
Article

A New Plastic Light Source: Electroluminescence

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For the last six decades or so synthetic oil-derived plastics - polymers - have been inexorably displacing traditional materials - metals, glass, cellulose - in an endless variety of applications. Indeed it would be difficult to maintain a "modern" living standard without the availability of plastics for packaging, transportation, construction, consumer articles, etc. One measure of the success of this "plastics revolution" is the fact that for several years now the total worldwide production of synthetic polymers has exceeded that of all metals combined.

Many of the applications of the versatile materials are regarded as somewhat mundane, even "low-tech", though in fact there are currently thousands of extremely sophisticated usages. Some of these applications rely on very carefully designed chemical structures, for example, contact lenses, whereas others on a highly refined processing technology as are modern synthetic fibres. We are now, perhaps, on the threshold of applications for plastics where these materials will compete with, or form an adjunct to, silicon and silicon-related semiconductor compounds which are rightfully regarded as the foundation of our current electronic "hi-tech" society.

The development of polymers with important electro-optical properties is one of the most active areas of academic and industrial research in materials science today. Of course polymers have been used in the electrical and electronics industry for decades, chiefly to take advantage of their superior properties - as insulators and dielectrics. More recently, however, polymers have been synthesized whose properties mimic those of classical metals, semi-conductors and even of electro-optically active inorganic crystals.

The class of polymers which are of the most interest in this regard are members of the so-called π -conjugated macromolecule family. The prototypical member of this class is polyacetylene, which is simply a long chain of CH moieties covalently bonded by alternating single and double carbon-carbon bonds (Fig. 1). This alternation is the critical element, and because of the versatility of organic chemistry there is literally an infinite number of polymer compounds that can be envisaged (and, in many cases, synthesized fairly easily) that display π -conjugation. The structure of another well known example, poly(phenylene vinylene) is also shown in Fig. 1.

About twenty years ago it was discovered that polyacetylene, when partially oxidized or reduced, shows remarkable electrical conductivity, in some extreme cases equalling or surpassing that of copper itself. This discovery led to an avalanche of research

both in academia and industry which continues in somewhat abated fashion to the present day. It must be mentioned, however, that the earlier promise of these "synthetic metals", for example, that they could displace classic metallic conductors such as copper or aluminum, has not been fulfilled as yet. Indeed the current uses of these polymeric electrical conductors are still relatively minor. The explanation is that in materials application it is typically a spectrum of properties rather than an individual property, no matter how spectacular or scientifically interesting, that dictates how readily, or if at all, a new material can displace an existing product.

Another property of certain π -conjugated polymers was discovered about eight years ago, that of electroluminescence, which is the capability of emitting light on the imposition of an electrical field. The conversion of electrical energy into light is surely amongst the most ubiquitous and important applications of technology incandescent and fluorescent lamps, and cathode ray tubes are obvious examples and the electro-luminescence of inorganic semi-conductor materials which display this phenomenon has been an important area of research and development for three or four decades. The light emitting diode (LED) seen as a pin-point of light, usually red, and based on gallium arsenide or a similar material, is very widely used and familiar to all. Thus it is now known that some of the same polymers that have high electrical conductivity or, in fact, certain organic low molecular weight materials, can display this phenomenon. Moreover, as already noted, these polymeric chromophores (the luminescing element in LEDs) are structurally very versatile which implies a ready tunability of the colour of the light output, and they are of course film forming, which implies at least the possibility of making large area devices, a distinct advantage over their inorganic counterparts. At the present time all these advantages remain to be proven as far as commercial devices are concerned. LEDs based on

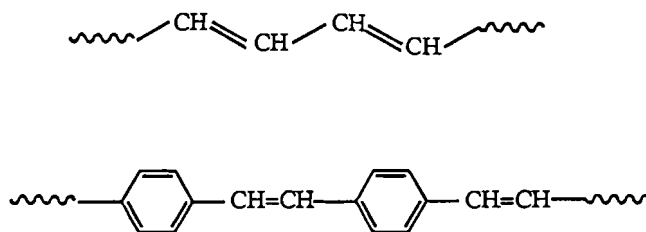


Fig. 1(Karasz) Chemical structures of representative sections of two typical π -conjugated polymers, polyacetylene and poly(phenylene vinylene).

low molecular weight organic chromophores, are apparently closer to commercialisation; it is said that the Japanese company Pioneer will market such devices later this year.

A basic polymer LED is illustrated schematically in Fig. 2. The device consists of an anode, usually a metal such as calcium or aluminum, and a cathode which for technical reasons discussed below is typically an inorganic conducting glass; the mixed oxide of indium and tin known as ITO is widely employed. Sandwiched between the anode and cathode is a very thin film of the polymer chromophore. When a voltage of the correct polarity and strength is applied to the anode and cathode, photons will be emitted from the polymer and in the example shown will emerge from the anode side, since ITO is transparent. It may be noted that for mechanical convenience the anode material is usually present as a thin film on a more robust substrate of ordinary glass. In a typical device the polymer film is of the order of 100 nanometers (one ten thousandth of a millimeter) thick; somewhat surprisingly, a film of this thickness with the required integrity (pin holes or nonuniformity, for example, must be totally avoided) can be prepared using relatively simple polymer processing techniques. At a typical operating voltage of 10v the electrical stress is quite severe; thus the film, amongst many other properties, must have outstanding dielectric strength. In practice, this means great attention must be paid to chemical purity and to the elimination of particulate matter. If a reactive metal is used for the anode it will also be necessary to seal the device in a vacuum or in an inert gas.

