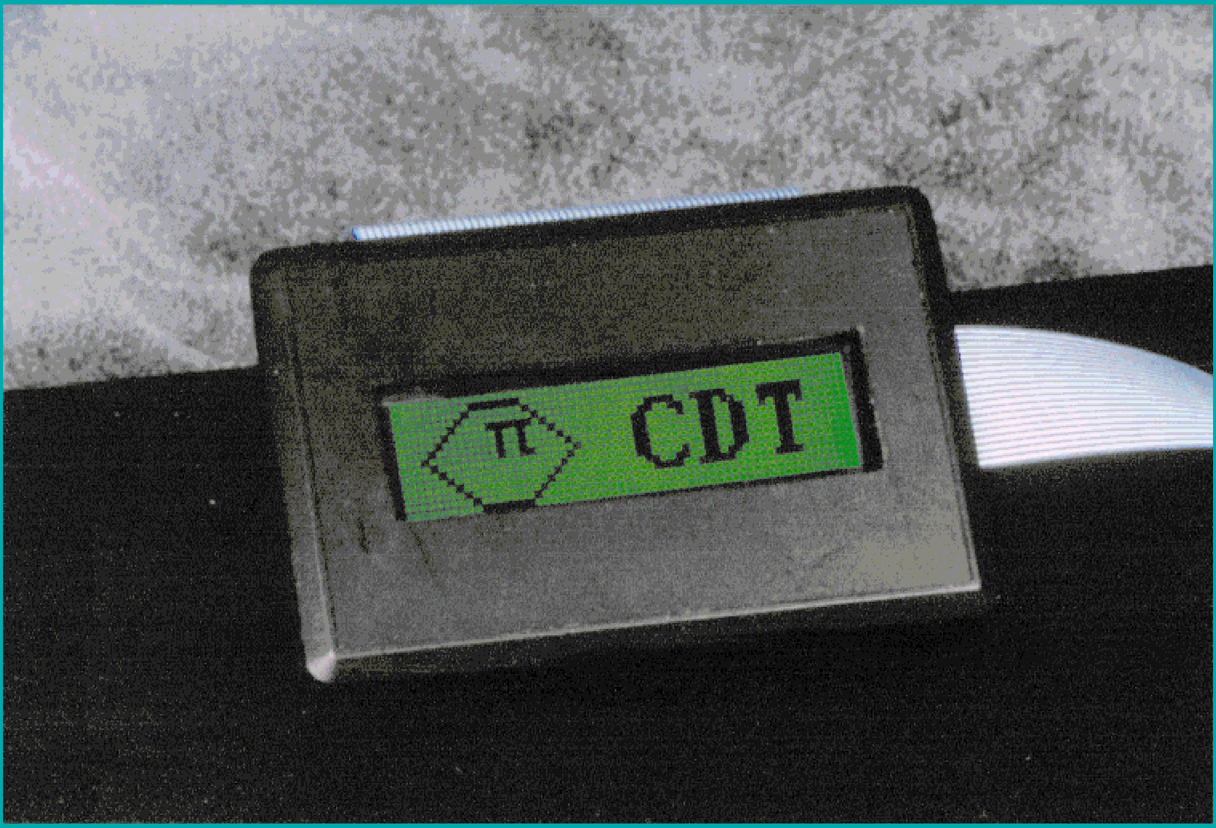
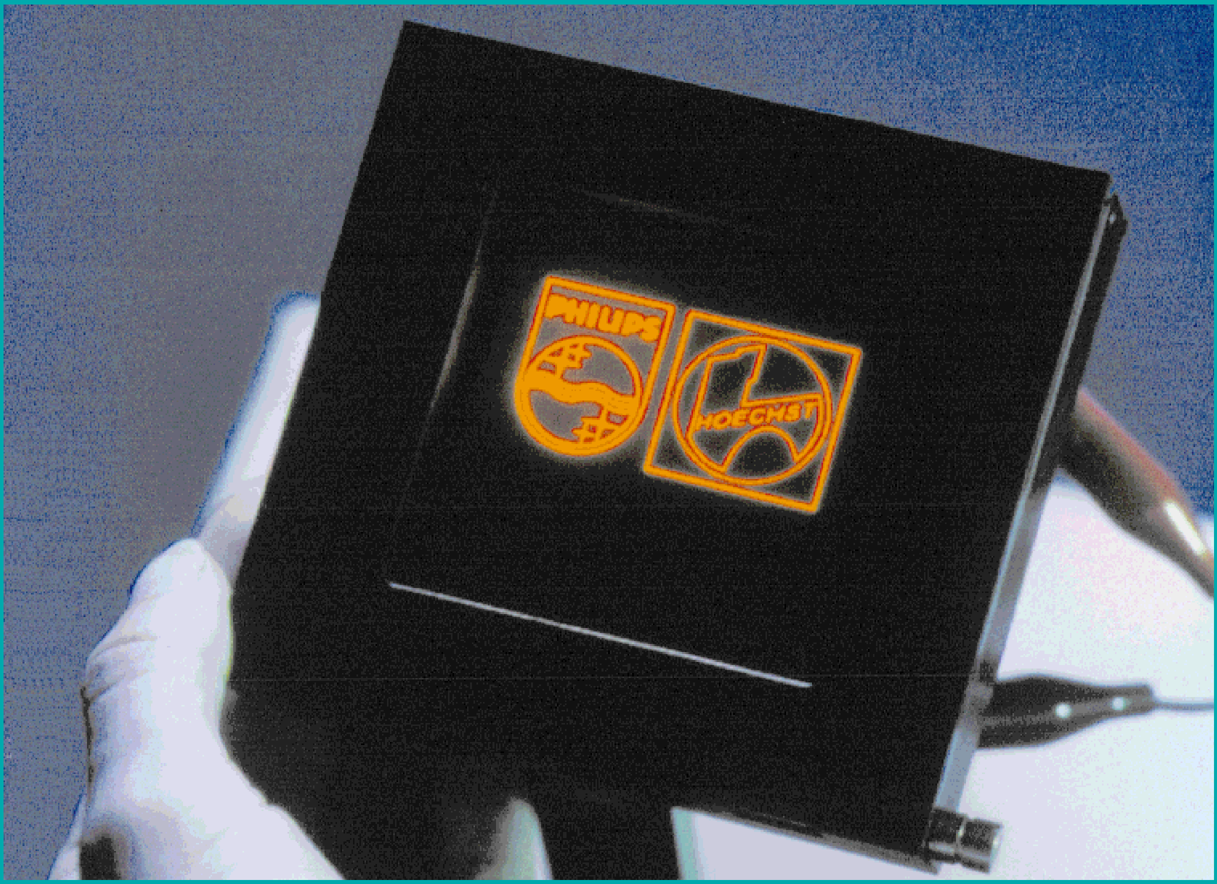


Cambridge Display Technology, photograph taken in the Photo Department at the University Chemical Laboratory of the University of Cambridge.

Green and red-orange are only two of the many possible colors that can be produced with polymer-based light-emitting devices.



Collaboration between Hoechst and Philips.

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Electroluminescent Conjugated Polymers—Seeing Polymers in a New Light

Arno Kraft, Andrew C. Grimsdale, and Andrew B. Holmes*

A major recent development in the field of molecular electronics has been the discovery of electroluminescent conjugated polymers—that is, fluorescent polymers that emit light when excited by the flow of an electric current. These materials may now challenge the domination by inorganic materials of the commercial market in light-emitting diodes. Conjugated polymers are particularly versatile because their physical properties (color, emission efficiency) can be fine-tuned by manipulation of their chemical structures. The development of polymer-based light-emitting devices has been accompanied by an increased understanding of the processes involved in device function and breakdown, and the systematic modification of the properties of the emissive polymers by synthetic design has become a vital component in the optimization of light-emitting devices. In this account we present an overview of the synthesis and properties of electroluminescent polymers and demonstrate through examples the development of the field. There are many aspects of fundamental science to be studied in order to realize commercial applications of this serendipitous discovery. Opportunities for synthesis abound.

Keywords: conjugation · electrochemistry · luminescence · materials science · polymers

1. Introduction

The role of polymers in the electronics industry has been traditionally associated with insulating properties, whether these be for isolating metallic conductors or for use in photoresist technology. From that starting point it was the pioneering work of MacDiarmid, Heeger, and Shirakawa et al. that inspired chemists and physicists to consider the opportunity of using polymers as conductors. While the scientific community had started to accept the concept of conjugated polymers as semiconductors, no-one was prepared for the discovery of the plastic sandwich that would emit light when simply connected to a battery. The discovery in Cambridge of electroluminescence (EL), that is the emission of light when excited by flow of an electric current, in conjugated polymers[1] has provided a new impetus to the development of light-emitting devices (LEDs) for display and other purposes.[2] Organic electroluminescent displays represent an alternative to the well-established display technologies based on cathode-ray tubes and liquid-crystal displays (LCDs), particularly with respect to large-area displays for which the existing methods are not well suited.

Inorganic electroluminescent materials have been known for many years, and LEDs based on these materials have been commercially available since the early 1960s. They have been widely used in a variety of applications. EL from molecular organic materials was discovered about the same time, but it was only in the mid-1980s that devices using fluorescent organic dyes showing brightnesses and operating voltages suitable for commercial applications were developed by Tang and Van Slyke,[3] and by Saito and Tsutsui et al.[4] Monochromatic displays based on such devices are reportedly due to be released on the commercial market in 1997 or 1998.[5, 6] Inorganic semiconducting and organic dye materials have to be deposited as thin films by the relatively expensive techniques of sublimation or vapor deposition, which are not well suited to fabrication of large-area devices. For these reasons, the possibility of using fluorescent conjugated polymers, which can be readily deposited from solution as thin films over large areas by spin-coating or doctor blade techniques, is most attractive. Considerable research efforts have gone into the development of electroluminescent polymers for use in LEDs, and in this review we aim to give an overview of the progress made in this area. Polymer LEDs are expected to have commercial applications as backlights

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[**] A list of abbreviations is given in the Appendix.

for liquid crystal displays and as the emissive material in alphanumeric displays within the near future.

Aspects of the properties of conjugated polymers and organic electroluminescence have previously been reviewed. These reviews are listed in Table 1.

Table 1. Recent reviews on conjugated polymers and electroluminescence.

First author	Topic
May	polymer electronics[2]
Patil	optical properties[7]
Friend	polymer LEDs[8]
Bradley	electroluminescent polymers[9]
Holmes	EL in conjugated polymers[10]
Fox	light-emitting plastics[11]
Baigent	conjugated polymer EL[12]
Yam	polymer electronics[13]
Greenham	physics of conjugated polymers[14]
Gymer	organic EL displays[15]
Rothberg	organic EL[16]
Salbeck	EL with organic compounds[17]
Salaneck	conjugated polymer interfaces[18]
Sheats	organic EL devices[19]
Lovinger	organic transistors[20]
Feast	synthesis of conjugated polymers[21]
Yang	polymer EL and LECs[22]
Friend	polymer device structures[23]
Díaz-García	plastic lasers[24]
Deussen	organic LEDs[323]
Hide	photonic applications[324]

2. Poly(phenylene vinylene)s—A Case History

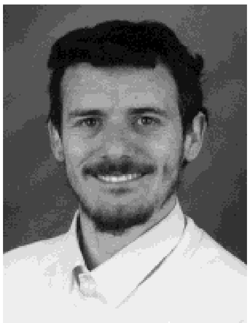
Electroluminescence in conjugated polymers was first discovered during investigations into the electrical properties of poly(1,4-phenylene vinylene) (PPV; **6**),[1] the simplest and cheapest poly(arylene vinylene).

2.1. The Synthesis of Poly(*p*-phenylene vinylene)—Precursor Polymer Routes

PPV (**6**) is a bright yellow, fluorescent polymer. Its emission maxima at 551 nm (2.25 eV) and 520 nm (2.4 eV) are in the yellow-green region of the visible spectrum. The polymer is insoluble, intractable, and infusible. Any synthesis of PPV directly from a monomer produces an insoluble material, which cannot be easily processed; solution processing by spin-coating is, however, particularly desirable as it yields high-quality transparent thin films for the production of polymer


A. Holmes


A. Kraft


A. Grimsdale

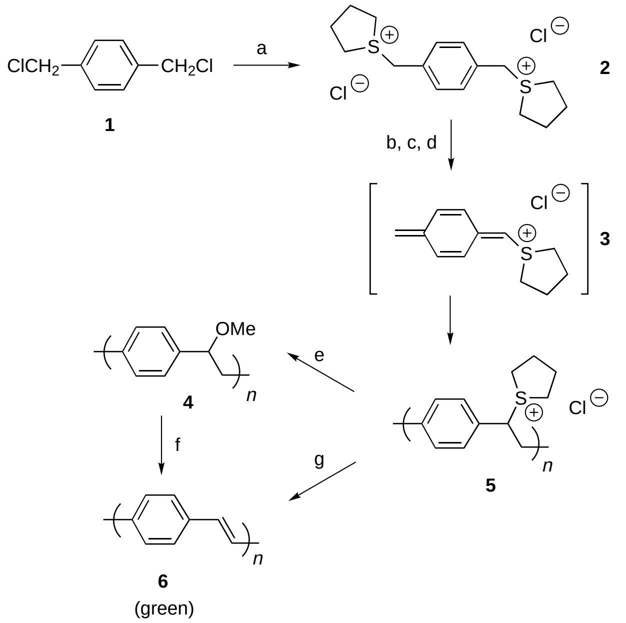
Andrew Holmes was born in Melbourne, Australia, in 1943 and received his early education at the University of Melbourne. He obtained his Ph.D. in 1971 in the field of annulene chemistry with Prof. Franz Sondheimer at University College London, and then carried out postdoctoral research at the Eidgenössische Technische Hochschule, Zürich with Prof. A. Eschenmoser on the total synthesis of vitamin B_{12}. *In 1972 he was appointed University Demonstrator (Assistant Lecturer) and in 1977 Lecturer in the University Chemical Laboratory at the University of Cambridge. In 1989 he commenced a collaboration with Prof. R. H. Friend in molecular electronics, which led to the discovery of electroluminescence of poly*(para-phenylene vinylene). *Dr. Holmes has been the Director of the Melville Laboratory for Polymer Synthesis since 1994. Current research interests embrace the synthesis of functional macromolecules and biologically active natural products.*

Arno Kraft, born 1961 in Darmstadt, Germany, studied chemistry at the Universität Würzburg. He then worked in the group of Prof. M. Christl on the synthesis of and NMR spectroscopic investigations of benzvalene derivatives, and obtained his Ph.D. in 1989. After a brief stay with Prof. G. Erker, he joined Andrew Holmes as a postdoctoral research fellow. During the following three years he worked on the development of electroluminescent polymers and charge-transporting materials. He left Cambridge in 1993 to start independent research for his habilitation at the Universität Düsseldorf. His current interests include highly soluble and, at the same time, highly self-associating and self-assembling dendrimers and branched macromolecules.

Andrew Grimsdale, born 1963 in Waiouru, New Zealand, is a graduate of the University of Auckland. He worked on the synthesis of analogues of biologically active drimane sesquiterpenes with Prof. R. C. Cambie and obtained his Ph. D. in 1990. He then joined Prof. A. Pelter at the University of Wales in Swansea, where he investigated photochromic and electroactive organic materials. In 1994 he moved to Cambridge where he began research with Andrew Holmes into novel electroluminescent polymers. In 1997 he returned to Auckland.

EL devices. This dilemma is conveniently resolved by the use of a solution-processible precursor polymer. The sulfonium precursor route to PPV was introduced by Wessling and Zimmerman,[25, 26] and was subsequently modified and optimized by other groups.[27–29] The principle has been applied, not only to PPV and its derivatives, but also to a whole range of PPV-related copolymers.

