**ADVANCED MATERIALS**

Progress with Light-Emitting Polymers

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Light-emitting polymers have been studied intensively as materials for light-emitting diodes (LEDs). Here research efforts toward developing these materials for commercial applications are reviewed. The Figure shows the preferred two-layer device structure for commercial polymer LEDs as well as polyfluorene, one of the polymers discussed.
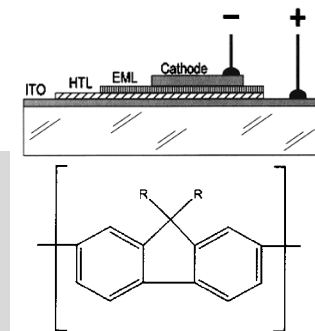
1. Introduction

Polymeric electroluminescence (EL) is a phenomenon based on amorphous, disordered organic semiconducting materials that has stimulated technological activity across a wide interdisciplinary reach within academic, industrial, and governmental sectors. Efforts aimed at developing associated technology have created a rare opportunity to develop high-value products and have contributed fundamental scientific insight in this area, which is poised for commercial success. Recent materials advances have endowed the concept of "plastic light" with the optical, electrical, and mechanical characteristics that truly make it disruptive technology within the display and lighting industries in that it is compatible with conventional device replacement and it offers new opportunities for exploitation. We review the materials science and engineering of this field within the framework of anticipated impact on product definition, as well as highlight contributions to the field originating from within The Dow Chemical Company.

2. Background

We confine our description of light-emitting polymers (LEPs) to the unique class of aromatic organic molecules that exhibit semiconducting behavior and give off light when electrically stimulated. They are, consequently, electroluminescent as well as photoluminescent when stimulated by long-wave ultraviolet (UV) irradiation. Electroactive devices based on LEPs typically operate at or below 5 V direct

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current (DC), have demonstrated high efficiencies in excess of 20 lm/W, and are approaching average operating lifetimes of 10 000 h at 200 cd/m^2 intensity. As polymers, these materials exhibit mechanical, electrical, and luminescent properties that hold great potential for display application. The mechanical properties of polymers enable them to be cast in a variety of shapes and sizes, and their simplified processing offers fewer steps to manufacture, thereby providing economic advantages over many other more elaborate device fabrication techniques. Given the recent and rapid development of materials and devices designed for efficient manufacture, many corporations see this technology as holding promise for the next generation of flat-panel displays.

Light is produced in the polymer by the fast decay of excited molecular states, the color of which depends on the energy difference between those excited states and the molecular ground level. A light-emitting device comprises a thin-film structure of one or two layers typically no more than 0.1 μm thick, sandwiched between two electrodes. Optimal device efficiency is achieved if the two electrodes are dissimilar, specifically where the respective electrode materials possess Fermi levels or electronic work functions that closely match the valence (ground) and conduction (or excited state) energy levels in the polymer. It is also necessary that one of the electrodes is transparent to the wavelength of light generated. This can be achieved with very thin metal films or more preferably the oxide of indium–tin, which retains good electrical conductivity but which is transparent in layers below 0.2 μm thick. Completely packaged units have a low product profile, with device thickness between 2 and 4 mm commonly achieved, depending on the complexity of the display. Such devices are also called polymeric light-emitting diodes (PLEDs), as they demonstrate nonlinear rectification with a minimum turn-on voltage that is analogous to the forward voltage drop of a diode. We shall use this nomenclature to describe light-emitting devices based on long-chain, high-molecular-weight polymeric solids to differentiate them from

devices based on smaller, low-molecular-weight organic films, which are often called organic LEDs or OLEDs.

LEPs have progressed considerably over the past 10 years. At their present stage, PLEDs are broadly comparable in brightness and efficiency to inorganic LEDs based on Group III–V elements. PLEDs are also advancing rapidly in their applicability for functional lighting in architectural applications as well as general signage. The NASDAQ Supersign, installed in 1999 in New York City's Times Square district, has approximately 19 million red, green, and blue inorganic LEDs as the operating emissive medium. For such display applications, many individual LEDs must be individually picked, mounted, and wired in a dot–matrix array. A modern alphanumeric display alone requires 35 LEDs each and is limited in resolution to the individual LED. The economics of display application with finer pitch resolution for personal viewing are formidable indeed, with application markets targeted toward military use.

PLEDs offer a low-cost, two-layer, thin-film approach with reduced manufacturing process complexity. Current limitations in PLED development towards laptop and desktop displays are lifetime-related, but at the present stage of development there is no foreseeable upper limit to device lifetimes that can be achieved. LEPs continue to be developed with increasing performance and associated light-generating efficacy. As a result, PLEDs are enjoying much commercial interest with product targets in portable electronics, display manufacture, digital cameras and camcorders, lighting, consumer goods, automotive systems, and communication systems.

Theoretical models that describe the complete and detailed physics of operation do not yet exist. Unlike crystalline inorganic semiconductor material, organic semiconductors are not perfectly suited to the electronic energy band theory. More recent work on amorphous semiconductors would be closer to analogous applicability. The area of organic luminescent semiconductors offers a unique opportunity to explore nature at the interface between chemistry and physics, and such cross-disciplinary areas as solid-state chemistry and soft-condensed matter are forming from these and related intellectual opportunities. With the advent of commercial interest in the past decade, the recent availability of materials, and the fairly inexpensive equipment required to create demonstrable devices, there is an explosion of activity in academia in the general area of organic electroluminescence. Chemical Abstracts lists over 5000 titles in the area during the 1990s alone, with most of them occurring in the last years of the decade.

The market potential for PLED displays alone is high, with corroborating studies offering expected global forecasts approaching a billion US dollars annually by 2005. Additional revenue is expected in the areas of indicators, backlights, and general lighting. The liquid crystal display (LCD) market has the greatest potential for penetration, beginning at the low end of complexity. This includes cell phone displays and personal digital assistant consumer devices. Laptop and desktop computer displays will most likely not be targeted until the PLED technology matures. Pioneer Electronic Corporation in Japan has developed a 256×64 pixel display based on the Kodak small-molecule technology, which has been available on a
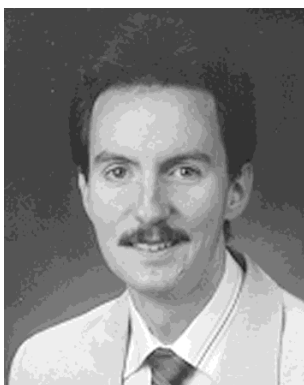
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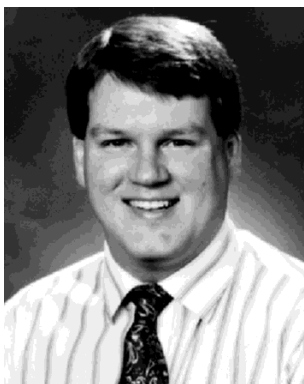
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limited basis for car radio consoles since late 1997. Philips Electronics has a PLED pilot production facility in Heerlen, The Netherlands, and is preparing to launch a product shortly. Virtually every large original equipment manufacturer that sustains a corporate R&D effort and whose product line involves a display of some kind is engaged in this new area of organic emissive technology.

This article addresses the developments in the area of light-emitting polymers as it impacts PLED performance offered from the commercial reference frame. Adequate justice to all contributions in the field cannot be hoped for, much less attained, given the surplus of references to published contributions in the field. An objective way to adequately credit work is to cite the patent literature, of which we make use. We will also highlight present activity in LEPs within Dow. We will seek to touch upon areas fairly well developed, and indicate others requiring a more detailed look. We will also address peripheral areas of engineering that impact PLED product development, and conclude with attempting to forecast future developments.

