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Electroluminescent polymers

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Dedicated to Professor Frank E. Karasz of UMASS

Abstract

Electroluminescent polymers are reviewed in terms of synthesis and relationships between structure and light emission properties.

The main concepts, problems and ideas related to the subject as a whole and to each class of electroluminescence (EL) polymer, have been systematically addressed. The elements of device architecture were considered, such as electrode characteristics and transport layers. The main mechanisms for light emission were approached, and the relevant issues related to color tuning were discussed in general terms and taking into account the structural features of each polymer structure, as well. The main routes for the synthesis of each EL polymer class are described, illustrated with numerous examples, including PPV and PPV related structures, polythiophenes, cyanopolymers, polyphenylenes, silicon-containing polymers, conjugated nitrogen-containing polymers, polyfluorenes, polyacetylenes and polymers with triple bonds in the main chain, condensation polymers.

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1. Introduction

Organic polymers that emit light on the imposition of an electric field have commanded increasing attention in the last decade both for their scientific interest and as potential materials for electro-optical and opto-electronic applications.

Electroluminescence (EL) was observed for the first time in inorganic compounds (ZnS phosphors) as early as 1936 by Destriau [1]. The discovery in 1947 that a transparent anode could be constructed by depositing a layer of Indium Tin Oxide (ITO) onto a glass surface opened the possibility of obtaining light-emitting planar surfaces [2,3].

The fact that many aromatic organic molecules are photoluminescent suggested their use as electroluminescent materials. EL for an organic semiconductor was first reported by Pope et al. [4] in 1963. They observed emission from single crystals of anthracene, a few tens of micrometers in thickness, using silver paste electrodes and required large voltages to get emission, typically 400 V. Similar studies were made by Helfrich and Schneider [5] in 1965 using liquid electrodes. Considerable effort has been expanded to understand the basic mechanism [5,497] as well as to provide stable electroluminescent devices, and the most relevant result was the establishment that the process responsible for EL required the injection of electrons from one electrode and holes from the other, the capture of one by another, and the radiative decay of the excited state produced by this recombination process. Development of organic thin-film EL advanced with the study of thin-film devices. In 1982, Vincett et al. [6] reported blue EL from anthracene sublimed onto oxidized aluminum as one electrode, and thermally evaporated semitransparent gold as the other electrode, and were able to reduce voltage considerably, for example, to 12 V.

In 1983, the discovery of EL of poly(vinyl carbazole [7] led to a search for other electroluminescent materials covering other ranges of the visual spectrum. However, the development of electroluminescent organic devices was not successful at that point due to the relatively poor lifetimes and relatively low efficiencies. Organic electroluminescent devices proved not to be competitive with incandescent light sources, and essentially all research was focused on traditional inorganic electroluminescent materials, since light-emitting devices (LEDs) based on these materials have been commercially available since early 1960s.

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During 1987–1989, the seminal work of Tang and Van Slyke [8] demonstrated efficient EL in two-layer sublimed molecular film devices comprised of a holetransporting layer of an aromatic diamine and an emissive layer of 8-hydroxyquinoline aluminum (Alq₃). This result provided a basic design for lightemitting diode architecture which was applicable to systems employing low molecular weight electroluminescent materials either in neat form or in inert polymer matrix, or to electro-optically active polymers or copolymers. Indium–tin oxide (ITO) was used as hole injection electrode and a magnesium– silver alloy as electron-injecting electrode.

Although the low molecular weight organic devices operated at voltages as low as 10 V, another problem was still present: the short lifetime, which was attributed to the rearrangement of the molecules caused by the heat generated, leading to crystallization and so compromising interfacial contacts. Advances including vacuum deposition of amorphous transport layers separating polycrystalline materials from the electrodes [9-12] or dispersing the chromophores in a polymeric matrix [13,14] in solid solution partially circumvented these problems. The use of intrinsically emitting polymers was then the most obvious way to improve morphological stability in organic LEDs, in spite of the higher impurity levels of polymers, which still presented certain drawbacks. In fact, advancements in semiconducting polymers have progressed steadily, since their discovery in 1977 by Heeger et al. at the University of Pennsylvania [15]. Poly(phenylene vinylene) (PPV) has been one of the most studied polymers. These facts led to the discovery in 1990 by the Cambridge group in England that it was possible to use PPV as the emitting element in a polymer-based LED [16]. The optical absorption, photoluminescence (PL) and EL spectra of PPV are shown in Fig. 1. The PL and the EL spectra are consistent, indicating that the emitting species are the same when excited by light or electric current. This was a breakthrough improvement since it made it possible to combine the good mechanical and processing properties of polymers with semiconducting behavior (providing processibility under well established techniques, such as spin or dip coating). The ease in oxidation or reduction (abstraction or addition of one or more electrons, usually from the π manifold), forming cations or anions (polarons)



Fig. 1. Optical absorption, PL and EL of poly(phenylene vinylene) (PPV). Reprinted with permission from Springer proceeding in physics, vol. 81. 1996. p. 231. © 1996 Springer-Verlag[483].

without significantly affecting the σ bonds responsible for the polymer's physical integrity is a fundamental feature of electroluminescent polymers. Another interesting property of polymer LEDs is the possibility of fabricating flexible devices by casting a polymer film on a plastic substrate, enabling the obtainment of displays in a variety of unusual shapes. One example is the 'plastic LED' made by Heeger et al. [17–19] in which the anode is a polyaniline film deposited on Mylar (PET) film.

A number of reviews on electroluminescent polymers focusing the basic physics [20-24] synthesis and properties [25,26], device operation and materials [27-30], design and synthesis [31] blue emitting structures [32] have been published. Some books are also out on the subject [33-36].

Apart from intrinsic electronic features, the color emitted by small organic molecules depends on micro-environment characteristics, such as its location in the device and medium polarity. When attached to a polymer chain, the mobility of the chromophore is restricted in all directions, and the emission becomes dependent on the structural features of the macromolecule (including the molecule's architecture, such as regioregularity, location and distribution of chromophores, etc.). This restriction opened a new avenue in the development of electroluminescent polymers: color tuning could be achieved by introducing variations in the polymeric structure, since in doing so the energy gap of the $\pi-\pi^*$

transition responsible for the color emitted is changed, and a broad range of colors can be achieved with one polymer. Several strategies for this purpose have been employed, and will be discussed later.

In this survey, we shall review the different classes of macromolecules that exhibit EL. Since essentially all this research has focused on the potential incorporation of these polymers into light-emitting diodes (LEDs), we first present the essential elements of the design and function of these devices. It may be noted that both low and high molecular weight organic EL materials are now under wide study. The perceived advantages of the former include the possibility of a definitive chemical structure, chemical purification at high purity levels by sublimation and facile manufacture of complex 3D architectures, while polymers are favored for their mechanical properties, principally the ready formation of robust films and their processibility using easily accessible technology for simple device architectures. The two classes of materials are not infrequently used together in multicomponent chromophoric layers.

A typical design of a polymer LED is shown in Fig. 2.

The basic device architecture consists of a lightemitting polymer film, an optically transparent anode and a metallic cathode, together with a DC or AC power source, which may be operated in a continuous or (to reduce heating) intermittent mode. The anode is most often, but not exclusively [37], indium/tin oxide (ITO) coated glass, while the cathode is typically a low work function metal, such as Ca, Mg or Al. The polymer may be deposited on the ITO by spin- or dipcoating from solution, and is typically of the order of 100 nm thick. The cathode metal is evaporated onto the polymer film in vacuo. More elaborate architectures may vary from this basic scheme, and may involve the use of a multicomponent chromophore and one or more transport layers (see below).

Recent advances include microfabrication of diode pixel arrays [38], patterned light emission with sizes of the order of 0.8 μ m [39], polarized EL based on stretch or, rub aligned Langmuir–Blodgett deposited polymers, or specifically synthesized liquid crystal polymers [40–46]. The application of ultra-thin and self-assembling films is an important development in LED technology. In this case the film in the device is not cast using a traditional processing technique such as spin coating, but using electrostatic layer-by-layer selfassembly methodologies, involving Coulombic interactions between oppositely charged molecules [47–50].

A new technique of constructing multilayer assemblies by consecutively alternating adsorption of polyelectrolytes has been developed [51,52]. This means that recent advances in the molecular level processing of conducting polymers have made it possible to fabricate thin film multilayer heterostructures with a high degree of control over the structural



Fig. 2. Design of a polymer LED showing optional HTL and ETL.

features and thickness of the deposited layers. As the dimensions of the individual layers approach molecular scales it may be possible to approach quantum effects in these multilayer contacts.

As an example, the spontaneous self-assembly of conjugated polyions was utilized in a substrate alternating layers of the sulfonium PPV-precursor (polycation) (PPV) and sulfonated polyaniline (polyanion) (SPAn). The layers were deposited on ITO covered glass, and after thermal conversion a LED was made using an Al cathode [53]. The SPAn/PPV monolayer LED emitted greenish-yellow light but the SPAn/PPV multilayer emitted bluish green. These results were interpreted in terms of the confinement effect of carriers in the superlattice structure consisting of the SPAn/PPV multilayer system.

Further progress is represented by the development of surface light-emitting devices (SLEDS), in which both anode and cathode lay underneath the electroluminescent layer, so that no transparent materials are required in the LED construction. These SLEDS were microfabricated using conventional silicon processing [54]. The patterning of light-emitting layers is the most important step in the manufacturing of multicolor organic electroluminescent devices, and should combine large area coatings with device patterning. One very promising methodology employs an ink jet patterning process [55–57].

2. Electroluminescent devices and mechanisms for light emission

Light-emitting devices as shown in Fig. 2 can be operated in a continuous DC or AC mode. They behave like a rectifier, the forward bias corresponding to a positive voltage on the ITO electrode and are also called light-emitting diodes in analogy to p-n junction devices. Light emission is transmitted from the transparent side normal to the plane of the device. The polymer layer is usually deposited by spin coating, but dipping techniques can also be used. After solvent evaporation the film thickness is in the 1000 Å range. The ITO coated glass substrate has a resistance of $10-25 \Omega/\Box$. Metal evaporation (cathode) is made under a vacuum of typically 5×10^{-7} - 10^{-6} Torr with an evaporating rate of 1-5 Å to typically 2000 Å thickness.

In a variation of this architecture, a layer of polyaniline doped with polymeric or small molecules was cast from a variety of solvents between the emissive layer and ITO to reduce the oxidative degradation rate [17-19,58,59]. However, polyaniline is too resistive as compared to ITO, and this limitation precludes its widespread use.

The cathode injects electrons in the conduction band of the polymer (π^* state), which corresponds to the lowest unoccupied molecular orbital (LUMO). and the anode, injects holes in the valence band (π state), which corresponds to the highest occupied molecular orbital (HOMO). The injected charges (polarons) can travel from one electrode to the other, be annihilated by any specific process such as multiphonon emission, Auger processes, or surface recombination. These concepts have been extensively studied in inorganic systems and may also apply to polymer systems. The physics underlying the processes involved in organic LEDs have been extensively explored in the literature, and is beyond the scope of this survey. A simplified description involves the formation of a neutral species, called an exciton, through the combination of electrons and holes. The exciton can be in the singlet or triplet state according to spin statistics. Because only singlets can decay radiatively, and there is only one singlet for each three triplet states, the maximum quantum efficiency (photons emitted per electron injected) attainable with fluorescent polymers is theoretically 25%. This limit can be overcome by using phosphorescent materials that can generate emission from both singlet and triplet excitons [60]. As a result, the internal quantum efficiency can reach 100%. Forrest et al. [61] reported highly efficient phosphorescent LEDs by doping an organic matrix with heavy atoms containing phosphorus. Polymer devices were also fabricated by using polyfluorene [62] or poly(vinyl carbazole) [63] as the host for the phosphorescent dye. LUMO levels can be determined by cyclic voltametry in conjunction with UV/vis spectrometry [64]. The singlet exciton decay time is typically in the ns timescale, whereas the triplet survives for up to 1 ms at low temperatures [65]. A major fact determining the internal quantum yield for luminescence (ratio of radiative to non-radiative processes) is the competition between radiative and non-radiative decays of the electron-hole pairs created within the polymer

layer. These pairs can migrate along the chains and are therefore susceptible to trapping at quenching sites where non-radiative processes may occur. They may also undergo a phonon emission and lose energy in a thermal burst, or transfer energy to 'impurities', or convert into a triplet by intersystem crossing and eventually lose energy non-radiatively. In the radiative process the released photon has an energy characterized by the energy gap between the LUMO and the HOMO levels of the chromophore. For organic polymeric chromophores this energy gap ranges from 1.4 to 3.3 eV corresponding to light wavelengths between 890 and 370 nm, covering the visible range. Charge recombination within the chromophoric polymer results in exciton states which decay and emit photons. The color of the emitted light is controlled by the band gap energy $(E_{\rm g})$, while the charge injection process is controlled by the energy differences between the work functions of the respective electrodes and the electron affinity (E_a) (cathode injection) and ionization potential (I_a) (anode injection) of the polymer. The I-V relationship of the diode is typically highly non-ohmic. Above the 'turn-on' voltage (which depends on contact resistance and the material's resistance to charge injection), there is an increasing current flow of both electrons and holes, and light is emitted. In this simplified heterojunction device there are four basic parameters: the two work functions for the electrodes and the two involving the electronic properties of the polymer. The band gap energy of the polymer (where carrier recombination takes place) determines the color of the emitted light, as noted, while the work functions of the electrodes vis-à-vis I_a and $E_{\rm a}$ (related as $E_{\rm g}=I_{\rm a}-E_{\rm a}$) of the polymer determine the respective barriers to charge injection and hence the 'turn-on' voltage. This is also a factor in the quantum yield of the device, since for a given polymer maximum recombination probability is obtained when the two carrier concentrations are of equal level thereby permitting a complete carrier recombination. In practical terms it is also desirable to minimize the barriers by appropriate material selection and hence minimize the 'turn-on' voltage and maximize the charge flux for a given electric field. The ratio between the probability of singlet exciton radiative decay and the sum of all competing nonradiative decay processes (i.e. the PL quantum yield) together with the exciton concentration determines the overall quantum efficiency. For the prototype electroluminescent polymer PPV, it was suggested that only about 10% of the photoexcited species were singlet excitons, and the rest were spatially indirect polaron pairs which did not result in radiative decay [65,66]. Quantum efficiencies are often referred as internal or external. Absolute values for the internal efficiency are estimated using an integrating sphere to measure the optical power in the forward direction only and multiplying by $2n^2$, where *n* is the material's refraction index. External quantum efficiencies are measured using a calibrated integrating sphere to account for light emitted in all directions from the device, including that waveguided out the substrate.

The sequence of charge processes leading to exciton formation is charge injection, transport, and recombination. These processes are difficult to separate on the basis of the device electrical characteristics, and the transport mechanism affects the other two. Two modes of injection mechanisms have been discussed for the operation of LEDs: thermoionic emission over a Schottky-like contact, and tunneling into the transport bands [21]. Theoretical modeling of charge injection has been attempted by several approaches [67–73].

Direct tunneling of charge carriers into the transport bands was described by Parker, who assembled a great deal of evidence to explain the $I \times V$ characteristics in 'foward' mode of operation. The effects of using different contact metals on the diode's current–voltage and light current characteristics were explained in terms of an ideal Schottky barrier model with charge carrier injection via Fowler–Norheim tunneling and that the current intensity vs. voltage characteristics of polymer LEDs were controlled by charge injection [68,74]. The temperature dependence of the current vs. voltage characteristics found in some cases favored the assumption that charge injection takes place via tunneling [75].