Scheme 1 outlines the standard preparation of PPV (**6**).[28] Treatment of 1,4-bis(dichloromethyl)benzene (**1**) with tetrahydrothiophene results in the formation of the bis-sulfonium salt **2**. Other sulfides such as dimethyl sulfide can be employed, but unwanted side reactions occur at sulfonio groups during subsequent steps.[27] Polymerization of a methanolic solution of monomer **2** is induced by the addition of slightly less than 1 mol equivalent of aqueous sodium hydroxide at 0–5 °C. If more base is used, the resulting polymer solutions become brightly colored owing to partial base-induced elimination of the sulfonio groups. The mechanism of this polymerization deserves further investigation. Studies[26, 30] have shown that the presence of radical trapping agents such as oxygen can severely lower the molecular weight of the polymer, which would suggest that the *p*-quinodimethane intermediate **3** undergoes radical polymerization, although anionic propagation cannot be completely excluded. The reaction is in practice best performed under an inert atmosphere and is terminated by neutralization with dilute hydrochloric acid. The almost colorless solutions of precursor polymer **5** are then dialyzed against distilled water to remove impurities having low molecular weight. The molar mass of the precursor polymer **5** cannot be determined easily by gel-permeation chromatography owing to the polyelectrolyte nature of the polymer. Treatment with refluxing methanol gives a neutral polymer **4** which on gel-permeation chromatography characterization shows a number-average molar mass M_n of ≥ 100000 g mol^{-1}.[31]

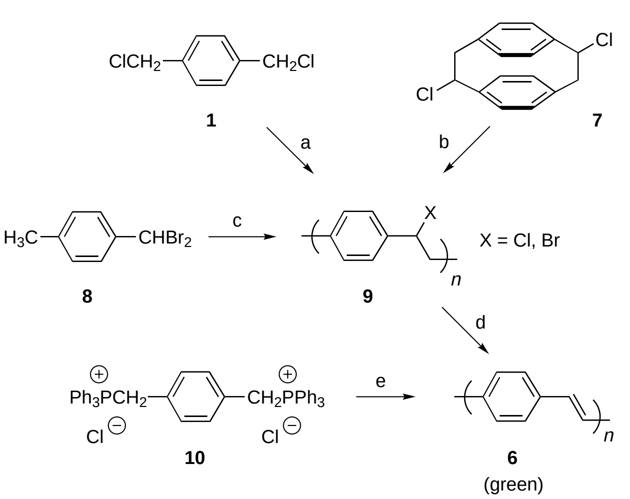


Scheme 1. Synthesis of PPV (**6**): a) tetrahydrothiophene, MeOH, 65 °C; b) NaOH, MeOH/H_2O or Bu_4NOH, MeOH, 0 °C; c) neutralization (HCl); d) dialysis (water); e) MeOH, 50 °C; f) 220 °C, HCl(g)/Ar, 22 h; g) 180–300 °C, vacuum, 12 h.

The precursor polymer **5** is converted into PPV (**6**) by heating thin films (spin-coated with thickness of typically 100 nm) in the temperature range of 180–300 °C for 12 h under vacuum (10^{-6} mbar).[1, 28] Under these conditions the by-products of the elimination (tetrahydrothiophene and hydrogen chloride) escape easily. It has been reported that traces of oxygen during the conversion step reduce the luminescence quantum efficiency in the final PPV film. This has been attributed to the formation of carbonyl groups that are believed to quench luminescence.[32–34] The formation of such groups was reported to be suppressed by performing the conversion in a reducing atmosphere of nitrogen and hydrogen.[32, 33] PPV prepared under these conditions has higher fluorescence and EL quantum efficiencies.[35] Our own experience is that a nitrogen atmosphere suffices. When conducting the elimination step under argon, Schwoerer et al.[36, 37] found that conversion already occurred at 160 °C. Vanderzande et al.[38] and Müllen et al.[29] then showed that the conversion temperature could be further reduced by using the bromide instead of the chloride salt of precursor polymer **5**, which allows the conversion to occur at temperatures as low as 100 °C. This enables LEDs to be fabricated on flexible polymer foil substrates, for example on indium-tin oxide (ITO)-coated poly(ethylene terephthalate) (PET). Films of PPV can also be deposited by Langmuir–Blodgett techniques[39] and by simple dip-coating. The resulting PPV shows remarkably good luminance properties given that these techniques contaminate PPV with surfactant residues.[40–43] Highly aligned free-standing thin films and fibers of PPV can be formed by pre-ordering the precursor polymer **5** in a lyotropic liquid-crystalline phase before thermal conversion.[44] This type of nanocomposite might show promise for polarized emission.

Other methods have also been exploited to prepare PPV suitable for LEDs. The materials produced by these routes, however, may differ from PPV prepared by the Wessling route in molar mass, molar mass distribution, film quality, nature and amount of defects and impurities, output of waste materials etc., and of course the resulting device efficiency and lifetimes may also vary considerably. A modified Wessling (quinodimethane) synthesis, based on the elimination of sulfinyl or sulfonyl groups instead of sulfonio groups, has been reported by Vanderzande et al.[45–47] Galvin et al.[48] favored a xanthate precursor polymer soluble in organic solvents and claimed that it gave better quality PPV films and higher device efficiencies than the standard route.

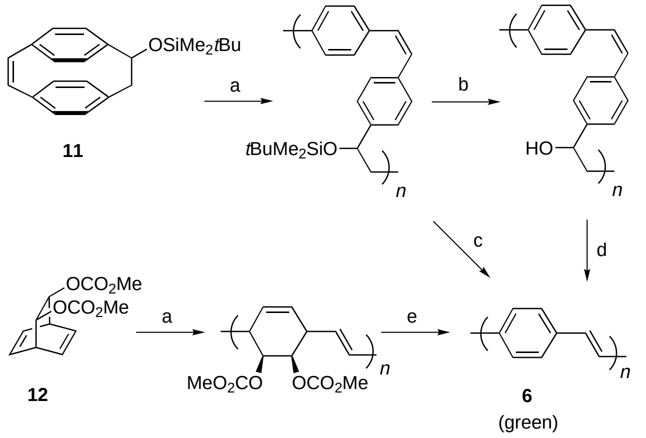
PPV films are also accessible by chemical vapor deposition (CVD) of compounds of type **1**[49] and **8** or of chlorinated cyclophane **7**.[50] In all cases the intermediate α-halo-precursor polymer **9** film is further converted to PPV **6** at 200 °C under vacuum (Scheme 2), but LEDs made with these films showed quite low (0.002 %) efficiencies (see Section 2.2).[49, 51] Electropolymerization of **10** gave PVV films, but absorption and emission spectra were blue-shifted with respect to material produced by other methods, indicating that the electropolymerized material had a shorter conjuga-



Scheme 2. Alternative synthetic routes to PPV (**6**): a) 500–700 °C, 0.01 mbar; b) 580 °C, 10 Pa; c) 800–900 °C, 0.01 mbar, then 60 °C, 0.1 mbar; d) 200 °C, vacuum; e) CH_3CN, 5.5 V.

tion length owing to incomplete elimination of the phosphonio groups.[52]

Ring-opening metathesis polymerization (ROMP) in principle offers the opportunity for precise control of polydispersity and microstructure. Applications to conjugated polymers such as polyacetylene are well-documented,[21] and promising routes to PPV are also emerging. The siloxy-substituted cyclophane **11**[53] or bicyclic monomer **12**[54] are typical substrates for ROMP and afford well-defined precursor polymers, which are converted to PPV **6** by thermal elimination (Scheme 3).



Scheme 3. ROMP routes to PPV (**6**): a) $[Mo(=NAr)(=CHCMe_2Ph)\{OCMe(CF_3)_2\}_2]$; b) Bu_4NF; c) HCl(g), 190 °C; d) 105 °C; e) 280 °C.

2.2. Simple Electroluminescent Devices Based on PPV—A Basic Polymer LED

As a material, PPV has several advantages over classical inorganic light-emitting semiconductors. First the ease of processing permits PPV to be spread onto large areas and curved surfaces. Second PPV shows the tensile properties expected for a chain-extended polymer: its elastic moduli and tensile strength are almost as high as those of polyaramide fibers. This, of course, helps the polymer "to survive" under the harsh conditions prevailing during device operation.

In a light-emitting diode (LED) or electroluminescent device (Figure 1), the thin film of light-emitting material is sandwiched between two electrodes, one of which has to be semitransparent. Under an applied bias (voltage), oppositely charged carriers (electrons and holes) are injected into the emissive layer(s) from the opposing contacts, and are swept through the device by the high ($>10^5\,V\,cm^{-1}$) electric field. Some of the electrons and holes combine within the emissive material to form triplet and singlet excited states. The singlets are indistinguishable from the excited states of photoluminescence (PL), the fluorescence process resulting from photoexcitation of the ground state (Figure 2).

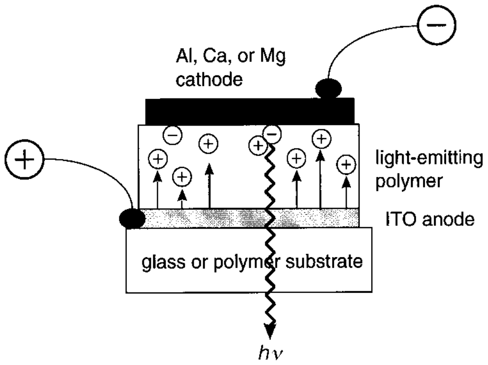


Figure 1. Schematic drawing of a single-layer electroluminescent device. An applied electric field leads to injection of holes (positive charges; the majority charge carriers in polymers such as PPV) and electrons (usually the minority charge carriers) into the light-emitting polymer film from the two electrode contacts. Formation of an electron-hole pair within the polymer may then result in the emission of a photon. Since holes migrate much more easily through PPV than electrons, electron-hole recombination takes place in the vicinity of the cathode.

A common measure of the efficiency of electroluminescent devices is the number of photons emitted per electron injected. This is the internal efficiency, which is based on the assumption that all the light generated is received by the viewer. External efficiencies are a factor of $2n^2$ smaller than internal efficiencies, where n is the refractive index of the polymer.[55] For a polymer having a typical refractive index of 1.4 this factor would be four, and external quantum efficiencies for the current family of polymers fall within the range 0.1–5 %.

It should also be noted that EL efficiencies are dependent on the distance of the emitting dipoles from the metal electrode.[56] Power conversion efficiences ($W\,W^{-1}$) are quoted by device engineers. These values are reached by multiplying the external quantum efficiency by the ratio of the photon energy and the drive voltage. The power efficiency should be as high as possible in order to maximize device longevity, and, at the same time, devices have to be bright at low current and low electric field. The luminous efficiency ($lm\,W^{-1}$) is the power conversion efficiency multiplied by the luminous efficacy (in lumens per watt).[19] The luminous efficacy is a conversion factor that takes account of the fact

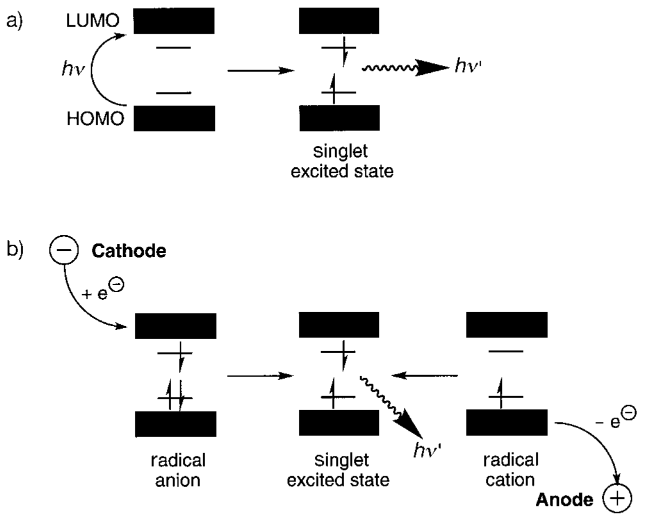


Figure 2. a) Irradiation of a fluorescent polymer excites an electron from HOMO to LUMO. In a typical conjugated polymer, two new energy states are generated upon relaxation within the original HOMO – LUMO energy gap and are each filled with one electron of opposite sign (singlet excited state). The excited polymer may then relax to the ground state with emission of light at a longer wavelength than that absorbed (photoluminescence). b) In a polymer LED, electrons are injected into the LUMO (to form radical anions) and holes into the HOMO (to form radical cations) of the electroluminescent polymer. The resulting charges migrate from polymer chain to polymer chain under the influence of the applied electric field. When a radical anion and a radical cation combine on a single conjugated segment, singlet and triplet exited states are formed, of which the singlets can emit light.

that the eye is more sensitive to green than to red and blue light. Current values reported for luminous efficiencies range between 1 – 2 lm W^{-1}, and values as high as 10 lm W^{-1} for the best devices have been reported. Luminance (cd m^{-2}) and luminance per unit of current density are also measures of device efficiency. Typical luminances for laptop displays are about 100 cd m^{-2}, but much higher luminances would be required for a matrix addressing scheme that avoids the need for thin film transistors behind each pixel.

The choice of the correct electrode combination is crucial to the operation of a polymer light-emitting diode (Figure 1). There has been considerable progress in understanding the dopant behavior of negatively charged metal contacts at the metal– polymer interface.[18] Single-layer devices are typically fabricated by solution-coating a thin film of polymer on indium-tin oxide (ITO)-glass and by vacuum evaporation of a cathode. These device structures will be denoted as ITO/polymer/metal in the remainder of this review. An early device configuration ITO/PPV/Ca had an average internal efficiency of 0.1 %.[57, 58] Glass or PET substrates with a thin (ca. 15 nm) transparent ITO layer are commercially available. The mixed-metal oxide has a high work-function, which matches the HOMO energy level of PPV and makes it convenient for hole injection (i.e. removal of an electron from the HOMO) into the polymer.

Other metals and oxides such as gold,[1] Al/Al$_2$O$_3$,[1] and SnO$_2$[59] have also been tested for electroluminescent polymers but in only a few cases gave better performance. Calcium as a result of its reactivity (especially its moisture sensitivity) may not be the preferred electrode for use in commercial devices unless excellent encapsulation can be realized, and a less reactive low-work-function metal would generally be favored. Aluminum has been a compromise, but the internal efficiency of a PPV light-emitting device using ITO and Al electrodes is only 0.01 % owing to poor electron injection.[58] Introduction of a thin layer of aluminum oxide between the PPV and Al layer (i.e., Al/Al$_2$O$_3$ as cathode) can result in a marked improvement in device efficiency as a result of carrier confinement.[60]

Heterostructure LEDs made from self-assembled multilayers of PPV and polyanions such as sulfonated polyaniline have also been constructed and found to emit bright yellow-green light with low turn-on voltages.[61–66] The self-assembled multilayer technique so far seems to enable exceptional control of the device thickness, and has recently been extended to include ruthenium-based complexes.[67] The improvement of power efficiency and stability of EL devices by addition of an extra charge-transporting layer between the PPV and the cathode[58, 68–77] is discussed in Section 3.2.