3. Historical Development

In the 1950s, Bernanose, who applied a high-voltage alternating current (AC) field to crystalline thin films of acridine orange and quinacrine,[1–4] first observed EL in organic material. In 1960 two researchers at The Dow Chemical Company also prepared AC-driven electroluminescent cells using doped anthracene, a π-conjugated, three-ring, fused aromatic system. This work resulted in the first patent on EL devices based on polynuclear aromatic organic compounds.[5] Later in the decade, Pope prepared a DC EL cell using single crystals of anthracene, which was observed to fluoresce in the blue by applying 400 V across the specimen.[6] In these early days, preparation techniques were used that now appear primitive, and latent material impurities were responsible for creating conditions requiring several hundred volts to stimulate light emission. The requirement for high operating voltages was a key factor prohibiting commercial interest.

In the late 1960s and early 1970s, advances were made in organic EL device structure, two of which we cite here. In 1969 the first use of a reactive cathode in organic EL devices was demonstrated.[7] This cathode structure was fabricated to permit the facile injection of electrons into the EL material, which was observed to increase device efficiency. In 1975 the first organic EL devices made with polymer, polyvinyl carbazole (PVK) doped with perylene, tetraphenylbutadiene, or acridine orange for increased luminescence, were tested using an alkali cathode whose work function more closely matched the electron affinity of the EL layer.[8] The work on cathode structure by Digby, Schadt, and Partridge enabled OLEDs to operate at lower voltages, which was a significant improvement in the general design structure. This and related early work in the field is reviewed in a 1982 publication by Vincett and co-workers.[9]

The development of organic luminescence progressed to the point of practical importance through the effort of Tang in the Kodak Research Laboratories, culminating in the 1987 demonstration of a two-layer structure of vacuum-deposited, small-molecule films.[10–12] Tang and co-workers employed a transparent hole-injecting electrode of indium tin oxide (ITO) on glass to improve the extraction of light. They sandwiched a p-type, hole-transporting molecular film of aromatic diamine and an emitting layer of the n-type, electron-transporting metal chelate tris-hydroxyquinoline aluminum (Alq_3) between the ITO anode and a low work-function alloy of magnesium as the electron-injecting cathode. Both the diamine and Alq_3 possess conjugated carbon bonds and were prepared using train sublimation techniques available to purify small-molecule compounds. The use of magnesium as the cathode was important for the same reason given for the reactive cathode mentioned earlier, namely to more closely match the π^* energy band of the luminescent semiconducting material to achieve electron injection with lower applied electric fields. The use of this two-layer structure, purified materials, and properly chosen electrodes permitted OLEDs to operate at voltages below 10 V for the first time. To date, OLEDs based on vacuum-sublimated small molecules follow this Kodak teaching.

Shortly afterwards, in 1990 the Cambridge group of Friend announced that they had achieved green–yellow EL using the conjugated polymer poly(p-phenylene vinylene) (PPV) in a single-layer device structure.[13] PPV, with its aromatic phenyl ring and conjugated vinylene linkage, was first synthesized by Wessling at Dow in 1968,[14–16] and has a π–π^* electronic energy gap of about 2.5 eV. PPV is insoluble in common solvents, and as such requires special processing steps to produce a conjugated thin film necessary for EL device application. A precursor polymer that is soluble is first prepared, then a film is applied from solution by spin casting, which is then thermally converted to the conjugated form. Cambridge Display Technology (CDT) was founded in 1992 to exploit a key patent of Cambridge University in light emission from conjugated polymers.[17] CDT has been active ever since in materials and technology issues to promote the commercial development of PLEDs. As a result of this activity, chemical companies began to further explore the PPV polymer, including a synthetic chemistry group in Hoechst. This group later formed part of a spin-off company, which was to evolve into Covion Organic Semiconductors in 1999, and whose materials portfolio remains largely PPV-based.

In 1991 Heeger and co-workers at the University of California at Santa Barbara announced the EL application of a soluble derivative of PPV, namely poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] or MEH-PPV.[18] MEH-PPV has a π–π^* electronic energy gap of about 2.2 eV, which is red-shifted from that of PPV. Owing to its dialkoxy side chain, MEH-PPV offered the advantage of being soluble in conjugated form in organic solvents. However, due to its susceptibility to photo-oxidation, this material has since fallen out of favor as a candidate for commercial use.[19,20] The Santa Bar-

bara group also employed calcium as the reactive cathode metal for improved device efficiency. UNIAX, a commercial venture spun out of the University of California at Santa Barbara and recently acquired by DuPont, was established to develop optimal process manufacturing guidelines for the commercialization of PLED-based devices.

In the last decade, other conjugated polymers have been used for EL application, including polythiophenes[21–23] and polyphenylenes.[24] Yoshino and co-workers prepared the wide-bandgap polymer polyfluorene[25] using the ferric chloride oxidative route, which was applied in a blue electroluminescent cell by Fukuda et al. in 1991.[26] Molecular weights of this polymer were low, with some degree of branched polynuclear structures present and hence poor regiospecificity given the synthetic method employed.

In the early 1990s, researchers at Dow developed a family of 9,9-dialkylfluorene homo- and copolymers that exhibit purity levels unattainable over a decade ago. At that time, it was believed that ultra-high material purity desired for optimal EL device efficiency could only be achieved with vacuum-sublimated small molecules, because distillation-like techniques such as train sublimation could be utilized ad infinitum until the degree of material purity desired was achieved. In general, polymers are difficult to purify to the level of a few parts per million of metals and heavy atoms (present as end groups). Work at Dow resulted in the development of a modified Suzuki polymerization process,[27] which provides a wide range of high-molecular-weight (50 000 to 600 000 Da), low-polydispersity (<2), fluorene-based homopolymers and copolymers in high yields and purity. Poly(9,9-dioctylfluorene) or PFO, for example, has a π–π* energy gap of 3.68 eV[28] and is an efficient blue emitter with a primary emission peak at 436 nm.[29] This improved Suzuki coupling process has permitted the preparation of a portfolio of fluorene-containing copolymers that emit colors spanning the entire visible range.[30]

4. Device Structure

At present, the two-layer structure represents the preferred embodiment for the commercial PLED device, and it is illustrated in Figure 1. The hole-transporting layer (HTL) material film is laminated over the transparent ITO anode structure, over which is applied the emitting layer (EML) film. A cathode possessing a low work function is deposited to provide electron injection into the π* band of the EML. Afterwards, the whole device may receive an encapsulation of some kind to improve its durability.