Nevertheless, some experimental results showed that this model was not strictly operative and the deviations were attributed to the contribution of thermoionic emission to the current [75] and to band-bending effects at the interface [76]. A Fowler–Nordheim analysis gave inconsistent results for poly(3-octyl thiophene) based devices [77]. Recent

results have shown that for low barrier heights and most voltages used, thermoionic injection rather than tunneling more correctly describes charge injection [78]. An analytic theory considering the injection current as a function of electric field, temperature and energetic width of the distribution of hopping states was presented, and at high electric fields it resembles the current calculated from the Fowler-Nordheim tunneling theory, although tunneling transitions were not included in this theory [79]. Assuming that both mechanisms are operative with the feature of thermoionic backflow, good quantitative results have also been reported [80]. Experimental data related to MEH-PPV-based devices have shown that injection is thermoionic with Schottky barriers for some electrode metals that are low enough to be considered ohmic [81]. The interface of copper and a bilayer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(4-styrenesulfonate) (PEDOT-PSS) and MEH-PPV showed ohmic behavior [82]. Except for diodes with large barriers for charge injection, either by thermoionic emission or tunneling, the injection of charge is not the limiting factor for current flow. Depending on the magnitude of the energy barrier for charge carrier injection from the electrode(s), the current flowing through a light-emitting diode can be either space charge limited or injection limited. Due to low mobility of charge carriers in semiconducting polymers (on the order of 10^{-5} cm² V⁻¹ s⁻¹) the current flow is bulk limited, mainly due to the buildup of space charge [83]. A variety of dependences of EL intensities on current flowing through the device has been observed. Linear, supralinear, and sublinear functions have been addressed in terms of injection and generation of emitting states [84-86].

A description by Vlegaar for the $I \times V$ characteristics proposes that the behavior of PPV-based LEDs is dominated by the bulk conduction properties of the polymer; the hole current being governed by spacecharge limited conduction and the electron current being limited by the presence of traps [87,88]. The charge carriers motion and radiative recombination are thus limited by trapping on quenching centers where they recombine non-radiatively. Conjugated polymers exhibit low carrier mobilities and therefore are very favorable media for the formation of a space charge. Some authors have mentioned space-charge limited current as a likely mechanism for supralinear regime in $I \times V$ curves. This model was applied to PPV-based LEDs and the extracted mobilities were in good agreement with those measured independently by time-of-flight photoconductivity [89]. Modeling of space-charge limited current is more involved than the modeling of charge injection due to a strongly field dependent mobility [90] and to the influence of bipolar currents on the reduction of the bulk space charge [91]. Apart from these two factors, only when diffusion and trapping of charge carriers can be ignored and when both electrodes provide ohmic contacts can a complete solution be obtained [67,92].

The theoretical modeling of the recombination process of electrons and holes has been approached by several groups using the Langevin theory [67,91,93] In this mechanism, which occurs for low carrier mean-free paths, an electron and hole that approach each other within a distance such that their mutual binding Coulomb energy is greater than kT will inevitably combine. The model implies that electron–hole capture process is spin independent.

2.1. Interchain excitons

In LEDs the polymers are thin films, leading to the possibility of electronic interactions between neighboring chains and the creation of new excited state species. This topic has been the subject of many recent investigations [94–97] mainly related to PPV [98,99] PPV derivatives such as poly(2-methoxy-1,4-PPV) [100], MEH-PPV [101-106], CN-PPV [96,101,107], poly(p-pyridyl vinylene) [105,108], acetoxy PPV [109] and other light-emitting polymers [94, 110-114], showing good evidence to suggest that interchain excitations play a significant role. The importance of these interchain excitations continues to be one of debate: if they are non-emissive, then they are detrimental to device operation, but if they are emissive, they can be used effectively [115]. Recently, transient and steady state PL results along with absorption, nuclear magnetic resonance [116] and scanning tunneling microscopy [106] have shown that MEH-PPV exits in two distinct morphological species: the isolated and the closed packed forms. The degree of interchain interactions can be controlled by varying the solvent, polymer concentration, and film forming conditions such as casting and annealing. The final morphology has a direct effect on

the performance of MEH-PPV based LEDs. Higher degrees of interchain interactions enhance the mobility of charge carriers at the expense of lower quantum efficiencies for EL. The reduction in efficiency in well packed regions is attributed to rapid formation of nonemissive interchain species without the involvement of ground state dimers or aggregates [106,116].

2.2. Transport layers

Single layer device architecture is typically employed and is appropriate for evaluation of new polymer chromophores and for measurements of their EL and PL spectra. In the simplest cases the two spectra are quantitatively identical, although in numerous cases their non-coincidence reveals a more complicated exciton formation and decay related to the differing modes of energy input. In devices which are intended to maximize photonic output and efficiency, however, it is established practice to employ additional layers of organic material (polymeric or low molecular weight) interspersed between chromophore film and the electrodes using materials chosen for their functional ability to facilitate charge transport and block (localize) carriers, avoiding their crossing the device without recombination. Usually the carriers do not form junctions with identical (or zero) barrier heights and therefore one carrier will be preferentially injected. If the two junction barriers are not identical, higher electric fields would be required near the junction with the greater barrier energy in order to equalize the injected current density from each contact [117]. For the three layer structure of Fig. 3(a)the current is likely to be carried predominantly by one charge carrier species and therefore it has a higher probability of crossing the EL layer without forming an exciton with an oppositely charged carrier, thus reducing the device efficiency. The LED efficiency is also reduced if the excitons are formed at the interface of the polymer and the electrode, lowering the carrier injection. This location is also where the greatest number of defects are expected and can act as quenching sites [118,119]. The transport layer also decreases exciton quenching near the metal electrode by acting as spacer separating the metallic contact from the active luminescent layer. To confine holes in the emissive layer an electron-conducting-hole

blocking layer should be used (electron transport layer, ETL). Its valence band should be lower in energy than the EL layer and its electron affinity should be equal to or greater than the EL layer as indicated in Fig. 3(b). In this way holes are confined between the emissive layer and the ETL, and the space charge formed provides a higher electric field across the interface with a more uniform distribution of charge, thus improving the balance between carriers [117]. The same reasoning is valid for the use of hole transport layers (HTL). A simple layer device using a poly(cyanoterephthalydene) derivative required a field of about $1.2 \times 10^6 \text{ V cm}^{-1}$ to obtain current densities of $5 \,\mathrm{A}\,\mathrm{cm}^{-2}$ and had an internal quantum efficiency of 0.2% obtained with both Al and Ca contacts. With the insertion of a PPV layer, which acts as an HTL, the field was lowered to 4×10^5 V cm⁻¹ and the quantum efficiency increased to 4%, which is comparable to the best sublimed low molecular weight organic devices [120].

Apart from injection problems, time of flight experiments showed that deep traps and holes exist in PPV, and that electrons are severely trapped, resulting in unbalanced charge transport [121]. Fig. 4 depicts examples of representative hole (Fig. 4(a)) and electron (Fig. 4(b)) transport materials.

The use of transport materials represents an improvement in device stability since it makes it possible in certain cases to change from a lower work function (ϕ_w) metal electrode as Calcium ($\phi_w = 2.9$ eV) which is unstable in atmospheric conditions to a higher work function material as aluminum ($\phi_w =$ 4.3 eV) and add it directly to the emitting polymer. For example, by dispersing PBD (Fig. 4(b)) in the yellow emitter poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene) (BCHA-PPV) it was possible to obtain quantum efficiencies of about 0.25%. This represented an improvement by a factor of five in relation to similar devices made without the addition of the electron transporting material [122]. In most cases the transport layer is prepared by dispersing the low molecular weight compound in an amorphous, nonemitting polymer such as poly(methyl methacrylate) or polycarbonate. Or, the transport materials can be attached to a polymer backbone in the main chain [123,124] or as pendant groups [125]. In this case their concentration can be higher than when compared to a dye-doped matrix, because of aggregation problems.





Fig. 3. Schematic band diagrams of EL diodes under a forward bias of voltage V, without (a) and with (b) and an electron conducting-hole blocking layer (PBD) between the EL polymer (PPV) and the low work function electron injecting contact. $\Delta E_v^{\rm H}$ is the energy difference between the high work function contact, of work function ϕ_1 , and the PPV valence band, and $\Delta E_c^{\rm L}$ the difference between the low work function contact, of work function band. Reprinted with permission from Appl Phys Lett 1992; 61(23): 2793. ©1992 American Institute of Physics [117].











Fig. 4. (a) Examples of hole transport materials TPD [484]: *N*,*N*[']-diphenyl-*N*,*N*[']-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine; PPV [117]: poly(phenylene vinylene); PMPS [485]: poly(methyl phenyl silane); PVK [456]: polyvinyl carbazole; TPTE [486]: triphenylamine tetramer, and TPD as a pendant group on a PMMA main chain: TPD-PMMA [125,249]. (b) Electron transport materials PBD [487]: 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole; Alq₃ [488]: tris-(8-hydroxyquinoline) aluminum complex; TAZ [489]: 3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-butyl phenyl)-1,2,4-triazole. In the polymeric structures the ET units are linked as pendant groups on a poly(methyl methacrylate) (PMA) backbone; PPD: 2-phenyl-5-phenyl-1,3-oxadiazole; DSB: distyrylbenzene; PDPyDP [490]: 2,5-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yil] pyridine. DPQ [487]: 2,3-diphenylquinoxaline; STR: substituted triazine. Polymeric structures with pendant groups [491]: PMA–PPD, PMA–PBD, PMA–DSB, PMA–DSB–PBD.



Fig. 4 (continued)

Materials for ETL are electron deficient and the most used are oxadiazole compounds in the 'free' form as PBD or grafted to a polymer main chain. Apart from PPV, a variety of electron-accepting polymers such as poly(vinyl carbazole) (PVK) [126,128], poly(pyridine-2,5-diyl), poly(1,10-phenanthroline-3-diyl) or poly(4,4'-disubstituted-2,2'-bithiazole-5,5'-diyl) have been used as HTL materials. The incorporation of the transport/blocking material can also be made directly by blending them with the emissive material [129], as in the case of the green emitter poly(2-cholestanoxy-5-hexyldimethylsylyl-1,4-phenylene vinylene) (CCS-PPV). By dispersing PBD in the emitter layer and using aluminum as electrode, quantum efficiencies of

about 0.3% photons per electron were obtained, better by a factor of 18 than similar devices without the addition of the electron transport dopant [130]. With the combination of PVK as HTL and PBD as ETL it was possible to achieve an internal quantum efficiency in excess of 4% for a polyquinoline ether emitting in the blue (450 nm) region [131].

Several p-doped conjugated polymers have been used as hole injecting electrodes, like polypyrrole, polythiophene derivatives, and polyaniline [18,19,58, 59,66,132] which have high work functions, providing low barriers for hole injection. The devices showed better efficiency and improved uniformity and durability [133,134]. There are reports of stable operation over long times for devices using polymeric dopants, which are expected to be relatively immobile. These include polystyrenesulfonic acid used to dope poly(dioxyethylene thienylene) (PEDOT) [22]. Recently, high T_g amorphous poly (imidoaryl ether sulfone) and poly(aryl ether ketone) have been reported as efficient host materials for TPD, a hole transport molecule that is morphologically unstable when vacuum sublimed as a thin film [135].

2.3. Color tuning

Initial results for polymer LEDs demonstrated that various colors could be realized with impressive efficiency, brightness, and uniformity. As the color of the emitted light depends on the band gap of the π - π^* transition which is a function of the polymer's structure, modifications with any specific purpose will affect band gap and consequently the emitted color.

3. PPV and PPV-type structures

3.1. Precursor routes

3.1.1. The Wessling method

Like most highly conjugated materials, semiconducting polymers show poor solubility in organic solvents. Structural changes have been made to overcome this difficulty. The first highly structured electroluminescent polymer, PPV, a green-yellow emitter, was prepared via a precursor route because its insolubility in poly-reactions resulted in only oligomeric materials (a review on polycondensation routes such as Wittig, Knoevenagel and Siegrist methods was published by Kossmehl in 1979) [136]. The precursor route involves the preparation of a soluble polymer intermediate that is cast in the appropriate substrate and after thermal treatment is converted to the final product in situ. This involves producing a polymer in which the arylene units are connected by ethylene units. The saturated units in the precursor contain a group which not only solubilizes the macromolecule and allows for processing, but also acts as a leaving group, thus affording the unsaturated vinylene units of a fully conjugated polymer.

One of the most important soluble precursor routes to PPV was developed by Wessling and co-workers in the 1960s [137,138] based upon aqueous solvent synthesis of $poly(p-xylylene-\alpha-dialkylsulfonium$ halides) from α, α' -bis(dialkyl sulfonium salts), followed by thermolytic formation of the final conjugated polymer, as shown in Fig. 5. The charged sulfonium groups solubilize the polymer and are removed during the conversion step. Molecular weights for the polyelectrolyte are in the 10,000 to >1,000,000 range, which may be precipitated or dialyzed to give typical yields of about 20% high molecular fraction. The mechanism is believed to proceed according to a chain growth polymerization via the in situ generation of the monomer, a pquinomethane-like intermediate, [139,140] based on the facts that high molecular weight is formed very quickly, within the first minutes of the reaction and also that various radical inhibitors limit or prevent formation of long polyelectrolyte chains. However, the initiation process was not unequivocally identified [141-145].

Reviews of the various mechanisms proposed for the Wessling process have been given elsewhere [146–149]. Manipulation for the equilibria that leads to xylylene formation helps to optimize polyelectrolyte formation. Wessling [137] and Garay [150] showed that use of an aqueous immiscible cosolvent to remove dialkylsulfides from the reaction mixture could increase the yield and molecular weight of the polyelectrolyte. Adjustment of solvent systems that optimize the synthesis was described by Denton [141]. Fig. 6 depicts the radical chain mechanism for PPV synthesis [151].

A modified Wessling route where the solubilizing and leaving group is an alkoxy group has been



Fig. 5. The sulfonium precursor route (Wessling) to PPV. A substituted *p*-xylylene (also known as *p*-benzoquinodimethane) intermediate polymerizes to give water or methanol soluble poly(xylylene- α -dialkylsulfonium)halide, a polyelectrolyte. The xylylene precursor then undergoes elimination giving the final insoluble PPV.

developed and gives methoxyprecursor polymers, which are soluble in polar aprotic solvents as chloroform, dichloromethane and tetrahydrofurane [152,153]. The generation of precursor copolymers containing randomly placed methoxy and acetate groups (which are expected to be more labile to elimination) was an approach used to prepare poly(2,5-dimethoxy-*p*-phenylene vinylene)



Fig. 6. Mechanistic processes for the sulfonium precursor synthesis of poly(phenylene vinylene)s, showing the ylide, the xylylene and the poly(*p*-xylylene- α -dialkylsulfonium halide) (PXD). Substituents X and Y can be alkyl, alkoxy and aryl groups. Reprinted with permission from Synthesis, properties of poly (phenylene vinylene)s, related poly (arylene vinylene)s. 1998. p. 61. chapter 3. © 1998 Marcel Dekker Inc. [147].



Fig. 7. Precursor route to PPV-containing randomly placed acetate and methoxy groups which can be selectively eliminated as a means to control conjugation length. Reprinted with permission from Synth Met 1999; 101:166. © 1999 Elsevier Science [154].

(DMPPV) of controlled conjugation length [154,155] as shown in Fig. 7.

A soluble PPV derivative which could be used directly without a second step treatment was a natural development since it would simplify device fabrication and at the same time allow for less imperfections in the final structure since the conversion process inevitably introduces defects (chemical, morphological, etc.) into the chain with the result that there is a distribution of effective conjugation lengths and these are far shorter than the nominal degree of polymerization. In fact, the different precursor polymers above discussed all give PPV, but the structural and hence electronic properties can vary quite dramatically depending on which precursor polymer was utilized [156].

Derivatization of PPV with long alkyl and/or alkoxy ramifications (RPPV, ROPPV) was the first approach for the obtainment of soluble electroluminescent polymers. The solubility by derivatization is due to the lowering of the interchain interactions, which should not in principle change the rigid rod-like character of the main chains.

A variety of PPV derivatives can be obtained from p-xylylenes by analogous routes used to obtain PPV. The 1,4-relationship of the exocyclic methylene groups seems to be important in the intermediates involved, as for the xylylenes. A wide variety of substituents are tolerated by the soluble sulfonium precursor route affording alkoxy [157–161], alkyl

[162,163], alkyl and aryl [164] substituted PPVs. These materials are soluble in organic solvents, which is a very useful feature in the preparation of polymer LEDs. Strongly electron deficient substituents tend to give polyelectrolytes that do not eliminate easily and do not give large molecular weights, but which can still be used to give homopolymers and copolymers such as 2,5-dicyano-PPV [165] and copolymers of 2nitro-PPV with parent PPV [166]. One of the first PPV soluble derivatives, prepared by the Santa Barbara group in California via the precursor route, was methoxy-ethylhexyloxy PPV (MEH-PPV), which emitted a red-orange color [167,168]. However, the desirable high molecular weight fraction of this polymer was not soluble at room temperature, and another PPV derivative with the bulky cholestanoxy group was prepared, namely the poly[2,5-bis(3α -5 β cholestanoxy)-1,4-phenylene vinylene] (BCHA-PPV). A blue shift was observed in relation to MEH-PPV; BCHA-PPV emitted in the yellow region [122,169].