2.3. Solution-Processible Poly(phenylene vinylene)s—Direct Deposition of Electroluminescent Polymers

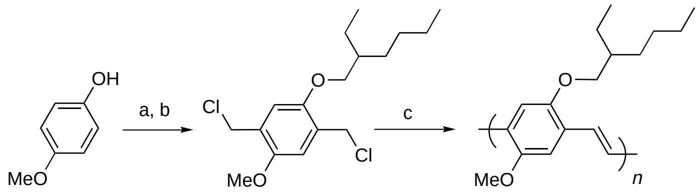
Following the discovery of electroluminescence in PPV, LEDs from PPV derivatives that are soluble in the conjugated form were reported independently by Ohnishi et al. at Sumitomo,[78] and by Braun and Heeger at Santa Barbara.[79, 80] Such soluble polymers no longer require thermal treatment during device fabrication, which is the drawback of the PPV precursor route, although they tend to have lower glass transition temperatures. It should be pointed out that, while the precursor polymer **5** is usually processed from methanolic solutions (and, like PPV, does not dissolve or swell in chloroform), almost all soluble PPV derivatives used in EL devices are processible from solvents that do not cause swelling of PPV or its precursor polymer **5**. This difference in solubility can be applied advantageously to the design of multilayer devices that consist of sandwich structures with layers of different polymers, for example, PPV and substituted PPVs (Section 3.3.).[81, 82]

Poly[(2,5-dialkoxy-1,4-phenylene)vinylene]s with at least one long, solubilizing alkoxy side chain (e.g., 2-ethylhexyloxy, 3,7-dimethyloctyloxy, 2-methylpentyloxy, or dodecyloxy)[78, 79, 83–87] dissolve in various organic solvents such as chloroform or tetrahydrofuran. In addition, their emission maximum is red-shifted [to ca. 590 nm (2.1 eV)] compared with that of PPV. The long side chains, which keep the conjugated polymer backbones apart from each other, apparently have a beneficial effect on the polymers' fluorescence and electroluminescence quantum yields.

Dialkoxy-substituted PPVs can be prepared by a sulfonium precursor route as described for the synthesis of PPV.[28, 86, 88–90] Although the Wessling route may be used to make soluble PPV derivatives, a dehydrohalogenation – condensation polymerization, first developed by Gilch et al.,[91] is generally preferred. It proceeds through base-promoted 1,6-elimination of 1,4-bis(halomethyl)benzene derivatives.[78, 84, 85, 92]

This shortens the preparation of the conjugated polymer by two steps, and can result in substantially increased yields. As with the Wessling procedure, the polymerization mechanism could involve a quinodimethane, an anionic intermediate, or a carbenoid species. Molar masses of soluble poly[(2,5-dialkoxyphenylene)vinylene]s, obtained by the polymerization of bis(chloromethyl) compounds with potassium *tert*-butoxide, are comparable with those obtained by the sulfonium precursor route.

Scheme 4 shows the synthesis of the most studied dialkoxy-PPV: MEH-PPV (**14**).[84, 86] The branched side chain in MEH-PPV has a favorable effect on the solubility of the polymer—indeed, the polymer dissolves easily in solvents such as tetrahydrofuran, chloroform, or xylene. A related polymer **17** (OC_1C_{10}-PPV) with a 3,7-dimethyloctyloxy side chain has been been the subject of investigation by workers at Philips and Hoechst.[17]



13 **14** (red-orange)

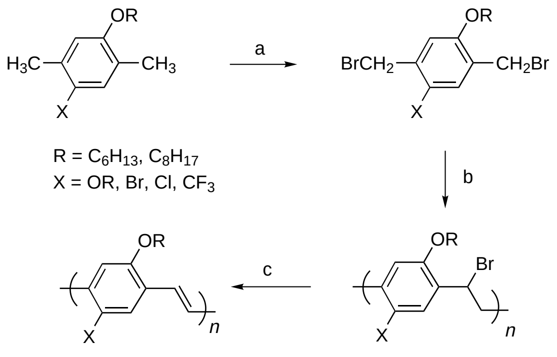
Scheme 4. Preparation of MEH-PPV (**14**): a) 3-(bromomethyl)heptane, KOH, EtOH, reflux, 16 h; b) HCHO, concd. HCl, dioxane, 20°C, 18 h, reflux, 4 h; c) KO*t*Bu, THF, 20°C, 24 h.

The bis(chloromethyl) compound **13** is synthesized by alkylation of 4-methoxyphenol followed by chloromethylation.[79, 83, 84, 86] Polymerization of the monomer **13** is induced with a tenfold excess of potassium *tert*-butoxide in tetrahydrofuran and gives the bright red-orange MEH-PPV (**14**). Careful control of concentration is needed to avoid gelation. Purification involves several reprecipitations in methanol. A simple electroluminescent device (ITO/MEH-PPV/Ca) already achieves a quite respectable efficiency of 1.0%.[79, 93] Insertion of a thin hole-blocking layer of poly(methyl methacrylate) film by Langmuir–Blodgett deposition is reported to give up to a fourfold increase in quantum efficiency with aluminum cathodes.[94] Devices have also been constructed with doped silicon as anode, thus opening the possibility of integrating polymer LEDs with silicon-chip technology.[95, 96]

Most of the reports of polymer LEDs described ITO on glass as the hole-injecting contact. Polyaniline (PANi), a long-known conducting polymer, presents an interesting alternative to ITO in devices using MEH-PPV, as, although it is deeply colored, it has an optical window coinciding with the maximum of emission for MEH-PPV. Using a layer of acid-doped PANi on ITO reduces the drive voltage of the device and causes an increase in device efficiency by a factor of 30%. Such devices can produce peak luminances of over 10000 cd m^{-2} at drive voltages of 5 V, with external quantum efficiencies of 2–2.5%, and luminous efficiencies of 3–4.5 lm W^{-1}.[97] Furthermore, replacement of the ITO-coated glass substrate by a polyaniline-coated PET sheet enables the manufacture of a flexible electroluminescent device.[83, 98] As the PET/PANi/MEH-PPV/Ca device consists of flexible polymers (with the exception of the calcium cathode), it can be safely deformed even during operation (inside a glove box). While this is an interesting application of PANi, it should be noted that ITO-coated PET is commercially available as an alternative flexible anode of reasonable mechanical stability.[36] A cylindrical polymer LED with layers of a transparent polyaniline electrode and MEH-PPV wrapped around a cylindrical metal cathode has been constructed; in this example the reactive electrode is protected by a sandwich of polymers.[99]

A significant recent development has been the introduction of a sulfonic acid-doped polyethylenedioxythiophene conducting polymer either in combination with ITO glass or alone as an anode. Quite spectacular improvements in device efficiency and reduction in drive voltage are observed in two-layer devices fabricated with this material.[100, 101] Gel-processing of a blend of MEH-PPV in polyethylene gives access to oriented films that show anisotropies of 60:1 in their fluorescence emission spectra; the preferred direction of emission is parallel to the draw axis.[102, 103] Rubbing alignment of a poly(dialkoxyphenylene vinylene) is the most effective way of orienting material to achieve polarized EL.[104, 326] Such oriented emission might find use for back-lighting in a liquid-crystal display. Orientation is also possible using Langmuir–Blodgett techniques for film deposition.[105]

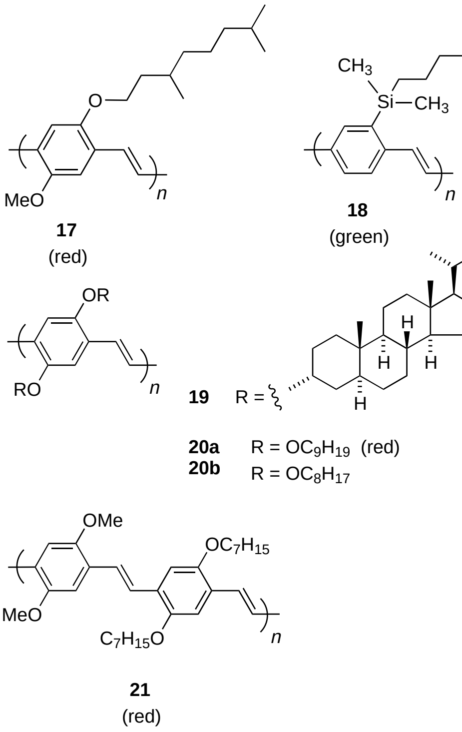
Electroluminescent poly(2,5-dialkoxy-1,4-phenylene vinylene)s other than MEH-PPV have been similarly prepared.[85, 86, 106, 107] If less than one equivalent of base is used, a soluble α-halo precursor polymer **16** is obtained that can be converted into the conjugated polymer **15** (Scheme 5)[85, 108]—this is known as the halo-precursor route and has some advantages if the precursor polymer is more soluble, if vapor deposition methods are used, or if incomplete conversion to a partially conjugated polymer is envisaged (Section 3.1.).



15 **16**

Scheme 5. The halo-precursor route to substituted PPVs: a) NBS, CCl_4, *hν*; b) KO*t*Bu, THF; c) 160–220°C, vacuum, 4 h.

Branched side chains, as in MEH-PPV, generally enhance solubility more than linear ones of identical length and number of carbon atoms or heteroatoms. With increasing size of the alkoxy group, EL efficiency passes though a maximum and decreases again with even larger side chains;[78] very large substituents, for example cholestanoxy as in **19**,[106, 109] seem to overpower and "dilute" the semiconducting properties of the conjugated polymer (Scheme 6). The highest external EL efficiency reported to date for a single layer device using dialkoxy-substituted PPV derivatives is 2.1 % for a device made by Philips with **17**.[17] This polymer EL device has a luminance of 100 cd m^{-2} with a luminous efficiency of 3 lm W^{-1} at a drive voltage of 2.8 V. A group at Hoechst has achieved the same quantum efficiency and luminance with a flexible device using an ITO anode on PET, with a slightly lower luminous efficiency of 2 lm W^{-1} at a driving voltage of 3.4 V and a current density of 4.5 mA cm^{-2}.[17] The introduction of a silyl group as in DMOS-PPV (**18**) widens the band gap so as to give emission of green light.[110–114] Yoshino et al.[115] have employed poly(2,5-dinonyloxy-1,4-phenylene vinylene) (**20a**), which forms a nematic liquid-crystalline state upon melting. When cooled to room temperature, the polymer remains oriented and has a lower energy gap (2.08 eV) than in an unoriented film (2.21 eV) formed by casting from chloroform solution. Rubbing of a film of this material also induces molecular orientation, and gives rise to oriented electroluminescence.[116] This technique has also been applied to a smectic liquid-crystalline copolymer of distyrylbenzene linked by long chain polyester flexible spacer groups.[117]



Scheme 6. Examples of soluble, dialkoxy-substituted PPV derivatives.

Other polycondensations have been used to prepare soluble PPV derivatives. Wittig condensation of terephthaldicarboxaldehydes with arylene–bisphosphylidenes furnishes alternating PPV copolymers.[118] An alkoxy-substituted PPV copolymer (**21**) prepared in this manner was found to show orange (585 nm) emission.[118] Similar PPV copolymers have been prepared by Heck coupling of dihalobenzenes with divinylbenzenes.[119]

3. Improvement of Device Efficiency—Making EL Polymers Competitive

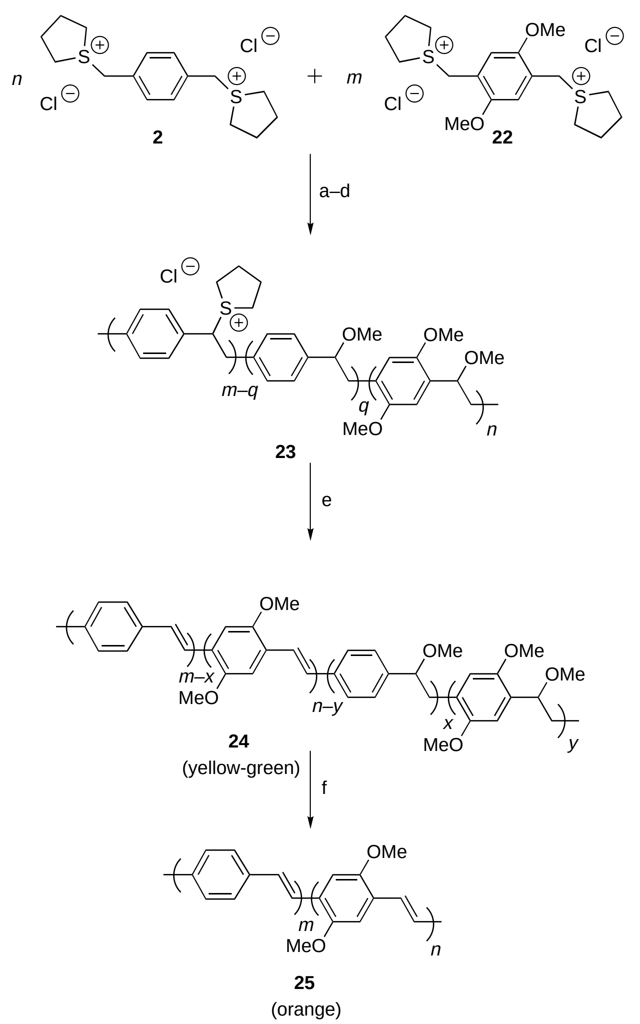
High efficiencies and reliability are the principle requirements of molecular and polymeric light-emitting materials for commercial applications.[19] The optimum goal is to obtain maximum power efficiency and brightness at minimum drive voltage and current density. This combination should afford devices having long lifetimes. The improvement of EL devices therefore requires optimization of the electroluminescent polymer and/or the device structure. Whereas it took about thirty years for an inorganic semiconductor to reach luminous efficiencies of several lm W^{-1}, organic light-emitting polymers have reached this level of performance in less than ten years. It is evident that the efficiencies of molecular and polymer organic LEDs have been dramatically improved in a short time, and are beginning to compete with those obtained for conventional inorganic LEDs.

3.1. The Use of Copolymers—Finessing the Properties

For the majority of conjugated polymers investigated so far, electron injection has proved to be more difficult than hole injection, that is, the polymers are more easily oxidized than reduced. This has been largely remedied by the use of metals with a low work-function (especially Ca) as the cathode material. However, calcium is highly susceptible to atmospheric degradation. Although this can be retarded by encapsulation, it would be beneficial to use less moisture- and oxygen-sensitive metals. If the barrier for electron injection from such metals is to be lowered, the polymer must be modified so that the energy of its LUMO matches the work function of the cathode. Copolymers of one kind or another present an attractive solution to this problem.

Copolymers containing a combination of different arylene units can be much more versatile than homopolymers and may even be chemically tuned to provide a range of materials with considerably improved EL properties. This was for the first time exemplified by statistical copolymers of PPV and poly[(2,5-dimethoxy-1,4-phenylene)vinylene], although other copolymers having interrupted conjugation have also been investigated.[57, 120–123]

By a modification of the sulfonium precursor route the two monomers **2** and **22** are copolymerized in the presence of sodium hydroxide in a water–methanol mixture (Scheme 7). The ratio of the units in the resulting (presumably statistical) copolymer **23** depends on the feed ratios of the two sulfonium salt monomers. The use of a solvent mixture leads to selective substitution of the sulfonio groups by methoxy groups. This occurs at a faster rate at those benzylic carbon atoms that are attached to the more activated dimethoxyphenylene rings. As a result, copolymer **23** has two leaving groups at the benzylic carbon atoms; the methoxy groups are adjacent to all the dimethoxyphenylene and a few phenylene units, and sulfonio

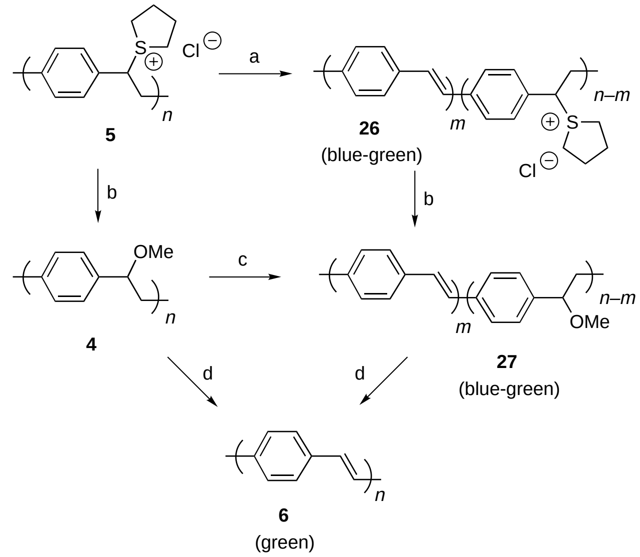


Scheme 7. Synthesis of PPV/dialkoxy-PPV copolymers: a) NaOH, MeOH/H_2O, 0 °C, 1 h; b) HCl; c) dialysis (water); d) MeOH; e) 220–300 °C, vacuum, 12 h; f) 220 °C, HCl(g)/Ar, 22 h.

groups are next to most of the phenylene units. Thermal conversion of thin (typical thickness 100 nm) films of **23** results in complete elimination of the sulfonio and only partial elimination of the methoxy leaving groups, which gives polymer **24** with interrupted conjugation. Complete elimination of all leaving groups to furnish the fully conjugated polymer **25** requires thermolysis under acidic conditions.

