

Brite-EuRam
Contract BRE2-CT93-0592 / Project BE-7762

PolyLED

Polymer Light-Emitting Diodes and Displays

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Publishable Synthesis Report

1 Introduction

The objective of this project is the development of electroluminescent materials and the industrial technology for the production of efficient polymeric light-emitting diodes and displays in the red, green and blue spectral ranges.

As a result of the **PolyLED** project the following has been achieved by the partners:

- ▶ A range of soluble conjugated polymers and soluble precursor polymers, model systems and non-conjugated sidechain polymers with well documented syntheses and characterization methods for these materials.
- ▶ A standard device geometry and a procedure to test these devices has been designed and implemented to allow comparison of materials and procedures between the partners.
- ▶ Well-documented procedures to fabricate electroluminescent devices, as a single pixel or as an array of pixels in a display and their characterization, both optically and electronically. Also special effects have been **observed**, e.g. polarized emission from devices with oriented polymer layers.
- ▶ Models have been generated, based on the study of our devices, that describe the mechanism of injection of the charge carriers and their recombination.
- Various demonstrator devices were presented, a 5x7 display and iconized displays, in various **colours**. We have also assembled the driving electronics for these devices.
- ▶ A procedure to prepare one of our materials, a soluble dialkoxy-substituted PPV, as well as some options to prepare **PolyLED** devices on a large scale, as a first step to device manufacturing technology.

More quantitatively the results are:

- ▶ Polymer materials that allow fabrication of **PolyLED** devices with an external quantum efficiency of more than 2 %
- ▶ Electroluminescent intensity of **PolyLED** devices well over 100 Cd/m², with peak brightness over 10,000 Cd/m²
- ▶ A durability of the devices, at 100 Cd/m², of over 1000 hrs
- ▶ Electroluminescent intensities of over 100 Cd/m² at voltages of less than 4 V
- ▶ All **colours**, red, green and blue, are available

The development of these new polymer light-emitting diodes will not only offer new opportunities to the manufacturers of these devices and to the end users of these displays, but will also open new markets for specialty chemicals. Potential products for the chemistry industry are; **(semi)conducting** polymers, transparent conducting layers, electrode materials. A more attractive option for the chemical industry is the manufacturing of stacks of thin layers on large substrates which could be transformed into the required product by a display manufacturer.

2 Profile of consortium

The consortium of this Brite-Euram project consists of two research institutes, the University of Cambridge (Prof. Dr. R.H. Friend and Dr. A.B. Holmes) and the Max Planck Institute Mainz (Dr. Prof. Dr. K. Müllen) who have outstanding reputation in the field of materials chemistry and physics of (semi)-conducting polymers, and three companies, Hoechst AG (Dr. H. Schenk), Thomson-CSF (Dr. P. Le Barny) and Philips (Dr. E.G.J. Staring). The Universities of Linköping and Mons participated on the basis of minor subcontractor (Linköping, Prof. W. R. Salaneck), or by direct contract (Mons, Prof. Dr. J.-L. Bredas) to one of the partners. This cooperation between these universities and research institutes, and the chemical and electronic industry is essential for the development of commercial products based on electroluminescent polymers.

3 State-of-the-art in the rest-of-the-world

Polymer light emitting diodes and displays can have a large impact on the market for flat panel displays, a market with a huge economical potential. These new devices and displays offer the following attractive features:

1. They are flat, leading to reduced volume e.g. for portable and hand-held equipment;
2. They emit light, there is no need for backlighting to obtain the required brightness;
3. A full range of colours is available, presently electroluminescent displays suffer from a poor brightness in blue and green;
4. It is possible to make large area displays;
5. The display shows no view angle dependence, contrary to liquid-crystal displays;
6. Flexible substrates can be used, for which there is no alternative technology;
7. Cost effectiveness, due mainly to simple processing and simple technology during manufacturing.

As a result of the economic potential of the PolyLED technology, numerous companies, universities and research institutes are active in this area.

Recent advances in the work on polymer Light-Emitting Diodes outside the PolyLED consortium come from the USA, in the groups of Swager, MacDiarmid and Epstein'. The design and layout of materials and devices allows the use of AC-voltage, and the use of stable electrode metals, as opposed to the use of e.g. calcium for the more traditional materials and devices. Likewise, the Santa Barbara group of Heeger reported a new principle, the so-called Light-Emitting Electrochemical Cell*. This principle allows the fabrication of in-plane polymer Light-emitting Diodes. Their paper on the subject also indicates that it might be easier to generate the various colours of the visible spectrum by this device design.

Also in Japan, polymer light-emitting diodes are studied in companies and universities. Leading in the field are the chemical companies Sumitomo and Idemitsu Kosan. The effort at Idemitsu

¹H.L. Wang, J.W. Park, D.K. Fu, M.J. Marsella, T.M. Swager, A.G. MacDiarmid, Y.Z. Wang, D.D. Gebler, A.J. Epstein, "Symmetrically configured alternating current light emitting devices, use of copper as an electron- and hole- injecting electrode", Polymer Preprints, 1995, August, Chicago meeting, page 45

²Q. Pei, G. Yu, C. Zhang, Y. Yang, A.J. Heeger, "Polymer Light-Emitting Electrochemical Cells", Science 269, 1086-1088, 1995.

Kosan is aimed at applications in future displays, e.g. in addition to, or to replace LCD's. Scientists from this company have described a 16 x 16 pixelated colour (RGB) display³. In a closely related field, low-molecular-weight and vacuum-evaporated organic thin films for electroluminescence, the Japanese companies Pioneer and TDK have shown impressive progress. Pioneer showed two types of devices, segment and dot matrix types⁴. Some specifications of these devices are the following:

Dot-matrix type:

| | |
|-------------------|--|
| number of pixels: | 64X 256 dots |
| size: | 21.1 mm x 94.7 mm |
| colour: | green |
| luminance: | 200 Cd/m ² |
| life time: | over 10,000 hours (starting luminance is 300 Cd/m ²) |

Pioneer announced a full-colour (RGB) pixelated display of 4" diameter for the beginning of 1997. TDK already showed a full-colour display of comparable size at an exhibition.

In the US the Kodak company also has a very active program in the Organic LED area, based on evaporated films. They have shown impressive lifetime data, over 10.000 hrs for their devices⁵.

Although the work on these low-molecular-weight systems is ahead of that on polymer systems, we think that this is to a large part due to the longer research and development programmed in this area, which started in the years 1985-1986, as opposed to the polymer effort which started in 1991. We are confident that similar result will be obtained using the polymer-based technology developed within the consortium.

³M. Matsuura, H. Tokailin, M. Eida, C. Hosokawa, Y. Hironaki, T. Kusumoto, "Performance of RGB multi-colour organic EL display", Proceedings of the fifteenth international display research conference, Display Asia '95, October 16-16, 1995 at Hamamatsu, Japan, pag. 269-272.

⁴H. Nakada, T. Tohma, "Applications of Organic LEDs -256 x 64 dot matrix display", at the 8th International workshop on Electroluminescence, 13-15 August 1996, Berlin, Workshop Proceedings "Inorganic and Organic electroluminescence", Ed. R.H. Mauch, H.-E. Gumlich, Wissenschaft und Technik Verlag Berlin

⁵C.W. Tang, "Electroluminescence of vapor-deposited organic thin films", at the discussion meeting "Electronics with molecular materials: from synthesis to device", 4-5 June, 1996, The Royal Society, London.

4 Design and synthesis of materials

Standard Preparation of Poly(*p*-phenylenevinylene) PPV

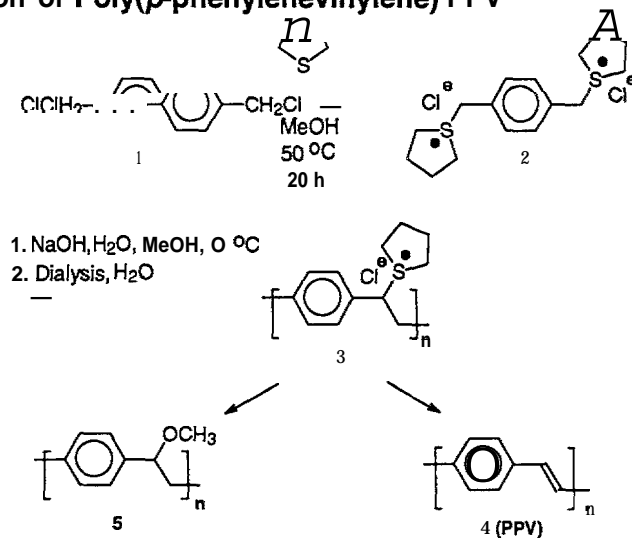


Figure 1. Standard Preparation of Poly(*p*-phenylenevinylene) PPV

A standard protocol for the synthesis of the reference material, poly(*p*-phenylenevinylene) (PPV) 4 prepared by the sulfonium precursor route was developed. The synthetic protocols were defined according to the well established *Organic Syntheses* format such that any trained synthetic chemist, skilled in the art, could follow the procedure reproducibly. The procedure was optimised particularly by careful dialysis of the sulfonium precursor polymer to remove impurities, The synthetic procedure was published in a special report.

