Introduction

Electroluminescent (EL) polymers are organic polymers that emit light upon the incidence of an electric field. The first discovery of electroluminescence for inorganic compounds was by Destriau in 1936 [1]. In 1947, it was found that a transparent anode of a layer of Indium Tin Oxide (ITO) deposited on glass could be used to allow for light emitting devices on a planar surface. The first observation of electroluminescence in organic crystals was made in 1963 for crystals of antracene using silver paste electrodes and several hundred volts for emission to take place [2]. The characteristics of devices using such technology were considerably worse than those of inorganic devices which consequently received greater focus. Interest in the electroluminescent polymers was revitalized when major works from Tang and van Slyke [3] and Saito and Tsutsui et al. [4] were published in the late 1980s which concerned new light-emitting diodes (LEDs) with organic fluorescent dyes. Advances in semiconducting polymers aided the construction of organic LEDs with much research being focused on poly(p-phenylenevinylene) (PPV) as the active material.

Polymer LEDs in their basic form consist of the electroluminescent polymer film, a transparent anode (most often ITO coated glass substrate), a metallic cathode, and a power source which can be either AC or DC. The cathode is an electropositive low work function metal such as calcium, magnesium, or aluminum and is evaporated onto the polymer in vacuo. The EL polymer may be deposited on the anode by spin or dip-coating to a thickness of about 100nm. When an external voltage is applied at the electrodes, charge carriers called ‘holes’ at the anode, and electrons at the cathode, are injected into the polymer film past the threshold voltage for the active material. After imposition of an electric field, the charge carriers move through the active film and are discharged without radiation when they arrive at the electrode. But if a hole and an electron meet while traveling through the polymer material, singlet and triplet states are excited and excitons are formed. Radiation occurs to relax the singlet state and light passes through the transparent anode.

The purpose of this review paper is to examine recent advances in electroluminescent polymers in LEDs, specifically methods for their construction as well as their features and potential applications.

Microfabrication of diode pixel arrays

The fabrication of microscopic LEDs to create pixel arrays of organic LEDs is an important concept in the development of flat panel electroluminescent displays. Using photoablation, a micron sized pixilated array or polymer was created [5]. The polymer used in the microfabrication was a conjugated copolymer of benzene and pyridine units – copoly-(1,4-phenylenevinylene-2,6 pyridylenevinylene) or co(PV-PyV). An increased DC voltage led to a shift from the green-yellow region to the red for the main emission band, demonstrating that the emission properties could be adjusted and that superimposing AC voltage on small biased DC
Voltage enhances EL emission by multiple magnitudes, yielding an EL spectrum similar to that of PPV.

The setup of the array utilized an electron microscope bar grid on a layer of ITO coated on a glass substrate. An excimer laser between the thresholds of the ITO ablation and glass substrate was used to replicate the dimensions of the grid onto the ITO anode. Layers of the polymer were baked and spin coated on the ITO and laser ablation was performed for the cathode layer and partly for the polymer layer over the bar grid. Light intensity had significant improvements over past investigations of thin film LEDs with the same electrodes under the same conditions. The electroluminescence from the pixel array was improved likely because of enhanced electric fields at the pixels. Using voltage tuning to adjust emission properties, multicolor displays of high resolution are a definite possibility.

3. Patterned light emission

Several methods for creating patterned light emission have been investigated. One such technique is microcontact printing. In a recent method [6], a patterned elastomer (PDMS) was first molded with a relief structure. The self-assembling monolayer (SAM) was formed by conformal contact between the inked PDMS stamp and the ITO. The PPV was selectively deposited on hydrophilic regions of the SAM. A clear topographical contrast-pattern was observed in this process of relative simplicity and low cost.

Rogers et al. [7] developed a system for microfabrication of patterned polymer LEDs through solvent assisted micromolding. An elastomeric mold was formed from casting and curing a prepolymer against a relief structure. This was used to generate a PPV precursor film with the surface relief of the mold. The process demonstrated a way to use patterned layers to spatially modify the intensity of the emitted light. It was achieved using the most basic materials for single layer polymer LEDs, but can be applied for electron-transporting, hole-transporting, or insulating layers.

4. Multi-color organic EL devices

Fabrication of patterned light-emitting layers is important for the creation of multi-color devices. Following are specific techniques in constructing multi-color devices. In an effort to create a red, green, and blue (RGB) polymer OLED, soluble polymers with oxetane sidegroups crosslinked photochemically to form insoluble polymer networks with photore sist properties were used [8]. A recent procedure [9] was used to synthesize the RGB light emitting oxetane-functionalized spirobifluorene-co-
6. Polarized electroluminescence

The state of polarization of emitted light may be controlled by using liquid crystalline polymers [13]. Besides the anisotropic characteristic, liquid crystalline polymers in LEDs also yielded spontaneously homogenous monodomain films. Linear or elliptical polarized emission was obtained due to the inherent structure of the liquid crystalline polymer and its optical properties, which may be used to control the polarization. Further research should lead to higher macroscopical orientations. An issue concerning elliptical polarized emission is that a high degree of ellipticity requires larger than ideal film thicknesses.

7. Surface light emitting devices

An interesting alternative to the conventional setup of an EL polymer between a transparent anode and a cathode is the surface light emitting device (SLED) where both the anode and cathode are underneath the polymer, rendering transparency of the anode unnecessary. A recent study used EO-PT, a conjugated polymer based on polythiophene with oligo(ethyleneoxide) side chains as the EL polymer [14]. The two methods of constructing the SLED are vertical (V-SLED) and lateral (L-SLED) and are shown in Fig. (1) [14].

![Image of V-SLED, L-SLED, and sandwich electrode configuration with electrode separations and arrows for the direction of light emitted](image)

The closer the electrode spacing, the greater the current transmitted and hence more light was emitted. SLEDs constructed with ITO and aluminum had lower turn-on voltages and greater currents than those with gold-silicide and aluminum electrodes as well as better stability. The addition of salt to the polymer resulted in an increase in the current and brightness, a decrease in turn-on voltage, and the current-voltage characteristics to be symmetric.

Microfabrication of surface light-emitting diodes on silicon substrates [15] was totally compatible with conventional silicon processing. This was because the polymer was spin coated last and the light was emitted from the top of the diode. The voltages needed for light emission were still not much greater than those of the standard sandwich LEDs.

8. Conclusions

The potential for the numerous recent developments in electroluminescent polymers in LEDs is quite promising. With continued attention, the techniques described here could lead to a number of fruitful uses. As techniques for organic LEDs progress, greater control over characteristics such as polarization, emission intensity, and resolution will emerge, as well as various applications – namely inexpensive large-area multicolor displays.

References