The electroluminescent device efficiency of polymer **24** varies with the composition of the copolymer and has its peak with a copolymer prepared from a 9:1 feed ratio of salts **2** and **22**. The maximum internal efficiency in this case is 0.3%, demonstrating a 30-fold improvement compared with that of PPV (0.01%) in the same device configuration (Al-Al_2O_3/polymer/Al).[120, 124] The shortening of the conjugated segments actually improves fluorescence yields and electroluminescence efficiency, probably originating from a reduction in nonradiative processes such as diffusion of the excited states to quenching sites. On the other hand, a large fraction of interruptions in the conjugated chain will lower the mobility of charged carriers. Somewhere in between lies an optimum for electroluminescence efficiency. The principle has been applied to other copolymers.[123] Alkoxy- and alkyl-substituted poly(phenylene vinylene)s prepared by the dehydrohalogenation route also yield interrupted copolymers having relatively high EL efficiencies.[123] In addition, statistical copolymer **23** has found use in forming lithographically patterned copolymers and waveguides.[120, 121]

A simple modification of the PPV synthesis gives access to PPV-derived blue-shifted light-emitting polymers with a high concentration of interruptions in the conjugated chain. Partial conversion of precursor homopolymers **4** or **5** produces statistical copolymers **26** and **27** with regions of saturated and unsaturated units (Scheme 8).[125, 126] The conversion of sulfonium precursor polymer **5** to **26** may be accomplished by either thermal or base treatment. Although **26** is prone to further elimination, Heeger et al. have found that conversion at 160 °C for 2 h gave a copolymer of the type **26** with fairly good long-term stability and emission efficiency.[127]



Scheme 8. Synthesis of partially conjugated PPV copolymers: a) Bu_4NOH, MeOH; b) MeOH, 50 °C; c) 300 °C, vacuum, 12 h; d) 220 °C, HCl(g)/Ar, 22 h.

Another approach to raising the efficiency of PPV is the introduction of disorder into the chain, thus interfering with polymer chain packing. Son et al.[128] have synthesized amorphous PPV by using a modified Wessling procedure with a xanthate leaving group. The resulting PPV has a mixture of *cis*- and *trans*-alkene units, which affects conjugation and interferes with packing. Internal efficiencies of up to 0.22% for single-layer devices with aluminum cathodes and 2% for double-layer devices using an electron-transporting layer (see Section 3.2) are reported. It is not clear whether the improvements in efficiency arise from interruptions to conjugation or from reduced intermolecular order owing to the presence of *Z* double bonds. The authors favor the latter explanation.

Hörhold et al have reported poly(arylene vinylene)/poly(phenylene vinylene) alternating copolymers in which the arylene substituent carries in-chain phenylamino groups. These have the effect of dramatically reducing the oxidation potential compared with that of PPV-based polymers (and are therefore photoconductors), and offer interesting possibilities as electroluminescent materials as well.[129]

3.2. Multilayer Devices—Raising Device Efficiency with Additional Charge-Transporting Layers

The electroluminescent conjugated polymer devices discussed so far were mostly single layer devices, that is, they have the conjugated polymer sandwiched directly between anode (high work-function electrode) and cathode (low work-function electrode). Unless the barriers between these contacts and the HOMO (or LUMO) of the polymer are identical or zero, one type of charge carrier (either holes or electrons) will be preferentially injected. For a discussion of factors affecting charge injection the reader is referred to the article by Blom et al.[130] and the excellent reviews by Greenham and Friend,[14] and Sheats et al.[19].

For PPV, the injection of holes predominates. To increase the efficiency of devices, electron injection has to be significantly boosted. The use of certain additional layer(s) of materials can promote the passage of electrons through the layer and, at the same time, provides a barrier to the passage of holes. Such a layer is called an electron-conducting/hole-blocking (ECHB) layer. A suitable ECHB material should have an electron affinity equal to or greater than the electron affinity of PPV. As illustrated by Figure 3, holes are increasingly confined in the PPV layer, and the site of recombination of holes and electrons (where the emission takes place) is then moved away from the metal–polymer interface, which is known to act as a quenching site. In contrast, hole injection is not a problem with devices made from PPV. When a device with a hole-transporting layer (between the anode and the PPV layer) was tested, the efficiency of the device actually decreased, indicating that the main limiting factor in PPV-based LEDs is indeed electron injection and transport.[131]

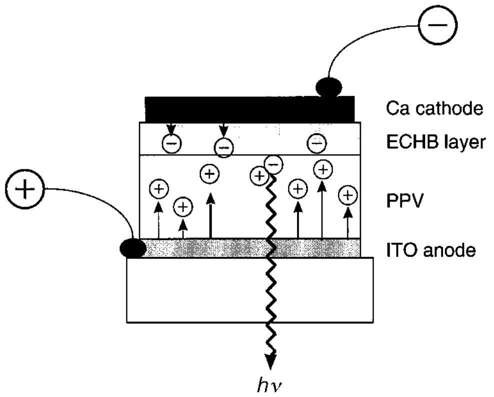
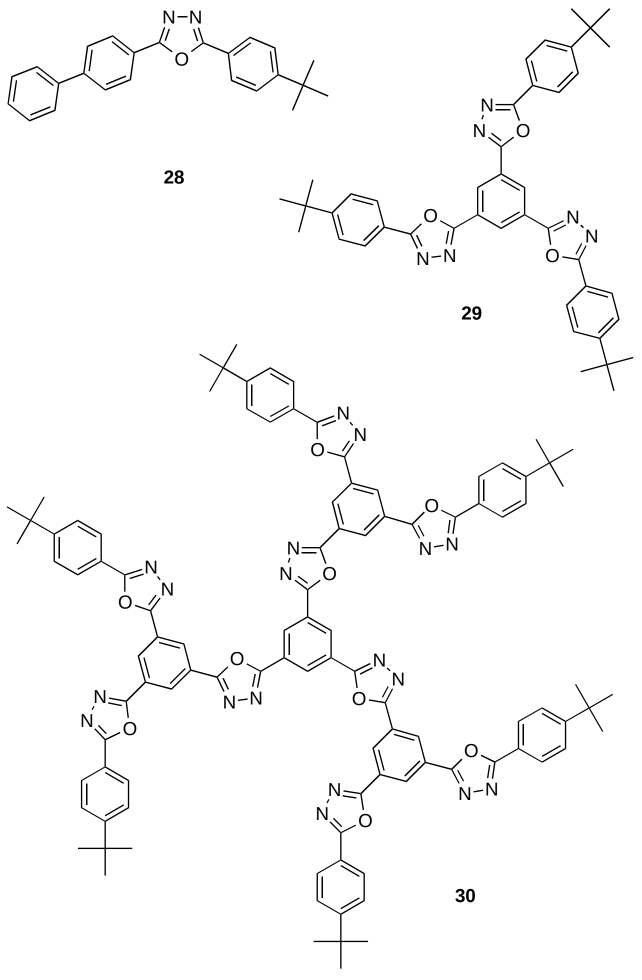


Figure 3. In this improved bilayer device structure for a polymer LED an extra ECHB layer has been inserted between the PPV and the cathode metal. The ECHB material enhances the flow of electrons but resists oxidation. Electrons and holes then accumulate near the PPV/ECHB layer interface. Charge recombination and photon generation occur in the PPV layer and away from the cathode.

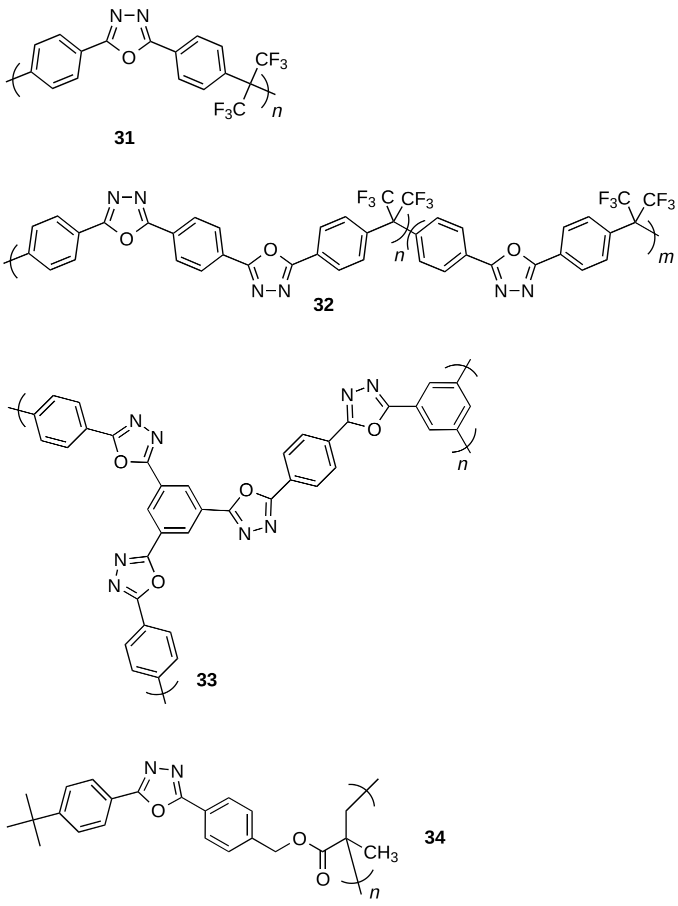
The principle behind the design of ECHB materials is well exemplified by oxadiazoles, the first and most extensively investigated class of ECHB materials. Following the successful use of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (**28**) in sublimed film EL devices,[3, 4] PBD has long been a favored compound (Scheme 9). Oxadiazoles are electron-deficient, making PBD an extremely poor hole acceptor. It has a number of advantages: it is available in high purity, sublimes, can be spin-coated as a dispersion in a range of standard polymers such as poly(methyl methacrylate) (PMMA),[68] and can be blended with electroluminescent polymers.[112, 132–134] However, some incompatibilities with polymers exist that may lead to phase separation or crystallization especially at higher temperatures. Crystallization may be retarded by using a solid dispersion of PBD in an insulating polymer (PMMA).[68] As the ITO/PPV/PBD-PMMA/Ca device then becomes thicker owing to the extra layer, the voltage required to drive the device needs to be increased. This drawback is outweighed by a rise in internal EL efficiency from 0.1% (for an ITO/PPV/Ca device) to 0.8% (for ITO/PPV/PBD-PMMA/Ca). However, higher current densities cause a drop in device efficiency as a result of quenching by the high amount of accumulated holes at the PPV/PBD-PMMA interface.



Scheme 9. Examples of oxadiazole-containing electron-transporting materials.

The incorporation of identical redox sites within the same molecule has been used successfully in the design of charge-transporting compounds for electrophotography (photocopiers and laser printers). Since electron hopping is the main charge-transport mechanism in ECHB materials, increasing the number of (in this case) oxadiazole units would therefore seem a promising way to improve the charge-transporting properties.[135] The idea was extended to the design of branched and highly symmetrical compounds such as the radialene **29**,[136] starburst structures,[137, 138] and small dendrimers like **30**.[138, 139] These materials have high glass-transition temperatures and form stable glasses, which minimize the problems of crystallization. Although the large numbers of branches in these materials should have made electron-transfer more efficient because of enhanced charge migration opportunities, they have not shown any improvement over PBD.

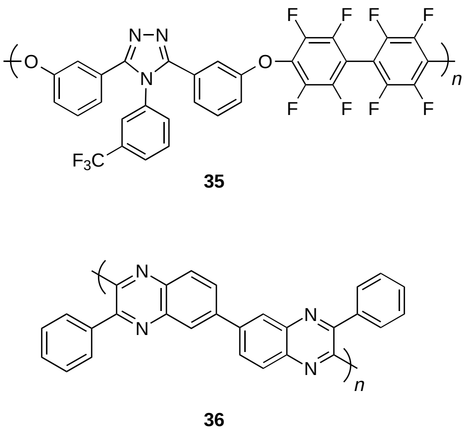
While low molar mass compounds are much easier to purify, incorporation of the active electron-transporting moieties into amorphous polymers should at least mitigate the problem of crystallization. Several polymeric analogs of PBD have been prepared with the oxadiazole unit either in the main or the side chain. A number of examples of poly(aromatic oxadiazole)s with satisfactory performance have been reported.[70, 72, 77, 136, 140] Solubility is mainly influenced by the frequency of solubilizing flexible spacer groups as in **31**, or the use of copolymer structures as in **32** (Scheme 10). A hyperbranched oxadiazole polymer **33**, which is soluble in trifluoroacetic acid, was prepared by a one-step procedure, but its electron-transporting properties were mediocre, perhaps caused by defects within the polymer.[136]



Scheme 10. Examples of oxadiazole-containing electron-transporting polymers.

Poly(methacrylate)s with ECHB-active oxadiazole side chains (e. g., **34**) have been prepared by radical polymerization and show good film-forming properties.[77, 141–143] However, their device performance has not fulfilled expectations, as higher drive voltages are required to achieve the improvement in efficiency.

Since oxadiazoles have not proved entirely successful as ECHB materials, attention has turned to other classes of materials. Nitrogen heterocycles such as 1,2,4-triazoles, 1,3,5-triazines,[325] or quinoxalines are of particular recent interest. The turn-on voltage in devices with an ECHB layer consisting of the polymer **35**, which contains a 1,2,4-triazole unit, is surprisingly unaltered from LEDs without an electron-transporting layer (Scheme 11).[69, 76] The electron-deficient nitrogen atoms in poly(phenyl quinoxaline) (**36**) also enhance the electron affinity of the polymer. This material has been shown to greatly enhance the efficiency of devices that use soluble PPV derivatives.[144] The materials discussed above have undoubtedly made a significant contribution towards improvement in device efficiency. A more successful approach may be to increase the electron affinity of the emissive polymer as will be discussed in Section 4.



Scheme 11. Examples of a triazole- and a quinoxaline-containing electron-transporting polymer.