3.1.2. The chlorine precursor route

An important soluble precursor route for PPV and related polymers involves the polymerization of 1,4-bis(chloromethyl) (or bromomethyl) arenes by treatment with about one equivalent of potassium *t*-butoxide in non-hydroxylic solvents like tetrahydrofuran. This methodology was first used by Gilch and Wheelwright [170] as one of the most successful



Fig. 8. The dehydrohalogenation route to PPV derivatives illustrated in the synthesis of (a) $poly[2,5-bis(3\alpha-5\beta-cholestanoxy)phenylene vinylene]$ (BCHA-PPV). CHA: cholestanol, DEAD: diethylazodicarboxylate, PPh₃: triphenyl phosphine, LAH: lithium aluminum hydride, SOCl₂: thionyl chloride, *t*-BuOK: potassium *tert*-butoxide and (b) poly(2,3-diphenyl-1,4-phenylene vinylene) (DP-PPV) and (c) poly(1-methoxy-4-(2-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV).



Fig. 8 (continued)

early PPV synthesis. Hörhold and co-workers elaborated fairly extensively on this method and recently applied it to synthesis of PPVs with large solubilizing groups on the aryl ring such as cholestanoxy (Fig. 8(a)) [169], high molecular weight [171,172], highlyphenylated PPVs [171-177] such as the diphenyl-4biphenyl ring substituted PPV which showed green EL [178], poly(2,3-diphenyl-1,4-phenylene vinylene) (DP-PPV) [174,179-181] (Fig. 8(b)). The soluble precursor is a side chain chlorinated (or brominated) polymer that, after thermal elimination, gives PPV. Without the presence of solubilizing side chains on the arene ring, premature precipitation can occur, but otherwise the method has the advantage of producing a precursor that is soluble in organic non-hydroxylic solvents, and therefore useful for electronic applications that require processing.

The chlorine precursor route has been also applied to the synthesis of the extensively explored poly(2-methoxy 5-(2-ethyl hexyloxy polyphenylene viny-lene) (MEH-PPV) (Fig. 8(c)) [182,183].

Although the sulfonium precursor route described above has been more extensively used than the chlorine precursor method, in part due to the greater number of substituents allowed, the latter affords substantially defect-free polymers [146]. A plausible source of defects in the precursor routes resides in the remaining saturated linkages between aromatic links, which can lead to localized traps via hydrogen abstraction, causing premature device decay. When the 1,4-bis(alkylsulfoniomethyl) arenes used in the sulfonium or chlorine precursor routes are asymmetrically substituted, regiorandomized PPVs are formed, although there may be some preference shown for which the benzylic proton is abstracted in the initial, ylide forming step of the polymerization, as illustrated by the X and Y substituents in Fig. 6 [141, 184,185]. Larger substituents seem to favor regioselectivity. For example, 2-bromo-5-hexyloxy-PPV synthesized by the sulfonium precursor route appears to be largely regiorandom [186] whereas poly(2bromo-5-dodecyloxy-1,4-phenylene vinylene) was found to be highly regioregular [187]. The regiochemical randomness associated with the Wesslingbased routes [186,188-190] is an important point since it affects the solid state morphology and states connected with molecular electronic architecture.

The preparation of precursors with two different leaving groups requiring different conditions for removal lead to partially methoxy substituted PPVs. This strategy enabled the formation of lithographically patterned LEDs [191,192]. In another variation of the Wessling route, non-ionic sulfinyl groups in the ethylene moiety are the leaving groups. This precursor showed better thermal stability and was soluble in organic solvents enabling structural characterization and study of the elimination mechanism [193,194]. The selective elimination of the sulfinyl group was used to give PPV with restricted conjugation lengths [195]. A modification of the Wessling route introducing a step of partial elimination of the sulfonium groups which can be transformed into methoxy groups that can be eliminated in a further step giving the final PPV was reported [196]. The PPV thus prepared had an improved chain ordering, which caused large changes in the electronic structure. The intrinsic electronic excitations were much more extended than in PPV prepared by the 'standard' Wessling route. A PPV polyelectrolyte precursor consisting of a random copolymer with acetate side groups and tetrahydrothiophenium groups with bromide counter ions was used to fabricate encapsulated single layer devices using ITO and Ca as electrodes, which have been operated in air for more than 7000 h at 20 °C without noticeable degradation [197].

In addition to the substituted aryl rings that can be incorporated in PPVs by the soluble precursor routes, it is also possible to use other aryl rings, like condensed ones, as long as they are derivable from *p*-xylylenes or their monocyclic analogs.

The obtainment of PPVs with aryl or alkyl substituents at the phenylene or vinylene group of PPV can also be accomplished by the palladiumcatalyzed coupling of dihalogenoarenes and ethylene [198].

It is a general trend that when electron donating alkoxy groups are attached to phenylene rings of PPV the bandgap is reduced and the wavelength of the emitted light shifts to red from the green region [163, 167,169,199,200]. RO PPVs where the alkoxy RO– length varied from C₅ to C₁₂ showed increasing EL intensity with increasing side chain length. This was attributed to the reductions of non-radiative decay processes due to preventing migration of excitons to traps [162]. Usually this substitution is at the 2, 5-hydrogens of the phenyls; recent work placing t-butoxy groups at the 2,3-positions in the ring showed substantial blue shift in relation to the 2,5-analog. The steric hindrance between the RO groups hindering the effective overlap of the oxygen lone pair with the aromatic ring and chain distortion were invoked as the main causes for this effect [201,202]. Halogenated derivatives of PPV as fluorine [203], chlorine, and bromine [186] substituted PPVs showed a red-shifted emission in relation to unsubstituted PPV. For monofluoro ring substitution the spectrum was similar to that of PPV itself, but for disubstitution a considerable red-shifted maximum was observed. This contrasted with results for copolymers of PPV and tetrafluoro PPV, where a slight blue shift was observed [204]. The red shift was assigned to the electronic effects of fluorine aryl ring substitution and the blue shift to shortening of effective conjugation length. The chlorine and bromine substituted PPVs vielded red emitting films (emission at 620 nm). Electrochemical measurements of copolymers of 2,3,5,6-tetrafluoro-1,4-phenylene vinylene and MEH-PPV moieties showed an increase of the oxidation and a decrease in the reduction potentials upon the increase of the fluorine content, as expected from the electron withdrawing effect of fluorine on the conjugated π -electron system. The copolymers showed emission in the red-orange region with lower turn-on voltages and higher EL efficiencies for lower fluorine contents [205]. Apart from electronic effects, intermacromolecular packing is a major factor in determining emission color and photoluminescence efficiency (PLeff). Since this quantity is a key factor in LED efficiency (along with balanced charge injection and carrier mobility as seen above), steric effects are important in the design of EL polymers. Fig. 9 shows the influence of side groups on the emission characteristics of some important PPV derivatives [206]. As a general trend close packing as in BEH-PPV (due to its lateral symmetry) results in reduced PLeff, whereas polymers bearing bulky side groups show increased PLeff, as BCHA-PPV, despite the symmetry which gives higher order in the polymer films.

Energy migration from a large band gap polymer to another with lower band gap is possible when the absorption of the latter overlaps with the emission of the former to a certain extent, and the result is an





563nm (Yellow)

Fig. 9. Influence of side groups on the emission properties of some important PPV derivatives. Reprinted with permission from Synth Met 1997; 85(1–3):1275. © 1997 Elsevier Science [206].

enhancement of the lower band gap emission. The dynamics of the excitation transfer process, measured in the picosecond timescale using an ultrafast Ti/sapphire laser, indicate that the energy transfer was completed in 10 ps when m-EHOP-PPV (poly[2-(meta-2'-ethylhexoxyphenyl)-1,4-phenylene vinylene]) was used as the host with BCHA-PPV (poly[2,5-bis(cholestanoxy)-1,4-phenylene vinylene]) and BEH-PPV (poly[2,5-bis(2'-ethylhexyloxy)-1,4phenylene vinylene]) as the guests [207]. Mixtures of poly(2-methoxy-5-(2-ethylhexyloxy-1,4-phenylene vinylene) (MEH-PPV) which emits at 600 nm (yellow -orange) with poly[1,3-propanedioxy-1,4phenylene-1,2-ethenylene(2,5-bis(bimethylsylyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene]) a conjugated-non-conjugated block copolymer, DSiPV) which emits at 450 nm (blue), yielded only the large wavelength emission. By varying the ratio DSiPV/MEH-PPV from 9/1 to 1/15 the relative quantum efficiency increased by a factor of 500. This was attributed not only to energy migration of the excitons from DSiPV to MEH-PPV but to a dilution factor as well. As the EL active MEH-PPV is diluted by DSiPV, the intermolecular non-radiative decay is diminished by blocking of the charge carriers. This effect was proved by diluting the pure polymer in a PMMA matrix, and obtaining an increase of eight times the quantum efficiency [208]. Time resolved fluorescence measurements supported the energy transfer mechanism, which was faster than the radiative and non-radiative decays. The spectral overlap between the emission of the donor (400-550 nm) and the absorption of the acceptor (420 -580 nm) was large enough for efficient energy transfer [209].

4. Conjugation confinement

4.1. Conjugated-non-conjugated block copolymers

So far we have seen that introducing substituents in the PPV molecule leads to various EL polymers, emitting in various regions of the visible spectrum according to their chemical structures. A theoretical study of the effects of derivatization can be found in Ref. [210]. From the red shift of the peaks in PL found with increasing chain length, the effective conjugation length for long chain precursor route samples of PPV are theoretically estimated to be 10-17 repeat units [211]. However, experimental work with oligomeric models led to the conclusion that the effective conjugation length of the solid polymer is not larger than 7-10 units [212].

Thus fully conjugated polymers may have chromophores with different energy gaps because the effective length of conjugation is statistically distributed. However, in the mixture, the chromophores with lower energy gaps will be the emitting species because of energy transfer. To solve this problem several approaches have been developed. The confinement of the conjugation into a well-defined length of the chain is one of the most successful strategies developed so far. Illustrative examples of EL structures exploring the concept of conjugation confinement are shown in Fig. 10 [213–215].

Copolymers in which a well-defined emitting unit is intercalated with non-emitting blocks have demonstrated that the emitted color was not affected by the length of the inert spacers but the EL efficiency of the single layer LEDs fabricated with the copolymers was a function of the length of the non-conjugated blocks; copolymers with longer spacers yielded higherefficiency devices [216]. A PL efficiency of 96% was achieved by intercalating 1,6-hexanedioxy segments with oligomethoxy PPV ($2\frac{1}{2}$ units). The effectiveness of the exciton confinement was proved through the independence of PL yield on temperature [217]. Those conjugated – non-conjugated copolymers (CNCPs) are soluble, homogeneous in terms of conjugation length, and can be designed to emit in any portion of the visible spectrum [216,218-220]. In such structures energy transfer from high band gap to lower band gap sequences in which excitons may be partially confined will provide higher luminescence efficiency when compared to similar structures of uniform conjugation. It has been demonstrated, for example, that the random interruption of conjugation by saturated groups in the prototypical electroluminescent polymer poly(phenylene vinylene) (PPV) [221] increased the devices efficiency by up to 30 times in relation to the corresponding PPV devices [222]. The fluorescence quantum yield in solution rapidly decreased with increasing average conjugation length in MEH-PPVs. This polymer was prepared by selective elimination of acetate groups













Fig. 10. Examples of El polymers exploring the concept of conjugation confinement. (a) An aliphatic spacer separating PPV type blocks [226]; (b) aliphatic spacer separating ethynylene–anthracene–phenylene blocks [234]; (c) dimethylsilane groups separating PPV type blocks [232]; (d) partially eliminated MEH-PPV [155]; (e) hexafluoroisopropylidene non-conjugated segment separating polyquinoline emitting units [131]; (f) adamantane moiety as spacer [215]; (g) kink (*meta-*) linkages in MEH-PPV [228]; (h) the planarity is interrupted by the twisted *p*-phenylene groups, schematically illustrated with the wiggled lines [233].



of a precursor containing various amounts of methoxy and acetate groups [223]. In soluble poly(dialkoxy-*p*phenylene vinylene)s, the systematic variation on the degree of conjugation showed that PL and EL increased with the fraction of non-conjugated units. The highest external electroluminescent efficiency (1.4% photons/electron) was measured for a polymer having about 10% non-conjugated units [224]. These effects are attributed to the decrease of interchain interactions with interruption of the conjugation, resulting in higher quantum efficiencies for photo and EL, as discussed above under Interchain Excitons (Section 2.1).

At the same time, confinement of the effective conjugation has proved to be an efficient means for blue shifting the spectrum because the conjugated emitters can allow charge carriers to form but not to diffuse along the chain, thus limiting the transport to quenching sites [225,226]. This electronic localization results in a large $\pi - \pi^*$ band gap which decreases with conjugation length [191].

A widely used route to CNCPs involves the Wittig type coupling of dialdehydes with bis(phosphoranylidene)s [227,228] as schematically shown in Fig. 11. This method was used to prepare a welldefined CNCP, having *p*-phenylene vinylene blocks (so called $2\frac{1}{2}$ PPV units) intercalated by an aliphatic spacer which was the first blue soluble emitter (465 nm) [229]. A series of CNCPs was prepared, varying the $-O(CH_2)_nO-$ spacer length, and chromophore's structure (PPV type) and length allowing to correlate conjugation length with emission color and device efficiency [216,218-220]. Changing the aromatic ring from a *p*-phenylene to a *p*-thienylene residue caused band gap shifts in which the emission changed from blue to yellow [219,229,230]. The effects of molecular architecture and chromophore substituents on the optical and redox properties of



x = 2,4,6,8,10,12, ...

Fig. 11. Wittig route to conjugated non-conjugated block copolymers (CNCPs). Reprinted with permission from J Macromol Sci, Pure Appl Chem 1998; A35(2): 233. © 1998 Marcel Dekker Inc. [216].





Fig. 12. Examples of EL polymers with emitting pendant groups (a) stilbene chromophores linked to a polystyrene backbone [111], (b) PPV type segment linked directly to a polystyrene backbone [244], (c) fluorinated oligo-*p*-phenylene as side chains in polystyrene [245], (d) anthracene derivatives linked to a poly(methyl methacrylate) backbone [249], (e) naphthalimide based chromophore as side chain in poly(methyl methacrylate) (f) poly(methyl methacrylate) containing carbazole and PV chromophores bearing electronwithdrawing nitrile groups [251], (g) 9,10-diphenylanthracene linked to a PPV type structure [253], (h) same as in (g) but separated from the main chain through hexamethylene spacers [253].





Fig. 12 (continued)

PPV-based alternating copolymers with an aliphatic spacer was recently reported [231]. The introduction of non-conjugated segments not only confines the π -electrons in the conjugated part but also imparts solubility and improves the homogeneity of the films. The Wittig route (as with other condensation routes) does not lead to high molecular weight polymers because these become insoluble after a certain degree

of polymerization is reached. In CNCPs the solubility provided by the spacer permits the obtainment of high molecular weight materials. Structures combining chromophores in a linear fashion with non-conjugated spacers have been made, like the copolymers with the short spacer $[-(CH_2)_3-]$ and $2\frac{1}{2}$ PPV units. In this case, it was necessary to attach flexible long alkoxy side groups or trimethyl silyl groups for solubility.

The latter showed blue EL (470 nm) and a red shift was observed for the alkoxy substituted polymer [232]. An analogous structure bearing two octyl side groups, a blue emitter, showed lasing properties [233]. The blend of the CNCPs, poly[9,10(1,3-bis(4-ethynylphenoxy)propane)anthracene] (Fig. 10(c)) or poly[1,2(tetra-2,5-thienylene-1,2-vinylene)dimethylsilylethane] with PVK/PBD afforded blue-green to red LEDs [234]. A series of rigid-flexible copolyethers containing blue and yellow emitting conjugated segments separated through aliphatic spacers have been prepared using the phase-transfer catalyst tetrabutylammonium hydrogen sulfate. As blue chromophores dihexyloxy-substituted quinquephenyl units, styrylbiphenyl segments laterally attached to the main chain, or *m*-distyrylbenzene were selected, representing different ways to increase solubility. As a yellow chromophore, the acetoxy functionalized 9,10distyrylanthracene unit was selected. Energy transfer from the blue to the yellow emitters was observed, in all excitation wavelengths. The mechanical (stressstrain curves) and dependence of the loss modulus (E'') with temperature were reported as well. These properties, which are important to describe the material's behavior towards mechanical stresses needed for device performance, were not addressed before [235].