All PLED devices rely on the transparent charge-conducting film of ITO as the transparent anodic material to facilitate hole injection while permitting light to exit the device in an effective manner.[31–33] ITO possesses a Fermi energy level taken to be approximately 4.5 to 5.0 eV relative to the vacuum state.[34,35] The material is non-stoichiometric, and as such the electronic properties are strongly dependent on the preparation and cleaning methods employed. The extent of oxygen
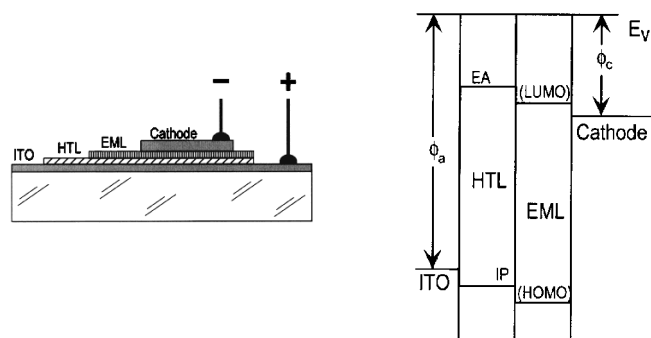

Fig. 1. Schematic illustration on the left depicting the general structure of a two-layer PLED device. On the right is depicted a simplistic electronic energy band diagram for the structure. Shown are the ITO anode, HTL, EML, and cathode structures. The energy band diagram illustrates the equivalence of the valence band with the ionization potential (IP) and HOMO, as well as the equivalence of the conduction band with the electron affinity (EA) and LUMO. The work function, ϕ, is also shown with reference to the vacuum potential, E_v.

enrichment of the surface can modify the conductivity of the material as well as increase its electronic work function by as much as 0.5 eV.[36] In addition, the ITO surface microstructure varies greatly with preparation method, which can have an impact on device performance. For flexible substrates made of plastics, the deposition process has to be modified to accommodate the glass-transition temperature of the plastic. Proper preparation of the ITO substrate is critical to the construction of a good PLED device, and any residual film or deposits from substrate handling or cleaning will result in imperfections within the emissive area on the device. Much of the early published work in PLEDs devoted discussion to the origin of black spots in the emissive area. We have correlated seven different causes for the black-spot defect, four of which can be controlled with proper substrate cleaning and handling.

PLED device architecture comes in two varieties: single-layer and multiple-layer structures. Single-layer devices rely on the emitting material to carry out the efficient injection and transport of both electrons (the minority charge carrier) and holes (the majority charge carrier) as well as facilitate the radiative decay of a narrow distribution of excited molecular states to ground. There are published accounts of single-layer PLED devices being operated using both PPV and its derivatives as the active medium. Unique difficulties arise for devices based on a single organic layer, however. It is difficult to balance the injection and transport of the two charge carriers in a single-material matrix over a reasonable voltage range. Any imbalance results in a relative increase in drive voltage and the subsequent loss of luminance efficiency from ideal conditions. Also, oxygen as well as metal ions are leached out of the ITO matrix into the EML under long-term action of the applied electric field, which can be as high as 10^7 V/cm. This leads to oxygen poisoning of the organic layer[37] and generates metallic quenching sites for EL. We have experimented with single-layer devices using a variety of materials, and our analytical research has revealed mass loss from the ITO layer specifically in the active pixel region of devices that were run in lifetime tests, with further elemental depletion of

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indium in the remaining ITO. This material has presumably migrated into the active material of the polymer. It is therefore desirable to buffer the active layer from metal ion contamination and oxidation from the ITO anode.

The motivation behind developing a multilayer PLED system is to separate the active layer from the ITO and accommodate charge-transport specialization for both carriers using different molecular structures. Three layers or more can accomplish the functional separation of an ion-buffering layer over the anode from the hole- and electron-transporting media as well as provide an emitting layer. However, the cost associated with manufacturing increases commensurately with the number of layers. With device design for manufacturability as a guide, a two-layer design becomes the minimum number of layers that provides anode-ion buffering and charge-carrier transport differentiation. The first polymeric film over the anode becomes both the HTL and the ion-buffering layer, and the second film becomes both the electron-transporting layer and the EML. The OLED field has moved to adopt a two-layer PLED structure as the preferred embodiment. This two-layer device is an analog to the p–n junction LED, although in this case we are limiting ourselves to considerations employing only undoped intrinsic semiconductor systems.

Organic polymeric materials tend to possess low electron affinities, and for that reason the majority of conjugated semiconductors exhibit hole-transporting properties.[38,39] Their properties are intrinsic to the native molecular structure and need not be caused by external additives or dopants. For this reason they are also referred to as undoped electroactive polymers. The electron affinity of a semiconducting polymer corresponds to the lower profile of the conduction band or π^* state density and therefore to the lowest unoccupied molecular orbital (LUMO). Likewise, the upper profile of the valence band or π state density (and therefore the highest occupied molecular orbital, or HOMO) corresponds to the ionization potential of the material. The ionization potential of most organic material can be modified by choice of structure, and for the common conjugated polymers lies in the 5–6 eV range. As this corresponds to the relative magnitude of the work function of ITO, the ITO–organic semiconductor contact is, in some cases, close to ohmic. As amorphous organic films are disordered, the notion of a band edge seems oversimplified, especially when these materials can easily possess impurities left over from the synthesis process, which gives rise to inner gap states. In reality, the density of states possesses some distribution about the mean quoted value.

There are several polymers that have been preferred as hole-transporting materials. PVK is one that has been studied extensively. In some cases, PPV has been used as a HTL, including structures employing an evaporated low-molecular-weight emitter. An alternative to using an intrinsic HTL is to use a conducting polymer to transport holes to the EML. The internal electric field in a conducting polymer is much lower than in a semiconducting polymer, and as such will slow the migration of unwanted ions from the ITO through the HTL over much longer operating time frames. Two popular con-

ducting polymers are polyaniline (PANI)[40] and poly-(3,4-ethylene dioxythiophene) (PEDOT).[41] PEDOT has a π–π^* electronic bandgap of 1.6–1.7 eV and possesses a conductivity between 1 to 10 S cm^{-1}. Recently, a commercial grade of PEDOT has become available from Bayer.

Different cathode metals have been employed in device architecture with varying degrees of success. The most obvious change to the choice of electron-injecting media is to vary the electronic work function and observe device performance. Michaelson has summarized metallic electronic work functions,[42,43] from which we tabulate those relevant metal properties that could be encountered in various PLED design configurations in the accompanying Table 1.

Table 1. Electronic properties of typical electrode metals (from [43]).

Element	Ionization potential [eV]	Preferred work function [eV]
Cs	3.89	2.14
K	4.34	2.30
Ba	5.21	2.70
Na	5.14	2.75
Ca	6.11	2.87
Li	5.39	2.90
Mg	7.65	3.66
In	5.79	4.12
Ag	7.58	4.26
Al	5.99	4.28
Nb	6.88	4.30
Cr	6.77	4.50
Cu	7.73	4.65
Si	8.15	4.85
Au	9.23	5.10

For most electroluminescent polymers, calcium is observed to provide an effective polymer–metal junction from which to effectively inject electrons into the organic matrix. Varying the choice of metal toward increasing the work function has the direct effect of increasing drive voltage and reducing device efficiency. This observation substantiates the tunneling model for cathodic charge injection through the Schottky barrier, whose width increases with increasing difference between the cathode work function and the electron affinity of the polymer.[44–46] For the most part, varying the cathode metal to lower work functions than Ca appears to have little to no effect, indicating that an ohmic contact has been established at the cathode. We have been able to modify the injecting efficiency for polymers so that cathodes up to magnesium can provide an ohmic contact to select materials, but we have not yet been able to go beyond this. For now, calcium remains the cathode of choice for laboratory-scale devices, with alternative schemes under development for manufacturing scale-up and product design.