3.3. Multilayer Devices with More Than One Electroluminescent Polymer—Towards White Light Emission

Other multilayer devices than those discussed in Section 3.2 can be constructed from at least two electroluminescent polymers. If carefully chosen, they show light emission from more than one layer provided that the polymers have small and controlled variations in energy gap from one layer to the next. This is necessary to avoid any build-up of space-charge at the interfaces between polymer layers. The first example of this type of LED consisted of an ITO/MEH-PPV/PPV/copolymer **24**/Ca device.[81] When one polymer is coated on top of another polymer layer, it is important that the process does not cause swelling or dissolution of the already deposited layer, and that good quality interfaces are obtained. Since

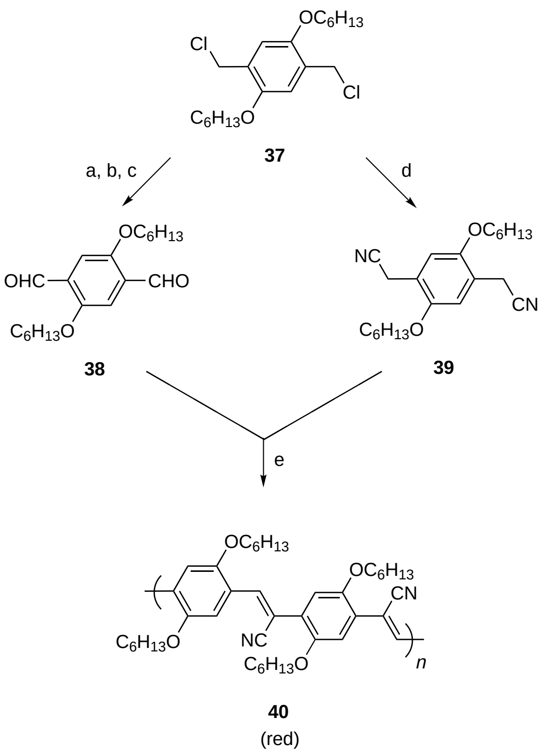
PPV and the sulfonium copolymer precursors are insoluble in chloroform, and MEH-PPV is insoluble in methanol, such a multilayer structure could be produced by spin-coating successive layers onto ITO without intermixing between MEH-PPV and the precursor layers. The precursor polymers **5** and **23** were then converted into the conjugated polymers and, after deposition of calcium, the device emitted orange light with the emission spectrum stretching from 800 nm (1.55 eV) through to 490 nm (2.5 eV). It was therefore concluded that electroluminescence occurred from both the red-light-emitting MEH-PPV, which was furthest away from the cathode, and from PPV, which showed yellow-green EL. The broadening of the emission spectrum further suggested how, in principle, to fabricate a white light source from a sandwich of several EL layers. A more recent multilayer device design developed by Yoshino et al.[145–147] uses layers of the blue-emitting polymer **75a** and of red-emitting materials such as the poly(3-alkylthiophene) **49a** separated by a charge-transport layer. Depending on the bias either red or blue light is emitted, while under alternating current bias emission from both materials is observed.

4. Polymers with Higher Electron Affinity—Luminescent Transport Layers

The ideal light-emitting polymer should be both fluorescent and avoid the need for an extra electron-transporting material. It should also function with cathode metals other than calcium. Calculations[148] have shown that a cyano substituent (and presumably other electron-withdrawing groups) on the ring or vinylene moiety of PPV lowers the HOMO and LUMO energies and increases the electron affinity of the polymer, thus improving the efficiency of electron injection and the potential efficiency of a polymer LED. Unfortunately, the Wessling (quinodimethane) route to poly(arylene vinylene)s is unsatisfactory when electron-withdrawing substituents are involved, and alternative polymerization or polycondensation methods need to be employed.

4.1. CN-PPV—Highly Luminescent Electron-Deficient Polymers

CN-PPV (**40**), a dialkoxy-substituted PPV derivative with cyano-groups on the vinylene units should be regarded as an alternating copolymer in this context. It is readily available by a Knoevenagel condensation[149] between equimolar amounts of the terephthaldehyde **38** and the benzene-1,4-diacetonitrile derivative **39**, both obtained from the same starting material **37**. The condensation reaction takes place upon addition of excess tetrabutylammonium hydroxide (or potassium *tert*-butoxide) in a tetrahydrofuran/*tert*-butanol mixture at 50°C (Scheme 12).[150] Polymer **40** precipitates and can be easily isolated. Careful control of reaction conditions is required to avoid Michael additions (and consequently crosslinking), which may lead to polymers with inferior EL properties, and purification by reprecipitation is essential to obtain high quality polymer. CN-PPV is a brilliant red, fluorescent material with a molar mass typical for polycondensates.



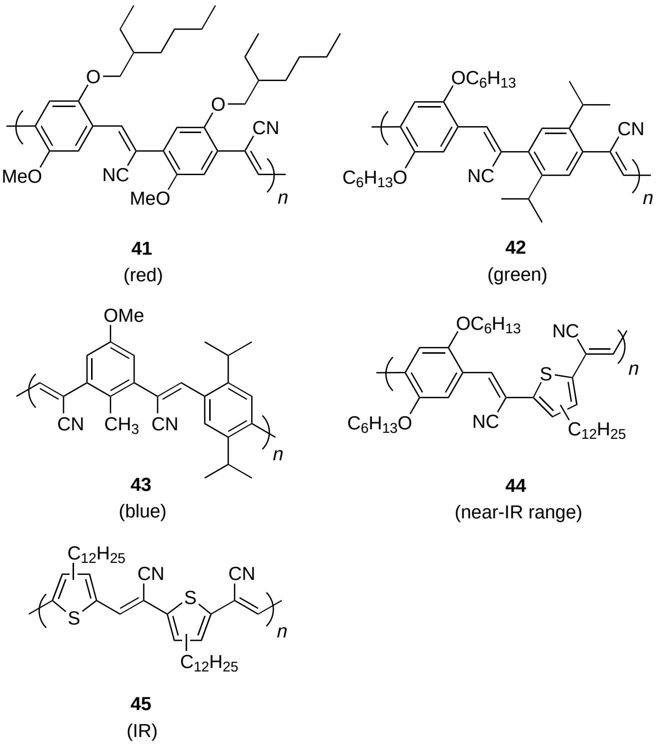
Scheme 12. Synthesis of CN-PPV (**40**): a) NaOAc; b) KOH, EtOH; c) pyridinium chlorochromate; d) NaCN; e) KO*t*Bu or Bu_4NOH, *t*BuOH, THF, 50°C.

The HOMO–LUMO gap of CN-PPV (590 nm; 2.1 eV) is mainly determined by the effect of the alkoxy substituents, which also serve to promote solubility in chloroform, and thus ensure processibility of the conjugated polymer; the cyano substituents contribute only to an increase in the electron affinity of the polymer compared with PPV. Cyclic voltammetry studies show that the cyano groups shift the onset of reduction by about 0.6 V.[136] The low HOMO–LUMO gap of CN-PPV also indicates that the nitrile groups do not introduce any significant steric torsion in the conjugated poly(2,5-dialkoxyphenylene vinylene) chain.

Internal efficiencies of red-emitting ITO/CN-PPV/cathode devices can reach 0.2% with calcium as well as aluminum cathodes. This is particularly noteworthy because other conjugated polymers such as PPV suffer from at least a tenfold reduction in efficiency when the electron-injecting contact is changed from Ca to Al. Since CN-PPV shows much higher electron affinity than PPV owing to the introduction of cyano groups, the device efficiency is now determined by hole injection at the ITO electrode. As a result of this, the introduction of a hole-transporting layer improves EL efficiencies considerably. PPV is a suitable hole-transporting polymer, and CN-PPV can be easily spin-coated on top of an insoluble PPV layer. Two-layer electroluminescent ITO/PPV/CN-PPV/cathode metal devices operate with very high internal (4%) efficiencies.[151, 152] Significant lifetimes were only observed with high-quality polymer, demonstrating once more the importance of purification. The emission ($\lambda_{max} =$

710 nm) occurs exclusively from the lower energy CN-PPV, with no evidence of electroluminescence from the PPV layer. Although this appears to be in contrast to the multilayer devices discussed in Section 3.3, CN-PPV apparently acts more like a sink for charge carriers and excited states rather than to permit any emission from another EL polymer (namely PPV) to occur.

The synthetic route is extremely flexible and lends itself to considerable variation, enabling the synthesis of many other α-cyano PPV derivatives (Scheme 13).[123, 153] Some of these show similarly high emission efficiencies in double-layer devices with PPV.[12, 154] In particular, MEH-CN-PPV (**41**) is processible in solvents such as toluene and exhibits very high EL device efficiencies. The improvement in processibility clearly contributes significantly to the improved device efficiency. A double layer device ITO/PPV/**41**/Al produces red-orange (600 nm) light with a power efficiency of 5 cd A^{-1} corresponding to a luminous intensity of over 1000 cd m^{-2} at a drive voltage of 6 V.[12, 154] This corresponds to a luminous efficiency of 2.5 lm W^{-1}.

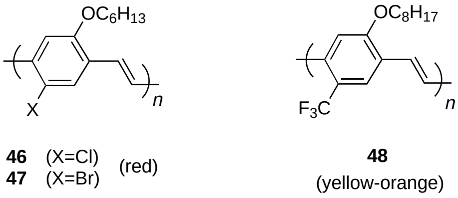


Scheme 13. Color range available for CN-PPV derivatives.

Color variations over a wide range of wavelengths have been demonstrated. The bulky isopropyl substituents of **42** cause a blue-shift and green light emission (510 nm), while incorporation of *meta*-linkages, as exemplified by those in **43**, results in blue fluorescence. The thiophene group in **44** reduces the HOMO – LUMO energy gap to 1.75 eV (740 nm), and the polymer shows substantial emission in the near infrared region. An ITO/PPV/**44**/Al device was the first polymer-based IR-emitting LED.[155] Replacement of both arylene rings with thiophene groups in **45** reduces the energy gap even further to 1.56 eV (800 nm).[153, 156]

4.2. Other High-Electron-Affinity PPV Derivatives—Electron-Deficient Building Blocks

Apart from CN-PPV, other PPV derivatives with electron-withdrawing substituents, this time on the arylene ring, have been investigated for EL applications (Scheme 14). Poly(phenylene vinylene)s **46** and **47** bearing halide and alkoxy groups on the ring are accessible through the Wessling method.[157] High molar masses required rigorous purification of the monomers and optimization of the polymerization conditions. We have found that PPV derivatives with bromo (**47**)[158] or trifluoromethyl (**48**) substituents[159, 160] can be readily obtained by a bromo-precursor route (see Scheme 5) or by Horner – Wittig polycondensation.[159] Polymer **48** in particular shows higher electron affinities than PPV. The halogen-substituted PPVs **46** and **47** were found to emit red (λ_{max} = 620 – 630 nm) light,[157] while the trifluoromethyl derivative **48** emits yellow to yellow-orange (λ_{max} = 540 – 570 nm) light. The PL quantum yields for **48** are much lower than for PPV and single-layer devices gave only weak emission, and EL internal efficiencies reached 0.01 % in double-layer devices with PPV as hole-injecting layer and Al as cathode.[160, 161] In view of their poor PL quantum yields these materials are more likely to prove useful as ECHB than as emissive materials.



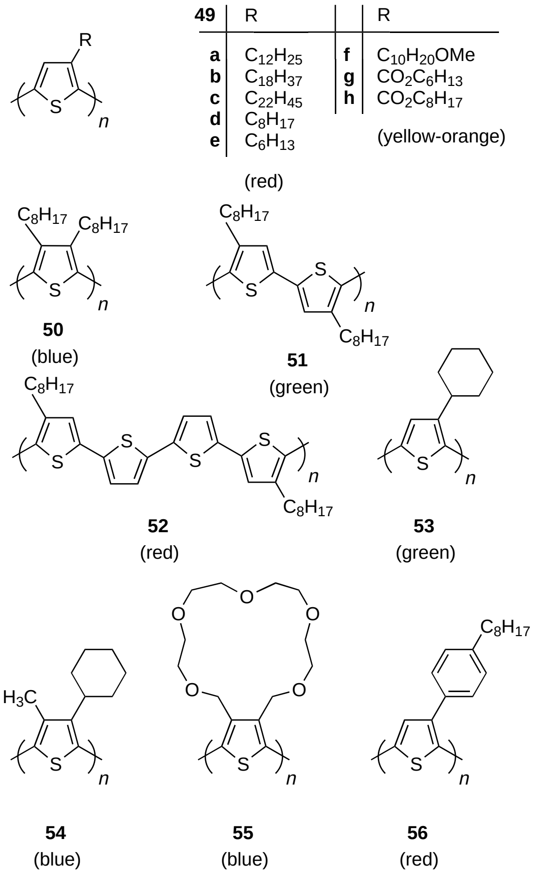
Scheme 14. High-electron-affinity PPV derivatives with electron-withdrawing groups on the aromatic ring.

5. Color Tuning—Varying the HOMO – LUMO Gap

A major advantage of polymers as EL materials is the ease with which their structures can be altered, thus enabling the chemist to tune the properties by modifying their structures. In this section we wish to illustrate both the wide range of polymer structures, which can be used for EL purposes, and also to show how the properties, especially the emission color, can be adjusted by varying the aromatic ring, the substituents, and the regioregularity of the conjugated polymer.

5.1. Poly(3-alkylthiophene)s—A Good Red

Poly(3-alkylthiophene)s provide a good example of how the color of emission can be varied in polymer LEDs by modifying both the polymer structure and the design of the devices (Scheme 15). Soluble poly(3-alkylthiophene)s **49** are readily prepared by the polymerization of the corresponding

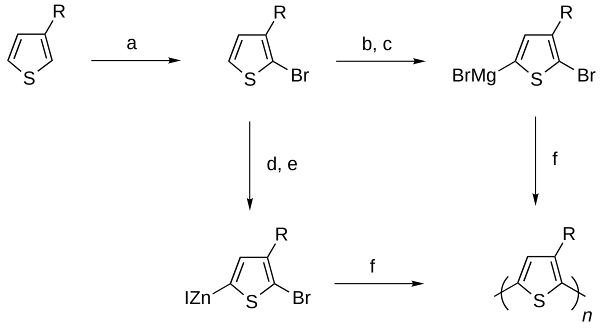


Scheme 15. Poly(alkylthiophene) derivatives and their emission color range.

3-alkylthiophene monomers in the presence of excess ferric chloride,[162] or by nickel-catalyzed coupling of dihalothiophenes with thiophene-bis(magnesium halide)s.[163, 164] Red electroluminescence (emission maxima at about 640 nm) from **49a–e**, which have alkyl chain lengths varying from 6 to 22 carbon atoms, has been reported by various groups.[165–169] The emission intensity became larger with increasing chain length, possibly owing to the improved confinement of excitons. Homopolymers based on 3-alkylthiophenes exhibit good red color purity, but they tend to have rather low fluorescence quantum yields. The use of charge carrier confinement layers[166] or doping with fluorescent dye materials[170] markedly increases device efficiency. Substitution of the hydrocarbon side chains as in **49f–h**[171, 172] produced a slight blue shift in the emission maximum and gave yellow-orange emission.

The emission frequency depends considerably on the nature and regularity of the side chains on the polymers. Hadziioannou et al.[173] studied alkylated polythiophenes **50–52** and reported that there was a correlation between their emission maximum and the inverse number of thiophenes between two consecutive head-to-head (2,2′-coupled) dyads. Thus the polymer **50** showed an emission maximum at 460 nm (2.7 eV), while **51** and **52** had emission maxima at 530 (2.35 eV) and 550 nm (2.25 eV), respectively. Similarly, the emission maximum for Holdcroft and Xu's[174, 175] poly(3-hexylthiophene) (**49e**) was blue-shifted with increasing amounts of head-to-head dyads. Similar blue shifts can be obtained by introducing bulky substituents; the cyclohexyl substituted polythiophene **53** has its emission maximum in the green (555 nm).[176–178] Blue emission can be obtained by substitution at both the 3- and 4-positions as in **54** (460 nm)[177–179] or **55** (470 nm).[180] Bilayer devices containing the 4-octylphenyl-substituted poly[α,α'-bithienyl] analogue of **56** and a thick layer of PBD **28** emit white light due to the simultaneous emission of three colors.[181] The red and green emission can be suppressed in favor of near ultraviolet emission (397 nm) for a device using a blend of the polythiophene **56** and **28** with a further layer of **28** as emissive material.[134] The blue shifts can be attributed to the twisting of the conjugated backbone out of coplanarity due to the bulky substituents.

Greater control of emission colors requires the ability to control polymer regioregularity. When thiophenes are polymerized with ferric chloride or by Grignard coupling reactions, the resulting polymers are regiorandom, with a preponderance of head-to-tail (2,5′-) coupling, varying from 52 to 80 % according to the method used.[164] Some control can be obtained in specific cases. For example, coupling of oligomeric alkylthiophenes results in regioregular copolymers,[173, 182] while polymerization of a 3-arylthiophene with ferric chloride under carefully controlled conditions can give high-molecular-weight, regioregular (94 % head-to-tail) polymers such as **56**[183] because the aryl group preferentially stabilizes the cationic charge in the intermediates at the 2-position. More general routes for the synthesis of regioregular (head-to-tail) poly(3-alkylthiophene)s have been developed by McCullough et al.[184–187] and Rieke et al.,[188, 189] who utilized nickel-catalyzed coupling of 2-halo-5-metallothiophenes (Scheme 16). These routes require extremely pure monomers for high molecular weights to be produced.