Long aliphatic spacers have also been used, like polyethylene glycol ($M_n = 900$) linking distyryl (PPV model oligomer), producing a blue emitter with lasing properties [236] and polystyrene linked to poly-pphenylene and to poly(3-hexylthiophene). The turnon voltage of the latter was four times lower than that of a similar device based on the respective homopolymer, and the external quantum efficiency was about 10^{-4} photons/electron, a very high figure for LEDs utilizing poly(alkyl thiophene)s [237]. Liquid crystalline behavior was observed in copolymers with methylene sequences up to 10 units intercalated with ring substituted distyryl blocks. The orientation was achieved by using rubbed polyimide surfaces, making them potentially useful for the fabrication of LEDs emitting polarized light [238].

Conjugation confinement can also be achieved by tailoring the polymer structure in other ways, like inserting kink (*ortho* and *meta*) linkages or imposing steric distortions. Alkoxy substituted PPVs usually carry the alkoxy groups at the 2,5-positions in the ring

and are red shifted in relation to unsubstituted PPV. By placing these substituents at the 2,3-positions and the ring in a meta-configuration it was possible to obtain blue emitting alkoxy-PPVs [202]. The irregular chain structure with meta-linkages also reduces interchain interactions that often limit PL efficiencies through the effects of aggregation and excimer formation [239,240]. It is interesting to note that the insertion of a meta-phenylene linkage influenced the band gap more than the aliphatic spacer $\left[-(CH_2)_6O^{-1}\right]$ in alkoxy substituted PPV type block copolymers [219] and that ortho links have been reported to influence the electronic structure of MEH-PPV-co-PPV in a comparable way as *cis* bonds in PPV [228]. Steric interactions induced by side chains have also been used as a means to interrupt conjugation [241]. The combination of these strategies in the same polymer chain is not uncommon [219,221,222].

4.2. Chromophores as side groups

An extension of the concept of CNCPs is the attachment of the fluorofore as a pendant group to a non-emitting random coil polymer. This idea should in principle present several advantages: the synthetic route would be simpler than that used for main-chain polymers, the solubility would be dominated by the nature of the backbone, the emission wavelength would be predetermined, and crystallization of the chromophore with concomitant degradation of the diode (in comparison with small molecular weight sublimable systems) would be prevented. In addition, an electroluminescent group could be placed on every repeat unit or in a controlled frequency along the backbone. Some representative EL structures with emitting pendant groups are shown in Fig. 12.

Using polystyrene as the main chain, stilbene groups were attached to every repeat unit [109], in every other repeating unit, or in every third repeat unit (Fig. 12(a)) [110,242,243], resulting in blue emitting polymers. Grafting 4-vinyl-*trans*-stilbene [244] (Fig. 12(b)) or fluorinated oligo-*p*-phenylene [245] (Fig. 12(c)) into this same backbone also resulted in blue emitting polymers [244]. High PL quantum yields for solution cast films (95%) were obtained for the former structure (2–4 rings inserted) indicating that intermolecular quenching effects were non-existent [246]. Blue emitting polymers bearing diphenylanthracene as

a side chain chromophore linked to a polynorbornene backbone were prepared via ring opening metathesis polymerization using a commercially available molybdenum initiator, giving polymers in a controlled (living) manner [247]. Several lumophores have been attached to poly(methyl methacrylate) (PMMA) as pendant groups, like carbazole and fluoranthene, alone or combined in the same chain [248]. In this case only the fluoranthene emission (yellow green, 521 nm) was detected, due to energy transfer. Grafting anthracene derivatives (2,3,7,8-tetramethoxy-9,10-dibutyl anthracene) (Fig.12(d)) and N-methyl naphthalimide (Fig. 12(e)) gave blue and green PMMA based lightemitting materials. An orange device was obtained by doping the latter compound with the DCM orange dye. The blue device had a turn-on voltage of only 6 V which is an interesting value since blue emission corresponds to high molecular energies, and the green device gave a 30% PL quantum yield for solution cast films [249,250]. A series of carbazole (25%) and phenylene vinylene (75%) fully substituted PMMA based copolymers (Fig. 12(f)) showed greenish-blue emission (474 nm). When nitrile groups were attached to the double bond of the phenylene vinylene moiety, the emission shifted to the yellow (526 nm); the turn on voltages were in the 15–20 V range [251]. Charge transfer and emission from associated forms (ground state dimers or excimers) are common events in pendant chromophore structures. Examples include the pyrene excimer only emission of polysiloxanes bearing a pyrene group in each mer and the suppression of carbazole emission of copolymers containing carbazole and pyrene attached to a polysiloxane backbone or carbazole and fluoranthene attached to a PMMA main chain [248]. PPV has also been used as a backbone for grafting of lumophores, giving rise to a structure with more than one simultaneously emitting center, like PPV containing the electron accepting trifluoromethyl stilbene moiety. This group emits in the violet, but the substituted PPV showed only the PPV characteristic emission, due to energy transfer [252]. On the other hand, an interaction between the π electrons of the main PPV chain and those of an attached anthracene derivative (9-phenyl anthracene) (Fig. 12(g)), has been observed. A broad PL emission spectrum was observed, due to the anthracene and PPV simultaneous emissions, by placing a hexamethylene spacer between the PPV main chain and 9,10-diphenyl

anthracene (Fig. 12(h)). In contrast, the EL emitted light was due mostly to the main PPV chain [253]. The concept of pendant chromophores has been also explored to afford better transport properties, by covalently attaching charge transport groups to the emitting polymer, therefore avoiding problems such as crystallization or aggregation of the dispersed transporting molecules. The hole transporting carbazole and the electron transporting 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole) (PBD) were placed as side groups in each mer of PPV. A slight interaction between the π -electrons of the PPV backbone and those of the pendant groups was detected. Also, blueshifted absorptions indicated that steric effects partially disrupted the conjugation in PPV; both copolymers showed overlapped emissions of the main chain and the side groups. The direct PBD attachment to PPV improved the EL efficiency to a great extent, but the carbazole insertion resulted in an increased imbalance in carrier transport, since PPV itself accepts and transports holes more readily than electrons [254,255].

The random copolymer poly[(benzodithiazole)-(1,4-(2-hydroxy)phenylene))-*co*-(benzodithiazoledecamethylene)], in which the EL is provided by a mechanism of electrically generated intramolecular proton-transfer [256], is also an example of rigid active blocks separated by aliphatic spacers.

To prevent intermolecular aggregation in quaterphenyl and sexiphenyl block copolymers, an aliphatic spacer with long alkoxy chains (12 carbon atoms) perpendicular to the polymer backbone was reported [257].

Apart from designing a molecule capable of emitting light in a defined region of the visible spectrum, a very interesting approach is to design structures that can emit light over a broad spectral range so that the color emitted is white or close to it. With this objective polymers carrying more than one chromophore were prepared like the ring anthracenyl substituted PPV shown in Fig. 12(g) [253].

White color emission was obtained by blending MEH-PPV with a side chain luminescent polymer, an alkoxy(trifluoromethyl)stilbene-substituted PMMA derivative (CF₃PMA). The EL peak of the MEH-PPV rich blend ranged over 580-800 nm (orange-red) and that of the CF₃PMA rich blend ranged from 380 to 800 nm, as shown in Fig. 13 [258].



Fig. 13. White light emission of a blend of MEH-PPV and CF₃–PMA. Reprinted with permission from Macromolecules 1997; 30:7749. © 1997 American Chemical Society [258].

5. Polythiophenes

Among various polymers for LED fabrication poly(3-alkylthiophene) (PAT) [77] has stimulated much interest because it was the first soluble and even fusible conducting polymer, and it demonstrated novel characteristics such thermochromism [259] and solvatochromism [260]. EL in these materials was first reported by Ohmori [261,262], and it is now possible to tune the emission of substituted polythiophenes from ultraviolet to IR by changing the substituent [263].

Yoshino et al. [264] have reported the anomalous dependence of PL in PAT on temperature and alkyl chain length. LEDs made with PAT emitted a redorange color [75] peaking at 640 nm. For the series in which the side chain is an aliphatic branch of 12, 18 or 22 carbons the EL intensity increased linearly, the latter (22 carbons) being five times brighter than

the former (12 carbons). This was explained in terms of confinement of carriers on the main chain where longer substitutions accounted for greater interchain distance decreasing the probability for quenching [248,265]. The emission intensity of PAT-based LEDs increases with increasing temperature (20– 80 °C) contrary to inorganic GaAs and InGaP semiconductor diodes [266]. This was explained in terms of changes in effective conjugation length with temperature due to changes in the main chain conformation which decreased the non-radiative recombination probability [262]. Some representative polythiophene structures are shown in Fig. 14.

Polythiophene and substituted polythiophenes can be prepared by chemical or electrochemical routes [267]. The eletrochemical method gives crosslinked materials, and chemical synthesis is most straightforward, in the iron chloride oxidative polymerization route. A particular point in this aspect is that of obtaining regioregular polymers, since regioregularity strongly influences the optical and transport properties of polythiophenes [268]. A study on the effects of the conditions of sample preparation in the extent of conjugation in non-regioregular poly(3-hexylthiophene) has been reported [269]. Electrochemically deposited poly(3-methyl thiophene) and chemically produced poly(3-phenoxymethyl thiophene) have been employed as the top electrical contact on porous silicon LEDs. The polymer-capped devices emitted white light, as opposed to the uncapped devices, which emitted orange color [270].

The dihedral angle and thus the π -orbital overlap between adjacent thiophene rings along the polymer backbone determine the conjugation length along the polymer chain. Short conjugation gives a blueshifted emission and long conjugation gives a redshifted emission. Three main strategies have been used for controlling the conjugation length and band gap in polythiophenes. In the first the conjugation length is modified by adding different substituents on the repeating unit, imposing continuous steric torsions of the main chain [271]. In Fig. 14 polythiophenes bearing substituents at positions 3 and 4 in the ring are shown and illustrate the shifts in emission resulting from different degrees of torsion. The larger substituents give a large dihedral angle between the rings, and short conjugation along the polymer backbone is achieved, resulting in blue-shifted emission. This way emission from the blue (PCHMT), green (PCHT), orange (PTOPT) to red (and NIR) (POPT) were observed [54,272]. With mixtures of these polymers it was also possible to obtain voltage controlled EL and white light emitters [272]. For poly(3-(2,5-octyldiphenyl)thiophene) (PDOPT) the bulky side chains efficiently separates the backbones giving the polymer a high PL yield (0.37 in solution and 0.24 in film). PTOPT has a lower density of side chains, and the PL yield reduces from 0.27 to 0.05 going from solution to thin film. PMOT is twisted out of planarity by sterical hindrance and shows blue-shifted absorption and emission [273]. Substituted polythiophene-containing electron transporting groups such as benzotriazole, chlorobenzotriazole and fluorene have also been reported [274,275].

Poly(3-octyl thiophene), which can be obtained as a 95% regioregular material, offers an example of how super structure can affect the electronic properties of an emissive polymer. When spin coated from solution a metastable film (POPT^{*} in Fig. 14) is obtained, which can be converted (POPT** in Fig. 14) by a short thermal treatment or by exposure to solvent. The conversion is accompanied by a strong shift of the optical properties, the color of the film changes from red to purple, and the EL emission changes from orange-red to near infrared, from 670 to 800 nm. It is possible to shift the absorption maximum continuously between those two states. This conversion is also evident in X-ray diffraction studies of thin films using synchrotron radiation, where an enhanced crystallinity has been observed after conversion [276].

The importance of the solvating alkyl groups in the electronic properties of P3ATs was addressed in terms of the excited state dynamics, the nature of the excited states, and their influence on the solvato- and thermochromic properties of these polymers [103]. Changing from poly(3-hexylthiophene) to poly(3-dodecylthiophene) increased the maximum efficiency from 0.05 to 0.2% with calcium electrodes [277]. The role of the solvating alkyl groups in polythiophenes was studied by using quantitative time-resolved and steady-state luminescence spectroscopy in PATs [103] and in the structures shown in Fig. 14.

The phase structure in blends of one or more polythiophenes with a PMMA matrix allowed



Fig. 14. Effect of substitution on the emitting properties of polythiophenes. POPT* and POPT* * are different forms of the same polymer, as explained in the text.

the fabrication of nanoLEDs giving white light emission [206]. The insulating polymer (PMMA) was used to diminish the energy transfer from high band gap to low band gap components [263]. Other approaches to tune the emission color of polythiophene LEDs are the preparation of completely coplanar systems with controlled inclusion of head-to-tail dyads or the preparation of alternating

block copolymers. In the first approach the head-totail dyads interrupt the conjugation length, which varies from 1 to 4 mers. These materials were prepared as shown in Fig. 15(a), and give emission spectra spanning from 460 to 650 nm in EL [278]. The synthesis of these polymers was carried out by reacting 3,3'-dioctyl-2,2'-bithiophene with two equivalents of *n*-BuLi to give the corresponding dilithium salt. The addition of magnesium bromideetherate afforded the corresponding di-Grignard compound, which was coupled with dibromo-oligthiophenes to provide the regiospecific polymers [278]. Recently Heeger et al. [279] reported the synthesis of a structure consisting of head-to-head thiophene dyads linked to a p-phenylene ring, with different substituents on both thiophene and phenylene. The insertion of the latter enhanced by 29% the PL efficiency, in comparison with other polythiophenes, and by changing the substitution on both the phenylene and thiophene rings, the electronic spectrum of the polymers could be tuned, emitting blue to green light. Another approach to regioregular polythiophenes bearing alternating alkyl and fluoroalkyl side chains made use of the regioregular polymerization of the suitable substituted bithiophene [280].

Alternating block copolymers in which oligosilylene blocks alternate with oligothiophene blocks have been prepared in attempts to chemical tune the emission of polythiophenes [281]. These electroluminescent polymers are conceptually similar to the conjugated-non-conjugated block copolymers of the PPV type with regard to the notion of exciton confinement: the oligothiophene blocks exhibit a delocalization of the electron density, while the oligosilylene blocks could be considered as intrinsically non-conjugated. It was observed, however, that conjugation extended across the oligosilylene blocks and that the $\pi - \sigma$ conjugation decreased with the length of the oligothiophene block. The chemical tuning in this case was based on the size of the oligothiophene block. The stabilization of the photoexcited states on these blocks was assisted by the oligosilylene substituents [281–283]. The synthesis of a poly(silanylene)hexathiophene with two octyl substituents in non-adjacent rings is shown in Fig. 15(b), through a nickel-catalyzed Grignard cross-coupling polymerization.

Block copolymers containing thiophene units of several lengths alternating with aliphatic spacers [125] and polyesters [284–287] have been reported. The emission of a series of p-n diblock copolymers with good electron-transporting properties where oligothiophenes were linked with oxadiazolyl-dia-lkoxybenzene units could be tuned from blue to green to orange by increasing the number of thiophene rings from 1 to 3 [288,289].

The thermochromism and the temperature dependence of the optical properties in polythiophene derivatives containing an urethane side chain with strong inter- or intra hydrogen bonds have been addressed by Tripathy et al. [290]. Within a limited temperature range the EL and PL intensities increased with increasing temperature and this was attributed to the thermally induced deformation of the ordered portion of the polymer chain [290].

As previously mentioned, the use of the electron transporting material PBD as a thin layer in LED fabrication can increase notably the quantum efficiency compared to devices without a PBD layer. When used as a 1100 Å thick layer in combination poly[3-(4-octylphenyl)-2,2'-bithiophene] with (PTOPT) as another layer (400 Å thick), multiple peak emissions were observed [291]. The device had the ITO/PTOPT/PBD/Al configuration and the EL spectrum was characterized by three peaks: 400 nm (blue), 530 nm (green) and 610 nm (red-orange) which appeared as a bluish white to the eye. The first emission was assigned to the PBD and the last to PTOPT but the intermediate could not be assigned by singlet recombination to either of the components. The interesting feature is that this intermediate emission in the EL was not present in the PL spectra of ITO/PTOPT/PBD structures. It was proposed that the enhanced concentrations of active species at the interface between the hole transport and the ETLs, in combination with the high electric field, may allow infrequent transitions to occur under PL conditions. The green peak was assigned to a transition between electron states in the PBD and hole states in PTOPT, i.e. radiative transfer of electrons generated in PBD to holes in the polymer [291].

