Electronic Transport In Polyphenylene-Vinylenes

János Veres, Heinrich Becker, Hubert Spreitzer, Horst Vestweber, Willi Kreuder
AVECIA (Manchester/UK) & COVION (Frankfurt/Germany)

Abstract

We describe some novel poly(p-phenylene vinylene) (PPV) derivatives of improved lifetime and luminescence. Electronic transport in these light emitting polymer materials has been studied using transient time-of-flight techniques. The effect of defects arising from the polymerisation process was investigated on carrier mobility and trapping. The same defects play crucial role in the lifetime of organic electroluminescent devices.

Introduction

During the last few years polymer light-emitting diodes (PLEDs) have made dramatic progress; starting with external quantum efficiencies well below 0.1% and lifetimes in the range of minutes[1], the cutting-edge of research is now exceeding 5% of external quantum efficiency and several thousand hours of operational lifetime. Power efficiencies beyond 15 lm/W have triggered considerable efforts to commercialize this technology in e. g. displays, back-lights, and lighting applications[2]. Recently we introduced a novel class of PPVs with exceptional properties prepared via solution based polymerization: soluble phenyl-substituted PPVs[3]. We reported luminance efficiencies of almost 15 Cd/A at relatively low voltage, allowing power efficiencies of up to 16 lm/W. With improved device architecture these materials were pushed even further: more than 23 lm/W were reached[4].

The most widely recognized hurdle for the commercialization is the operational lifetime of the devices, especially the stability at elevated temperature to fulfill customer specifications (e. g. operational stability at 70 or 85°C). By understanding[5] and improving[6,7] the microstructure of the polymers employed we were able to strongly improve material stability. A significant step forward was made by reducing the number of defects which dramatically extended the lifetime of PLEDs. It was suggested that these defects lower carrier mobilities and lead to charge carrier build-up in the device[6]. We decided to investigate the transport properties of some of the latest PPV derivatives with different defect contents and compare them to their performance in PLED devices. It seemed that time-of-flight experiments will be better to visualise carrier transport than standard I-V curves due to the very large impact of the device processing. In parallel, we looked at accelerated device degradation.

Material Development and Properties

In the recent years we have developed a series of materials based on the PPV basic structure with varying side-groups in order to enhance the properties of the materials, and in parallel those of the device. A selection of these compounds is shown in Figure 1.

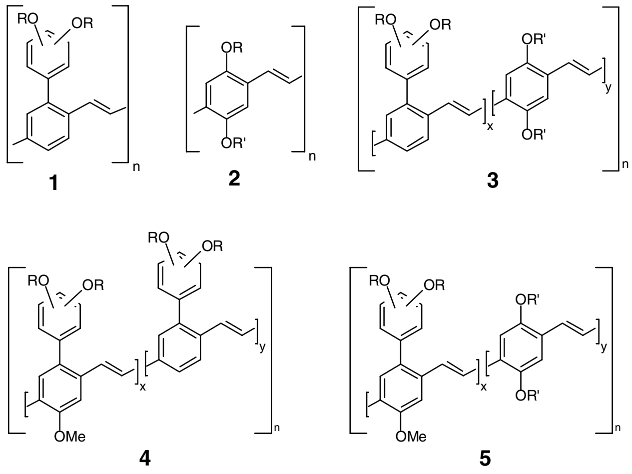


Figure 1. PPV derivatives of different colours

Using these polymers emission colours ranging from green to a deep orange are achieved: polymers of types **2**, **3**, and **5** show emission in the orange, polymers of type **4** in the yellow, and polymers of type **1** in the green part of the spectrum. Exact colour coordinates (e. g. needed for special customized applications) can easily be adjusted by varying the co-polymerization ratio, especially for polymers of type **3** to **5**.

Due to the synthetic procedure (Gilch polymerization[8]) the polymers are of very high molecular weight (i. e. $M_w > 10^6$, $M_n > 2 \times 10^5$); this enhances the mechanical stability and allows applications on flexible substrates. Nevertheless, the polymers show a good solubility in standard organic solvents, e. g. toluene, THF, and are therefore useful for standard coating processes, like spin-coating or even advanced printing techniques.