Standard Preparation of MEH-PPV 9

The dialkoxy-PPV 9 polymer poly-1,4-(2-methoxy-5-(2-ethyl)-hexyloxy)-phenylene-vinylene, MEH-PPV for short (Figure 2) was selected as a soluble and conjugated reference material. The standard preparation of MEH-PPV is very similar to that reported in Santa Barbara by Heeger and Braun⁶ and a modification of the route first developed by Wudl⁷. MEH-PPV 9. The standard preparation of MEH-PPV was optimised by conducting the polymerisation in dilute THF solution and by purification of the polymer. The procedure was published in a special report.

In parallel, "we have prepared a whole range soluble conjugated poly-1,4-(2,5-dialkoxy-phenylene-vinylene) 10 and poly-(2,5-dialkyl-1,4-phenylene-vinylene) 12 polymer materials.

⁶ Heeger, Alan J.; Braun, David (University of California, Santa Barbara) *PCT Int. Appl. Appl. WO* 9216,023 (cl. HOI L33/00), 17 Sep 1992, US Appl. 662,290,27 Feb 1991; *Chem. Abst.*, 1993, **118**, 157401 j.

⁷ Wudl, F.; Allemand, P.-M.; Srdanov, G.; Ni, Z.; McBranch, D. in *Materials for Non-Linear Optics; Chemical Perspectives*, Eds. Marder, S. R.; Sohn, J. E.; Stucky, G.D. *ACS Symp. Ser.* **1991**, **455**, 683.

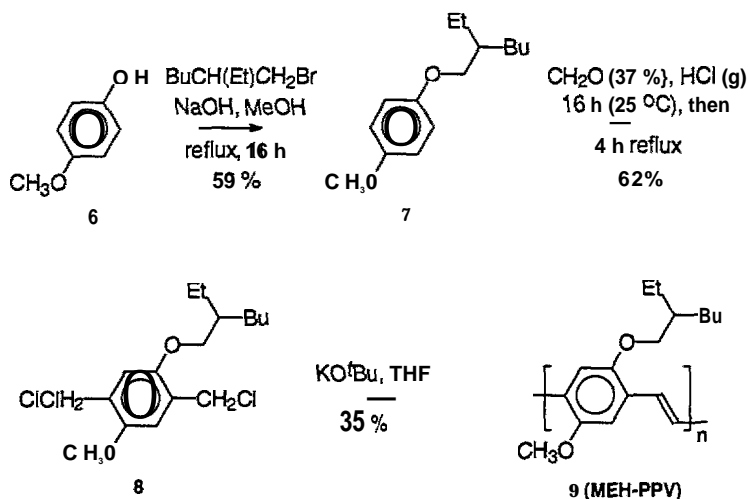


Figure 2. Synthesis of MEH-PPV

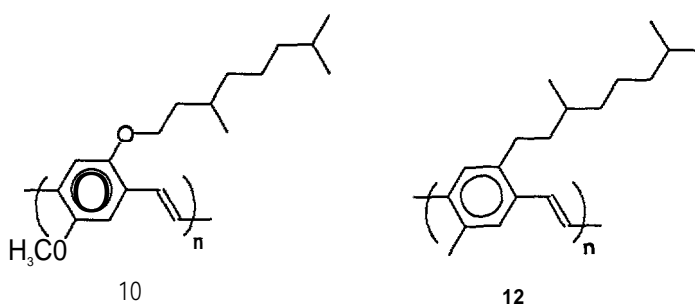


Figure 3. Dialkyl- and dialkoxy derivatives of PPV.

Poly(cyanoterephthalydene)s

The high electron affinity polymers **13-15** serve as a transport layer and a luminescent material. Polymer **13** is solution processible in solvents such as toluene. This leads to high quality thin films of polymer 13. This material, when incorporated in a two layer device with the configuration ITO/PPV/Polymer **13**/Al exhibits some of the highest EL emission efficiencies (up to 10% internal efficiency) measured to date. Polymer **14** was synthesised and analysed in collaboration with Philips. There are subtle differences in processibility and emission characteristics between polymers **13-15**.

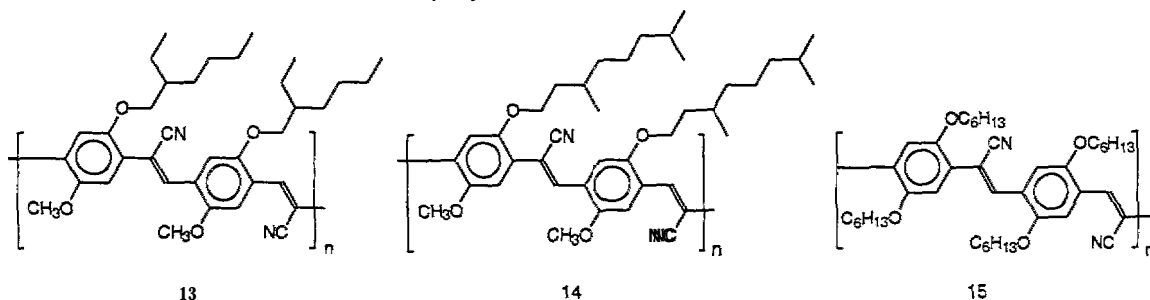
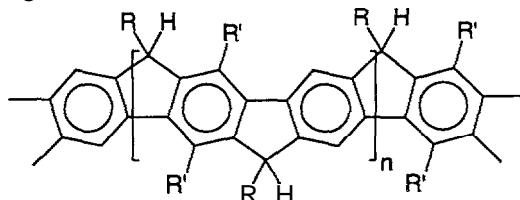


Figure 4. Structure of various Poly(cyanoterephthalydene)s

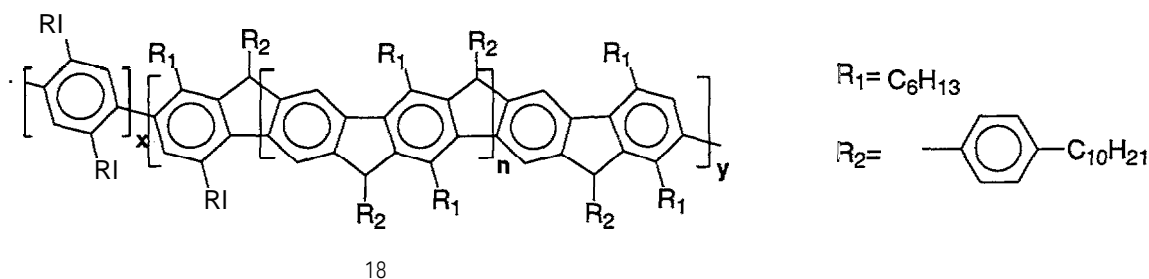
Synthesis of Ladder-Type Poly(*para*-phenylene)s

For blue LEDs, the use of conjugated polymers with a HOMO/LUMO energy difference (band gap) of 2.7- 3.0 eV is necessary. In this project, novel poly(*para*-phenylene)-based ladder polymers [R: -1,4-C₆H₄-alkyl, R': -alkyl) with an E_g of ca. 2.75 eV were, therefore, used as active layer in light-emitting diodes⁸.