When blended with the blue emitter ladder poly(*p*-phenylene), enhanced yellow emission was obtained from poly(decyl thiophene) (PA10T).The effect was



b)

904



R: Me y: 1,2,4 and 8 R: Bu y: 1,2

Fig. 15. (a)Synthetic route to regiospecific polythiophenes in which the alkyl substituents are in a head-to-tail configuration and the length of the coplanar blocks was varied systematically [278], (b) synthetic route to poly[(silanylene)hexathiophene]s [281]. Reprinted with permission from Adv Mater 1994; 6:132, Macromolecules 1995; 28:8102. © 1994, 1995 VCH Verlagsgesellschaft mbH, American Chemical Society [278,281].

attributed to energy migration from the blue emitter to the polythiophene [292].

octylphenyl)thiophene) (POMeOPT) the currentvoltage characteristics of single layer devices were measured in two regimes: contact limited current and bulk-limited current. The passage from one regime to

In a recent study [293] of the transport properties of a polythiophene derivative, poly(3-(2'-methoxy-5'-

another was done upon insertion of a conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT-PSS) between the metallic electrode and the POMeOPT. The measured mobility was seven times higher than that for MEH-PPV in the same conditions, illustrating the good transport properties and high mobility that can be attained with regioregular substituted polythiophenes.

6. Cyanopolymers

Most of the electroluminescent polymers are suitable as hole-injecting and transporting materials [20]. To set an adequate balance in the injection flows coming from each side of the device it has been necessary to use electron transporting layers and/or low work function metals at the cathode, like calcium, which is unstable at atmospheric conditions. The synthesis of polymers with high electron affinity as the solution processable poly(cyanoterephthalydene)s which are derivatives of PPV with cyano groups attached to the vinylic carbons has provided the material necessary to complement the existing hole transport PPVs [103,120,210,294-299]. Poly(arylenevinylene)s bearing electron withdrawing groups are not easily available by application of the Wessling and related procedures and thus these cyano derivatives of PPV were synthesized via a Knoevenagel condensation route between an aromatic diacetonitrile and the corresponding aromatic dialdehyde [300,301] as exemplified in Fig. 16(a), or by copolymerization of dibromoarenes in basic medium (Fig. 16(b)). This approach permits adjustment of the band gap by varying the proportion of the two comonomers [302].

The synthesis of fully conjugated PPV type structures containing cyano groups attached to the ring afforded a more perfect structure when a Wittig type condensation was followed (Fig. 16(c)), as compared with the Knoevenagel route, emitting orange light (3000 cd/m² at 20 V) in a double layer device with PPV as HTL [303].

A variety of monomers with different substituents in the ring as alkyl or alkoxy solubilizing groups (as hexyloxy or methoxy-ethyl-hexyoxy as in MEH-PPV) were used to prepare cyano PPV like polymers emitting in the full-visible spectrum. The inclusion of thiophene units in the main chain lowers the band gap and shifts the emission to the infrared [304]. Examples of various EL polymers bearing cyano groups are given in Fig. 17.

The electron withdrawing effect of the cyano group is calculated to increase the binding energies of both occupied π and unoccupied π^* states, while at the same time keeping a similar $\pi - \pi^*$ gap [305]. Experimental results for a two layer device made with PPV as the HTL and CN-PPV as emitter gave an external quantum efficiency for light emitted in the forward direction of 2.5% and estimated internal quantum efficiency in excess of 10% with a luminance of 100 cd/m² at 5 V bias [296,306]. The increase in binding energy of the cyano polymer in comparison to MEH-PPV measured by cyclic voltametry was about 0.5 eV [299] and solid state PL efficiency was around 50% [224,307] while PPV showed efficiency of 27% [200]. Emission mechanisms in solution and in the solid state using time resolved spectroscopy [107,308] were also studied in connection with HTLs and silicon-based anodes [304]. The higher PL quantum yield of solutions (0.52) in comparison with films (0.35) and the much longer lifetime of emitting species in films (5.6 ns) than in solution (0.9 ns)strongly indicated that in cyano-substituted PPV the emission originates from interchain excitations [103, 107,308] that could come from a (physical) dimer or an excimer. The photophysical behavior of these polymers indicated that the excimer was probably the emitting associated form. The minimum energy configuration of a stack of five face-to-face polymer segments, each long enough to accommodate three phenyls, was calculated by applying a Monte Carlo cooling algorithm. An interchain distance of 3.3 Å was found, less than that found for other polymers such as MEH-PPV which showed an interchain distance of 4.04 Å. The molecular registry was such that the cyano group in one chain overlaps the edge of a ring in the nearest chain. The smaller distance between CN-PPV chains, due to the high electron affinity of the cyano group, would lead to a larger excimer emission probability, calculated to be 16-20 times larger than MEH-PPV [95].

Another class of cyano substituted PPV lightemitting polymers was developed in which the chromophores were isolated from each other through a flexible spacer. Copolymerization improves polymer



solubility in volatile organic solvents and decreases crystallinity, improving the film forming properties, and also increases the band gap by confining conjugation. It also brings about molecular dilution of the emitting centers, decreasing self-quenching probability. Polymers having an octamethylene spacer between methoxy-PPV segments containing cyano groups in the double bond or in the 2,5-positions in the aromatic ring [303] emitted an orange-red or yellow light, respectively, in contrast with a similar structure



Fig. 16. Synthetic routes to CN substituted EL polymers: (a) Knoevenagel route leading to CN placement in the double bond, (b) copolymerization of dibromoarenes in basic medium, (c) Wittig route used to place the CN group in the aromatic ring in a conjugated-non-conjugated block copolymer.



Fig. 17. Examples of various EL polymers bearing the CN group in the double bond or in the aromatic ring. (a) and (b) [296], (c) [300], (d) [245], (e)–(g) [303].

without the cyano group which emitted in the blue region. The observed bathochromic shift is due to the lowering of the conduction band and in the case of the poly(cyano terephthalydene)s the LUMO was lowered by 0.9 eV (and HOMO by 0.6 eV) in relation to the non-substituted analogs [120]. Similar structures without the methoxy groups in the PPV type segment emitted in the green region [309]. Segments of 2,5-dicyano-1,4-phenylene vinylene interspersed among MEH-PPV sequences showed improved performance in comparison with MEH-PPV, in single layer devices, also emitting in the orange [302].

7. Poly-(p-phenylene)s (PPP) and polyfluorenes

7.1. Polyphenylenes

Poly-(*p*-phenylene) (PPP) is an interesting material for electro-optical applications as its band gap is in the blue region of the visible spectrum and its thermal stability is combined with high PL. However, it is insoluble and infusible making it difficult to fabricate thin films. In the early stages of the search for PPP synthesis the limitations were related to the difficulties in the preparation of polymers possessing a defined architecture. Oxidative coupling of benzene via the Kovacic method [310] leads to branched, low molecular weight products that are infusible and insoluble in organic solvents. Other routes, such as the reductive conversion of poly(cyclohexa-1,3-diene), also proved not to be effective [311].

The first devices based on PPP were prepared via a precursor route, which resulted in 10% ortho-linkages (defects) [297]. Since only a few 'classical' organic reactions are known to generate a direct link between aromatic units, metal catalyzed coupling reactions are commonly used for this purpose. The most successful routes are the Yamamoto route and the Suzuki crosscoupling reactions (SCC). The Yamamoto route involves the Ni mediated coupling of arenes by the reaction of the correspondent dibromo-substituted compounds [311]; the SCC involves the palladiumcatalyzed cross-coupling reaction between organoboron compounds and organic halides. When applied to polymer synthesis, it proved to be a powerful tool to prepare poly(arylene)s and related polymers. In this case, SCC is a step-growth polymerization (Suzuki cross-coupling polymerization, SCP) of bifunctional aromatic monomers. The general method has been reviewed [312] and a wide variety of polymer structures prepared through this method [313]. In Fig. 18 a schematic representation of the step growth SCP is shown.

Recently, blue EL devices have been prepared by the vacuum-deposition of linear PPPs bearing 8-9 phenylene rings, which was known to be an effective conjugation length. The oligomers were prepared by the polycondensation of dihalogenated aromatic compounds (X-Ar-X type) with a zero-valent nickel complex. After removing the low molecular weight products, the thin PPP film was deposited onto an ITO substrate by heating the powder to 500 °C under a vacuum of 2×10^{-6} Torr [314–316]. A series of copolymers consisting of *p*-phenylene and *m*-phenylene units randomly placed was prepared from the mixture of the corresponding Grignard reagents from 1,4- and 1,3-dibromobenzenes (Fig. 19). Their condensation was accomplished in the presence of the dichloro(2,2'-bipyridine)nickel(II)catalyst (Yamamoto route). Soluble products were obtained when the concentration of para-units was below 60%. Thin films were combinatorially deposited by vacuum evaporation with a fixed mask and slit masks, allowing optimization of bilayer films [317]. Alkylated, soluble PPPs prepared via coupling reactions using the Yamamoto [311] or Suzuki [318] routes yielded significant torsion angles. The inter-ring twisting significantly changes the electronic structure as well as the conjugation length [319].

Copolymers consisting of oligo *p*-phenylene sequences linked by ethylene, vinylene or units have been reported. By the combination of different AA/BB type monomers in various concentrations in a Suzuki coupling as polymerization route, a variety of well-defined structures were prepared with high quantum yields in solution [320] as shown in Fig. 20.

Monodisperse fractions of low molecular weight alkoxy-substituted PPPs were analyzed by matrixassisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) and HPLC. The results indicated that the effective conjugation length in these substituted PPPs was around 11 phenylene units [321].

One way of obtaining a planar conjugated backbone was to incorporate the phenyl rings into

$$(RO)_{2}B \longrightarrow Ar \longrightarrow B(RO)_{2} + X \longrightarrow Ar' \longrightarrow X \xrightarrow{Pd(0)} (Ar \longrightarrow Ar' \longrightarrow Ar$$

Fig. 18. Schematic representation of the SCP. -Ar- represent aromatic units, typically benzene derivatives.

a ladder-type structure where four C-atoms of each phenyl ring are connected with neighboring rings (LPPP) in combination with an additional attachment of solubilizing side groups, thus creating a solution processable structure. The synthesis followed a Suzuki coupling, in which unsubstituted or alkyl substituted aromatic diboronic acids reacted with 2',5'-dibromo-4-alkyl-4'-(4-alkylbenzoyl)benzophenone as shown in Fig. 21 [322-327]. The forced planarity of the molecule led to a high degree of intrachain order, with a conjugation length of about eight phenyl rings [328,329]. The EL spectrum of the structures showed two emissions: a blue (461 nm) and a yellow (600 nm). The latter was attributed to the formation of excimers. The relative height of the blue emission and hence the emission color in the bluegreen region could be controlled by varying the intensity of the applied field [330]. To decrease the excimerization, a modification of this structure was made by inserting oligo(*p*-phenylene) spacers, which caused a distortion of the rigid ladder type subunits [331,332]. The oligo phenylene spacers were introduced as a third dibromoarylene comonomer in the synthetic route showed in Fig. 22 [333]. Similar structures carrying phenanthrene units were recently reported [334]. The electronic states in excited LPPPs have been addressed in Refs. [335,336]. The same methodology was employed to synthesize alternating copolymers of p-phenylene sequences and poly(ethylene glycol) (Fig. 23(a)). The solubility limit was set at seven rings in the *p*-phenylene block [337]. Similar structures in which quaterphenyl and sexiphenyl pphenylene groups were linked by a spacer group with a long alkoxy chain perpendicular to the polymer



Fig. 19. Synthetic route to random copolymers of *p*-phenylene (PP) and *m*-phenylene (MP): poly(PP-ran-MP-*m*/*n*) [317].



Fig. 20. Polymers containing oligo-*p*-phenylene sequences linked by ethylene (E), vinylene (V) or ethynylene (A). The numbers correspond to the degree of polymerization of the phenylene sequences. The monomers were connected through the Suzuki coupling method.

backbone were used to fabricate bright blue LEDs (Fig. 23(b)) [257]. A blue emitting PPP copolymer was reported in which tri-(p-phenylene) (LPP) and oligo(phenylene vinylene) (OPV) segments were linked in an orthogonal arrangement (Fig. 23(c)) to decrease quenching processes by aggregation of emissive units [333]. Energy transfer from LPP to OPV was observed in these structures. Analogous structures with oligo(p-phenylene) units orthogonally and periodically tethered to a polyalkylene main chain have been prepared by the polymerization of oligomeric fluoreneacenes via an S_N2 type of mechanism [338] (Fig. 23(d)). Another class of PPP-type polymer is exemplified by the poly(benzoyl-1,4-phenylene) in a head-to-tail configuration. Single layer devices

showed blue emission with brightness in the order of 100 cd/m^2 [339].

Polyelectrolytes based on PPP have been synthesized as both anionic or cationic materials. The anionic derivative was the di-sodium salt of poly[2,5bis(3-sulfonatopropoxy-1,4-phenylene-*alt*-1,4-phenylene] (PPP-OPSO₃) and the cationic counterparts were poly[2,5-bis(3-{N,N,N-triethylammonium}-1oxapropyl)-1,4-phenylene-*alt*-phenylene]dibromide (P-NEt₃⁺) and poly[2,5-bis(3-{N,N,N-trimethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-phenylene]dibromide (P-NEt₃⁺), (Fig. 23(e)). The neutral polymers, prepared via a Pd catalyzed Suzuki coupling, were soluble in organic solvents, and the quaternary ammonium functionalized PPPs were


Fig. 21. Synthetic route to ladder poly(phenylene vinylene)s (LPPP)s.





R': n-hexyl

Fig. 22. Ladder poly(*p*-phenylene) containing linear sequences of alkylated *p*-phenylene. These groups effect a twisting in the chain, hindering aggregation. Reprinted with permission from ACS Symposium 1997. chapter 4. p. 358. © 1997 American Chemical Society [322].

water soluble and showed blue luminescence with an intensity that varied with ionic composition. The polymers formed compatible blue emitting devices via layer-by-layer polyelectrolyte self-assembly, for hybrid ink jet printing fabrication of pixilated LEDs [340].

Efficient yellow LEDs were prepared from blends of a blue emitting ladder PPP (m-LPPP), (Fig. 23(f))

Fig. 23. Examples of EL polymers containing phenylene sequences: (a) block copolymers with segments of five *p*-phenylene rings and polyethyleneglycol of $M_w = 1000$ g/mol [337], (b) copolymers with sexiphenyl units and a spacer [257], (c) El polymer combining ladder type tri(*p*-phenylene) and oligo(phenylene vinylene) segments [333], (d) ladder-type oligo(*p*-phenylene) tethered in a periodic orthogonal position to a polyalkylene main chain [poly(alkylenefluoreneacene)], m = 4-6 or 8 [338], (e) luminescent cationic polyelectrolyte based on poly(*p*-phenylene): poly[2,5-bis(3-{*N*,*N*,*N*-triethylammonium}-1-oxapropyl-1,4-phenylene-*alt*-1,4-phenylene]dibromide [340], (f) blue emitting methyl substituted ladder type PPP (*m*-PPP) [342].



and small amounts (0.5-2.0%) of the orange emitting poly(decyl thiophene). The external EL quantum efficiency increased from 2.0% (pure *m*-LPPP) to 4.2% (blend). PL excitation spectra supported the assignment of the emission to Förster type excitation energy transfer [341,342].

The fabrication of red-green-blue and white emission devices was achieved by means of the deposition of layers of *p*-hexaphenyl oligomer, methyl substituted ladder type poly-*p*-phenylene (Fig. 22) and poly(perylene-*co*-diethynylbenzene) [343]. EL emission colors over the entire visible range have been obtained by controlling the composition of molecular beam deposited layers of oligophenylene vinylene and oligophenylene [344].