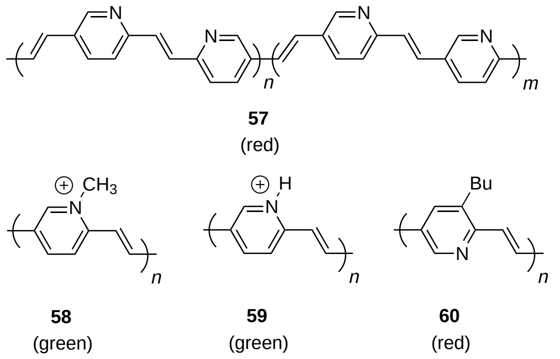
Scheme 16. Routes to regioregular poly(3-alkylthiophene)s: a) Br_2, HOAc, 15 °C; b) LiN*i*Pr$_2$, −40 °C; c) $MgBr_2$, diethyl ether, −40 °C; d) I_2, HNO_3, CH_2Cl_2; e) Rieke zinc; f) $[Ni(Ph_2PCH_2CH_2PPh_2)]Cl_2$ or $[Ni\{Ph_2PCH_2CH(CH_3)PPh_2\}]Cl_2$.

High regioregularity and a minimum amount of head-to-head dyads greatly influence the color of emission, and it is no surprise that the UV/Vis absorption spectrum of regioregular poly(3-hexylthiophene) (**49e**) indicates a longer conjugation length than observed for the corresponding regiorandom material.[190] McCullough et al. found that regioregular **49e** also showed a higher EL quantum efficiency than its regiorandom counterpart.[191] Comparison of regioregular and regiorandom **49a** and **49e** prepared by us, however, showed no significant differences in their emission spectra or efficiencies.[192, 193]

The emissive properties of regioregular statistical copolymers can be tuned by varying the length of the alkyl side chain and the relative ratios of the organometallic monomers.[186, 194] We have also prepared poly(3-alkylthiophene) copolymers with side chains containing terminal azide groups which have enabled us to cross-link the deposited films so as to produce insoluble materials for use in multilayer devices.[195] Polarized emission from stretch-oriented polythiophenes has been observed.[196] An oriented film of poly[3-(10-methoxydecyl)thiophene] (**49f**) has been deposited by Langmuir–Blodgett techniques and shown to emit polarized electroluminescence.[197]

5.2. Electron-Deficient Aromatic Rings

Color control by alteration of substituents and regioregularity is also illustrated by the pyridine-based analogue **57** of PPV and its derivatives (Scheme 17). Stille coupling of 2,5-dibromopyridine and 1,2-bis(tributylstannyl)ethylene [198] gives **57** as an orange powder that is soluble in *m*-cresol. Alkylation and protonation furnish the N-alkylated **58** and N-protonated **59** derivatives, respectively. Both are soluble in chloroform although **58** tends to decompose in the presence of nucleophiles. Coupling of 3-butyl-2,5-dibromopyridine gives the substituted polymer **60**,[199, 200] which is soluble in conventional organic solvents.



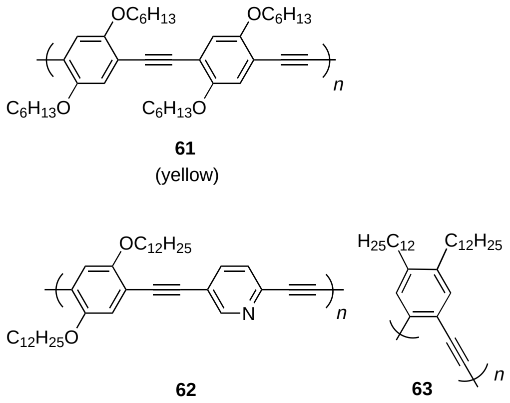
Scheme 17. Pyridine-based analogues of PPV.

The parent polymer **57** has a PL maximum in the red region (590 nm). The C-alkylated polymers **60** exhibit a red-shift to 630 nm, whereas a blue-shift to 540 nm is seen for the N-alkylated polymer **58**. Protonated polymer **59** has a more complex spectrum with emission maxima at 535 and 570 nm.

Owing to the lower symmetry of the pyridine ring, polymer **57** can exist in three regioisomeric forms: head-to-tail, head-to-head, and random. Swager et al.[201] have prepared the regioregular head-to-tail and head-to-head polymers and found that the three isomers show different UV/Vis absorption, PL, and EL emission spectra, with EL emission maxima of 575 nm (random), 584 nm (head-to-tail) and 605 nm (head-to-head).[202]

5.3. Poly(phenylene ethynylene)s—Stiffening the Polymer Chain

LEDs based on poly(phenylene ethynylene)s such as **61** (the dehydro-analogues of PPVs) are typically prepared by Sonogashira coupling of diethynylbenzenes and dihalobenzenes (Scheme 18).[203, 204] The synthesis and properties of poly(arylene ethynylene)s have recently been reviewed by Giesa.[205] Poly(phenylene ethynylene) **61** shows yellow emission with maxima around 600 nm,[203, 206, 207] whereas the corresponding dialkoxy-PPVs give rise to red or red-orange emission. Incorporation of a 2,5-pyridinediyl unit (**62**) gives a blue-shift and blue-green emission ($\lambda_{max} = 480$ nm).[208] Blue (410 nm) emission is obtained from poly(3,4-dialkyl-1,6-phenylene ethynylene)s **63**,[209] prepared by palladium cross-coupling reaction of a 3,4-dialkyl-1,6-diiodobenzene and a 3,4-dialkyl-1,6-diethynylbenzene. Steric interactions may cause twisting of the polymer chain which reduces the effective conjugation length, but other factors also probably contribute to the overall emission characteristics. The poly(phenylene ethynylene)s have received some attention in the patent literature, but have been generally rather disappointing in EL applications.



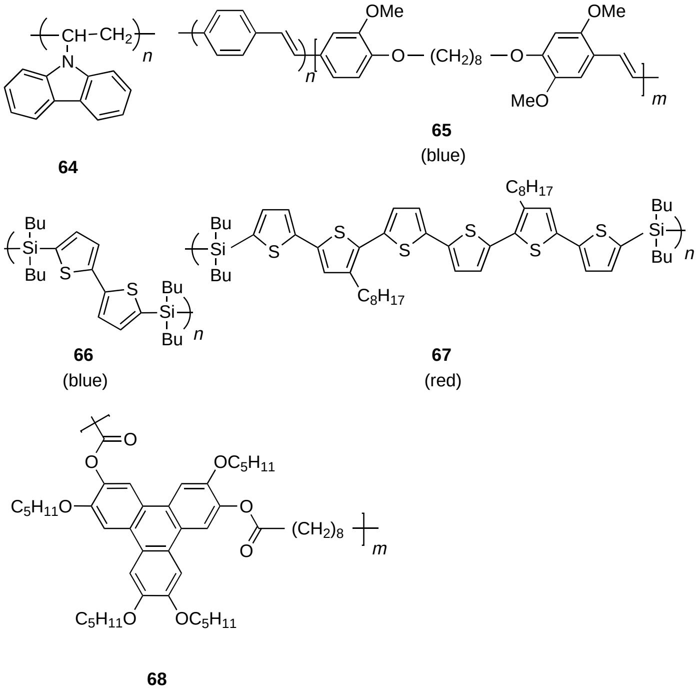
Scheme 18. Examples of poly(phenylene ethynylene)s.

5.4. Polymers with Isolated Chromophores—The Best of Both Worlds?

An alternative approach to designing a polymeric EL material is to blend a fluorescent dye in an inert polymer matrix such as polystyrene. Unfortunately, such blends often do not electroluminesce because the volume fraction of the electroactive species is too low. However, if an electroactive polymer such as poly(vinyl carbazole) (PVK) **64** is included, blends with tiny amounts of luminescent material can yield quite bright electroluminescent devices. An extension of this concept is to link the luminescent chromophore covalently to a polymer.

In polymers with isolated chromophores, the color is determined by altering the conjugation length of the chromophore. For example, Klavetter et al.[210] has prepared copolymers of type **65** by Wittig condensation using varying amounts of a flexible-chain dialdehyde and a bis-ylide

(Scheme 19). The emission peak of **65** ranges from 2.75 eV (460 nm) (blue) to 2.25 eV (550 nm) (yellow-green) depending on the amount of flexible linker content. Thus, the emission color can be easily altered by simply changing the comonomer feed ratio.



Scheme 19. Examples of polymers with isolated chromophores.

Hadziioannou et al. have prepared oligothiophene-dibutylsilane copolymers such as **66** or **67**[211–214] whose emission maxima range from blue (415 nm) for **66** to red (612 nm) for **67** according to the number of thiophene and silane units. The red-shift produced by increasing the number of silane units is slight and the emission color is mainly determined by the number of thiophene units. At present the advantages of the embedded chromophore polymers over the more traditional fully conjugated materials remain to be demonstrated.

Polymers that have special features of processibility in addition to high luminescent properties are particularly attractive. Much can be expected from improving supramolecular order. The recent work of Ringsdorf, Haarer et al. on discotic columnar phases involving triphenylene stacks shows much promise.[215] For example, the liquid-crystalline polymer **68** incorporating these structural features had a particular tendency to orient parallel to the film surface. Perhaps not surprisingly, this material showed steep current–voltage curves, low threshold fields, and high charge carrier mobilities.[216, 217]

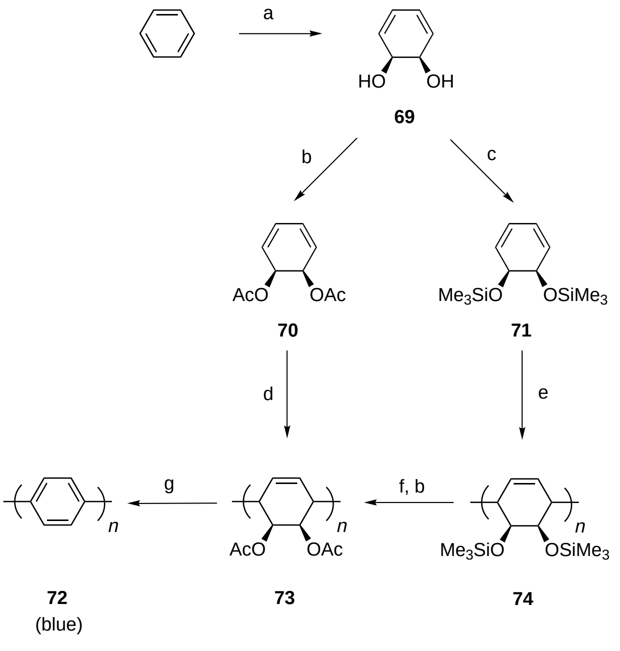
6. Blue Light-Emitting Polymers—The "Holy Grail"

The preceding sections outlined how a wide variety of conjugated electroluminescent polymers gives access to a whole range of emission colors. Multicolor display applications require at least three basic colors: red, green, and blue. Blue EL—already difficult to achieve with inorganic semiconductors—has been sought in conjugated polymers having a high HOMO–LUMO energy gap, and in copolymers containing high HOMO–LUMO, short conjugated segments. The search for a stable, highly efficient, bright blue light-emitting polymer continues. The following milestones have been passed.

6.1. Poly(*para*-phenylene)s—The Blue Paradigm

The design of blue-emitting electroluminescent polymers based on PPV-type materials with interrupted conjugation (Section 3.1) suffers from the drawback that emission occurs usually from the more conjugated segments, and the emission spectrum is therefore broadened and red-shifted. The alternative use of short, defined PPV oligomers will be discussed in succeeding sections (6.2 and 6.3). High HOMO–LUMO gap polymers are required for blue light emission. The first blue-emitting ($\lambda_{max} = 470$ nm) polymer LED was made by Yoshino et al.[218] using poly(9,9-dihexylfluorene) (**75a**) by oxidative coupling of the fluorene monomer with ferric chloride.[219, 220] This material has a poly(*para*-phenylene) (PPP) backbone, and derivatives of PPP **72** have been the focus of much research into the development of blue-emitting polymers. Higher polyarylenes have been little studied, possibly owing to the difficulties associated with their synthesis.

Leising et al.[221, 222] were the first to describe the use of PPP **72** as a blue light emitter [$\lambda_{max} = 459$ nm (2.7 eV)]. Like PPV, unsubstituted PPP is insoluble and not processible. Although films of oligomeric (9–10mer) poly(phenylene)s can be obtained by vacuum deposition,[223] the preparation of the polymer again requires suitable precursor routes (a topic recently reviewed by Gin and Conticello[224]). The original synthesis of unsubstituted PPP employs the ICI route based on *cis*-1,2-cyclohexadienediol (**69**) as starting material (Scheme 20).



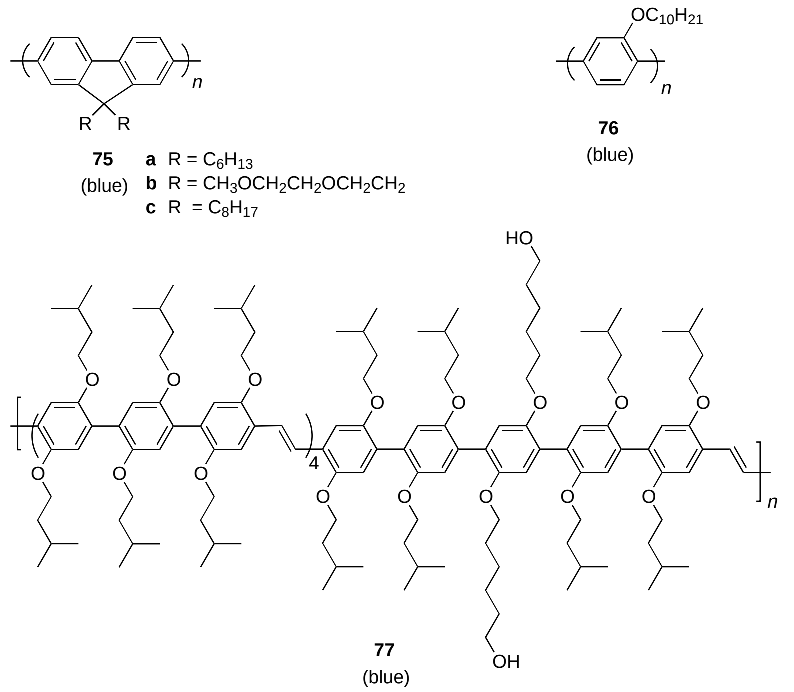
Scheme 20. Precursor routes to PPP (**72**): a) *Pseudomonas putida*; b) Ac_2O, pyridine; c) Me_3SiCl, DMAP, pyridine; d) azoisobutyronitrile AIBN, 70 °C; e) bis[(η^3-allyl)(trifluoroacetato)nickel(II)]; f) Bu_4NF, MeOH; g) 310–340 °C, Ar.

Radical-initiated polymerization of diacetate **70** furnishes the PPP precursor polymer **73**, which suffers from lack of stereoregularity and contains about 15% of 1,2-linkages.[225, 226] Thermal elimination of acetic acid finally gives the conjugated polymer **72** accompanied by some oligomer formation through chain scission. A number of other diesters have been polymerized by the same method (again with 10–15% of 1,2-linkages in the polymer) and thermally converted to PPP, of which the dimethyl carbonate and dipivaloyl esters yield the polymers with the highest molar masses.[227] Regioregular PPP is accessible through a nickel-catalyzed stereoregular polymerization of **71**. Despite the regioregularity and low polydispersity of the resulting polymer **74**, there are only limited reports on the electroluminescence of PPP derived from it.