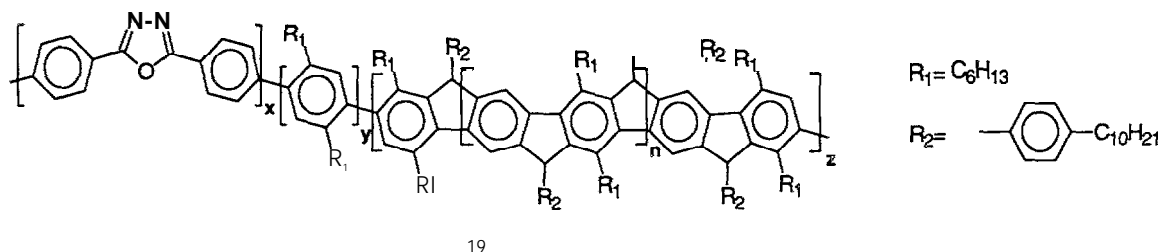


Their solubility in common organic solvents allows for a processing to thin transparent films by spin coating or casting. Their rigid, regioregular and defect-free structure offers the chance for designing LEDs with low energy losses by nonradiative decay processes. The PPP-type ladder structures are, however, characterized by a two-component light emission. The blue component can be assigned to the electroluminescence of single molecules, a yellow component to the emission of intermolecular aggregates. A strategy to suppress the formation of aggregates on the way to blue emitting devices is the use of new PPP-type step-ladder structures 18 (R: -1,4-C₆H₄-alkyl, R': -alkyl)⁹. The distorted geometry of the step-ladder structures prevents an intermolecular aggregation. Internal quantum efficiency values of up to 1% for blue LEDs are very promising.

One often discussed strategy to facilitate the electron injection is a "tuning" of the LUMO level by means of an incorporation of electron-deficient aromatic subunits (oxadiazole subunits)



into the conjugated emitters. Following this strategy, a copolymer 3 (R: -1,4-C₆H₄-alkyl, R': -alkyl) was synthesized which shows an improved electron injection and internal EL quantum efficiencies of 2.5%¹⁰.



⁸Huber, K. Mullen, J. Salbeck, H. Schenk, U. Scherf, T. Stehlin, R. Stem, *Acts Polymer*. 45,244 (1994).

⁹J. F. Grüner, P. Hamer, R. H. Friend, J. Huber, U. Scherf, A. B. Holmes, *Adv. Mater.* 6,748 (1994).

¹⁰J. F. Grüner, R. H. Friend, J. Huber, U. Scherf, *Chem. Phys. Lett.* 251,204 (1996).

Synthesis of rigid rod-like polymers for the Langmuir-Blodgett Technique

A variety of substituted rigid rod-like polymers based on poly(p-oligophenylene vinylene)s has been synthesised and characterised". The preparation of polymers containing oligo(p-phenylene) units connected by various functionalities was made possible by extending the Suzuki¹² reaction to stilbene-, diphenylethynylene- and 1,2-diphenylethane derivatives. Examples of some of these polymers are given in Figure 5. The incorporation of new monomers now allows the synthesis of polymers containing alternating oligo-p-phenylene and vinylidene, alkynylene and ethylidene units, with varying absorption and emission wavelengths, by modifying the fraction of the vinylene units in the chain. High photoluminescence efficiencies were observed for polymers with an interrupted conjugation or with a variation of the electronic structure along the polymer backbone.

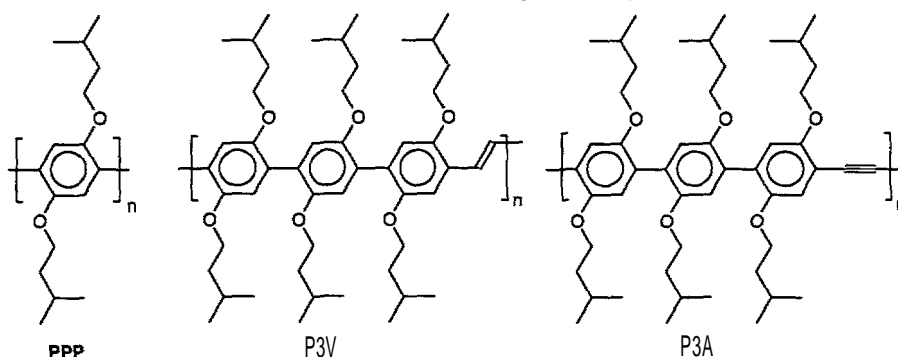


Figure 5. Structure of some selected rigid-rod polymers for LB-film formation.

Side-chain and non-conjugated polymers

A whole range of side chain EI-polymers and copolymers was prepared emitting in the blue, the green or the red-orange, mainly based on the polymethacrylate backbone. Synthesis of the different monomers was performed via multi step pathways which involved standard procedures. Nevertheless, most of the steps had to be adapted. The emitting units were chosen taking into account their emission wavelength and their photoluminescence quantum yield. The following chromophores were thus selected:

- ◆ 2,3,6,7-tetramethoxy-9, 10-dialkyl-anthracene for the blue
- ◆ N-phenyl-4-N,N-dialkylaminonaphthalimide for the green
- ◆ 4-(dicyanomethylene)-2-methyl--6-p-(dimethylaminostyryl)-4H-pyran (DCM) for the red-orange.

¹¹ M. Remmers, D. Neher, J. Grüner, R.H. Friend, G.H. Gelinck, J.M. Warman, C. Quattrocchi, D. A. dos Santos, J.-L. Bredas, *Macromolecules* 1996,29,7432

¹² M. Remmers, M. Schulze, G. Wegner, *Macromol. Rapid. Commun.* 1996, 17,239

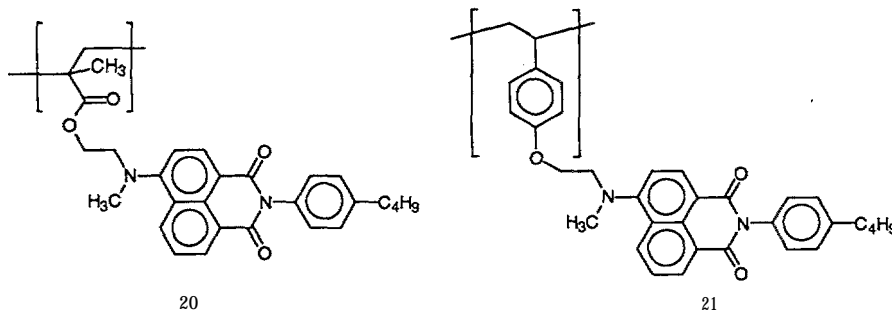


Figure 6. Structure of polymers 20 and 21

5 Processing of materials

Dialkoxy-PPV derivative 10 dissolves readily in toluene. Toluene is very suitable for spincoating of homogeneous layer over larger areas. We used a polymer that contained 15 % of non-conjugated segments, the material that we showed to have the highest electroluminescence efficiency so far. The concentration of the polymer was varied, 0.5, 1.0 and 1.5 % (w/w) in toluene. The results are shown in Table 1. The mean surface roughness is less than 1 nm over a $6.6 \times 6.6 \mu\text{m}^2$ area.

| % (w/w) in toluene | R_a / nm | R_m / nm |
|--------------------|------------|------------|
| 0.5 | 2 | 10 |
| 1 | 0.5 | 4 |
| 1.5 | 1 | 5 |

Table 1. Roughness values for the various spincoating experiments of dialkoxy-PPV 10 from toluene, as determined by STM.

For the measurement of the thickness variations on the macroscale, we prepared a film of the dialkoxy-PPV derivative 10, by spincoating from toluene (1 % w/w) on a 4" diameter silicon wafer. Thickness of the resulting film was measured by ellipsometry. The resulting thicknesses are displayed in Figure 7. The total layer thickness was roughly 920 nm. On a scale of 1000 nm thickness hardly any deviation from that value is observed. Variations fall within the 1 % range. On an enlarged scale, deviations are of course clearly visible, but there is no correlation with the sample point, There is no clear indication that the film is thinner at the edges or much thicker in the centre.

From the above we can conclude that, by spincoating, it is possible to obtain thin polymer films, with only small thickness variations, both on a macroscopic level as well as on a microscopic level. For in-line control of the spincoating techniques, viscosity data and optical density measurements can be used.