7.2. Polyfluorenes

Recently, polyfluorenes were introduced as a prospective emitting layer for polymer LEDs. These materials are thermally stable and display high PL efficiencies both in solution and in solid films [345-349] with emission wavelengths primarily in the blue spectral region. Their photostability and thermal stability are also found to be better than those of the poly(phenylene vinylene)s [347]. Polyfluorenes contain a rigidly planarized biphenyl structure in the fluorene repeating unit, while the remote substitution at C-9 produces less steric interaction in the conjugated backbone itself than in comparison with PPP, in which this interaction can lead to significant twisting of the main chain since the substituents used to control solubility are ortho to the aryl chain linkage, as is the case for the monocyclic monomers [350,351] discussed in Section 7.1. In this regard polyfluorenes can be considered as another version of PPP with pairs of phenylene rings locked into a coplanar arrangement by the presence of the C-9 atom. Liquid crystallinity was observed in poly(dioctyl fluorene), which is important for the obtainment of polarized EL [45,352]. Polyfluorene with octvl side groups can be melted to a liquid crystalline (LC) state at about 170 °C, become isotropic in the temperature range of 270-280 °C, and show a reversible transition between LC and isotropic phases. The polymer can be controllably prepared either as a glassy or a semicrystalline film at room temperature [353]. The relaxation of electronic excitations in polyfluorenes

have been addressed by time resolved fluorescence spectroscopy in the ps timescale [354].

A representative number of polyfluorenes and related structures are shown in Fig. 24.

In the early 1990s, Yoshino et al. [265, 355-357] reported the synthesis of blue emitting polyfluorenes which have been obtained from a simple chemical oxidation of the monomers using FeCl₃, in a similar procedure to that developed for the preparation of poly(3-alkyl thiophene)s. The polymers produced by this technique were of low molecular weight (DP ~ 10) [357] and it was difficult to remove all traces of the oxidant. Nevertheless, devices were fabricated with these polymers.

Thereafter, the nickel-mediated coupling of arylene dihalides, the Yamamoto route[311], has been used to prepare a variety of fluorene and substituted fluorene homo- and copolymers [345-349,358,359]. The use of a heterogeneous catalyst (nickel on charcoal, Ni/C), which is considerably less expensive than palladium, has been reported as effective in biaryl couplings [360]. As with PPPs, the SCP has been recently applied to the synthesis of a wide number of polyfluorenes and related structures. In the case of alternating copolymers obtained by SCP the optical and electronic properties of the polymers were tailored through selective incorporation of different aromatic units into the system. A variety of chromophores intercalated with fluorene has been reported, such as phenylene, naphthalene, anthracene, stilbene, cyanovinylene, thiophene, bithiophene, pyrazoline, quinoxaline, 1,2-cyanostilbene, pyridine, and carbazole [318,361].

Figs. 25 and 26 show the Yamamoto and the SCP routes to synthesize fluorene-based copolymers, respectively.

Well-defined monodisperse oligomers were prepared via SCP to access the effect of conjugation length on photoluminescent properties of polyfluorenes [362]. The Yamamoto route was also used to prepare 9-di-hexyl substituted oligofluorenes, containing 3–10 repeating units. The effective conjugation length was estimated to be 12 bonded fluorene units, by extrapolation of spectral data [363]. Substituted oligofluorenes in which the fluorene units alternate with triple bonds, namely



oligo(9,9-dihexyl-2,7-fluorene ethynylene)s, demonstrated strong EL, and their effective conjugation length was calculated to be around 10 fluorene units (Fig. 24(a)) [364].

Devices with fluorene polymers appear to have electrons as the majority carriers and their performance is notably improved when modified with an appropriate HTL. The Dow Chemical group has reported devices with lifetimes exceeding 1000 h at a brightness of 150 cd/m² with low voltages [361]. Hole transporting moieties such as tertiary amines [361] and TPD [365] (Fig. 4) have been incorporated to

polyfluorenes in attempts to optimize LED performance. The HOMO levels of fluorene-based poly (iminoarylene)s ($\sim -5.1 \text{ eV}$) were close to the work function of ITO, and their use as buffer layers has been suggested (buffer layers are inserted between ITO anode and HTLs, as TPD, due to the low T_g of this material and crystallization problems) [366]. On the other hand, the incorporation of the electronwithdrawing 1,3,4-oxadiazole units brought the electron affinity of the copolymers close to the work functions of Ca. These structures, shown in Fig. 24(b), prepared via the SCP, contained the oxadiazole evenly



Fig. 24. Examples of various fluorene based polymers (a) fluorene copolymer with triple bonds, poly(2,7-9,9-di-2-ethylhexylfluorenylene ethynylene) [365], (b) alternating copolymers of 9,9-dioctylfluorene and oxadiazole [367], (c) copolymer containing the electron-accepting moiety 2,7-diethynylfluorene and the electron-donating moiety tetraphenyl diaminobiphenyl (TPD) [367], (d) polyfluorenes with perylene groups in the main chain [370] and (e) as side chains [370], (f) copolymer of fluorene and anthracene [359], (g) a dendronized polyfluorene [368], (h) 9,9-dihexylfluorene as pendant group in the vinyl bridge of poly(bi-phenylene vinylene) [371], (i) 2,7-poly(9-fluorenone) [374], (j) crosslinked poly(fluoren-9,9-diyl-*alt*-alkan- α , ω -diyl) [377], (k) based-doped poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] [380], (l) poly-2,8-indenofluorene [382], (m) poly[2,2'-(5,5'-bithienylene)-2,7-(9,9-dioctylfluorene)] (PBTF) [383], (n) poly[2,2'-(5,5'-di(3,4-ethylenedioxythienylene))-2,7-(9,9-dioctylfluorene)] (PdiEDOTF) [383].







Fig. 24 (continued)





 \hat{l}

K+





R: octyl R: ethylhexyl





PdiEDOTF Fig. 24 (*continued*)





Fig. 25. The Yamamoto route to polyfluorene based block copolymers/nickel mediated coupling of 2,7-dibromo-9,9-dialkyl fluorene and various dibromoarenes.



Fig. 26. The SCP route to fluorene-based alternating copolymers: tetrakis (triphenylphosphine)palladium mediated condensation 9,9dialkylfluorene-2,7-bis(trimethylene boronate) and various dibromoarenes [318].

dispersed in the main chain, at every one, three, or four 9,9-dioctyl fluorene mers. All copolymers fluoresced in the blue range with quantum yields of about 70% in solution [367].

The combination of donor and accepting moieties in fluorene-based structures has been accomplished by alternating TPD (electron donating) with 2,7diethylhexyl fluorene or diethynylfluorene units (electron donors), as shown in Fig. 24(c) [365].

The Förster-type energy transfer was efficiently used to tune the solid state emission color of fluorenebased copolymers bearing perylene dyes as end groups or side chains, as shown in Fig. 24(d) and (e). The emission coming almost exclusively from the perylene dyes could be tuned from yellow-green (558 nm) to red (675 nm). These copolymers extended the emission of polyfluorene-based structures over the entire visible range [346].

One problem with polyfluorenes is the formation of aggregates and/or excimers after annealing or the passage of current. Miller and co-workers at IBM have managed to overcome this by incorporating anthracene units which show stable blue emission even after annealing at 200 °C for 3 days (Fig. 24(f))

[369]. They attributed this ability to the anthracene units acting as traps for the excitons, preventing excimer formation. Müllen et al. [370] at the Max-Planck Institute in Germany produced non-aggregating polyfluorenes by the insertion of dendron side chains, as shown in Fig. 24(g) [368], giving a polymer with pure blue emission, as the bulky side chains do not cause distortion between the fluorene units. The insertion of a 9,9-dihexylfluorenyl as a pendant group in a chain of poly(biphenylene vinylene) brought about steric interactions between adjacent rings, reducing conjugation length, but at the same time inhibited the formation of excimers (Fig. 24(h)). The polymer showed bright and stable blue emission [371]. A series of electron-deficient, oxadiazole-, quinoline-, quinoxaline- and phenylenecyanovinylene-containing copolymers bearing ethyl hexyl groups on the fluorene unit was recently reported. These materials possess low-lying LUMO energy levels (-3.01 to -3.37 eV) and low-lying HOMO energy levels (-6.13 to -6.38 eV), with sharp blue emission, and may be promising candidates for electron transport-hole-blocking materials in LED fabrication. The film emissions were only 7-11 nm red shifted in comparison with the solution emissions, indicating that excimer formation was suppressed. This was explained in terms of the prevention of molecular stacking by the presence of sterically demanding ethyl-hexyl substitutions at the fluorene unit [372].

Miller et al. [373] demonstrated that thermostability and excimer formation are both dependent on the molecular weight. Controlled end capping with either 2-bromofluorene or 2-bromo-9,9-di-n-hexyl fluorene allowed the preparation of copolymers with variable molecular weights. It was observed that lower molecular weights showed larger excimer formation after annealing, and this effect was attributed in part to the increase in chain mobility expected for the shorter chains. Moreover, the nature of the end groups apparently affected the tendency of the fluorene backbone to π stack, that is, polymers terminated with more sterically hindered end cappers as 9,9-di-nhexyl fluorene were less prone to excimer formation. At the same time, the non-substituted polymers bearing the benzylic hydrogens at the 9-position appeared to be prone to oxidation. The formation of fluorenone after annealing was demonstrated by comparison with the deliberately end capped with 9fluorenone-2-yil substituents of the same molecular weight [373]. Polyfluorenone (Fig. 24(i)) itself has been introduced as prospective material for ETLs. The work function of 2,7-poly(9-fluorenone) is located almost on the same level as that of magnesium and its insolubility in organic solvents would allow the fabrication of multilayer LEDs. Its synthesis followed a precursor route that led to a polyfluorene ketal which was converted to polyfluorenone after treatment with dichloro acetic acid [374].

The formation of a network is a useful strategy in the obtainment of various performance improvements in polyfluorenes. For example, the attachment of styryl end groups, via reaction of the bromoterminated polymer with bromostyrene in a Yamamoto coupling, allowed the deposition of a crosslinkable layer through the thermal polymerization of the terminal styrene groups. Apart from the added advantage of further casting other layers, the immobilization of the chains leads to suppression of intermolecular excited state interactions, hampering the ability to π stack [375,376]. Fluorene copolymers with emissive units separated by methylene sequences containing 4-12 carbons atoms were also crosslinked by chemical oxidation using FeCl₃. The resulting structure had the crosslinks placed between each fluorene unit (Fig. 24(j)) [377].

Energy migration has been explored in polyfluorenes to enhance emission intensity. For example, devices of poly(9,9-dioctylfluorene) mixed with the amine-substituted copolyfluorene poly(9,9-dioctylfluorene-*co*-bis-*N*,*N'*-phenyl-1,4-phenylenediamine), showed a blue emission with a luminance of 1550 cd/m² and a maximum external quantum efficiency of 0.4%. Similar devices using a Dow Chemical proprietary green emitting polymer when mixed with a similar amine containing copolyfluorene achieved a luminance of 7400 cd/m² and a external quantum efficiency of 0.9%. These figures were largely better than those relative to the pure components [378].

A recent aspect of the research in polyfluorenes is related to supramolecular ordering of these conjugated polymers by making rod-coil block copolymers. The rod-like conjugated polyfluorene was end capped on one or both ends with polyethylene oxide, forming di- or triblock

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copolymers. The solid-state fluorescence spectra of these materials had better resolution than the homopolymer, indicating an enhanced number of well-ordered rods in the films and an additional increase in long wave emission. Morphological studies showed a fibrilar structure which was thought to be governed by the solid-state packing of the conjugated rods. The width of the fibers seemed to correlate to the length of the polymer chain [370]. Another interesting class of polyfluorene derivatives carries carboxylate groups in the 2,7-positions as shown in Fig. 24(k). Upon deprotonation (base doping) these polymers generate stable polymeric anions counterbalanced by alkali metal cations which show interesting electric conducting properties, typically in the range 10^{-2} - 10^{-3} S/cm [379,380]. The strong polarization of the electrical conduction observed in these materials indicated a significant contribution of ionic transport.

Multilayer fluorene-based LEDs were reported by a Japanese group [381] where a three layer device having the structure ITO/N,N'-bis(2,5-di-tertbutylphenyl)-3,4,9,10-perylene dicarboxamide (BPPC)/N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'biphenyl-4,4'-diamine (TPD)/poly(9,9-dihexylfluorene) (PDHF) was able to emit either red or blue by changing the polarity of the applied voltage. TPD is a material mainly used for hole transport, BPPC is a red emitter, and the polymer emits in the blue region. The particular set of gap conditions in this system allowed the emission of blue light under positive bias conditions (ITO anode, Al cathode) and emission of red light under negative conditions. Furthermore, the device can be driven with an AC field and the emission color can be gradually modulated by changing the frequency of the applied AC field [381].

An intermediate structure between PPP and polyfluorene has been developed, the poly(2,8-indenofluorene), Fig. 24(1). This blue emitting polymer is stable up to 380 °C, and shows thermotropic LC behavior at high temperatures (250-300 °C) making it a good candidate as the active material in polarized LEDs [382].

Copolymers of fluorene and thiophene-containing moieties are shown in Fig. 24(m) and (n), respectively [383].

8. Silicon-containing polymers

The interest in silicon-based polymers resides in the delocalization of the σ electrons over a Si backbone providing electronically analogous properties to the π -conjugated polymers. Polysilanes are σ -conjugated polymers with a one-dimensional (1D) Si chain backbone and organic side chain substituents. Progress in understanding their electronic structure derived from both theoretical and experimental studies has revealed that they are quasi-1D semiconductors with a direct and wide band gap $(\sim 4 \text{ eV})$, and that the σ -conjugated electronic structure typically observed in silane high polymers appears in Si chains with more than 20-25 Si units [384]. Polysilanes exhibit photoconductivity, intense near-UV absorption, and strong PL of small Stokesshift and high hole mobility (on the order of $10^{-4} \text{ cm}^{-2} \text{ s}^{-1}$) [385]. Near-UV or UV emitting LEDs of diaryl, dialkyl, monoalkyl-aryl polysilanes have been reported [386-389], and the band gap energies tend to shift to lower values based on the size of substituents with aromatic side groups [390]. The emissions in polysilanes have been attributed to the $\sigma - \sigma^*$ transitions of 1D excitons in the Si backbone. Nevertheless, PL studies of poly(methylphenylsilane) demonstrated the existence of another emission due to a charge transfer state from the intrachain σ to pendant π^* groups which appears in larger wavelengths (400-500 nm) [391]. Being typical p-type semiconductors, polysilanes cannot transport electrons, and for this reason the incorporation of electron transporting groups with emitting properties seemed to be an interesting way of combining good properties. Polymethyl phenyl silane (PMPS), poly[bis(*p-n*-butylphenylphenyl)silane] (PBPS) and poly(2-naphthyl phenyl silane (PNPS) are examples of polysilanes, shown in Fig. 27(a). A blue emission (480 nm) with a PL of 87% was achieved with a poly(methylphenylsilane) containing anthracene units in the polymer backbone [392] (PMPS-AN) which was prepared by the condensation of 9,10-bis(methylpropylchlorosily-1)anthracene with methyl-phenyldichlorosilane as shown in Fig. 27(b).

Silicon-containing PPV derivatives have been developed in which the silicon unit acts a spacer to improve solubility, film forming characteristics and

confine conjugation, in analogy of the conjugatednon-conjugated block copolymers with an aliphatic spacer (Fig. 10(a)). While the aliphatic segments as spacers can act as a barrier to injection and mobility of the charge carriers, resulting in higher threshold voltages, the silicon units with an aromatic or flexible group are able to produce the same spacer effects with low operating voltages. It has been argued that the participation of the d-orbital of the Si atom could be assisting to increase the effective conjugation length, thus facilitating charge mobility, [393] although previous theoretical work has demonstrated that Si bonds breaks effectively the π -conjugation [394]. A variety of PPV related structures such as copolymers of diphenyl/dibutylsilane [278], dibutyl, butyl/methyl, diphenyl silanes [395] with PPV and alkoxy PPV [396] have been reported, in which the organosilicon groups are used as spacers [397]. Some representative examples are shown in Fig. 27(c). These structures were prepared by the well-known Wittig route, reacting the diphosphonium salts of the organosilicon moiety with the appropriate dialdehyde, as shown in Fig. $27(d_1)$, or via the Knoevenagel condensation, in which a diacetonitrile of the organosilicon moiety reacts with the dialdehyde in the presence of a strong base as shown in Fig. $27(d_2)$. The EL spectrum of the diphenyl substituted copolymer (SiPhPPV) gave the highest peak (450 nm) when the operating voltage of 9 V was applied. With 12 V applied bias a strong white color was emitted due to additional emissive bands [395]. This threshold voltage was further decreased to 7 V by the introduction of a CN group into the double bond of PPV [393]. Similar results were obtained in alternating copolymers of silane and carbazolvl or fluorenyl derivatives, peaking around 440-476 nm with operating voltages of 6-12 V [398].