Operated in forward bias, the electronic energy diagram for a bilayer PLED device appears as depicted in Figure 2. We believe that there is no band bending at the junction between polymeric semiconductors.[47] The HOMO and LUMO levels are shown as a distribution about the mean value. The initial barrier between the work function of either the anode or cath-
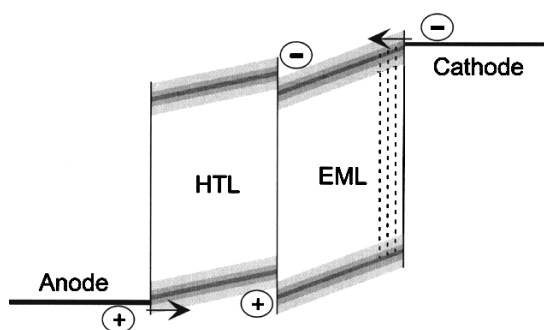
Fig. 2. Energy level diagram of a two-layer PLED device under forward bias. This illustration assumes a conducting HTL and illustrates charge tunneling through the electrode–organic interface barrier (Shottky barrier). Also shown is the "dead zone" associated with excitonic quenching in the proximity of the cathode.

ode and the respective density of states in the adjacent transport layer is overcome by tunneling injection into the transport level, whereupon charge transport is carried out by hopping along π orbitals under action of the applied field. Charge combination occurs in the emitting material in a zone extending between the HTL and EML junction and extending to within 20 to 30 nm of the cathode interface.[48] It is assumed that the extent of the combination zone is linked to the mobility of the minority carrier and the efficient balance of space charge limited current of both charge carriers in the device.

EL occurs when singlet excitons, formed by the coulombic combination of electron and hole pairs with opposite spin states, radiatively decay to the molecular ground state. This represents the same excited state that is formed when long-wave UV radiation is absorbed by the material in the photoluminescence (PL) process. The similarity (and differences) between the EL and PL spectra indicate the extent of similarity in accessing the associated electronic states of the molecular species (for examples, see the literature[49–51]). For more details of the physics of the polymeric EL phenomenon, the reader is advised to consult Bässler,[52–54] Friend,[55,56] and Heeger.[57]

5. Polymeric Luminescent Material Development

The design of luminescent materials for use in LED devices is as critical to device performance as the process of constructing the device itself. Processability, purity, thermal and oxidative stability, color of emission, luminance efficiency, balance of charge carrier mobility, and others are among many important materials properties required for a system to be viable in commercial LED device applications. Great strides have been made toward the development of new polymeric materials for luminescent applications.

Although electroluminescent materials have been known for decades, and some were available for purchase in the early 1960s, they were limited until recently to inorganic semiconductors and small-molecule organic dyes. To be used in diode display devices, these materials require deposition as very thin films by vapor deposition or sublimation processes. Such processes are expensive, equipment intensive, and do not adapt well for coating large-area substrates.

To overcome the device processing drawbacks of these emitting systems, a great deal of research has been focussed on the development of luminescent polymeric equivalents that offer the ability to coat substrates efficiently by any of a variety of common solution processes. A series of fluorescent polymers with extended conjugated backbones has emerged from this work. The year 1990 marked the discovery of the first electroluminescent polymer, PPV.[13] Since that time a variety of PPV derivatives with improved performance and processability have been developed. Other conjugated polymer systems such as polyfluorenes, polyphenylenes, poly(phenylene ethynylenes), and polyalkylthiophenes are also interesting emissive materials investigated over the past decade. Additional approaches to solution-processable polymeric emitting materials that have been explored include blending of inorganic semiconductors or organic dyes with polymers (inert and/or electroactive) as well as synthesizing polymers that bear discrete chromophores bound either pendant from or within the polymer backbone.

Out of the host of materials investigated, two classes of polymers have emerged as leading candidates for PLED applications, the PPVs and the polyfluorenes. Through fine tuning of their chemical structures via polymerization variations, both of these polymer families have achieved ease of processability, high purity, and tunability of emission color. Many high-efficiency, high-brightness, and long-lived devices have been constructed from these materials.

An excellent review of the state-of-the-art in electroluminescent conjugated polymer development was published by Holmes and co-workers in 1998.[58] The reader is referred to this review for an extensive overview of the classes of polymeric materials that exist, and as a reference to many other previous reviews. A summary of the synthetic processes that yield the emissive polymers, materials properties reported, as well as device structures and performances derived from them are well covered, especially for the PPV family. Polyphenylenes, poly(phenylene ethynylenes), polyalkylthiophenes, and other polymer systems containing isolated chromophores either in the polymer chain or pendant to it are also briefly described. Polyfluorene homopolymers are lightly mentioned primarily due to the early stage of their development in 1998. In the past few years, much progress has been made within this class of material.

The major groups of polymeric materials developed in the past decade will be summarized here. The discussion is by no means exhaustive (given the recent explosion of research in the field) and is limited to the groups of materials that have shown the greatest overall potential to date to be adopted as emissive materials in PLED applications: the poly(phenylene vinylene)s, the poly(fluorene)s, and the poly(phenylene)s, as illustrated in Figure 3. Polyfluorene homo- and co-polymers are intentionally highlighted since they have not been well reviewed in the past, much progress has been made very recently, and this class of material has quickly emerged as an extremely viable LED polymeric material of great commercial interest.
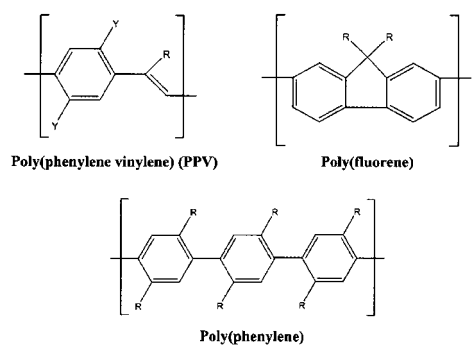
Fig. 3. Sample molecular structure classification described in text: PPV, poly-(fluorene) homopolymer, and copolymer, and poly(phenylene).

5.1. Polyfluorene-Based Luminescent Polymers

The first fluorene-based polymers, via ferric chloride oxidative polymerization of 9-alkyl- and 9,9-dialkylfluorenes, reported by Fukuda et al., appear to be relatively low in molecular weight, with some degree of branching and non-conjugated linkages through positions other than 2 and 7.[59,60] To improve regiospecificity and minimize branching, Dow researchers have accessed these homopolymers through transition-metal-catalyzed reactions of monomeric 2,7-dihalogenated fluorenes. The palladium-catalyzed synthesis of mixed biphenyls from phenylboronic acid and aryl bromide discovered by Suzuki and co-workers[61] is tolerant of a large variety of functional groups, is insensitive to the presence of water, is truly catalytic in metallic reagents, and can be used to prepare perfectly alternating copolymers.

Efforts at Dow have provided a large number of high-molecular-weight, very pure fluorene-based polymers. 9,9-Disubstituted 2,7-bis-1,3,2-dioxaborolanylfluorene is allowed to react with a variety of dibromoarenes in toluene in the presence of 2 M sodium carbonate, a phase-transfer catalyst, and a catalytic amount of (triphenylphosphine)palladium. The improved process yields high-molecular-weight polymers with low polydispersity (<2) in less than 24 h reaction time whereas the conventional Suzuki coupling process can take up to 72 h or more to provide polymers of modest molecular weights. Through the use of this very versatile synthetic process, polymers of ever-improving LED performance continue to evolve. An optimized green LED based on improved Suzuki polyfluorene chemistry, for example, has exhibited light emission exceeding $10\,000$ cd/m^2 at less than 6 V with peak efficiency of 22 lm/W.[56]

5.2. Polyfluorene Homopolymers

Polyfluorenes with C_6 or higher substituents at C-9 are soluble in conventional organic solvents such as aromatic hydrocarbons, tetrahydrofuran, and chlorinated hydrocarbons. Most high-molecular-weight polymers do not show very distinct glass transition, and those with straight alkyl substituents tend to be semicrystalline and exhibit liquid crystallinity. F8, for instance, has a very stable liquid crystalline state that persists up to 270 °C.[62] Polymers with branched alkyl substituents, e.g., 2-ethylhexyl, are amorphous. All are strong blue emitters when excited with UV either in solution or in the solid state. The absorption spectra are broad and featureless while the PL spectra show well-defined vibronic structures.[63] The Stoke's shift is typically less than 50 meV, indicative of an extended conformation.