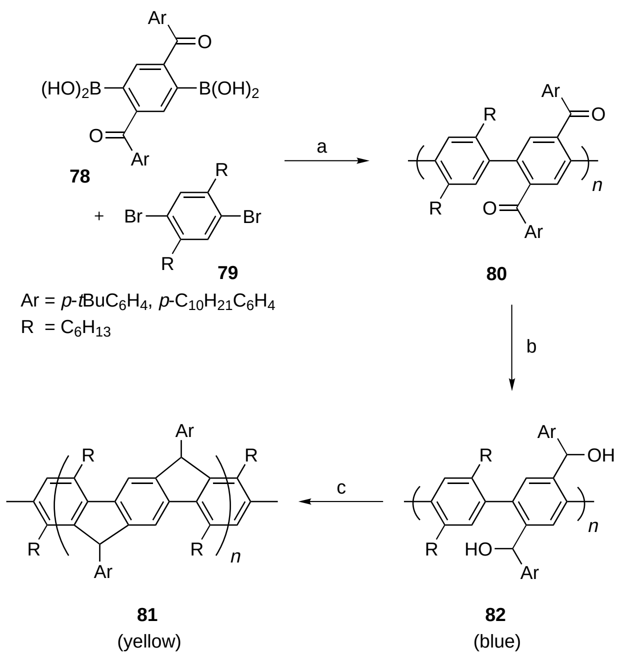
Much interest concentrates also on solution-processible poly(*para*-phenylene)s made soluble by suitable alkyl, aryl, alkoxy, or perfluoroalkyl[228] solubilizing groups. PPP derivatives with solubilizing alkyl side chains are the most important, and these are available through transition-metal-catalyzed polycondensations (reviewed by Schlüter and Wegner[229]), especially the Suzuki coupling of arylboronic acids and bromoarenes (optimized by Wegner et al.[230–232]), and the nickel-catalyzed coupling of substituted dihalobenzenes (reviewed by Yamamoto[233]), hydroquinone bistriflates,[234] or bis(mesylates).[235, 236] Although the degree of polymerization is usually rather limited, the molar masses of the polycondensates are sufficiently high (above 10000 g mol^{-1}) to form robust films for EL applications by spin-coating from solution. Various groups have used the resulting polymeric materials to make blue-emitting LEDs.[105, 237–242] The best devices so far reported have used the decyloxy derivative **76** (Scheme 21). External efficiencies of up to 3% have been achieved for double layer devices ITO/PVK/**76**/Ca, and of 0.8% with other, more air-stable, metal cathodes.[240] Polarized emission has been obtained from a device using an oriented Langmuir–Blodgett film of a dialkoxy PPP derivative.[105] Internal efficiencies of 4% have been measured for blue-emitting (460 nm) devices using the copolymer **77**, containing alternating terphenylene vinylene and quinquephenylene vinylene units, with calcium electrodes.[243]

The inclusion of solubilizing side groups on the PPP backbone has the drawback that the additional substituents twist the substituted phenylene rings considerably out of plane. This drastically decreases the interaction of the aromatic π-electron system, and an unwanted additional blue-shift in the emission spectrum compared with that for PPP is usually accompanied by a drop in fluorescence quantum yield. The twist cannot occur if the PPP backbone is planarized by incorporation into a ladder polymer. Scherf and Müllen were the first to show that structurally regular ladder-type polymers can be derived from a two-step route in which a soluble poly(*para*-phenylene) is prepared by a Suzuki aryl–aryl coupling of monomers **78** and **79**. After reduction of **80**, the resulting precursor polymer **82** is then subjected to another polymer-analogous intramolecular Friedel–Crafts ring-closing reaction to give **81**. The ladder formation occurs with surprisingly high regularity, and no indications of defects such as cross-linking or incomplete cyclization were found (Scheme 22).[244, 245] Molar masses of the structurally well-defined, soluble, ladder-type poly(para-phenylene)s (LPPPs) **81** are typically up to 20000 g mol^{-1}. The phenylene rings in the ladder polymers are almost planar and the homopolymer shows a broad emission between 650 and 450 nm in the solid state, in contrast to the polymer's sharp fluorescence emission around 450 nm in solution. The large Stokes shift (leading to yellow instead of blue light emission) is especially enhanced after annealing, and has been attributed to the formation of excimers owing to interchain interactions and π-stacking between the planarized conjugated segments.[246–249]

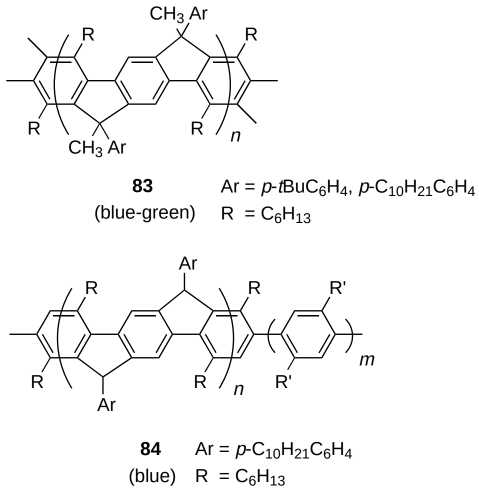
In some cases, blue emission has been observed from LPPP films but it remained unstable over time, again a result of the formation of yellow-emitting aggregates.[248] Slight structural variations have been suggested to inhibit the aggregation of planarized ladder-PPPs. After introduction of a methyl group at the methine bridge, the resulting ladder polymer **83**[250] shows stable blue-green emission with external efficiencies of up to 4% (Scheme 23).[251–253] Even more productive are random interruptions in the conjugated chain. In statistical copolymers **84**, called "step-ladder" copolymers, the conjugated chain is disrupted because the LPPP segments are connected by twisted oligophenylene spacers. These copolymers give stable films which remain blue-emitting even after annealing.[248] Pure blue emission with 0.1% internal efficiency can also be accomplished by diluting the ladder homopolymer (1–10 weight%) in a poly(vinylcarbazole) **64** hole-transporting poly-



Scheme 21. Examples of soluble PPP derivatives.



Scheme 22. Synthesis of ladder-PPP (**81**): a) $[Pd(PPh_3)_4]$; b) $LiAlH_4$; c) BF_3.

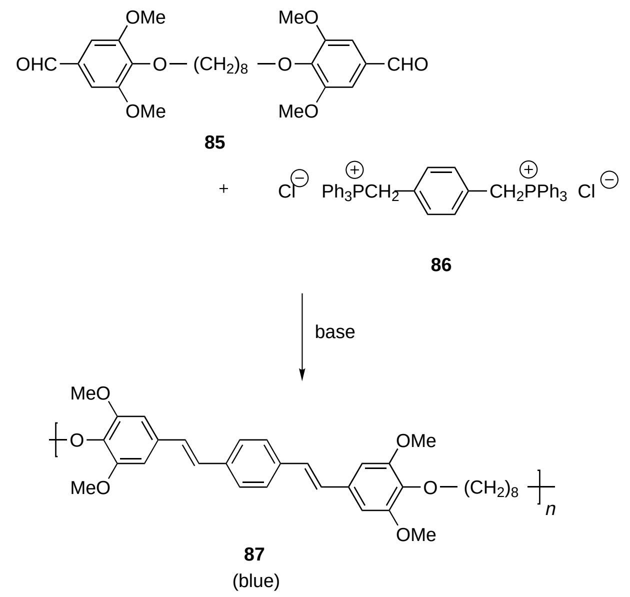


Scheme 23. Examples of blue-emitting, ladder-type PPP derivatives.

mer matrix.[254] This presumably inhibits aggregation. The above-mentioned poly(9,9-dihexylfluorene) (**75a**)[168, 218, 255] has a structure halfway between PPP and LPPP. A similar derivative BDOH-PF (**75b**) has been prepared by Pei and Yang.[256] Very little lifetime data is available for these materials as their development is in its infancy. However, the polyfluorene derivative **75c** has shown considerable promise in a number of applications.[257]

6.2. Polymers with Isolated Main-Chain Chromophores—Polycondensates by Wittig Reaction

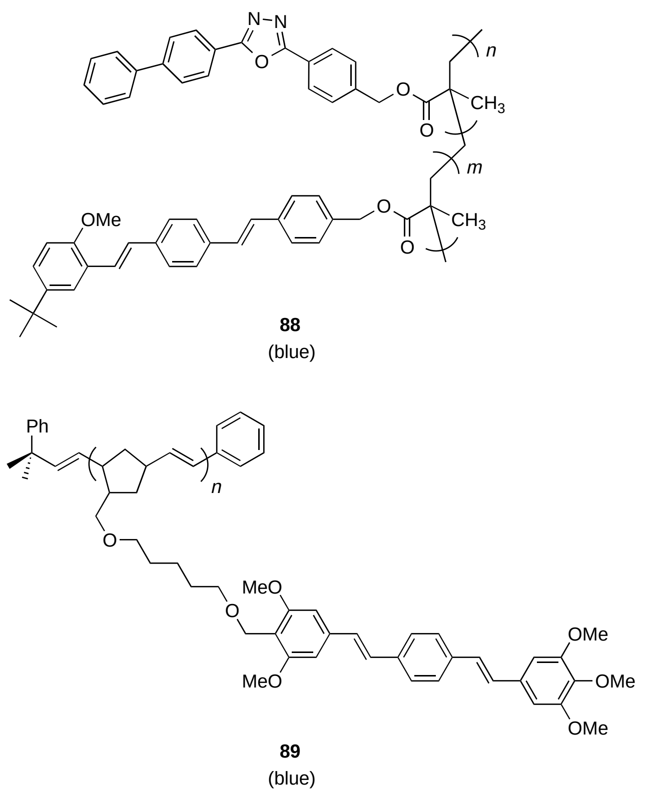
Since the wavelength of the emitted light is dependent on the conjugation length of the chromophore, lowering this length will result in a blue-shift in the emission. One way to achieve a blue-emitting polymer, therefore, is to interrupt the conjugation of the polymer at short intervals with nonconjugated segments in between. As was discussed in Section 3.1 above, simple modification of the PPV synthesis gives access to PPV-derived blue light-emitting polymers with a high concentration of a fluorescent chromophore and, at the same time, with a statistical range of short conjugation lengths (see Scheme 8). This method, however, only allows limited control of the conjugation length. Another way to polymers with well-defined fluorescent π-electron systems makes use of a Wittig condensation of an arylene bisphosphonium salt **86** with a bisbenzaldehyde **85** already containing a spacer unit (Scheme 24). This has been used, for example, to make polycondensate **87** in which the oligomeric PPV segments are separated by flexible polymethylene spacers.[258–262] Such polyethers give blue or blue-green emission ($\lambda_{max} = 470-495$ nm).



Scheme 24. Synthesis of a blue-emitting copolymers with isolated chromophore by Wittig reaction.

6.3. Polymers with Conjugated Side-Chain Chromophores—"Comb" Lumophores

Another approach towards polymers with well-defined chromophores is based on polymers with luminescent conjugated side chains. As the backbone can now be any nonconjugated "standard" polymer, this enables, in principle, utilization of the considerable body of expertise developed in classical polymer synthesis to adjust the physical properties of the polymer. Our own efforts have concentrated on polymethacrylates such as the copolymers **88** bearing diaryloxadiazole charge-transporting and distyrylbenzene emissive units as side chains (Scheme 25).[74, 136, 141] Bilayer devices with **88** as emissive layer and PPV as hole-transport layer showed blue emission ($\lambda_{max} = 457$ nm) (with a tail in the yellow-green region, owing to emission from PPV, and an efficiency of 0.037 %). The polymers **88** unfortunately were not very stable,



88 (blue)

89 (blue)

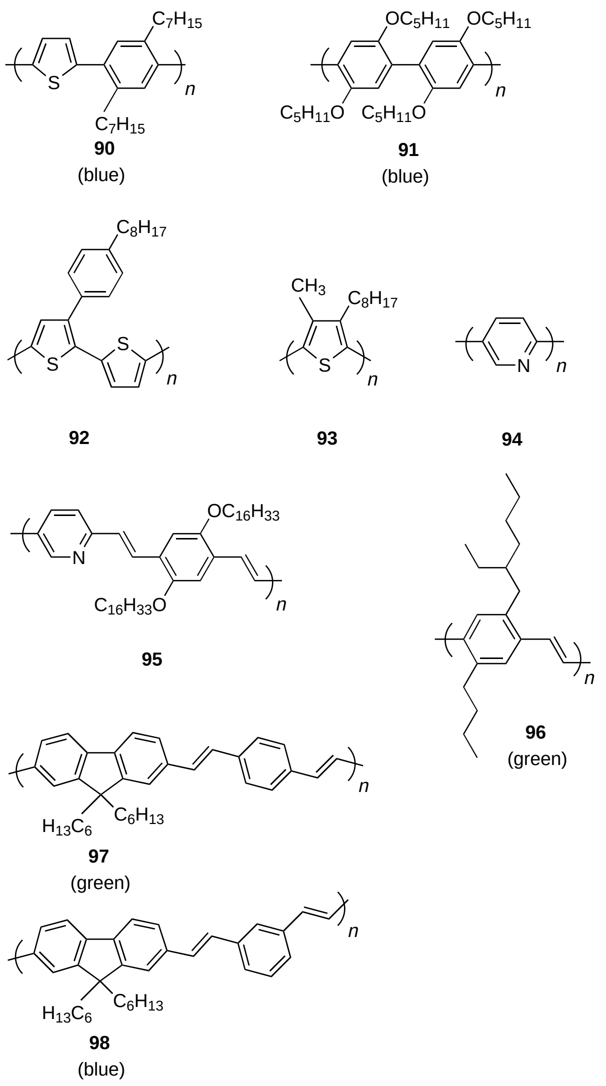
Scheme 25. Examples of electroluminescent polymers with side-chain chromophores.

degrading on storage, photoexcitation, and particularly during device operation. Significant improvements can be obtained by cross-linking.[143]

Schrock et al.[263] have used ROMP on a norbornene monomer with a side chain distyrylbenzene chromophore attached to produce polymer **89**, which shows blue (λ_{max} = 475 nm) electroluminescence with 0.3 % internal efficiency and a turn-on voltage of 12 V when calcium was the cathode. The efficiency increased to 0.55 % for a blend of **89** and an oxadiazole electron-transporting material although the turn-on voltage was also raised considerably.

7. Blends and Combinations of Polymers with Other Materials—A Potpourri of Electroluminescent Materials

Improvements in electroluminescence efficiencies have been made by blending conjugated polymers. For example, Nishino et al.[264] found that blending the red-emitting polymers MEH-PPV (**14**) and poly(3-hexylthiophene) (**49e**) gave an initial increase in LED external efficiency up to a maximum of 1.7 % (with a calcium cathode and 1 weight % of **49e**), which is twice the efficiency of a device made from pure MEH-PPV and three orders of magnitude higher than for pure **49e**. The emission spectra showed that the emitted light came from both polymers. Similarly, Salaneck et al.[265] have found that blue (2.6 eV, 490 nm) emission from the alternating copolymer **90**[266] was enhanced by blending it with the soluble PPP copolymer **91** (Scheme 26). A ratio of 1:9 for **90**:**91** produced the highest external quantum efficiency (1.9 %) with a peak emission at 474 nm at a bias field of 6 × 10^7 V m^{-1}. Polymer **91** (460, 400 nm) as a single-layer ITO/**91**/Ca device emits two peaks at a bias field of 6 × 10^7 V m^{-1} and current density of 0.2 mA mm^{-2}.



90 (blue)

91 (blue)

92

93

94

95

96 (green)

97 (green)

98 (blue)

Scheme 26. Examples of polymers used as blends, in SCALE and in other devices.