How does a polymer LED work? One may carry the analogy with the well-understood classical semiconductor LEDs quite far. For historical reasons the explanation is usually couched in the terminology of solid state physics and adopts the band theory of metals and semiconductors. Thus we postulate that the electrons in the π -conjugated polymers can occupy both valence and conduction bands, the latter being of higher energy. The magnitude of the energy difference, the so-called band energy gap of the polymer will ultimately dictate the colour of the emitted light. The function of the anode and cathode is then simply to inject positive charges, "holes", and negative charges, electrons, into the valence and conduction bands, respectively, of the polymer chromophore. These charges of opposite sign will migrate in opposite directions because of the presence of the electric field and in a properly designed LED, will recombine within the polymer film forming a spectroscopically excited state or "exciton". The relaxation of this exciton to the ground state releases the energy in the form of a photon. The injection process is one that requires the surmounting of or tunnelling through a potential energy barrier. This means that current will not flow, nor will light be emitted, until a critical voltage is applied - the so-called "turn-on" voltage. Above this level the light emission and current flow both increase very rapidly until, usually, the device breaks down due to dielectric failure. Electroluminescence is actually quite analogous to the well-known fluorescence effect that is found in many organic materials. In the latter case, however, energy is

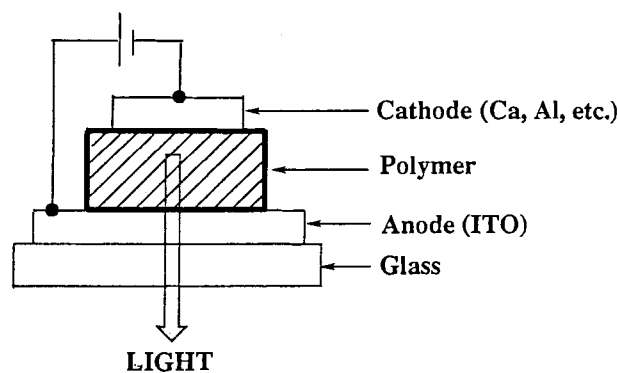


Fig. 2. (Karasz) Sketch (not to scale) of a basic polymer light emitting diode. The vacuum tight enclosure is not shown.

introduced into the material by irradiation with light, though not necessarily visible light: fluorescence is often induced in an organic material by illuminating with ultraviolet or "black" light.

In any LED a highly sought after feature is brightness of the light emitted and high efficiency measured in terms of the conversion of electrical into photonic energy. It turns out that brightness is quite easily achievable. Polymer LEDs have been reported with brightnesses orders of magnitude greater than, for example, that of the familiar cathode ray or "picture" tube used in TVs. Acceptable efficiency is harder to come by, however, and in order to improve the relatively poor efficiency of the simple single layer device described above, a substantially more sophisticated design and material selection process must be employed. For example, one must select electrode materials which optimize the injection of the respective charge carriers - electrons and holes - into the chromophore. Moreover it is important that the injection process is balanced. It is counter productive to have an excess of either charge carrier in the polymer. This requires the careful assessment of the electronic properties of the electrodes and the relation of these properties to the band energy levels of the polymer. It is customary to use additional polymeric films interspersed between the chromophore and the electrodes in a multi-layer architecture. The primary purpose of these so-called transport layers is two fold: to increase and at the same time balance the charge carrier flux into the chromophore, and also to provide the desirable feature of charge and exciton confinement. The latter is important because it is known that efficiency improvements can be achieved by preventing charge recombination anywhere other than in the chromophore itself. Moreover by using transport layers with the correct electronic properties it may be possible to reduce the operating voltage of a device. There are several other features that have been found to improve polymer LED efficiency. One is to use a carefully selected polymer blend instead of a single component as the all important chromophoric layer. Because of certain energy absorption and emission processes that can occur within such a polymer mixture, the final output of light from a blend may well be substantially brighter and the device efficiency greater than in single component devices. In some of the latest designs the chromophore blend may

even incorporate the transport layer materials discussed above. An LED based on such a multicomponent blend is obviously more readily fabricated than one in which several different polymer layers may have to be sequentially deposited.

A chromophore blend also offers a rather obvious approach to the design of a white light emitting LED. It is not too difficult to design and synthesize polymers of a selected band energy gap and hence with a selected colour emission. In principle, at least, one may blend chromophores emitting the three respective primary colours at the correct intensities so that the perceived output is pure white.

What is the commercial future of polymer LEDs? Indeed is there a future? In the context of the over-optimistic predictions for electrically conducting polymers alluded to above, one should be more than a little cautious. However, it seems reasonable to suggest that polymer

LEDs will eventually find application in display devices, in the so-called flat panel displays so widely sought after in electronics and communication. Perhaps one may even speculate that the inherent film forming properties of polymers may lead to an essentially all-plastic flexible flat panel display, which could form the basis of a sort of electronic newspaper. The same film forming capability also leads one to speculate that polymer electroluminescent devices could be developed for large area lighting in competition with conventional light sources. All this will depend on achieving a capability for the routine and inexpensive fabrication of bright, stable devices with satisfactory operating lifetimes (upwards of 1000 hours, depending on the application) and of higher efficiencies than those that are currently available. These are tall orders. However, progress in LEDs using organic materials has been very rapid from a laboratory phenomenon eight years ago to one that is on the verge of pilot plant production today.

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