5.3. Polyfluorene Alternating Copolymers

Tertiary aromatic amines have been known as excellent hole-transport materials and have found utility in photoconductors and in LEDs. With the Pd-catalyzed polymerization process, it is possible to prepare high-molecular-weight, alternating copolymers consisting of 9,9-dialkylfluorene and various aromatic amines. These alternating polymers are all blue emitters, excellent film formers, and soluble in conventional organic solvents. Films of these polymers show distinct and reversible oxidation potentials by cyclic voltammetry and can be cycled without any appreciable change. Hole mobilities of these amine copolymers are quite high (3×10^{-4} to 1×10^{-3} cm^2/V s)[64–66] equaling hole mobility values for small molecules such as tetraphenyl diamine (TPD) doped into polycarbonates. The high hole mobility of these materials suggests that they are potentially useful as photoconductors as well as hole transporters in LED devices.

In light of the success in creating polymers with unique properties, the alternating copolymer approach has been extended to other conjugated monomers, as Figure 4 exemplifies (e.g., thiophene, bithiophene, triarylamine, etc.). All copolymers are of high molecular weight, they are highly photoluminescent, and their emissive colors can be qualitatively correlated to the extent of delocalization in the comonomers. For example, the thiophene copolymer emits bluish green light, the cyanostilbene copolymer emits green light, and the bithiophene copolymer emits yellow light. Thus, the choice of comonomer in the fluorene-based polymer family has served as an excellent synthetic tool for designing polymers with well-balanced hole- and electron-transport properties and fine color control. A portfolio of fluorene copolymers that emit colors spanning the entire visible range has been prepared using the improved Suzuki route.[63] Rich red-, green-, and blue-emitting polymers are of highest interest. No other polymer class offers the full range of color with high efficiency, low operating voltage, and high lifetime when applied in a device configuration. Thus the polyfluorene-based molecules are the most viable LEPs for commercialization; and since making these materials available, we have received positive feedback from a variety of customers who have validated this concept to us.
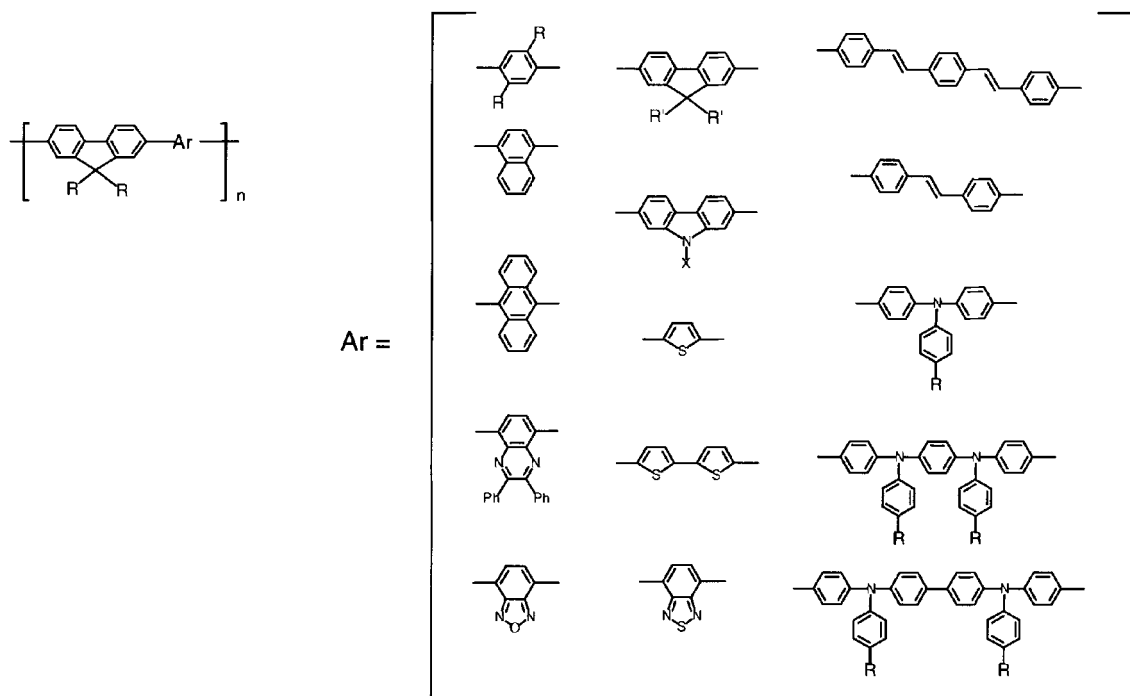
Fig. 4. Examples of monomers, Ar, used with polyfluorene in some of the copolymers developed at The Dow Chemical Company.

5.4. Poly(*p*-phenylene vinylene) and Derivatives

Since the discovery about a decade ago of the ability of PPV to emit light (yellow-green) under electrical stimulation, numerous research groups have continued to work towards optimization of this promising class of material. Improvements have developed primarily in ease of synthesis and processability, control of charge carrier balance, overall device power efficiency and lifetime, and to some extent emission wavelength tunability. A variety of solvent-processable precursor polymers (converted thermally to PPV following the coating process), solution-processable versions of PPV, and PPV copolymers (to facilitate electron injection and modulate color) have resulted from these efforts.

The first convenient synthetic route to PPVs was first described by Wessling et al. in 1968 via bis-sulfonium salt monomers.[14,15] Since these original accounts, many variations on the theme have evolved. Routes have primarily afforded the ability to reproducibly generate high-molecular-weight, high-purity polymers, vary functional groups bound to the parent backbone (particularly solubilizing groups and groups to enhance electron affinity), and produce PPVs with improved efficiency in LED devices. The chemistry has remained somewhat restricted in enabling development of rich, saturated red and blue emitters, and the chemical structure of the PPV backbone is inherently photo-oxidatively unstable due to the vinylene linkages. While these issues are likely to continue to challenge the introduction of PPVs into commercial display devices (particularly multi- and full-color applications) in the future, significant progress has been made

toward the optimization and tuning of these materials, making them very good candidates for PLED applications.

5.5. Poly(*p*-phenylene vinylene) from Soluble Precursors

PPV is the parent structure of the poly(arylene vinylene) series. Because of its linear rigid-rod-like structure, tendency to form crystalline morphologies, and lack of functional groups to enhance solubility, this system is intractable and not processable directly from solution, a feature shared by many PPVs.

Since solvent processability is a desirable attribute for polymeric emitting systems, soluble precursor systems to the PPVs that can be cast as films and subsequently converted to PPV by heating have been developed (vacuum or inert gas environment is required in order to maintain high EL efficiencies). The Wessling condensation route afforded soluble polymers bearing sulfonium chloride salt groups and represented the first system-processable PPV precursor; thermal elimination of tetrahydrothiophene and hydrogen chloride at temperatures between 150 and 300 °C yields high-quality PPV films. Research toward facilitating the elimination reaction at reduced temperatures has improved the process. For example, Müllen and co-workers demonstrated that through the use of sulfonium bromide salts, conversion to PPV can be initiated at temperatures as low as 100 °C.[67] Other modifications of the Wessling chemistry directed toward improving film quality and performance include reports of precursors eliminating sulfinyl and sulfonyl groups rather than tetrahydrothiophene.[68–70]

The need to convert precursor films to PPVs represents additional complexity to the processing of PLED devices and offers a variable that can significantly affect overall device power efficiency. For example, nearly complete conversion is required to achieve extended conjugation, and inert environments are needed to avoid formation of luminescence-quenching oxidation by-products. Nonetheless, high-quality films and highly efficient devices have been repeatedly demonstrated via this technical approach.