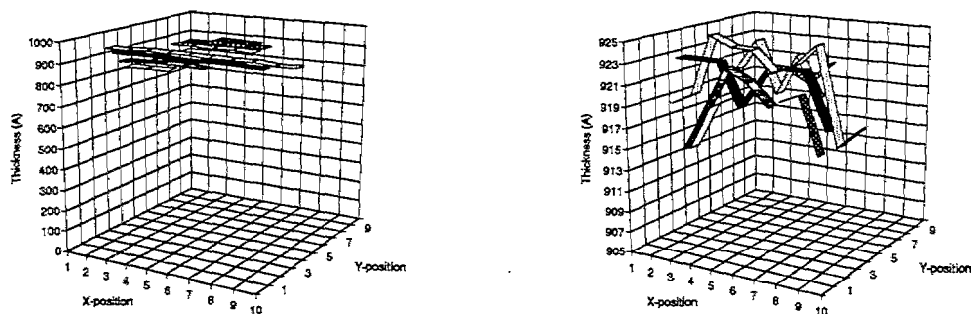


Figure 7. Thickness variation of the films, on an absolute and on an enlarged scale.

Characterisation of Langmuir-Blodgett Films of rigid rod-like fluorescent polymers

The behaviour of various polymers as summarised in Figure 5 at the air-water interface was characterised using a Lauda Filmwaage FW-1 in a laminar flow box. Solutions with concentrations of approx. 0.3 g/l in Chloroform (Merck Uvasol) were spread on the surface of Mini-Q water (conductivity: 10^{-18} S/cm) serving as subphase.

Figure 7 shows the surface pressure area diagram of a PPP, P₃V and P₃A Langmuir film on water. The clear step of the PPP at 17 mN/m in one indication of a good processibility of this material as a hairy rod molecule. However, the P₃V and P₃A did not exhibit an as pronounced step. An increase of the surface pressure of the P₃A can be measured at a relatively large surface area, but the collapse pressure is much lower than that of PPP and P₃V.

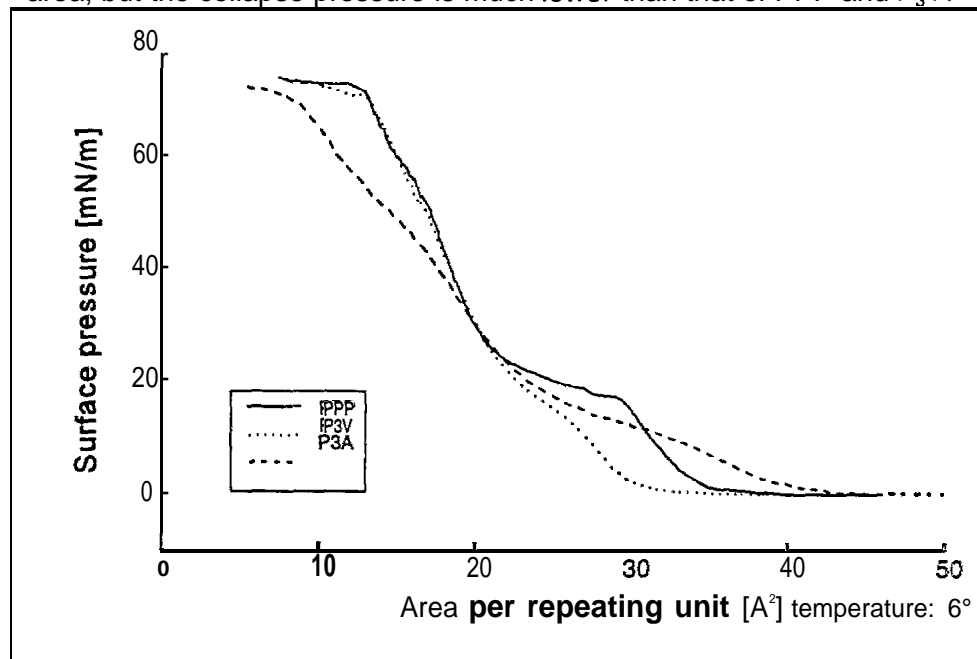


Figure 7. Surface-pressure-area-diagrams of PPP, P₃V and P₃A Langmuir films recorded at 6°C

Light emitting diodes were fabricated with an emission layer of PPP prepared by the LB technique¹³. The conditions for transfer onto the hydrophobic substrate were $\pi_c \approx 8$ mN/m at 6°C at a dipping speed of 0.9 cm/min. Under these conditions LB assemblies with 100 monolayers could be produced with a transfer ratio of 0.96 \pm 0.04. The film thicknesses were determined to be in the range from 120 to 130 nm with a surface roughness of only 0.5 nm from the analysis of the so-called Kiesig fringes in X-ray reflection experiment.

For LED devices 100 monolayer (130 nm) of PPP were deposited onto a fused silica substrate, which had previously been covered with 4 nm of chromium followed by 17 nm of gold or onto an ITO-covered glass substrate to form the semitransparent bottom electrode. An aluminium electrode was evaporated on top of the polymer films as the electron-injecting contact. Typical active areas were around 4 mm². The LED's were driven under constant bias. All measurements were performed in an inert atmosphere or in vacuum to prevent electrode oxidation.

6 Characterization of materials

A range of characterisations of optical and electrical properties of some of the new polymers now available have been carried out.

In a collaboration between the University of Cambridge and Philips, parallel facilities for the measurement of absolute efficiencies of photoluminescence, PL, and electroluminescence, EL, was set up. This has been achieved using an integrating sphere which allows the measurement of light emission from the sample device irrespective of the direction of emission (thus not requiring detailed knowledge of the angular distribution of the emitted light).

Results of the measurement of the PL efficiencies of a range of polymers have proved to be very interesting, not least because their values are considerably higher than had been anticipated. A selection of data is shown in table 2 below:

| Polymer | η_{PL} | Error | Excitation |
|------------|-------------|------------|------------|
| PPV | 0.27 | *0.02 | 458 |
| MEH-PPV | 0.10-0.15 | \pm 0.01 | 488 |
| P3HT-a | 0.018 | *0.004 | 488 |
| P3HT-b | 0.020 | *0.004 | 488 |
| CN-PPV | 0.35-0.46 | *0.02 | 488 |
| MEH-CN-PPV | 0.48 | *0.02 | 488 |

Table 2. PL efficiencies measured for a range of conjugated polymers.

Note that the PL efficiencies for the various PPVS are all very high. The value for PPV is of particular interest since previous reports had suggested that the PL efficiency might be considerably lower than the value listed in the table above (277.), and on the basis of this and on transient optical measurements, the AT&T group of Rothberg had suggested that

¹³ V. Cimrová, M. Remmers, D. Neher, G. Wegner, *Adv. Mat.* 1996,8, 146

intra-chain excitons might not be the dominant photoexcited state. These high values provide good support for the Cambridge model in which intra-chain excitons have a substantial binding energy (of order 0.4 eV). In contrast, poly(3-alkylthiophene)s are considerably less efficient, as reported in the table above for poly(3-hexyl thiophene), both regio-random (a) and regio-regular (b).

Photochemical stability of dialkoxy-substituted-PPV

At the Philips Laboratories, we have tried to quantify the photochemical stability of polymer **10**. Although it has not been proven, we are confident that MEH-PPV **9** will behave identical or at least closely similar.

We have derived a formula that allows a quantitative study of the photochemical degradation of PPV materials¹⁴. This is of interest because it will allow us to predict the stability of these materials in polymer LEDs, in the absence of other external factors that cause device degradation and failure. These electroluminescent devices operate by a similar mechanisms as the photoluminescence mechanisms presented in this study. The polymeric materials used in these devices will therefore undergo similar chemical processes, in the absence and in the presence of oxygen.

A thin film of polymer **10** is illuminated with a laser beam of known intensity distribution, power and wavelength. The setup can be placed in a closed chamber, to operate in vacuum, air, nitrogen or any other gas. As a quantitative measure for the photochemical degradation, a quantum yield for photodegradation is proposed, γ , being the inverse of the average number of photons a molecule can absorb before being destructed. The experimentally observed changes in transmission of the PPV films are fitted with a formula that contains γ as the only adjustable variable.

We have investigated the parameter dependence of γ , including parameters like: bleaching power, wavelength dependency and dependency on the bandgap of the electroluminescent polymer material. The experiments show that γ is independent of the optical power of the light source used in the bleaching experiments, and independent of the wavelength, as long as this wavelength falls within the absorption spectrum of the PPV material. In the presence of oxygen, the main degradation pathway is by photo-oxidation of the PPV material. Consequently, there is a strong dependence of γ on the oxygen concentration.