In contrast to alkoxy groups, the lack of electron donor capacity (and consequent red shifting of



Fig. 27. Examples of (a) polysilanes, where the main chain is made up of Si–Si bonds: poly(phenyl methyl silane) (PMPS) [390], poly(naphthyl methyl silane) (PMPS) [390], poly[bis(*p*-*n*-butylphenyl)silane] (PBPS) [384]; (b) synthetic route to poly(methyl phenyl silane) containing anthracene units [392]; (c) PPV related structures containing Si as spacers [395]; (d) copolymers with Si inserted between π -conjugated blocks: Wittig [216] (top) and Knoevenagel [393] (bottom) routes; (e) Si in a lateral chain: poly(2-dimethyl silyl-1,4-phenylene) (DMOS-PPV) and poly(2-dimethyl octyl silyl-*co*-2-methoxy-5-ethyl hexyloxy-1,4-phenylene vinylene) (DMOS-*co*-MEH PPV) [399].











SiBuCNPPV







SiPhCNPVK





SIHMCNPPV

Fig. 27 (continued)





the emission) of alkylsilicon groups has suggested the introduction of these groups as ramifications in EL polymers, improving processing characteristics [399–401] (Fig. 27(e)). In fact, poly(2-dimethyloc-tylsilyl-1,4-phenylene vinylene) (DMOS-PPV) produced high efficiencies in its single layer LED (ITO/Al). The turn-on voltages of poly(2-dimethyloctyl silyl-*co*-methoxy-5-ethylhexyloxy-1,4-phenylene vinylene) (poly(DMOS-MEH-PPV) decreased as the content of MEH-PPV in the copolymers increased, but the EL efficiencies decreased as well [402].

One of the unique properties of polysilanes is the Si-Si bond scission of the backbone chain under UV radiation. In the presence of oxygen it is accompanied by a Si-O-Si bond formation that leads to the conversion into an insulator, with no hole transport ability. Using this property, a patterning-image-display electroluminescent device was built. Before turning on the voltage, the anthracene-containing polysilane LED was irradiated in order to pattern an image onto the emission area, from the glass substrate side. Blue

patterned light was obtained, corresponding to the negative photomask used [392].

9. Nitrogen-containing conjugated polymers

9.1. Pyridine-containing conjugated polymers

Due to their strong electron acceptor character, nitrogen-containing groups of various kinds have been incorporated to conjugated polymeric structures. The most extensively studied structures carry the pyridine moiety, in homopolymers (poly(2,5-pyridine), poly(3,5 pyridine)) [403–407], in PPV-type structures (poly(*p*-pyridylene vinylene))s [408–410, 404], in copolymers with PPV (poly(phenylene vinylene pyridylene vinylene)s) [85,404] or in *p*-phenylene derivatives [411,412]. Fig. 28 shows the chemical structures of the repeating unit of the most representative pyridine-containing conjugated electroluminescent polymers.

Fig. 28(d) is a macrocycle-bridged copolymer of pyridylene and phenylene vinylene. The purpose of introducing the macrocycle bridges to the phenyl group is to further separate the polymer chains and reduce aggregate formation [413]. This effect was indeed observed but complete suppression of aggregate formation was not achieved [410]. Tuning of the emission by means of the external voltage applied was achieved with this copolymer [204] and its blends with *p*-sexiphenyl oligomer [414]. As compared to phenylene-based analogues, one of the most important features of pyridine-based polymers is the higher electronic affinity. As a consequence, the polymer is more resistant to oxidation and shows better electron transport properties. The higher electron affinity enables the use of relatively stable metals such as Al, Cu or Au or doped polyaniline as electrodes [404, 415]. The pyridine-containing conjugated polymers are highly luminescent, especially the copolymers with phenylene vinylene. The internal PL quantum efficiencies of these copolymers were in the range of 75-90% in solution and 18-30% in film form [410]. The solubility of polypyridines in organic solvents represents another advantage as compared to PPV for device fabrication. Time resolved studies showed that the presence of n, π^* states leads to enhanced intersystem crossing to triplet excitons for the powder

form, while aggregate formation plays a key role in the optical and electronic properties of the films [416].

The ability to protonate and quaternize the nitrogen makes it possible to manipulate the electronic structure and thereby the emission wavelength [403, 408,412,416,417].

The synthesis of poly(2,5-pyridine) and poly(3,5pyridine) is straightforward: one step coupling polymerization of the 2,5 (or 3,5) dibromopyridine using a metal catalyst [403]. Partially N-methylated poly(2,5-pyridine)s were prepared by reacting the polymer with methyl iodide in methanol, and the UV and fluorescence spectra were studied in solution and in the solid state. The emission maxima of these polymers shift to shorter wavelengths with increasing acidity. This blue shift is caused by an increasing torsional angle between the planes of the rings with protonation. Fluorescence intensity increases with the degree of protonation [403]. In Fig. 29 the various dimeric units of poly(2,5-pyridine) with the respective protonation possibilities are shown. It is proposed that two blue electroluminescent devices emitting at 420 and 520 nm [403] can be constructed by varying the degree of protonation. Another example illustrating the possibility of tuning spectroscopic properties by protonation of the lone pair of electrons of the pyridine ring is the red shift observed in the fluorescence and EL emission of poly(2,5-pyridylene-*co*-1,4-(2,5-bis(ethylhexyloxy)phenylene) [413]: a red-shifted emission is observed upon treatment with strong acids. Excitation profiles show that emission arises from both protonated and nonprotonated sites in the polymer chain. At the same time protonation is accompanied by intramolecular hydrogen bonding to the oxygen of the adjacent solubilizing alkoxy group, providing a new mechanism for driving the polymer into a near planar conformation, extending the conjugation and tuning the emission profiles [413]. Fig. 30 depicts the synthetic pathway to this polymer.

The PL and EL spectra of copolymers of 1,4phenylene vinylene and 2,6-pyridylene vinylene (co(2,6-PyV–PV)) could be tuned, respectively, in function of the excitation wavelength of the light and the external voltage applied in LED devices. The incorporation of the pyridine moiety increased the EL efficiency of the devices by a factor of 5 in relation to PPV [404,409,417,418].



Fig. 28. Pyridine-containing polymers: (a) poly(*p*-pyridine) (Ppy) (b) poly(*p*-pyridyl vinylene) (PpyV) (c) copolymer of PPV and Ppy, (PpyVP(R)₂V), (d) macrocycle-bridged copolymer of pyridylvinylene and phenylene vinylene (PPyVPV) [404].

Fig. 31 depicts the copolymerization route to obtain (co(2,6-PyV-PV)). The water soluble sulfonium chlorides (2,6-pyridyl-dimethylene-bis(te-tramethylene sulfonium chloride) and 1,4-phenylene-dimethylene-bis(tetramethylene sulfonium chloride))) copolymerize in basic medium forming the copolye-lectrolyte precursor copolymer which gives the <math>co(2,6-PyVPV) copolymers upon elimination [419].

A series of poly(2,5-dialkoxy-1,4-phenylene-*alt*-2,5-pyridine)s in which the [alkoxy phenylene– pyridyilene] structural unit acts as donor–acceptor pair was synthesized via a SCP, as shown in Fig. 32 [411]. The electron affinity of these polymers is ca. 2.5 eV, comparable to that of copolymers containing oxadiazole moieties. The electron withdrawing pyridinylene groups were able to lower

Head-to-Head



Fig. 29. Dimeric units of poly(2,5-pyridine) with/without protonation: head-to-head, head-to-tail, and tail-to-tail configurations. Reprinted with permission from Macromolecules 1997; 30:4633. © 1997 American Chemical Society [403].

the LUMO energy in such a way that these polymers may have similar electron injection properties as typical oxadiazole-containing electron transport polymers, when they are used as active materials in LEDs [411]. They showed strong blue EL in single layer devices and a bathochromic shift when protonated [411].

The Wittig and Wittig-Horner reactions have been employed to prepare copolymers containing bipyridine and silicon units. The organosilicon moiety improves the solubility and limits the conjugation length [420]. The synthetic pathway for these blue emitting copolymers is shown in Fig. 33.

9.2. Oxadiazole containing conjugated polymers

One of the best electron transport structures is the oxadiazole group, as noted above. The covalent attachment of the PBD moiety to an emitting polymer (Fig. 4(b)), was a natural development in LED technology, avoiding the problems with the deposition of an additional layer in diode construction and the anticipated phase separation after film preparation or under operating conditions. Some examples of oxadiazole-containing EL polymers are given in Fig. 34. Among the various examples found in the literature one can cite the use of oxadiazole incorporated in the main chain [255,421-429] or as



Fig. 30. Synthesis of 1,4 phenylene-2,5-pyridylene copolymers: (i) 2-ethylhexyl bromide, DMF, K₂CO₃, 100 °C; (ii) X stands for Br that is subsequently transformed into the corresponding boronic acid with triisopropyl borate; (iii) THF, Pd(PPh₃)₄, Na₂CO₃, reflux. Reprinted with permission from J Am Chem Soc 2002; 124(21): 6049. © 2002 American Chemical Society [412].

a pendant group [255,421,429–431]. In the first case the oxadiazole moiety was used as a comonomer in chromophoric imides [255,423,429,432], copolymers containing thiophene sequences [427], or in a PPVtype main chain [255,256,370,423–425]. Synthetic approaches for the oxadiazole-containing polymers were the Heck reaction [370] or via the formation of a polyhydrazide precursor [428]. Oxadiazole moieties linked to PPV [255,256,431], alkyl-PPV, and polythiophene [430] chains as pendant groups with improved EL efficiencies due to higher electron affinity, better injection, and transport properties have also been reported [433].

The insertion of electron transporting groups in ptype polymers brings about bipolar carrier transport ability. The combination of donor-acceptor groups in the same chain in attempts to achieve balanced electron-hole injection and transport avoiding the use of intermediate transport layers has been widely explored, such as the combination in the same chain oxadiazole and PPV [433,255] or oxadiazole and oligothiophenes [434] have reported for example for PPV type chains [253,433,435] or other chromophores like naphthalimide [432], fluorene [59], anthracene [59], triphenyl amine [59].

9.3. Polyquinolines and polyquinoxalines

Polyquinolines and polyquinoxalines are n-type (electron transporting) polymers and therefore offer alternative EL device engineering in conjunction with the extensively studied p-type (hole transporting) polymers such as poly(*p*-phenylene vinylene)s, polyphenylenes, and polythiophenes. A variety of





Fig. 31. Copolymerization route to obtain the co(2,6-PyV-PV) copolymers [419] (THT stands for tetrahydrothiophene). Reprinted with permission from Adv Mater 1996; 3:395. © 1996 VCH Verlagsgesellschaff mbH [419].

polyquinolines [373,436–439] and polyquinoxalines [440–444] has been reported in the literature, acting as the active emitting layer [373,437,438] or as the transport layer [439–442] in LEDs. Fig. 35 shows some representative examples of these emitting and electron-transporting polymers. The increased

electron deficiency of the quinoxaline ring due to an additional imine nitrogen, compared to the quinoline ring, enhances the electron-accepting ability of conjugated polyquinoxalines, thus improving electron transport properties [437,438]. Polyquinolines are usually prepared by the acid-catalyzed Friedländler



Fig. 32. Synthesis of poly(2,5-dialkoxy-1,4-phenylene-*alt*-2,5-pyridylene)s via the SCP. Reprinted with permission from Mocromolecules 2001; 34:6895. © 2001 American Chemical Society [411].

condensation of bis(*o*-aminoketone)s and bis(ketomethylene) monomers, have good mechanical properties and high thermal stability, and can be processed into high quality thin films. Variations in the polyquinoline backbone linkage (R) and pendant side groups (Fig. 35(c)) provided a means to regulate the intramolecular and supramolecular structures which in turn enabled tuning of the light emission from blue to red [439]. When the quinoline moieties of poly(2,6-[phenylquinoline]) and of poly(2,6-[*p*-phenylene]-4-phenylquinoline) were methylated or protonated by means of acidic solvents, intense blue emission was observed at 450 nm. When the positive charge on the nitrogen atom of the quinolines reached a critical value, intermolecular electrostatic repulsion prevented the aggregation, and the emission spectra were those of the isolated chain. The non-protonated forms



Fig. 33. Synthesis of EL copolymers containing bipyridyne and organosilicon via Wittig condensation.

formed LC structures, which formed excimers with emissions in the 550–600 nm range [442]. pH-tunable PL was also demonstrated in poly(vinyl diphenylquinoline), with emission maxima varying from 486 to 529 nm (blue to green). Intramolecular excimer emission was observed in acidic solutions but not in neutral solutions or thin films of the polymer. The polymer, which was obtained from a modification of polystyrene, was introduced as a prospective high T_g , electron transporting counterpart of the hole transporting side chain PVK [439]. The electron transporting properties of copolymers bearing fluorene and quinoline units with conjugation confinement varied with the chain rigidity and conjugation length and proved to be useful in double and triple layer devices [443].

A series of polyquinolines containing 9,9'spirobifluorene was recently reported [444], Fig. 35(e). The two fluorene rings were orthogonally arranged and were connected via a common tetracoordinated carbon. The incorporation of the spiro moiety provided good solubility due to a decrease in the degree of molecular packing and crystallinity while imparting a significant increase in both T_g and thermal stability by restricting segmental mobility.

Binary blends of the conjugated polyquinolines poly (2,2'-(2,5-thyenylene)-6,6'-bis(4-phenylquinoline))



Fig. 34. Oxadiazole-containing EL polymers: (a) poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene [424]; (b) poly(phenylene-1,3,4-oxadiazole-phenylene-hexafluoro isopropylidene) [427]; (c) alternating oxadiazole-*alt*-alkoxyphenylene and a aliphatic spacer [427]; (d) copolymers containing interspersed oxadiazole units between phenylene and phenylene vinylene-based units [369].

and poly(2,2'-biphenylene)-6,6'-bis(4-phenylquinoline)) showed enhanced EL emission by a factor of 30 in comparison with the parent components [445]. This result was attributed to the spatial confinement of excitons which led to increased exciton stability and electron-hole recombination efficiency. Energy transfer was negligible, but new emission bands indicated exciplex formation and molecular miscibility to a certain degree in the blends.

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Studies of supramolecular photophysics of selfassembled block copolymers bearing styrene-polyquinoline sequences demonstrated evidence of





Fig. 35. Examples of EL polyquinolines (a)–(d) [438]. Polymer (e) contains a 9.9^{\prime} -spirobifluorene unit where the bifluorene rings are orthogonally arranged and connected via a tetracoordinated carbon [493] (f)–(i) [494], (j) and (k) [495].







Fig. 35 (continued)







Fig. 35 (continued)



J-aggregation in well-defined, ordered structures such as micelles and vesicles. The polymers represent a novel class of functional luminescent materials [441].

In a recent contribution, Jenekhe reported a detailed study on voltage-tunable multicolor emission bilayer LEDs combining PPV (as typical p-type layer) with a series of polyquinolines, polyanthrazolines, polybenzothiazoles and a poly(benzimidazobenzo-phenanthroline) ladder, addressing the influence of the polymer-polymer interface in the diode

efficiency and luminance and showing that its electronic structure plays a more important role than the injection barrier at the cathode/polymer interface [445].