5.6. Solution-Processable Poly(*p*-phenylene vinylene) Derivatives

The general intractability of PPVs, and thus issues associated with their processability, combined with the good potential of these systems for PLED applications, has driven a great deal of research toward the development of soluble PPVs from which films can be cast without the need for subsequent thermal conversion. Heeger and co-workers in 1991 demonstrated the use of 2,5-dialkoxy functional PPVs.[56,71] It has been shown that when at least one of the alkoxy groups is long and/or bulky (at least C_4, for example), the polymers are soluble in a variety of organic solvents including xylene, chloroform, and tetrahydrofuran. There are now a series of fully conjugated PPV systems that are directly processable from solutions. The most highly studied of the series is the 2-methoxy-5-(2'-ethylhexyloxy) derivative MEH-PPV. In addition to enhancing solubility, the alkoxy substituents also impart a red shift of emission color. Thus, MEH-PPV exhibits an orange electroluminescence in contrast to the yellow-green of the parent PPV. The bulkier functionality has been reported to disrupt the tendency of PPV to order and results in an increase in EL efficiency.

The Wessling sulfonium salt route to PPVs may be applied to the synthesis of the dialkoxy PPVs; however, due to their soluble nature, more direct routes have been developed. A process that involves the direct base-initiated dehydrohalogenation polymerization of 1,4-bis(halomethyl)-2,5-dialkoxy-benzene monomers was first reported by Gilch et al. as early as 1966 as the preferred methodology.[72] High-molecular-weight, high-purity, soluble materials can be achieved in this manner. LED devices based on the soluble PPVs have shown very good performance and have led to considerable commercial interest in developing materials of this type.

Following the observation that alkoxy substituents on the PPV backbone effectively modulate important properties such as the electronics (color of emission) and disruption of semicrystalline ordering (improved EL efficiency), many PPVs bearing other functional groups have been developed with an emphasis on further enhancing EL performance. A few additional representative examples of such functionalization are: 1) a 2-dimethyloctylsilyl functional group on the PPV phenylene group shifts emission color to green by widening the polymer bandgap;[73] 2) introduction of cyano groups bound to the vinylene linkage of the PPV backbone results in

a polymer of much improved electron affinity and has allowed high-efficiency, PPV-based devices to be constructed without the need for an additional electron-transport layer;[74] and 3) copolymers (based on alkoxy and non-alkoxy monomer units) in which incomplete conversion to fully conjugated PPV (yielding isolated conjugated components) has enabled devices with significant efficiency gains relative to the basic PPV polymer.[75] These developments are only a minor subset of PPV-related advancements reported to date and described extensively in reviews cited herein.

5.7. Polyphenylenes

Poly(1,4-phenylene) (PPP) represents another class of conjugated polymer of interest to the PLED field. Wide bandgaps are typical for PPPs and allow emission of blue light. Since the design of efficient long-lived blue emitters remains a significant challenge to the field, these polymers, like the polyfluorenes, are attractive candidates for consideration. As with the PPVs, most PPPs are insoluble and intractable. Thus, research activities in the PPP field have emphasized routes to PPP films via soluble thermally converted precursor polymers, as well as the development of soluble PPPs.

A wide variety of processable PPP precursor routes have been described.[76] Similar to the PPV precursor chemistries, the PPP precursor routes typically involve the thermal elimination of a leaving group(s) to generate the fully conjugated system. For example, elimination of two equivalents of acetic acid (per monomer unit) from poly-1,4-(5,6-diaceto-2,3-cyclohexene) enables aromatization of the polymer chain rings and formation of the PPP structure. Relatively high temperatures are required to effect the conversion, and side reactions that can lead to reduction of molecular weight (and reduce polymer film integrity) are problematic. Therefore, progress in the precursor approach to PPP emissive devices has been slow and has met with very limited success.

A great deal of attention has been focussed on the preparation and characterization of PPPs derived from monomers functionalized with a variety of solubility-enhancing groups, including alkyl, alkoxy, and aryl units, analogous to the development of soluble PPV systems. Since the monomers and resulting polymers are soluble if appropriately long or bulky substituents are employed, the polymerization reaction can occur in solution using well-known aryl or Suzuki coupling approaches. Molecular weights high enough to cast films with good integrity have been achieved, and blue-emitting diodes have been constructed and demonstrated reasonable efficiencies.[77]

6. Operational Characteristics

The primary attributes of PLED device performance are its emissive ability or perceived brightness, color matching within targeted specifications, and control and longevity in operation. The term "brightness" is a physiological description of

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light intensity with respect to the wavelength sensitivity of the human eye. The average observer possesses daylight sensitivity to wavelength described by the photopic efficacy curve depicted in Figure 5.[78] The maximum of this response curve describes the yellow-green portion of the spectrum to which
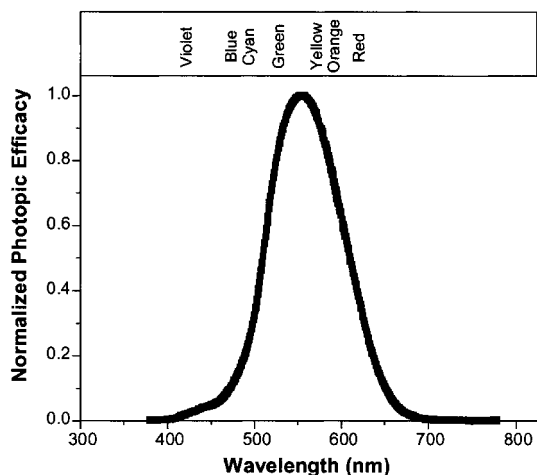

Fig. 5. The 1988 CIE photopic luminous efficiency function describing the spectral distribution of luminous energy and the efficacy upon the eye (adapted from [78]).

we are most sensitive. The response is almost Gaussian, falling off rapidly towards either the red or blue. This photopic response has significant implications for the materials designer of light-emitting polymers. For a green emitter, a given number of photons corresponding to a proportional number of electronic transitions will be perceived as attaining a certain brightness. For a red emitter, however, the material must support a significantly greater number of electronic transitions in the same time interval in order to be perceived at the same brightness level. For materials with similar quantum efficiencies, more emitted photons come at the expense of increased current, which is typically achieved at higher operating voltages. Matching similar operating characteristics and brightness levels require dissimilar material EL efficiencies.