All these polymers, and also the required monomers, are now routinely manufactured on a scale useful for industrial applications. The first products incorporating these types of materials will be commercialized by PHILIPS N. V. around the end of this year[9].

Polymer Microstructure and Defects

Key to the improvement shown has been the understanding of the microstructure of the PPVs. Detailed analysis of the polymers revealed the occurrence of only one significant polymerization defect for all PPVs prepared by the Gilch route[8]: Tolane-Bisbenzyl (TBB, cf. Figure 2)[5]. This structure is found in various amounts and depends strongly on the reaction conditions and the chemical structure. The occurrence of this defect is readily explained: Instead of the normally occurring head-to-tail connection of monomer units, head-to-head linkage takes place (cf. Figure 2).

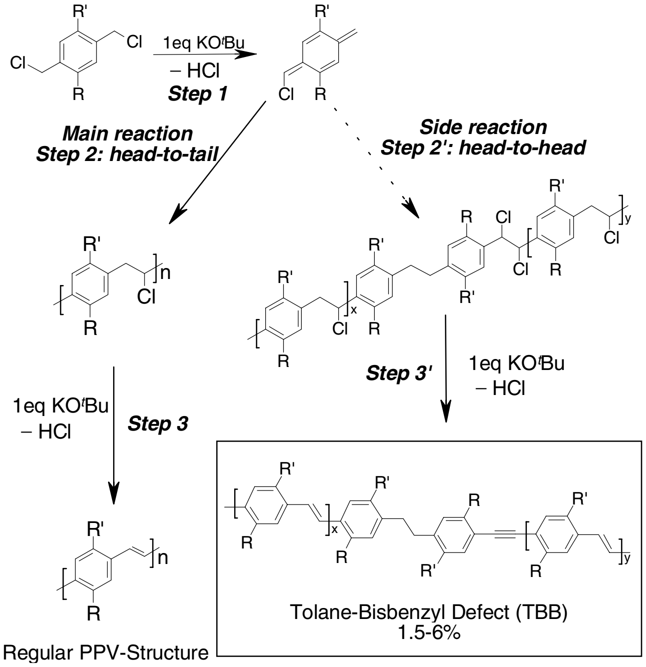


Figure 2. Defect formation in PPV synthesis

Depending on the polymer structure, 1.5–6% defects (this corresponds to 3–12% ”wrong bonds”) are found. It is not surprising, that the percentage of these defects strongly affects the properties of the PLED, especially (and most importantly) the useful operational lifetime. Fortunately, we found a way to strongly decrease formation of TBB by introducing an ”asymmetric” monomer unit. Sterical interaction between the monomer units prohibit the occurrence of head-to-head interactions and lead to a highly regular polymer.

Experimental

The structures of the polymers investigated are shown in Table 1. Mobilities were measured by the time-of-flight (TOF) technique. All TOF data presented here was obtained in the sandwich configuration. The PPV samples were prepared by spin coating from a toluene solution. Films of approximately 2 μ thickness were deposited onto a conductive electrode such as indium tin oxide (ITO) coated glass or mylar with a semitransparent aluminium layer. The top ~15-20 nm semitransparent metal was Al (vacuum evaporated) or a sputtered PtPd alloy, which is similar to Au in behaviour. Top-bottom electrode combinations (Al/Al, ITO/Al, ITO/PtPd, Al/PtPd) gave a good range of workfunction combinations for studying background currents and the choice of bias applied. In addition, the samples could be illuminated from either electrode side at both bias polarities. Such combinations help to reveal the nature of mobile carriers and allow us to look specifically, for example, for electrons.

A Model 437 Nanopulser flashlamp (Xenon Co.) was used for optical excitation giving a 10 ns duration pulse. Bandpass filters were used to vary the excitation wavelength. Absorption spectra of the PPVs are shown in Figure 3. The transients were amplified by a high speed current-feedback amplifier, which combined low impedance with very high sensitivity. Transients were recorded using a Tektronix TDS430A oscilloscope. The transit time was determined from the asymptotes to the plateau and the tail of the transients. Each polymer was measured at least on four different samples with different electrodes. All experiments were performed in air, at 22 °C.

Table 1. TBB defect contents in the materials studied.