Even greater enhancements in emission efficiency arise from blending conjugated polymers with partially conjugated polymers. Shim et al.[267, 268] found that blends of MEH-PPV (**14**) and a blue-emitting copolymer [similar to] **87** showed emission largely from **14**. The emission maximum was blue-shifted by 20–40 nm from that of MEH-PPV. The best efficiency (Al cathode, **87**:**14** = 15:1) was nearly 500 times greater than that for a device made from pure MEH-PPV. As blending of MEH-PPV with insulating polymers, for example polystyrene, enhances emission efficiency by a factor of less than 10, dilution effects clearly play only a minor part in the enhancement observed. The higher efficiency of the blend is therefore attributed to the charge-transporting properties of copolymer **87** leading to confinement of charge on MEH-PPV. Promising results with blends of the closely related polymers **97** and **98** offer opportunities for stable blue devices.[269]

Inganäs et al. have shown that blends of polymers with different emission colors are suitable for devices with variable-color, even white light emission. A blend of the polymers **53**, **54**, **56**, and **92** was used to construct a device in which emission can be tuned from red to green by controlling the applied voltage.[177, 178, 270] A similar blend of polymers **53**, **56**, and **93** in PMMA emits white light.[271] The PMMA acts as an insulating matrix and reduces the degree of exciton transfer between the polymers. Another approach employs a blend of a tristyrylamine in various host polymers such as the polyester Durel, polynorbornene, and poly(vinyl pyridine). The emission of the chromophore depends in this case strongly on the matrix.[216]

Devices can be constructed by using combinations of conjugated polymers and nonpolymeric materials. Yoshino et al.[272, 273] have shown that a device containing a mixture of red-orange-emitting **20b** and the green-emitting fluorescent dye tris(8-hydroxyquinolatino)aluminum produces a voltage-dependent variable emission of orange to green light. Blending of polythiophene **49e** with fluorescent dyes has been found to enhance the EL intensity at constant voltage by a factor of up to 70 with an increase in efficiency at constant luminance of up to 20-fold.[132, 274] With an oxadiazole dye as dopant, the emission color changed from red-orange to white when the voltage was increased.

8. Recent Advances

8.1. Degradation—Oxygen and Water

The one remaining obstacle to the widespread use of polymer LEDs is that, to date, their lifetimes remain lower than the best devices using inorganic or small-molecule organic compounds, although this gap is rapidly being closed. This is in part a result of the susceptibility of conjugated polymers towards oxidative degradation (a topic which has been recently reviewed by Cumpston, Jensen et al.).[275, 276] Studies on PPV have shown that photooxidation produces carbonyl defects that quench fluorescence.[33, 277, 278] Singlet oxygen has been implicated in the cleavage of vinylene groups in MEH-PPV (**14**) and bis (cholestanyloxy)-PPV (**19**), leading to ester or aldehyde groups.[279, 280] A study of PPV-based LEDs[281] revealed that exposure to air produced a drop in efficiency and an increase in threshold voltage, while degradation of the polymer is one of the primary processes involved in the breakdown of MEH-PPV-based LEDs.[282, 283] These results suggest that suitable protection from aerial oxidation may be a significant factor in improving the lifetime and efficiency of devices. Improvements in device design or encapsulation offer potential methods for achieving this. It should be noted that electrochemical dissolution of the metal electrodes at the electrode/polymer interface has been reported.[284] This is thought to lead to electrode failure due to corrosion.

8.2. Light-Emitting Electrochemical Cells—Lowering the Barrier to Charge Injection

A potentially significant new advance in the development of electroluminescent devices based on conjugated polymers has been the discovery[285–289] of light-emitting electrochemical cells (LECs) in which a conjugated polymer is blended with poly(ethylene oxide), a well-known ion-transporting polymer, and lithium trifluoromethanesulfonate as solid electrolyte. Application of a voltage above the bandgap energy (E_g/e), where e is the electron charge, results in p- and n-doping of regions adjacent to the anode and cathode respectively. A p-n junction is formed within the active layer, and positive and negative charge carriers combine with emission of a photon within the compensated p-n junction.[22]

With MEH-PPV (**14**) light emission is observed at a voltage <2.5 V, with external efficiencies of up to 2%. Green emission with a luminance of 100 $\text{cd}\,\text{m}^{-2}$ and an external quantum efficiency of 0.4% at a driving voltage of 4 V has been obtained from a device using PPV. Blue-green emission occurs when a soluble poly[9,9-bis(alkyl)fluorene] (BDOH-PF) (**75b**) serves as emitting polymer. Incorporation of the methoxyethoxyethyl substituents avoids the need for a two-phase blend with an extra ion-supporting polymer.[256] LECs have a high EL power efficiency, low operating voltages and allow the use of air-stable electrodes. A two-color LEC based on PPV and MEH-PPV has been made in which the emission color can be varied from red to green by altering the applied voltage.[290, 291] Some serious obstacles, still to be overcome in commercial realization of these devices, are the slow charging time (LECs are electrochemical batteries) and lifetimes under continuous operation, although promising results concerning these issues have been reported.[292, 293]

8.3. SCALE Devices—Using Alternating Current

Another new advance in device design has been the invention by Epstein and MacDiarmid et al.[294–300] of symmetrically configured, alternating current, light-emitting (SCALE) devices, which have the typical structure electrode/“insulating” polymer/emissive polymer/“insulating” polymer/electrode. The emissive layers used to date have been polypyridine **94** for blue and copolymer **95** for red light emission. Undoped (emeraldine base) polyaniline and polythiophene **49e** are typical “insulating” or electrode-modifying, nonemitting polymers for this type of device.

Use of **49e** with **95** as emissive layer gave a device in which the emission color varied depending on whether forward (590 nm) or reverse (635 nm) bias was applied. This is probably caused by charge recombination occurring at different interfaces in the two modes. With polyaniline, the EL spectra were essentially identical in both bias modes with a maximum at 635 nm. As with standard LEDs, one of the electrodes has to be transparent (ITO on glass), while air-stable metals such as Al, Cu, or Au have been used as the other electrode but, unlike standard LEDs, the two electrodes need not have dissimilar work-functions. Turn-on voltages are reported to be lower than those for the corresponding ITO/polymer/metal devices. Operation in alternating current mode also allows ion migration effects to be minimized. These devices remain to be developed to their full potential.

8.4. Lasers and Microcavities—Stimulated Emission and Superradiance

One method for the enhancement of emission in LEDs makes use of a microcavity structure in which the electroluminescent polymer is sandwiched between two planar, highly reflecting mirrors. When the polymer film thickness is of the order of the wavelength of the emitted light, the device acts as a resonator for a standing electromagnetic wave and produces a marked narrowing in the emission spectrum.[301–306] A microcavity device has been constructed by using ladder-type PPP **81** in which the emission color can be tuned from red to blue by altering the thickness of the polymer layer.[307]

Another microcavity device that uses PPV (**6**) as emissive layer has shown lasing activity with optical pumping, thus presenting the prospect of organic polymer-based lasers.[308] Similar optically pumped lasing and superradiance effects have been seen with other conjugated polymers.[309–317] Some investigators have questioned whether or not conjugated polymers will be capable of sustaining the high current densities necessary to realize electrically pumped lasing. The recent work by Bradley and Seidler and colleagues has shown that PPV films emitted light when a scanning tunneling microscope was used to inject charge at high current densities.[318]

9. Conclusion and Outlook

The prospects for the success of conjugated polymer-based LEDs as commercially viable display devices depend not only on the development of new materials, but also on progress in the design of devices. The three main factors (other than cost) that will determine the utility of polymer LEDs as light sources are their efficiencies (which control brightness for a given current), threshold or turn-on voltages (which affect power consumption), and lifetimes (over 10000 h are necessary for many commercial applications). With the appropriate choice of polymer and device design, external efficiencies of up to 4 % can be obtained, which are comparable with the best EL devices based on inorganic or small molecule organic materials, and even much lower values suffice to give emission that is visible under ambient lighting. Turn-on voltages of 5 V or below have also been achieved by the use of charge-transporting layers, enabling devices to be run from low-power sources such as batteries.

The current best results for green materials (Table 2) are from Cambridge Display Technology with two-layer devices based on PPV (550 nm) prepared from a polyelectrolyte precursor copolymer as the emissive layer.[101] Photoluminescence efficiencies of about 50–80 % have been reported for this material. Luminance efficiencies in excess of 2 lm W^{-1} and brightnesses in excess of 600 cd m^{-2} at 4 V and lifetimes of >1400 h at about 100 cd m^{-2} are now achievable. Another promising green polymer is the organic solvent-processible silylated DMOS-PPV (**18**) for which a respectable 0.1 % external efficiency in a single-layer device with an Al cathode has been reported.[114, 319]

Table 2. Summary of promising light-emitting polymers across the range of the visible spectrum.

Polymer	Color(λ_{max} [nm])	Efficiency [%][a]
MEH-PPV **14**[97]	red-orange (610)	2–4
OC$_1$C$_{10}$-PPV **17**[17]	red-orange (610)	2.1[b]
CN-PPV **40**[55, 150]	red (710)	0.87
MEH-CN-PPV **41**[12]	red-orange (600)	5.0
Polythiophene **49**[191]	red (662)	3.85×10^{-4}[b]
PPV **6**[101]	green (550)	0.3[c]
DMOS-PPV **18**[319]	green (500)	0.1[b]
BUEH-PPV **96**[322]	green (554)	3.2
BDOH-PF **75b**[256]	blue-green (450)	0.3[b]
PPP **72**[222]	blue (459)	0.01[b]
Blend **90**:**91** (1:10)[321]	blue (400–490)	2
DO-PPP **76**[240]	blue (440)	3
m-LPPP **83**[252]	blue-green (491)	0.1[b]
P3V/P5V **77**[243]	blue (460)	4[b]

[a] Unless otherwise indicated most devices are two-layer devices with a hole injecting layer between anode and emissive polymer. [b] Signifies single-layer device. [c] Estimated from the published data for a PPV device giving a luminous efficiency 1 lm W^{-1} at 4 V.

Exciting results for red emitters have emerged from three laboratories, all using closely related solvent-processible oxygenated PPV analogues. At UNIAX, MEH-PPV (**14**) (λ_{max} = 610 nm) in the configuration ITO/PANI-camphor sulfonate/MEH-PPV/Ca exhibited brightnesses of 100 cd m^{-2} at 2.4 V, 4000 cd m^{-2} at 4 V, and over 10000 cd m^{-2} at higher voltages. The external quantum efficiency was 2–2.5 % and the luminous efficiency corresponded to 3–4.5 lm W^{-1}. Operating lifetimes in excess of 2000 h at 400–500 cd m^{-2} initial brightness were reported.[97] Two European companies, Philips and Hoechst, have achieved comparable results with OC$_1$C$_{10}$-PPV (**17**).[17] Philips reported an external quantum efficiency of 2.1 % in the device configuration ITO/**17**/Ca.[87, 320] Luminous efficiencies up to 7 lm W^{-1} and lifetimes of several thousand hours at 100 cd m^{-2} were realized. Hoechst fabricated a flexible device based on a dialkoxy-PPV (probably OC$_1$C$_{10}$-PPV **17**) in the configuration PET-ITO/polymer/Ca, which demonstrated an external efficiency of 2.1 %, a luminous efficiency of 2 lm W^{-1}, and a luminance of 100 cd m^{-2} at 3.4 V with a current density of 4.5 mA cm^{-2}.[17] Calculations based on the data reported by the Cambridge group show that MEH-CN-PPV (**41**) has a luminous efficiency of 5 lm W^{-1}.[12]

Some of the most interesting blue materials are based on polyphenylene and polyfluorene derivatives, but the major progress has been largely from academic laboratories, and serious industrial evaluation has still to be carried out. One of the best results has been obtained with the poly(2-decyloxy-1,4-phenylene) (**76**) (λ_{max} = 440 nm), which showed 1.8 % external quantum efficiency in the single-layer device configuration ITO/**76**/Ca. Problems with polymer film quality were circumvented by using a second PVK buffer and hole injection layer. The two-layer device was more efficient (3 %) and turned on at 15 V to reach a brightness of 490 cd m^{-2} at about 30 V.[240] The blends of copolymers **90** and **91** have already been mentioned as emitting blue light with external efficiency of about 2 %.[321] The results highlight the general problem for blue emitters that the threshold voltage is not far removed from that which induces dielectric breakdown. This makes the problem of obtaining good lifetime data considerable. These reservations should be qualified in the light of the recently reported stable devices made from the polyfluorenes **75b** and **75c**.[256, 257]

During the past seven years, a wide range of electroluminescent conjugated polymers and copolymers have been made that are suitable for use in LEDs. Alteration of their chemical structures by synthetic design has stimulated the preparation of polymer-based devices emitting in any part of the visible spectrum, and also in the near infrared. By the use of precursor methods thin films of insoluble and intractable materials can be produced. In view of the recent advances in polymer LEDs, efficiencies are now comparable with inorganic or dye-based devices, and ongoing work into improvement of device lifetimes makes the future for these devices promising.

A number of tasks still remain to be performed before the apparent bright prospects of conjugated EL polymers can be realized. Of the wide variety of polymers that have become available in the last seven years, only a few have been extensively studied, and the best materials have yet to be identified. The study of polymer EL devices is an interdisciplinary research area, combining semiconductor physics, polymer chemistry, and materials chemistry, and challenging tasks remain in all of these fields. Although much is known about simple device structures and common electrode materials, devices have yet to be optimized. We also need improved methods (which includes making the polymers more eco-friendly) for the preparation and purification of EL polymers. High purity polymers are required, and the challenge in polymer synthesis is to meet these requirements. High molar masses are advantageous for ensuring good film-forming properties. The long-term stability of polymers and polymer blends during storage and especially in the high electric fields found in operating devices also need to be improved. It will furthermore be necessary to develop suitable encapsulations for the protection of polymers and electrodes from environmental degradative influences. These challenges imply continuing scope for exciting and innovative research into the preparation and application of conjugated electroluminescent polymers. We are confident that markets will emerge for commercial polymer LED devices having a low information content – such as for mobile telephone displays, alphanumeric and backlit LCDs. While the horizon for high information content applications (such as flat-screen color TV) is still several years away, we expect that polymer LEDs will ultimately have a significant input in this area as well.

Appendix: List of Abbreviations

BDOH-PF	poly[9,9-bis(methoxyethoxyethyl)fluorene] **75b**
BUEH-PPV	poly[2-(2′-ethylhexyl)-5-butyl-1,4-phenylene vinylene] **96**
CN-PPV	poly[2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene)] **40**
DMOS-PPV	poly[2-(dimethyloctylsilyl)-1,4-phenylene vinylene] **18**
DO-PPP	poly(2-decyloxy-1,4-phenylene) **76**
ECHB	electron-conducting/hole-blocking
EL	electroluminescence
HOMO	highest occupied molecular orbital
ITO	indium-tin oxide
LCD	liquid crystal display
LEC	light-emitting electrochemical cell
LED	light-emitting diode
LPPP	ladder-type poly(*para*-phenylene)
LUMO	lowest unoccupied molecular orbital
MEH-CN-PPV	poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylene-(1-cyanovinylene)] **41**
MEH-PPV	poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylene vinylene] **14**
OC_1C_{10}-PPV	poly[2-(3,7-dimethyloctyloxy)-5-methoxy-1,4-phenylene vinylene] **17**
P3V/P5V	copolymer **77**
PANi	polyaniline
PBD	2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **28**
PDAF	poly(dialkylfluorene)
PET	poly(ethylene terephthalate)
PL	photoluminescence (fluorescence)
PMMA	poly(methyl methacrylate)
PPP	poly(*para*-phenylene) **72**
PPV	poly(*para*-phenylene vinylene) **6**
ROMP	ring-opening metathesis polymerization
SCALE	symmetrically configured, alternating current, light-emitting (diode)

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