Color tuning is an important parameter when addressing the scope of LEPs. Due to the disorder of the polymer matrix, emission peaks will be broad, with a full width at half maximum (FWHM) approaching 60 to 70 nm for "monochromatic" sources. Color is calculated using the integral of spectral emission as a function of wavelength against the chromatic sensitivity of the eye. This results in a set of coordinates on a chromaticity graph defined by international standards maintained by the Commission Internationale de l'Eclairage (CIE). Figure 6 illustrates typical PLED device data from two different color emitters, one red and the other green. Identical device structures were employed to duplicate conditions that are present on a multicolor display. Both devices utilize 40 nm of PEDOT as the HTL and 80 nm of the respective EML. Both devices also use calcium as the cathode contact. The green device has a maximum EL peak at 534 nm and the red device has its maximum emission at 634 nm. The color coordinates according to the CIE 1931 chromaticity dia-
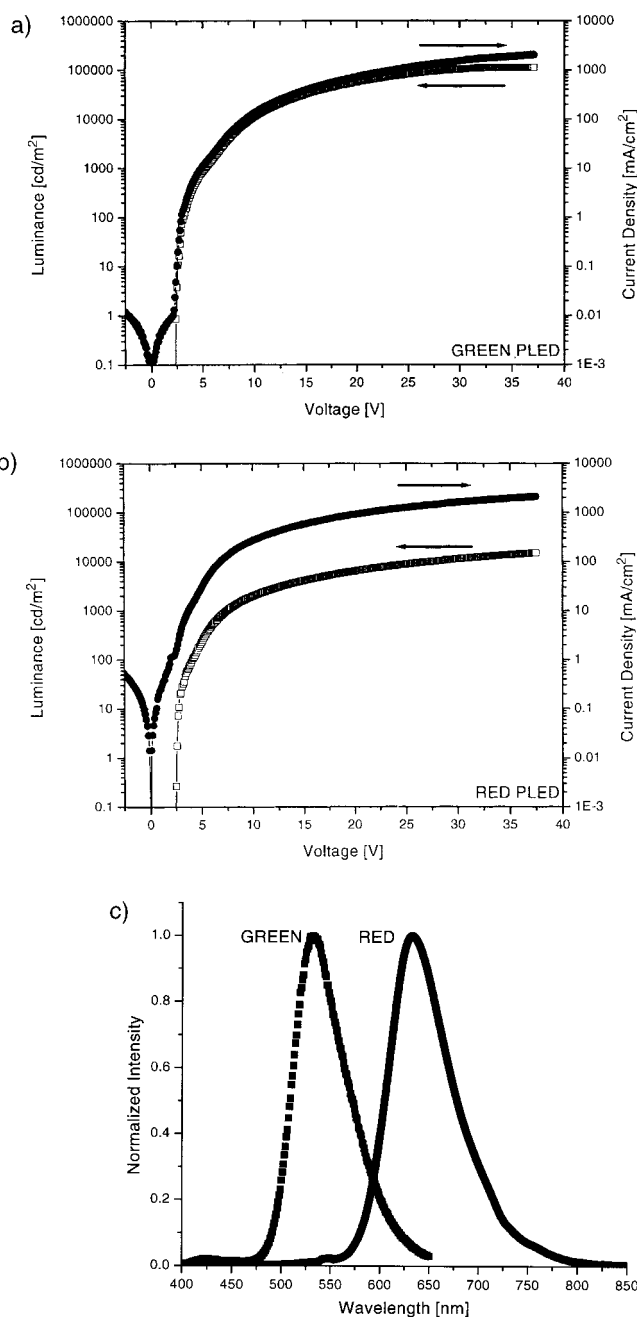

Fig. 6. Current–voltage–luminance determinations for two PLED devices: a) employing a green emitter, and b) using a red one. c) EL spectra for the two emitting materials.

gram for the green emitter are (0.385, 0.579), and for the red emitter the CIE coordinates are (0.683, 0.313).

A desirable feature with LEPs is that they can be fabricated into a device possessing a relatively constant efficiency over a wide luminance range. An example of the near-linearity of the material efficiency of the same green emitter described above is shown in Figure 7. The green emitter is more efficient, with higher luminance levels at lower voltage levels than can be achieved with the red emitter in an identical device configuration. If we approximate the relative EL spectral
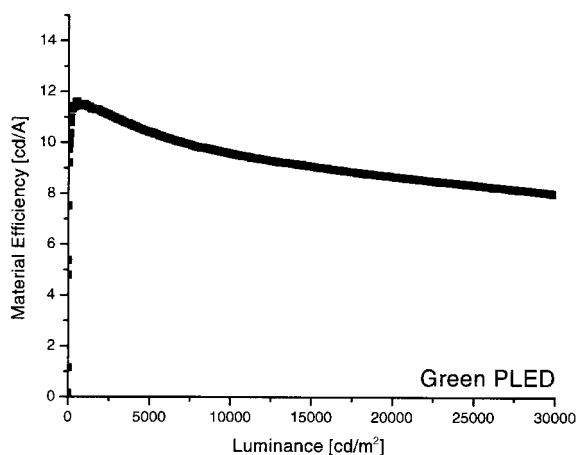
Fig. 7. Plot of material efficiency metric [cd/A] against luminance [cd/m^2] for the green emitter exemplified in Figure 6.

curves to follow the same shape, then according to the photopic efficacy model of the eye, the red emitter must produce four times more photons than the green emitter in the same period of time to stimulate an equal sensation of brightness. For deep-blue emitters, the relationship is less favorable.

Lifetime reliability is also an important characteristic of this technology. Although different end-users have their own unique lifetime tolerances, we shall adhere to the current definition that lifetime refers to that duration of operating time corresponding to the decay of device luminance to one-half of the initial value. We shall also describe lifetime parameters that are obtained under DC (or continuously ON) conditions.

When describing device lifetime, it is also important to specify the corresponding initial luminance level from which it is measured. For example, an early candidate for a polyfluorene-based red EL was measured for device lifetime, of which the results of one device are shown in Figure 8. The data were obtained using DC operation under constant current driving conditions. The initial luminance value was 100 cd/m^2 and was directly proportional to the current applied to the device. Of interest are both the voltage rise with time
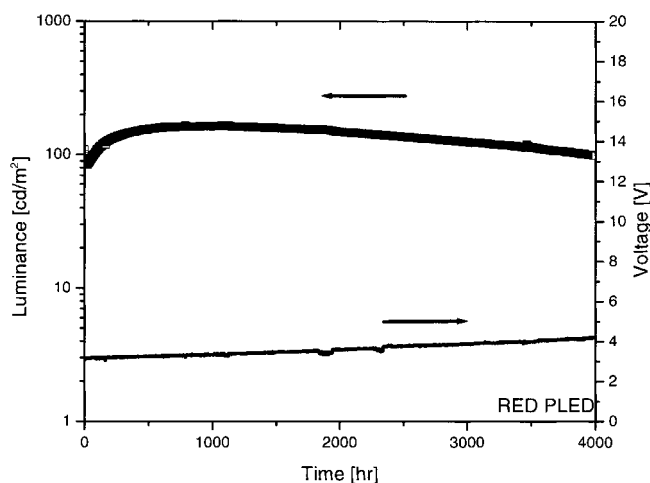

Fig. 8. Lifetime plot of a red EL emitter, showing luminance decay and voltage rise with time.

as well as the luminance decay. Varying the molecular design of EL polymers will permit long lifetimes, but with varying degrees of voltage change during the operational lifetime of a device. The lifetime of this specific device was later found to be approximately 5500 h. Such data were used to compile the engineering diagram shown in Figure 9. For the same red material, data were obtained from many DC lifetime evalua-
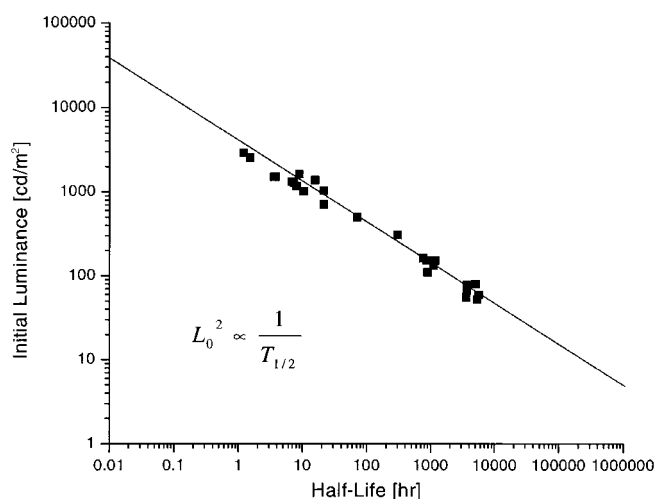

Fig. 9. Composite engineering plot summarizing initial luminance with device lifetime for the red EL material.

tions starting with various initial luminances, all at room-temperature and -pressure conditions. None of the data were extrapolated; all data represent empirical observations of device performance in the laboratory. The relationship between initial luminance and lifetime follows an inverse power law very well, with L_0 describing the initial luminance and $T_{1/2}$ representing the half-life. Note that lifetimes of 1 000 000 h are possible with this early material candidate with this specific device configuration, but only with an initial luminance value of 5 to 7 cd/m^2. Such graphical relationships are essential to the design engineer considering certain performance levels over a desired operating duration.