9.4. Carbazole-containing conjugated polymers

Due to its electro- and photo-properties, the carbazole molecule has been used in various technological applications [446,447]. Polymers based on this compound have been used to enhance

LED emission and also for color tuning. In Partridge's study of EL of dye doped PVK systems [7,498,499,500], the hole properties of this polymer was demonstrated. The EL was due to the radiative decay of exciplexes (or exterplexes) formed by combination of PVK units and cyanobenzene derivatives. The EL from PVK was observed by Kido et al. [128] in a multilayer device in which the peak at 410 nm was attributed to excimer emission by the carbazole group. Shortly after, a single active layer device with the ITO/PVK/Al (or Ca) structure was developed [219] in which the emitted light was violet with a maximum intensity at 426 nm and a part of the spectrum lay in the UV region. Devices in which the emitting layer was formed by PVK blended with other polymeric systems have shown remarkable increases in luminescence efficiency, as compared to those in which PVK was not incorporated. In blending poly(p-phenyl phenylene vinylene) (PPPV) with PVK the blue emitting device with the ITO/ polymer blend/Ca configuration showed a quantum efficiency of 0.16% which is a good result for a blue emitter [456]. When used in combination with an electron donor transporting material (PBD), as in a blend with a blue emitting copolyester containing isolated 1,2-dinaphthylene units, a quantum efficiency of 0.1% was obtained for an Al based device [447]. The blue emitting polymer (485 nm) and the electron transport molecule PBD were dispersed in PVK and the devices showed quantum efficiencies better by a factor of 10^2 than similar devices made only with the copolyester.

The intensity of the red-orange emission from poly(3-octyl thiophene) (P3OT) was also greatly increased by the incorporation of PVK in the emitting layer [448,449]. Blends of a PPV derivative with silane spacers and PVK yielded enhanced blue emission [397]. As in all cases of PVK blends, it was observed that there is an optimum molar ratio between the emitting polymer and PVK for the increase in EL intensity. In the case of the blend P3OT/PVK, in spite of the favorable spectral characteristics, energy or charge transfer from PVK to P3OT was ruled out by spectral evidence. It was proposed that holes in PVK (top level of valence band = 6.1 eV) could transfer to the neighboring

P3OT (top of valence band = 5.2 eV) according to:

 $P3OT^{-} + PVK^{+} \rightarrow P3OT^{*} + PVK$

$$P3OT^* \rightarrow P3OT + h\nu$$

The P3OT electrons will combine with the holes from PVK leading to an increase of the probability for electron hole radiative recombination. On the other hand, if the diode is doped excessively with PVK the conductivity is reduced, i.e. the carrier concentration decreases, because carrier mobility is much larger in P2OT than in PVK [262,450], resulting in a decrease in EL efficiency.

Apart from the homopolymer, the carbazole moiety can be incorporated in polymer chains as part of the main chain, like poly(2,5-dihexyl phenylene-*alt-N*-ethyl-3,6-carbazolevinylene),

which was combined with an electron transporting oxadiazole-containing structure [451]. Alternating structures containing units of 2,5-bis-trimethyl silylp-phenylene vinylene, or 2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene with N-ethyl hexyl-3,6-carbazolevinylene or 9,9-n-hexyl fluorenevinylene were prepared via Wittig polycondensation. Among the four combinations the silylsubstituted carbazole copolymers presented the most interesting properties, for example, its EL quantum efficiency was 32 times higher than the MEH-PPV analog (film quantum efficiency was 0.81, one of the highest reported). The participation of the silvl group in the PL enhancement and also to the blue shift observed was attributed to its sterical hindrance and lack of electron donating ability as compared to alkoxy substituents [451]. The hole conduction of the carbazole unit was studied by comparing polydiphenylacetylene derivatives without and with a carrier transport moiety as poly[1-(p-n-butylphenyl)2-phenylacetylene] and poly[1(p-n-carbazolylphenyl)-2-phenylacetylene], respectively. It was shown that hole mobility enhancement by the attachment of the carbazolyl side groups brings about a remarkable improvement in the EL devices [226].

9.5. Other nitrogen-containing conjugated polymers

Other electron affinity enhancer nitrogen-containing heterocyclic groups include the triazole [353],

bithiazole [452] and non-conjugated amino groups as substituents, such as $-N(CH_3,C_6H_{13})$ attached to the ring in (poly(2,5-bis(*N*-methyl-*N*-alkylamino)phenylene vinylenes) [453]. In this case the nitrogen atom does not participate in the conjugation system, and its electron donor character provides a stronger donor effect to the amino substituent than the corresponding alkoxy substituents.

As before mentioned (under transport layers Fig. 4), triamines have been used as hole transport materials.

In a recent report, this class of compounds have shown emissive capacity as well, when inserted as pendant groups in conjugated backbones. Single layer devices fabricated from these copolymers can emit light ranging from yellow to bright red, depending on the aromatic units incorporated [454]. These structures are shown in Fig. 36.

The attachment of carbazolyl groups as pendant groups grafted to a backbone as PMMA, which was blended with MEH-PPV, enhanced the emission four



Fig. 36. Arylamine pendants in EL polymers. The arylamine groups act as hole transporters and the emission color is tuned by the different aromatic units [454]. P1: yellow, P2: red, P3: red and P4: orange. Reprinted with permission from Macromolecules 2001; 34:6571. © 2001 American Chemical Society [454].



times when compared to that of the pure polymer [455].

Apart from hole transport ability, PVK can interact with low molecular weight compounds or polymers to form new emitting species as exciplexes [235], and consequently bring about a shift in the emission wavelength. In the case of PPPV/PVK [456] mentioned above, where PVK was used both as matrix and hole transport material, the EL spectra of the system tended to blue shift as compared to the respective pure PPP. It was speculated that this was caused by a change in molecular conformation or aggregation of the PPP in the PVK matrix. In blends of the conjugated-non-conjugated multiblock copolymer PPV derivative (CNMBC) (Fig. 37) [219] with PVK, the EL blue shifted according to PVK increments in the blend. The new emission was attributed to an exciplex formed by the two polymers. As the composition of the blend changed from a PVK-poor to a PVK-rich ratio the emitted light changed from green to blue. Further blends of composition 97/3 (wt%) PVK/block copolymer yielded an EL spectrum with a single emission peak in the blue region different in location from either single component, whereas for a certain range of composition the new peak coexisted with those of the pure components. An exciplex where an excited PVK combines with ground state copolymer was proposed [219].



Fig. 37. EL spectra of the CNMBC in blends with PVK, illustrating the shift of the emission color with the blend's composition [218,258]. Pure CMMBC (curve a) emits green light which gradually moves to violet with increasing amounts of PVK (curve j). Polymer ratios CNMBC/PVK: 89% (b), 75% (c), 50% (d), 17% (e), 8% (f), 3% (g), 1% (h), 0.24% (i). Reprinted with permission from J Appl Phys 1994; 76(4): 2419. © 1994 American Institute of Physcis [218].

Exciplexes can also form in heterojunctions of PVK and various compounds containing nitrogen atoms. For example, bilayers of PVK and poly(pyridyl vinylene phenylene vinylene) (PPyVPV) showed a single peak in PL which could not be assigned to either component alone. It was determined that the EL from the device was also due to exciplex emission, which enhances the internal efficiencies and brightness of bilayer devices compared to single layer [457].

Single active layer devices made with poly(3octylthiophene)-[bis(*N*-ethyl (or octyl)carbazolylene] multiblock copolymers were color tunable by changing the numbers of thiophene units in the thiophene block. An increase in external quantum efficiency in polymers with short thiophene segments was attributed to a more balanced charge injection [127]. Also, a bilayer device having the electron-transporting nonemitting poly(phenyl quinoxaline) (PPQ) and PVK as components showed a EL peaking at 650 nm [458].

The attachment of carbazolyl groups as pendant groups grafted to a backbone as PMMA, which was blended with MEH-PPV, enhanced the emission four times as compared to that of the pure polymer [456].

Apart from hole transport ability PVK can interact with low molecular weight compounds or polymers to form new emitting species as exciplexes [235], and consequently bringing about a shift in the emission wavelength. In the case of PPPV/PVK [448] above mentioned, where PVK was used both as matrix and hole transport material, the EL spectra of the system tended to blue shift as compared to the respective pure PPP. It was speculated that this was caused by a change in molecular conformation or aggregation of the PPP in the PVK matrix. In blends of the conjugated-non-conjugated multiblock copolymer PPV derivative (CNMBC) (Fig. 37) [219] with PVK the EL blue shifted according to PVK increments in the blend. The new emission was attributed to an exciplex formed by the two polymers. As the composition of the blend changed from a PVK-poor to a PVK-rich ratio the emitted light changed from green to blue. Further blends of composition 97/3 (wt%) PVK/block copolymer yielded an EL spectrum with a single emission peak different in location from either single component, in the blue region, whereas for certain range of composition the new peak coexisted with those of the pure components. An exciplex where an excited PVK combines with ground state copolymer was proposed [219].

10. Polyacetylenes and polymers with triple bonds in the main chain

10.1. Polyacetylenes

Polyacetylene is the first conjugated polymer to exhibit a metallic conductivity. However, polyacetylene shows a very low PL efficiency [459]. Recently, in contrast, a number of good lightemitting polyacetylene derivatives have been produced, covering the visible spectrum. The poor solubility of these rod-like structures with concomitant color tuning was addressed in three ways: by substituting the hydrogen atoms with alkyl or aryl groups as done in PPV, by means of copolymerization, or by a combination of both methods. In the first approach many of substituents were tried [460,461].

Monosubstituted polyacetylenes were often referred as non-luminescent polymers, but the insertion of mesogenic pendants afforded intense blue emitting materials [462] as shown in Fig. 38(a).

The emission observed from a series of alkyl and phenyl disubstituted polyacetylenes changed from blue-green to pure blue and the luminescence intensity was enhanced when the length of the alkyl side chain increased [463]. This effect was also observed in poly(3-alkylthiophene) [262] and in PPV derivatives [201], indicating that the $\pi - \pi^*$ interband transition increases with the length of the side chain, and at the same time the diffusion rate of the excitons to quenching sites is reduced by the longer interchain distances. Interchain interaction is also known to decrease radiative efficiency [201]. Examples of EL disubstituted polyacetylenes are given in Fig. 38(b).

Aryl-substituted polyacetylenes like poly(phenylacetylene) (PPA), poly(phenyl-*p*-ethynyl phenylacetylene) (PEPA), poly(*p*-phenylethynylphenylacetylene) (PPEPA) and poly[*p*-2-thiophenylethynyl)phenylacetylene) (PTEPA) (Fig. 38(b)) were stable to 200 °C in either air or nitrogen, according to thermogravimetric analysis [460].



Fig. 38. Examples of EL polyacetylenes: (a) monosubstituted [462]; (b) disubstituted [460]. Reprinted with permission from Synth Met 1997; 91:283. © 1997 Elsevier Science [460].

10.2. Poly(phenylene ethynylene)s

Some examples of EL polymers bearing triple bonds in the main chain are given in Fig. 39.

The HOMO–LUMO energy gap of some alkoxy substituted poly(phenylene ethynylene)s (ROPPE) is higher than that of the corresponding ROPPVs, indicating that introducing triple bonds in the main chain shortens the effective conjugation length. For example, poly(3,4-dialkyl-1,6-phenylene ethynylene) has a band gap of 3.1 eV [465]. Poly(*p*-phenylene ethynylene)s showed a lower energy barrier for electron injection than for hole injection, in contrast with the PPV analogs. This is an important feature for cathode stability, since more stable metals can be used [466]. For example, the poly(dialkyl-1,6-phenylene ethynylene) (Fig. 39(a))

was used for the fabrication of blue emitting LEDs [467]. A high quantum efficiency was obtained with poly(2,5 dialkoxy-1,4-phenylene ethynylene) (ROPPE) in which the triple bond is equivalent to the double bond in poly(2,5-dialkoxy-1,4-phenylene vinylene) (ROPPV) [468]. Bright blue-green EL was observed from an LED made with the copolymer ROPPE and pyridine (Py) (Fig. 39b) with Al/ROPPE-Py/ITO. In comparison with PPV it was suggested that the triple bonds in the chain were responsible for the blue shift and enhancement of the EL, due to the shortening of the effective conjugation length and effective confinement of the excitons. However, the effects of the triple bonds were suppressed by the introduction of electron-rich moieties in the chain, such as in poly(2,5-dialkoxy-1,4-phenylenediethylene-co-9,



Fig. 39. Examples of EL polymers with triple bonds in the chain (ROPPE) [464].



Fig. 40. Synthetic routes to poly(phenylene ethynylene)s: (a) Pd catalyzed coupling of diiodo benzene, norbonadiene and bis(organostannane) and subsequent retro-Diels–Alder reaction [469]; (b)Heck type coupling of 2,5-bis(hexyloxy)-1,4-diiodobenzene with 1,3-diethynylbenzene in the presence of $PdCl_2(PPh^3)_2/CuI/Et_3N$ catalyst [470] and (c) copolymerization via alkyne methatesis [496]. Reprinted with permission from Macromolecules 2000; 33:1487, 1998; 31:6730, Chem Mater 2001; 13:2691. © 2000, 1998, 2001 American Chemical Society [469,470,496].



Fig. 41. Examples of EL condensation polymers: (a) polyesters containing isolated 1,2-dinaphthylene units [214]; (b) copolyesters containing various types of chromophores [477]; (c) polyamide [475]; (d) polyimide [479]; (e) and (f) polyurethanes [482].





10-anthracenylene)(ROPPE-An) (Fig. 39(c)). In this case the insertion of the 9,10-anthracenyl group caused a delocalization of the π -electrons and enhancement of interchain interactions [465,469].

Linear copolymers containing phenylene ethynylene linkages have been synthesized using precursor routes [470], inserting *m*-linkages [471] or aliphatic spacers [472,473]. In the precursor route, regular building blocks of *p*-phenylene, norbonadiene, and diethynyl benzene made up the soluble precursor, which was converted to a polymer with enyne units upon the release of cyclopentadiene through a retro-Diels–Alder pathway [470] (Fig. 40(a)). The copolymer with phenylene with *m*-linkages made through a Heck-type route, using Pd as catalyst, shown in Fig. 40(b), displayed a PL four times stronger than that of the corresponding *p*-substituted analog [471]. This synthetic method is very often employed in a general way in poly(arylene ethynylene)s chemistry [474]. Copolymerization via alkyne methatesis is schematically depicted in Fig. 40(c).

11. Condensation polymers

Condensation polymers, as polyesters, polyamides, polyimides, and polyurethanes, as shown in Fig. 41, can also have emissive properties. These materials can be classified as block copolymers, have good processibility and film formation properties, and the structure of the emitting center can be determined prior to polymerization. Multiblock copolymers in which distyryl blocks were linked by different functional groups with non-conjugated spacers have been synthesized. By altering these spacers different

classes of photoluminescent polycondensates with identical chromophoric groups were obtained. Polyesters, aromatic and aliphatic polyethers, polycarbonates, polysulfones and polyurethanes were investigated [475]. The reaction of dihydroxy functionalized, substituted phenylene vinylene chromophores with a variety of dicarboxylic acid chlorides yielded high molecular weight electroluminescent polyesters emitting in the blue-green region [476,477].

Copolyesters with varying concentrations of isolated 1,2-naphthylene chromophore units (Fig. 41(a)), emitted in the blue to blue-green region [214]. Distyryl naphthalene, distyryl anthracene, and terthiophene units in the chain of copolyesters also emitted blue and green light (Fig. 41(b)) [478], and copolyesters with isolated dimethoxy quarterthiophene emitted in the orange region [287]. Polycondensation reactions of several benzimidazole-, benzoxazole- and diphenyl anthracenyl containing chromophores with *m*-phenylenediamine, isophthaloyl chloride and bisphenol A gave strong photoluminescent polyamides, the majority emitting in the blue region, showing potential use for LED applications [479].

Light-emitting chromophoric polyamides and polyimides are shown in Fig. 41(c) and (d). Aromatic polyimides prepared from 9,10-bis (*m*-aminophenylthio)anthracene and 1,3-bis(3,4-dicarbophenoxy)benzene or 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydrides (Fig. 41(d)) belong to the class of donor-acceptor polymers and have been shown to be efficient electron and hole conductors. LEDs with a brightness over 1000 cd/m² at 16 V were fabricated [480,481].

Polarized EL was observed in films of polyesters with substituted bis(styryl)benzene or biphenylene units spaced by aliphatic segments when cast from solution on rubbed polyimide [482].

Polyurethanes with a diphenylamino-substituted-1,4-bistyryl benzene which acted as an emissive and charge transport chromophore showed luminance of 35 cd/m^2 at 26 V (Fig. 41(e) and (f)). When cyano groups were attached to the chromophore the luminance increased to 1000 cd/ m² at the same bias. The two polyurethanes peaked at 505 and 590 nm and formed homogeneous blends [482].

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