XPS and UPS in PolyLED

The detailed chemistry of the interface between the active light emitting polymer medium and the metal electrode may be a determining factor in the commercialization of polymer-based LEDs. This statement comes from the results of a wide variety of studies of the surface physics and chemistry of n-conjugated polymers, as well as the interfaces between these

¹⁴ E.G.J. Staring, A.J.M. Berntsen, S.T.R. Romme, G.J.L.A. Rikken, P. Urbach, On the Photochemical stability of dialkoxy-PPV; a quantitative approach", Phil.Trans.R.Soc. Lend. A (1997), 355,1-11.

polymers and either metal electrodes^{15, 16, 17, 18, 19} or the ITO electrode. These studies have been carried out using both ultra-violet and X-ray photoelectron spectroscopy (UPS and XPS). Looking over the range of results, certain distinct trends have emerged. The chemistry which occurs at the metal-on-polymer interface varies with the nature of the metal involved, the polymer involved, and especially with the cleanliness of both the materials employed and the vacuum system used in the metalisation process. Of particular significance is the fact that, using the basic science results, certain guidelines have been developed to guide eventual fabrication of polymer-based devices.

In the case of calcium vapor-deposited upon clean surfaces in UHV, it was observed clearly, first for a model polyene molecular solid system and subsequently for substituted PPV²⁰, that calcium atoms diffuse into the near surface region, donate electrons to the n-system, and form Ca⁺⁺-ions. In contrast, cases where there are large numbers of oxygen-containing species at the surface of, e.g., PPV 2 or substituted PPVS²², an interracial layer of an oxide of calcium is formed initially upon the deposition of calcium atoms in UHV, followed by the deposition of calcium metal after the oxygen-containing species have been consumed by the initial calcium atoms. With this background, a series of studies were carried out to determine the best vapor-deposition conditions for calcium electrodes. Considering a figure-of-merit based upon device yield, turn-on voltage, brightness, and more, the optimisation of indicated that a vacuum of about 10⁻⁶ mBar is better than ultra high vacuum²³. The presence of a certain degree of oxidation, or other type of interracial barrier, is apparently necessary for the control of detrimental interracial effects at the metal-polymer interface.

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- ¹⁵ W. R. Salaneck and J. L. Brédas, "The metal-on-polymer interface in polymer light emitting diodes", *Adv. Mat.*, 8(1),48(1996).
- ¹⁶ W. R. Salaneck, S. Stafström, and J. L. Brédas, *Conjugated Polymer Surfaces and Interfaces*, 1996, Cambridge: Cambridge University Press.
- ¹⁷ J. L. Bredas, *Adv. Mat.*, 7,263 (1 995).
- ¹⁸ J. L. Brédas and W. R. Salaneck, *Characterization of the Interfaces between Low Work Function Metals and Conjugated Polymers in Light Emitting Diodes*, in *Organic Electroluminescence*, D.D.C. Bradley and T. Tsutsui, Editors. 1995, Cambridge University Press: Cambridge.
- ¹⁹ M. Lögdlund, P. Dannelun, and W. R. Salaneck, *Electronic and chemical structure of polymer surfaces and interfaces as studied by photoelectron spectroscopy*, in *Handbook of Conducting Polymers*, T. Skotheim, J. Reynolds, and R. Elsenbaumer, Editors. 1996, Marcel Dekker: New York
- ²⁰ P. Dannelun, M. Fahlman, C. Fauquet, K. Kaerijama, Y. Sonoda, R. Lazzaroni, J. L. Brédas, and W. R. Salaneck, *Interface formation between poly(2,5-diheptyl-p-phenylenevinylene) and calcium: Implications for light emitting diodes*, in *Organic Materials for Electronics: Conjugated polymer interfaces with metals and semiconductors*, J. L. Brédas, W. R. Salaneck, and G. Wegner, Editors. 1994, North Holland: Amsterdam. p.113.
- ²¹ Y. Gao, K. T. Park, and B. R. Hsieh, "X-ray photoemission investigations of the interface formation of Ca and poly(p-phenylenevinylene)", *J. Chem. Phys.*, 97, 69S1 (1 992).
- ²² P. Dannelun, *Private communication*, (1994).
- ²³ P. Bröms, J. Birgersson, N. Johansson, M. Lögdlund, and W. R. Salaneck, "Calcium electrodes in polymer LED's", *Synth. Met.*, 74, 179 (1995).

7 Device fabrication

For reasons of reproducibility from experiment-to-experiment and for comparison from partner-to-partner, we have defined a **lab scale** reference system and a standard device geometry and lay-out. The standard consists of glass substrate that have, on a 30 x 30 mm² area, 2 x 2 mm², 3 x 3 mm², 5 x 5 mm² and 9 x 9 mm² diodes, that have no common ITO or metal electrodes and can therefore be addressed independently. As evaporated metal electrodes, we used **calcium, aluminium and calcium/aluminium combinations**. The specific details of sample preparation were described in a separate report. The result of our device fabrication procedure, as an IV and VL curve of a PolyLED device is shown in figure 8.

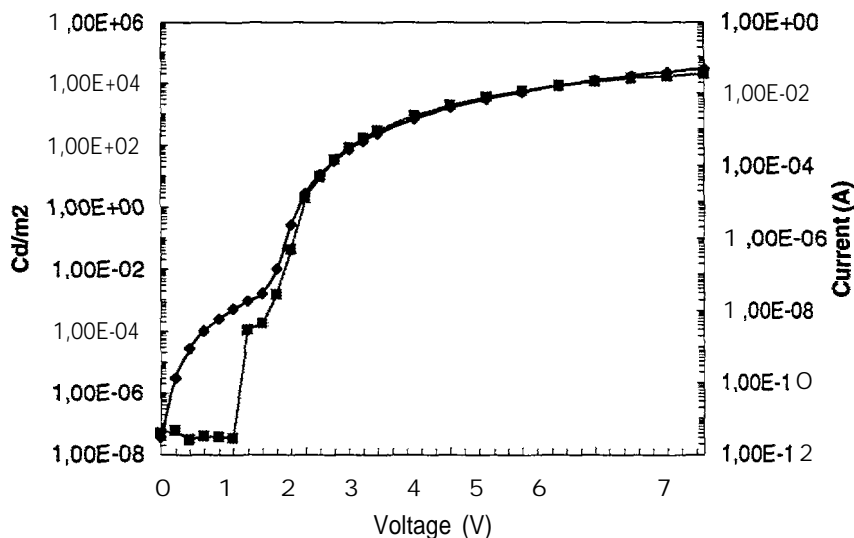


Figure 8. The figure shows the I-V (diamonds) and L-V (squares) characteristics of a 2 x 2 mm² PLED device, using a soluble dialkoxy-PPV as emissive layer, and Ca and ITO as electrodes. The maximum emission wavelength of the device is 610-620 nm. The onset of light-emission is at 1,6 V.

Multi layered Devices

For many conjugated polymers there is a significant barrier to electron injection. Organic conjugated materials have a highest occupied molecular orbital (HOMO) well-matched to the work function of iridium tin oxide (ITO), and the barrier to hole injection is therefore relatively low. Balanced charge injection is important for the operation of polymer LEDs with maximum efficiency. This can be realised by the use of one or more charge transport layers between the emissive layer and the electrodes.

The approach to balancing electron and hole injection in Cambridge has been to design highly luminescent high electron affinity polymers which serve as an electron transport layer. The prototypical example is the poly(cyanoterephthalylidene)s or CN-PPV family displayed in figure 4.

The polymers 11-13 function efficiently in a two-layer device using Al as the negative contact and a second layer of PPV as hole transport layer. PPV has the advantage that it can be processed as the precursor sulfonium polymer and then converted into the robust insoluble fully conjugated material. This allows deposition by spin coating of a solution of one of the

polymers **11** or **12** (from toluene) or **13** (from chloroform) without dissolution of the PPV layer. Good interfaces are formed between the polymer layers, and emission probably occurs in the two-layer device within a small interracial layer. **hetero** junction offsets play an important role in determining barrier levels. These can be estimated from **cyclic voltammetry** studies in conjunction with computational methods and optical band gap measurements.

Another approach is to use an electron **transport/hole** blocking layer between an emissive layer such as PPV and a negative electrode. In Cambridge **oxadiazole** side chain and main chain polymers have been extensively investigated. Although these materials improve device efficiency, they function largely as hole blocking materials, and hence significantly large drive voltages are required to allow the devices to function.