7. Engineering Aspects

Electroluminescent material applied to a transparent surface and excited to emission creates a Lambertian source of light, in that the surface can be adequately described by the surface integral of a two-dimensional array of diffuse point emitters, each generating light equally. As such, potential applications that are replacements of filament-based sources of light are not straightforward, especially if product specifications are defined in terms of the luminous intensity of localized point emitters. In these circumstances, different means of describing product performance are required. Descriptions of filament bulb performance describe luminance intensity in units of candelas (cd), whereby surface emitters are described in terms of luminance with units in cd/m^2. The two systems of photometric nomenclature can be reconciled by considering

the emitting area, but product requirements need to be redefined. For example, the luminance intensity for some safety indicators is specified on the central optical axis, which is directly in-line with the filament source. It is implicitly assumed that there will be some intensity drop-off at other spatial locations on the front lens. The same intensity available at all points over an extended emitter would be perceived as uncomfortably bright, even though that is what would be required to meet the defining product specifications. Therefore, as this technology is considered for incumbent technology replacement, existing product specifications will need to be broadened to include Lambertian sources.

Specific applications intended for the marketplace will require their own unique engineering and tooling. But given the commonality of the emissive medium, there are engineering aspects that are common to most application embodiments. Most applications of either monochrome or multicolor formats for information display will require pixelation of the emissive area. There are two primary methodologies associated with achieving this, and both require etching rows of ITO strips on the transparent substrate, and later depositing columns of cathode electrodes across the display. Where the cathode and anode overlap defines a pixel. Simple excitation of a given row and column defines passive-matrix operation. Passive-matrix driving schemes rely on pulsing each row of pixels in sequence where the entire display format is scanned with a period of less than 1/30 s. This corresponds to the limit of visual temporal resolution, otherwise known as the physiological persistence of the latent image. For a display built of N rows, each row will be pulsed $(1/N)(1/30)$ s each. In that way, the observer will not notice image flicker and will perceive a continuous image display.

The addition of individual thin-film transistors on the substrate for each pixel permits individual pixels to be independently turned on and off, and alleviates the need to raster each row sequentially within 1/30 s. This operation defines active-matrix driving. Fine display resolution is achieved with small, closely spaced pixels. For very fine resolution, neighboring pixels could be so closely spaced that interpixel communication could distort the intended operation with what is referred to as cross-talk. Cross-talk will result in a blooming effect whereby nearest neighbor pixels will display some unintended gray-scale activation state. The use of highly conducting polymers as the HTL can aggravate this problem by providing a low resistive path to nearest neighbor sites. This can be overcome by modifications to the conductivity of the HTL, or to the driver electronics, or both.

In the passive matrix display, a pixel that will be in the active state for $1/N$ of the scan period and which is designed to be perceived at a luminance of L will have to be pulsed to a luminance of NL for $(1/N)(1/30)$ s. In addition, improved image contrast from the display is achieved by using a polarizer front filter, which also reduces the perceived luminance by approximately 50 %. Therefore, a 64 × 128 pixel display running with a maximum perceived luminance of 100 cd/m² will be designed to operate with a maximum luminance of 200 cd/

m² (filter accommodation), and a given pixel will be required to emit with 12 800 cd/m² for 0.5 ms every 33 ms. Such pixels may require 150 mA/cm² given common materials characteristics. For portable displays with small pixel sizes operating under short pulse duration, this is not expected to introduce any undue Joule-heating effects. In fact, the pulsing operation will permit higher device efficiencies and luminance levels than would be achievable with DC (continuously ON) operation.[79] However, for large display formats where the number of rows is large, the pulsed requirements for a pixel can be substantial. For displays beyond approximately 6 inch (1 inch ≈ 2.5 cm) diagonal, active-matrix operation will be required. Then the minimum time for each pixel to be operated will be 1/30 s, and the maximum luminance will be the value required for observation (200 cd/m² if used with a polarizer filter). It is expected that the product lifetime based on an active matrix operation will exceed that achievable with a passive-matrix drive scheme.

Also common to PLED-based products will be the requirement for airtight device packaging. The PLED is a semiconducting optoelectronic device operating at fields near half a million volts per centimeter. With current flowing through the matrix, trapped chemisorbed water molecules can undergo electrolysis, liberating radical oxygen-bearing ions, which are detrimental to organic molecules. The preferred methods of device encapsulation will have to stay below the glass transition temperature of the polymers, because going above this precipitates device shorts and failure.[80] Therefore, device encapsulation schemes are not likely to greatly exceed 100 °C. The engineering of flexible displays offers greater challenges, but comes with greater rewards. Some of the issues that will need to be addressed include providing a substrate that seals against moisture and oxygen, maintaining flexibility while maintaining the adhesion and integrity of a conducting anode, and accommodating an encapsulation scheme with package flexibility. Dow is uniquely positioned with access to a broad portfolio of materials expertise across the company to address these and related challenges that face the final stage of product definition.

8. Summary and Outlook

The development of organic electroluminescent materials has attained a state commensurate with defining commercial product. At present, both the electroluminescent, low-molecular-weight solids and LEPs are capable of attaining approximately 20 lm/W, and approximately 10 000 h operating lifetime at 200 cd/m² luminance levels, with improving reproducibility. The mechanical and economic advantages shown by polymers as compared to low-molecular-weight solids position the high-molecular-weight, readily processable "plastics" with a clear, long-term advantage in product development.

On the horizon, we can see that color control in LEPs is clearly important in defining product characteristics. Further,

considerations in fabrication techniques (e.g., coating technologies) will require material modifications without sacrificing EL performance. Material advances such as increasing the upper temperature over which these devices can operate without accelerated deterioration will also be needed. Equally important, an improvement in transparent flexible substrates over those commercially available will enable the technology to expand to a wider range of consumer products with greater speed. These and related improvements in the field are anticipated with great commercial interest, and will probably come from the larger chemical-based companies that can address the multifunctional requirements with economically acceptable solutions to these materials challenges. Concomitant with these required advances in materials development is the need for improved understanding of the working principles governing device lifetimes. We believe that this fundamental work will involve the electronic role of the polymer interfaces during operation.

There is an optimal economic strategy that will accentuate the commercial success of LEP technology. Cell phones and personal digital assistants have a mean consumer life of about 2 years, with newer models replacing older ones within that time period. Therefore, these are likely target applications for the technology to be introduced. The first applications will be small and inflexible, with later developments extending to flexible display styles and larger formats. With further product improvement, as well as commensurate advances in design and development engineering, a multicolor and eventually full-color product will follow. Despite the intrinsic limits by which technology can develop, in our opinion these estimates are conservative and are so constructed to accommodate unforeseen larger economic forces beyond those immediately affecting the industry.

At present, no one has determined, either experimentally or theoretically, an upper limit to material and device performance that can be achieved, either in color, efficiency, or lifetime. This is due, in part, to the incomplete understanding of the underlying principles governing PLED device performance. Nevertheless, we anticipate that the next decade will surpass the last, with new and unexpected results in active and passive materials development that will continue to drive this technology forward.

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