gas then wiped once more with isopropanol to remove the water stains. The next step of cleaning involves an apparatus called the UltraViolet-Ozone (UVO) Cleaner. Before the samples are put in the machine, we decide which surface is going to be coated with the polymer then place the samples in the drawer with that particular surface facing up. For the next 15

minutes, the exposed surface is bombarded by UV-rays and bathed by ozone gas. This completes the cleaning procedure.

#### **b. Spincoating**

Once the substrates have been cleaned satisfactorily we commence the spinning process. In this procedure the ITO is placed on the spinning apparatus, which holds the glass down by using the generated by a vacuum pump. Next, several drops of polymeric matter are smeared over the surface. We keep hundreds of different polymeric solutions cooled in the fridge but so far most of the coating has been done using poly(9-vinylcarbazole) (PVK). Generally, the desired thickness of the polymer varies from material to material but PVK on ITO is optimum if the thickness is kept around a 1000 angstroms. The thickness is determined by coating a test glass first (it is not required to be clean). Once the coating is completed, a scratch is made on the surface then the sample is taken to the *Surface Scanner* for close inspection. This apparatus has a very sensitive needle that scans the surface very carefully along a chosen line then gives a 2-dimensional plot of thickness versus the path of needle. If the polymer is too thick on the surface, the spin rate is speeded up to make it thinner. If it is too thin, the rate is slowed down so the material has greater thickness on the ITO. Once the ideal spin rate has been determined, the cleaned ITOs are placed on the spinner, the polymer is spread on the surface then the samples are spun for 20 seconds at the determined spin rate. After spinning is complete the samples are visually inspected for

homogeneity and imperfections. If they pass the visual, we move on to the next step.

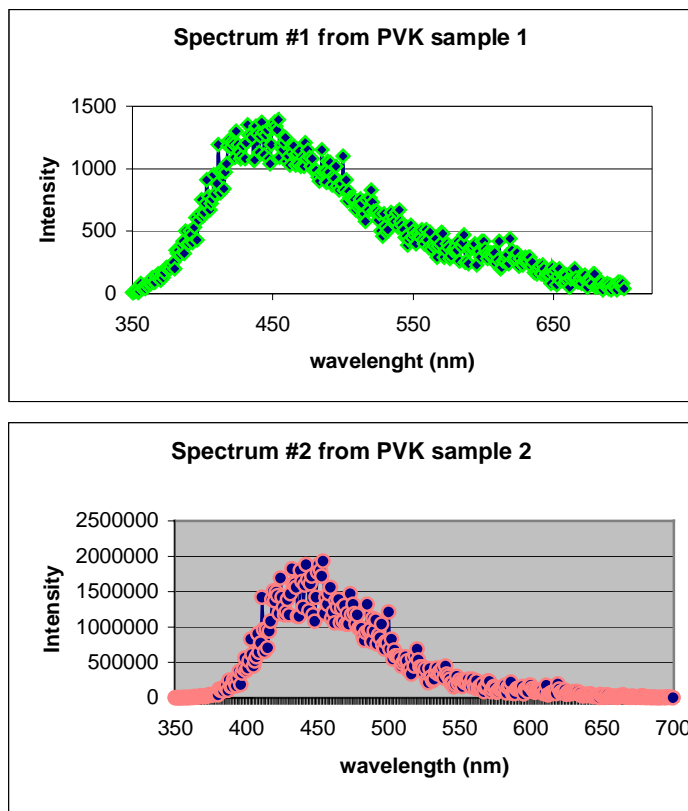
**c. Depositing**

The depositor is very much like a high vacuum environment that contains electrodes. The operational pressure is kept approximately at  $10^{-6}$  Torr. The samples are placed about 20 cm above the electrodes facing down. Special masks are used to shape the metal in anyway desired by the builder (grid, number or alphabetical patterns). The electrodes are connected via high resistance metal alloys. The material that needs to be deposited is placed on these connecting bridges. Once the voltage is increased over 20 volts the heat generated from the electrical resistance evaporates the metal. The airborne molecules scatter all over the inner surface of the dome. Some end up impacting the coated surface of the glasses and condense back to their solid state, thus forming the patterns seen in figure 5. The thickness of the metal depends on the properties of the glasses and the polymers. My research group used either aluminum or aluminum/lithium alloys with a general thickness kept a little below 1000 angstroms. The thickness is monitored by the “deposition box”, which is connected to a sensor in the chamber. Once the depositing is finished the vacuum chamber is filled with nitrogen until it is pressurized and the samples are taken for testing.



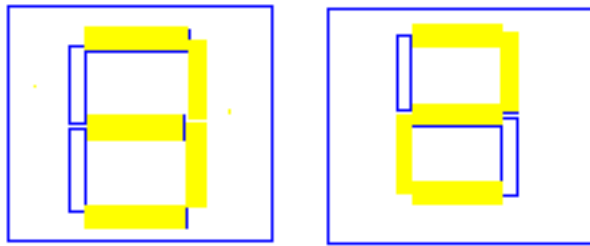
optical range is detected. On average, substances will light up between 8 to 15 volts. A small fraction might require higher or lower voltages. But one needs to be careful with incrementing the voltage too high. The electric field between the electrodes creates immense amounts of heat, which can cause the glass to crack or split to pieces. This sort of failures occur often.

If radiation has been detected within the optical range, the samples are placed in a spectrograph and the spectra of the emitted light is taken and displayed on a monitor for close inspection. There is always some noise in the system and a perfectly smooth radiation distribution is not possible. But in general, the smoother the curve is the better the LEDs perform.



**Figure 8:** Plots of intensity vs. wavelength for light from PVK. Notice the peak in the vicinity of 440 nm, which is blue light.

The devices that emit sufficient visible light and that display adequately smooth spectra find their place among the other survivors of this tedious and picky process, namely inside of a glove box where they will be preserved and protected from the harmful atmosphere. In many cases, what is done is solder one single positive lead from the battery to the glass and many negative leads to the metal electrodes, which may be arranged in numerical or alphabetical patterns. After the circuit is complete one can power up the desired wires, which would light up only certain metal electrodes. That way one can use the LED as a numerical or verbal display. (See figure below)



**Figure 9:** Polymeric numerical displays

## **Conclusion**

Light emitting diodes represent a novel class of devices that combine the electrical and optical properties of semiconductors with the mechanical properties and processability of polymers. After several years of research and development, the performance of polymer LEDs, such as device quantum efficiency, luminous efficiency and lifetime, has reached a stage of enabling some commercial products to soon become available. Like the inorganic semiconductors in the 1950s and 1960s, conjugated organics/polymeric electronic devices have potential applications in semiconductor

industry. Currently the technical challenges are device-stability studies and synthesis of new products that will be impervious to atmospheric oxidation.

This article first introduced the reader to polymers and their properties. Most important characteristic of these organic molecules is the fact that they are very large molecular chains made of hundreds of repeating units. We then explained the basics behind the physics of how doped polymers behaved like semiconductors thanks to  $\pi$ -conjugation. However, it should be remembered that this research group has done most of their major work in the field of experimentation. Therefore we felt inclined to also include the construction and testing processes so that the reader may acquire a better intuition for the distinction between the work of a theorist and an experimentalist.

### **Acknowledgments**

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