Devices based on LB-films with polarised light emission

The current voltage characteristics detected on the devices with 100 monolayer of PPP, an ITO hole injecting electrode and an aluminium top electrode exhibited typical diode-like behaviour. The onset of electroluminescence could be detected at an electric field of 10^6 V m^{-1} (according to an onset voltage of 13V). In the current voltage characteristics of the devices with **Cr/Au** electrode anomalies appeared in the low voltage region. External quantum efficiencies were approx. 0.05 % and the external power efficiency approx. 0.01 % for a device driven at 13 V. These are typical numbers for single layer diodes based on poly(p-phenylene vinylene)s^{24, 25}.

Polarised absorption spectra of the PPP emission layer showed the absorption maximum at 330 nm (Figure 9, left). The absorption A_{\parallel} , parallel to the dipping direction, is about five times larger than A_{\perp} , perpendicular to the dipping direction indicating a high in-plane anisotropy of chain alignment. Polarised photoluminescence spectra (PL) of the PPP LB film show a blue emission with the maximum at ca. 3.11 eV (395 nm) and with a tail extending down to 2 eV (600 nm). The ratio of light intensity being polarised parallel and perpendicular to the dipping direction was around 3-4, which is slightly smaller than the dichroic ratio found in the linear absorption experiment. This discrepancy might indicate the occurrence of energy transfer in the film after excitation

Polarised electroluminescence (EL) spectra of the device recorded through the ITO electrode show that the ratio of light emission intensity polarised parallel and perpendicular to the dipping direction was larger than three for both types of hole injecting electrodes in agreement to the values found in the photoluminescence experiments (Figure 9, right). The anisotropy of emission is quite large when compared to the results on stretched poly(thiophene) emission layers²⁶ and comparable to recent results on layers with rubbing-aligned poly(2,5-dinonyloxy-1,4-phenylene vinylene) (NO-PPV) films²⁷. Our result proves that electroluminescence occurs via the direct recombination of an intra chain exciton along the conjugated backbone.

24 G. Grem, G. Leditzky, B. Ullrich, G. Leising, *Synth. Met.* 1992,51,383

25 G. Grem, G. Leising, *Synth. Met.* 1993,55-57,4105

²⁶ P. Dyreklev, M. Berggren, O. Inganäs, M. R. Andersson, O. Wennerström, T. Hjertberg, *Adv. Mat.* 1995, 7,43

2. M. Hamaguchi, K. Yoshino *Appl. Phys. Lett.* 1995, 67,3381

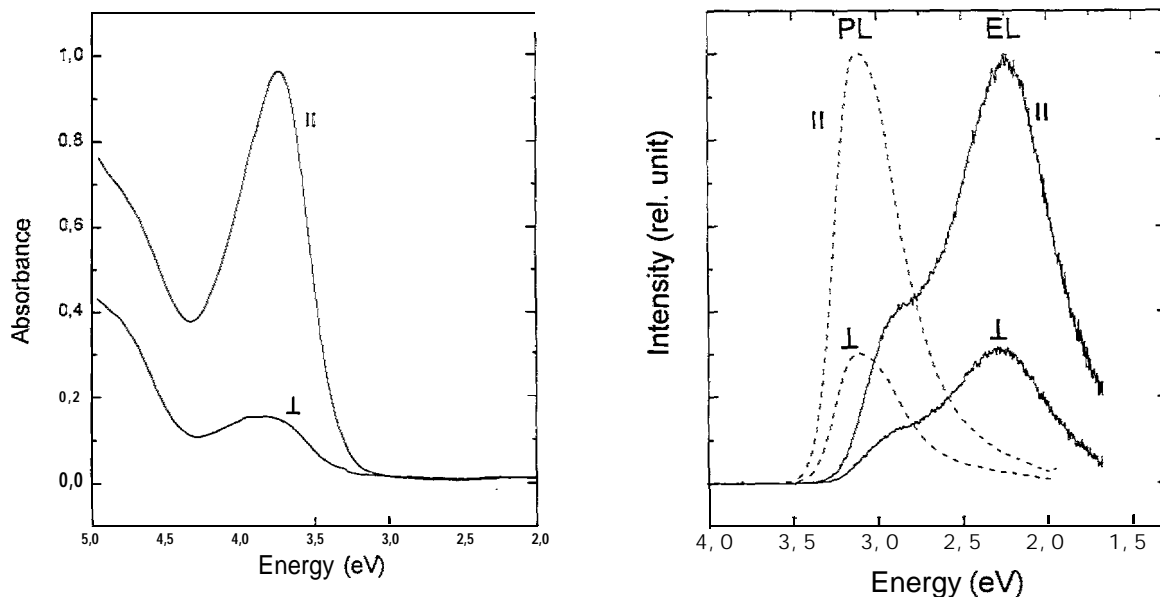


Figure 9. Left: Absorption spectra (parallel and perpendicular to the dipping direction) of a Langmuir-Blodgett film consisting of 100 monolayer of PPP; **Right:** PL emission spectra (dashed line) and EL spectra (solid line) of a light-emitting device (ITO/PPP 100ML/Al) prepared by the LB technique. Emission spectra are shown for the polarisation of light parallel and perpendicular to the dipping direction.

The EL emission, with the maximum of the parallel and perpendicular emission located at about 2.23 eV (536 nm) and 2.28 (524 nm), respectively, is strongly red-shifted with respect to the PL spectra. This large spectral shift can be explained by trapping of the injected charges into low lying recombination centres. A comparison to the emission characteristics of light emitting diodes of the same material but with the emitting layer prepared by spin-coating indicates that the existence of such radiative states correlates with the degree of order in the emitting layer.

PolyLED devices based on non-conjugated systems

Among all the side chain emitting polymers prepared so far, naphthalimide derivatives have given the best results in terms of brightness and efficiency and have hence been the subject of careful studies to improve their performance. More precisely, using polystyrene instead of polymethacrylate as polymer backbone was a real breakthrough, Cyclic voltammetry studies clearly shown that devices made with polymers 20 and 21 would exhibit better performance if an hole injecting layer (HTL) was introduced. Efficient green light emission was obtained with the following device: ITO/PVK/20/Ca. The results are summarised in table 3.

| Maximum luminance | | | L = 100 cd/m ² | | Ext. Quantum | Ext. Energetic |
|-------------------|------|------------------------|---------------------------|------------------------|--------------|----------------|
| L _{max} | V(V) | j(mA/cm ²) | V(V) | j(mA/cm ²) | efficiency | efficiency |
| 3830 | 14 | 322 | 9 | 10.8 | 1% | 0.2% |

Table 3. Performance of the bi-layer device based on PVK and 21

Quite high brightness was also obtained in the red-orange with guest-host systems based on polymer **20** doped with 20% DCM. The results are summarised in table 4.

| ITO/PVK/ 20 + 20% DCM/Al | | | | |
|---------------------------------|------|-----|--------------------------|----|
| Max Luminance | | | L = 100cd/m ² | |
| L _{max} | v(v) | j | V(V) | j |
| 1772 | 22 | 500 | 16 | 40 |

Table 4. Device performance of polymer 20 doped with DCM. (j in mA/cm²)

8 Device properties, measurement and modelling

Within this PolyLED program, we have studied and described the charge injection, transport and recombination phenomena. We have demonstrated that the electron and hole currents in PPV devices with low contact barriers are determined by the bulk conduction properties of the polymer, and not by the injection properties of the contacts^{28, 29, 30}. The conduction of holes in a film of the conjugated polymer PPV is governed by a combination of a field-dependent mobility and space charge effects. The mobility which is directly obtained from the *J-V* experiments is constant at low fields and exhibits a high field behaviour in agreement with the mobility of molecularly-doped polymers and organic glasses as observed in TOF. The electron transport is limited by traps which are exponentially distributed in energy with a density of 10¹⁸ cm⁻³. A device model for PLEDs is proposed which demonstrates that an unbalanced electron- and hole transport give rise to a bias dependent efficiency. The recombination in a PLED is mainly non-radiative, only 5% of the total number of recombination contributes to the light output of the device.

Molecular modelling and calculations

The theoretical studies performed in Mons within a collaboration with Hoechst AG in the framework of the PolyLED programme were focused on the investigation of various aspects of the electronic structure of conjugated polymers and molecules of interest in the PolyLED programme, in particular the spire-type molecules, the ladder-type arylene compounds, and the substituted polyparaphenylene and related copolymers with different numbers of rings between the vinylene groups along the backbone. Distinct theoretical approaches were exploited to provide a detailed characterization of the frontier electronic structure and lowest energy optical transitions in these compounds. The most stable structures were obtained with

²⁸ P.W.M. Blom, M.J.M. de Jong, J.J. M. Vleggaar, ApplPhys. Lett. 68,3308 (1 996).

²⁹ P.W.M. Blom, M.J.M. de Jong, M.G. van Munster, Phys.Rev.B. 55, R656 (1 997)

³⁰ P.W.M. Blom, M.J.M. de Jong, C.T.H.F. Liednbaum, J.J.M. Vleggaar, ICSM96, to be published in Synth. Met.

the help of semiempirical AMI and density functional theory (DFT) calculations. On the basis of the structural data, the electronic structure was investigated at the Valence Effective Hamiltonian (VEH) or DFT level; the optical absorption spectra, including the vibronic coupling, were obtained via the intermediate Neglect of Differential Overlap (INDO) method coupled to a single configuration interaction (SCI) technique.

We have characterized the electronic and optical properties of spiro derivatives of the PBD (2-(4-biphenyl)-5-(4-terbutylphenyl)-1,3,4-oxadiazole) and triphenyldiamine (TPD) molecules, in collaboration with the Linköping group, using a combined theoretical and experimental approach consisting of quantum-chemical calculations, ultra-violet photoelectron spectroscopy, Raman spectroscopy, and spectroscopic ellipsometry. The impact of the spiro architecture was investigated in detail, by comparing the results obtained for spiro-molecules with those of the corresponding non-spiro ones. The theoretical results reveal that, due to their geometric structure characterized by two perpendicular branches, the π electron systems associated to each branch in the spiro molecules appear to be nearly completely decoupled. The analysis of the VEH calculated frontier levels energies and the INDO/SCI optical spectra indicates that the small modifications on the electronic structure induced by the spiro architecture comes from the geometry modifications in the spiro molecules with respect to that in the non-spiro counterparts.

The electronic structure of ladder-type derivatives of poly(*p*-phenylene), or LPPP, was also investigated at the theoretical and experimental levels, in particular the interaction of the ladder-type LPPP with alkali metals, rubidium and potassium. A very good agreement was obtained between theory and experiment in the description of the pristine LPPP electronic structure. However, the description of the metal/polymer interaction at the theoretical level shows that both Rb and K play the role of dopant when interacting with single chains of LPPP, while the experimental data points to a distinct behavior, *i.e.*, only K is observed to dope LPPP. This discrepancy may indicate that solid-state packing, or the polymer morphology, play a role on the evolution of the electronic structure upon metal exposure.

Finally, we have undertaken the study of the geometric and electronic structure of copolymers of substituted polyparaphenylenes with different numbers of rings between the vinylene groups along the backbone, prepared by the MPI group³². The theoretical results allow us to rationalize the evolution of the main electronic parameters, as the ionization potential and energy bandgap, as a function of the molar fraction of vinylene groups along the polymer backbone; an overall very good agreement between the theoretical and experimental main electronic parameter values reported by the MPI group was obtained.

³¹ R.I. Johansson, D.A. dos Santos, S. Guo, J. Cornil, M. Fahlman, J. Salbeck, H. Schenk, H. Arwin, J.L. Brédas, and W.R. Salaneck, "Electronic structure and optical properties of electroluminescent spiro-type molecules", to be submitted.

³² M. Remmers, D. Neher, J. Grüner, R.H. Friend, G.H. Gelink, J.M. Warman, C. Quattrocchi, D.A. dos Santos, and J.L. Brédas, "The optical, electronic and electroluminescent properties of novel poly(*p*-phenylene)-related polymers", *Macromolecules* 29,7432-7445 (1996)

9 Demonstrator

For this project a number of demonstrators were prepared. The most challenging and desirable device is a flexible display, and it is described here. The full versatility of light emitting polymer technology can best be demonstrated by manufacturing all plastic displays. Such displays use a plastic film instead of a glass substrate. They open up completely new areas of applications and provide potential for a unique variety of innovative display designs. This has been recognized very early by the Cambridge group and first demonstrated by Heeger et al.³³ who used a two layer system with soluble polyaniline as hole-injecting layer and MEH-PPV as light emitting polymer. Somewhat later Schwoerer et al.³⁴ [2] used a Wessling-precursor PPV on a PET film for the same purpose. We have now demonstrated that it is in fact possible to manufacture single layer all plastic light emitting diodes which are almost as efficient as the best devices on glass.

The PET films were rinsed in an **alkalic** water solution with Extran AP 11 (from Merck) in an ultrasonic tank. The substrates were rinsed again in **Milliporewater** with ultrasonic power and dried with N₂. As photoresist the speciality resist AZ NOVA 2071 (Hoechst) was used. The samples were exposed in a FUHS electronic F1 501 equipment with a shadow mask. Subsequent development was done with MF 32 (Hoechst). Rinsing with **Milliporewater** and drying with N₂ was repeated. The ITO was etched with a mixture of hydrochloric and nitric acid in water. The photoresist was removed with acetone and the substrate dried with N₂. The solution of **dialkoxy-PPVs** were spin coated onto the PET substrate using a 5 µm filter. Finally the cathode was evaporated through a contact mask in a Balzers evaporator at a rate of 1 nm/s. For **electro-optical** characterization test devices with active areas ranging from 2 x 2 mm² to 9 x 9 mm² were fabricated. The light-emitting polymer typically used for this test was a single 80-140 nm layer of OC1 Cl 0-PPV.

Typical external quantum efficiency and the corresponding luminous power efficiency of an flexible LED device is displayed in Figure X. The device turned on at a voltage of about 2 V. The quantum efficiency had a maximum value of 2.2 % and the power efficiency had a maximum value of 2.5 lm/W. For 100 cd/m² brightness, the power efficiency was 2 lm/W at 3.4 V and 4.5 mA/cm². To demonstrate the mechanical performance of such device it can be bend while operating without being damaged.

These results were used to demonstrate the versatility of the light emitting polymer technology by manufacturing a companies logo as an example of a customized display (figure x) and a flexible pixelated display (figure x).

For the **pixelated** matrix the ITO on PET was structured to stripes with a width of 2 mm and a stripe spacing of 0.5 mm by photo-etching ITO. A single layer of light-emitting polymer was spin coated onto the structured ITO substrate. The cathodes were subsequently deposited by thermal evaporation using a shadow mask. They also consisted of stripes perpendicular to the ITO pattern with otherwise identical geometry. Thus, a matrix of 5x7 pixel with a pixel size of 2x2 mm² was formed by 5 columns of ITO electrodes and 7 rows of the cathode. The display was connected to a driver circuit unit modified from a commercially available electronic LED display sign board. The matrix display has high luminance and high

33 G. Gustafson,, Y. Cao, G.M. Treaty, F. Klavetter, N. Colaneri and A. J. Heeger, Nature 357, 477 (1992)

³⁴ M. Herold, J. Gmeiner, and M. Schwoerer, Acts Polym. 45, 392-395(1994)

visibility and does not suffer from any unintended activation of next neighbour pixels (cross talking).

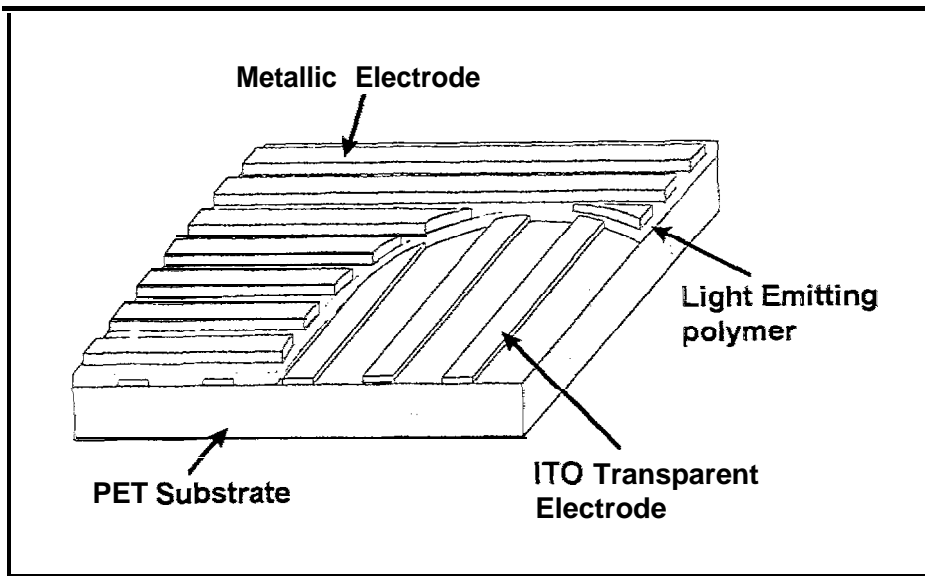


Figure 10. Structure of flexible PolyLED device

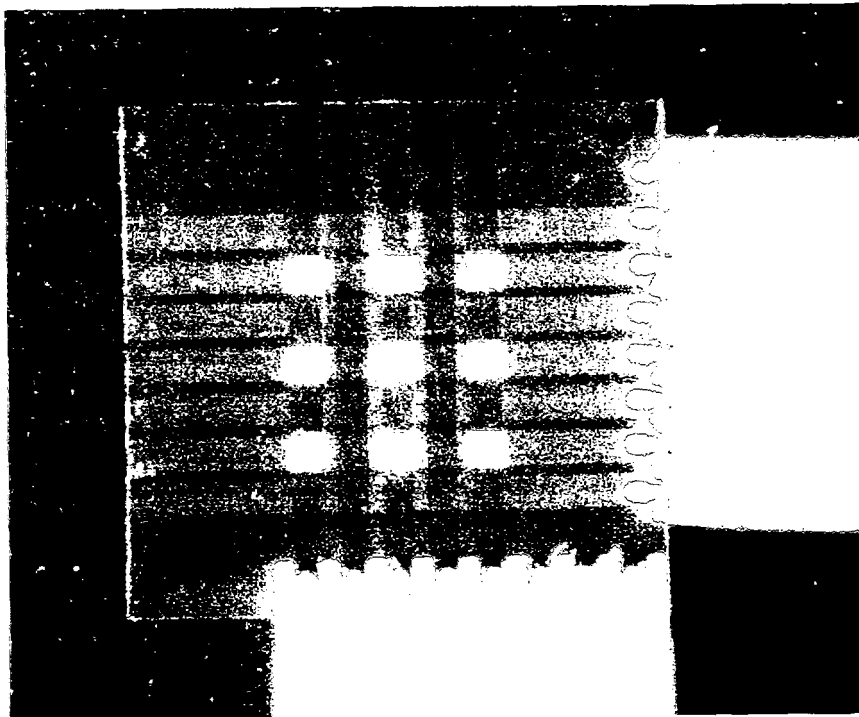


Figure 11. Example of working flexible PolyLED device

Reliability of the devices

The standard configuration of the polymer LED as used for lifetime measurements within Philips Research Laboratories, comprises a polymer layer of poly(dialkoxy-p-phenylenevinylene) as the active layer, serving for both charge transport and light emission. This layer is sandwiched between a calcium and iridium-tin oxide (ITO) layer that are used as the electron-injecting and the hole-injecting electrode, respectively. Though calcium is intrinsically instable with respect to moisture and oxygen, it is applied for its low workfunction. For operation under ambient conditions, the drawback of calcium application is the need for a proper encapsulation.

Lifetime measurements have been performed at constant brightness. The voltage and current are allowed to increase during this test. Probably as a result of increased heating of the device, the light output suddenly drops to zero. That moment is defined as the operational lifetime. The operational lifetime for a 1 cm² device under inert conditions is about 2500 hrs. This reflects the progress fine-tuning that was achieved over the last year in polymer synthesis and device fabrication.

Encapsulation of the devices is performed with a glass plate mounted with a light-curing epoxy adhesive (DELO KATIOBOND VE 1249). Application of a layer of this adhesive on top of a calcium layer (under inert atmosphere) does not show significant degeneration of the calcium layer, as measured by its resistivity. This demonstrates that the encapsulant does not react with calcium. In a next step the shelf life of a Ca/PPV/ITO device encapsulated with a glass plate mounted with a full layer of encapsulant, has been measured to be many thousands of hours. This proves the capability of the encapsulant as a barrier for oxygen and water from the atmosphere. However, when operating the encapsulated devices at 100 Cd/m² (under inert atmosphere), the lifetime does not exceed one hour !! Without understanding the exact nature of this failure mechanism, we found that the reduction of operational lifetime by the encapsulation process can be substantially reduced by applying an edge of adhesive between the glass cover plate and the substrate. Care has been taken not to contact the adhesive and the metal of the polymer LED. With such an encapsulation procedure we obtained an operational lifetime for a 0.3 cm² device at 100 Cd/m² of about 2500 hours.

10 Scale-up

As a part of the project, and described in detail in a special report, we have studied for options to produce PolyLED materials and devices on a large scale. Our work resulted in a number of options that we foresee and some of them have been tested. However, more work is required to come to a technology flow chart for actual production.

Our work provided strong evidence that a scale up of the materials synthesis to an industrial scale should in principle be possible. Process parameters need to be fitted and purification steps were identified to be the time-consuming bottle-neck, because a photoresist-like purity is desired. Before stepping into polymerizations in the kilogram-range a clear need for an intermediate size polymerization equipment (50 g = 10 l) was identified. Thus major effort still have to be undertaken to fully proof compatibility with environmental and economical requirements.

Evaluation of the industrial manufacturability of these devices comes at a relatively early stage, because research is still continuing, and we are in an early stage of development. Therefore we have concentrated on device production techniques that are applicable in the

distinct PolyLED manufacturing steps. These techniques are investigated, evaluated and compared with respect to specific requirements for PolyLED device manufacturing, Especially in the case of polymer layer application large scale-up possibilities exist, compared to the presently used single substrate spincoating process. Printing technologies would certainly offer high throughput and the possible use of flexible substrates would facilitate production of polymer layers enormously.

However, years of study and experience in this field has shown time and time again, that with the introduction of a new process step, which improves for instance the optical quality of the polymer layer, interaction within the fabrication process may decrease the LED performance. Therefore, before we can come to an industrial viable process, many experiments and optimisations still have to be performed. But we are optimistic that scale-up of the PolyLED production to an industrial scale is feasible,

11 Conclusions

The technical progress in the project has been excellent. Our project has received considerable attention both in the scientific and industrial world. We believe our work has emphasised the important role of Europe in the area of polymer LED research. The project has created a strong interaction and collaboration between leading laboratories in this field of research. The devices based on the technology developed in the project represent the best that can be achieved at the moment. Moreover, we created a realistic outlook on the possibility to prepare Polymer LED devices on an industrial scale at a later stage.

As a result of the project we now have available materials for red, green and blue electroluminescence, and materials for charge transport, to facilitate the charge injection in the PolyLED devices. The design and synthesis of these materials was an important part of the PolyLED project. Most of the materials were fully characterized and processed into device structures.

Two of the materials, a soluble, dialkoxy-PPV for red emission, and precursor PPV for green emission, were prepared on a larger scale and studied in great detail. They were selected as standard materials and distributed among the partners for device fabrication. A standard protocol to make PolyLED devices was proposed and used in the partners' Labs. With the standard material dialkoxy-PPV we were able to make devices with excellent performance: Quantum Efficiencies over 2 %, Luminous Efficacy of over 2 Lm/W, at a Voltage below 4 Volt. Peak brightness of these devices is over 10.000 Cd/m². At a brightness level of 100 Cd/m², the lifetime of the devices can be as high as over 2000 hrs. These data represent the best that have been reported, and we think we are leading in that respect.

The characterization of materials and devices allowed us to propose a model for charge injection, charge recombination and device operation. These models will certainly help us to develop better, more efficient devices.

The scale-up of materials and device production techniques was studied in the final year of the project. The first results indicate that development of the PolyLED technology on an industrial scale is feasible.

Final results, deliverables and demonstrators from our project were presented at the final meeting of the consortium and at various other occasions, at conferences, and in the companies and universities of the partners. One of the examples that were shown is included as photograph in this report.

Also, many publications and manuscripts were generated, and the various partners have contributed to scientific conferences, This also contributed to the high esteem and high profile this project has gained in the past three year period.