Polymer Sample	Chemical type	Colour	TBB content
A	4	yellow	~5%
B	4	yellow	~4.5%
C 1,2	3	orange	~8%
D 1,2,3,4	5	orange	~4%

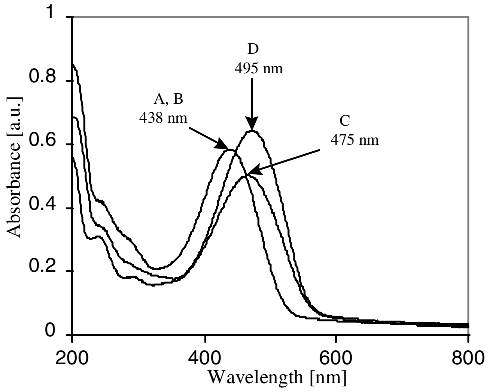


Figure 3. Absorption spectra of the PPV films

To ensure that TOF transient were genuine in the thin samples the illumination intensity was varied. Signals did not change in duration. The wavelength of the light was also varied, and it became clear that carriers were generated in the vicinity of the metal/polymer interface.

Details of PLED preparation and procedures for degradation tests are described elsewhere[6, 10].

Results and Discussion

The yellow compounds A and B are clearly unipolar hole transporters. Electron current is not detected at any electrode configuration or illumination, despite the high sensitivity of our experimental setup. No initial electron motion was seen, which would at least appear as an initial transient. This suggests that electron transport is limited indeed.

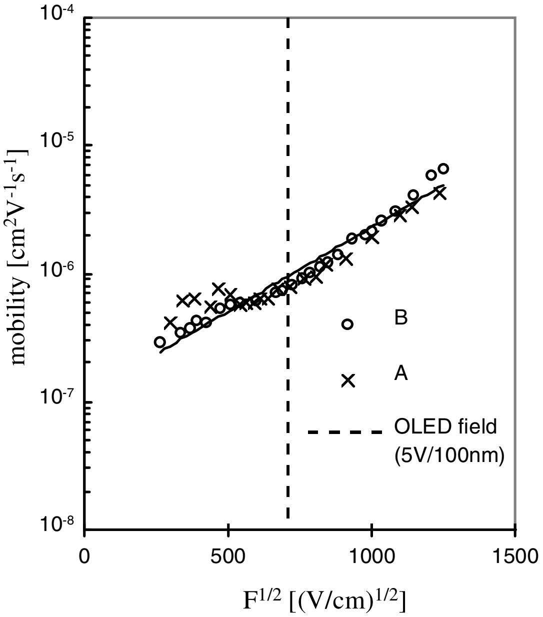


Figure 4. Hole mobilities of the yellow PPVs A and B against square root electric field

The hole mobilities in polymers A and B are virtually identical (Figure 4). The mobility follows the usual quasi-Pool-Frenkel dependence characteristic for organic disordered solids. Both yellow PPVs exhibited somewhat dispersive signals, but the shoulder of the transit time could clearly be identified without a log-log plot. The position of this shoulder did not change with light intensity; this is a measure of a true transit time. There was a noticeable difference in signal shapes. Polymer A gave more dispersive transients, with evidence of charge accumulation when repetitive TOF signals were generated. Figure 5 compares dispersive features at low fields, where they are most apparent. These signals are recorded in the small signal regime after dark resting. The shoulder points for B are more clear (at about 1.1 ms on the graph). This shoulder for polymer A occurs roughly at the same time, but it would only develop at higher excitation intensities, when the larger carrier packet accelerates under its own field. Note that signals exhibit the shoulders very clearly at higher fields.

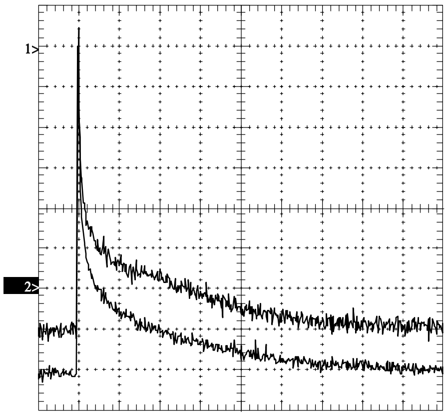


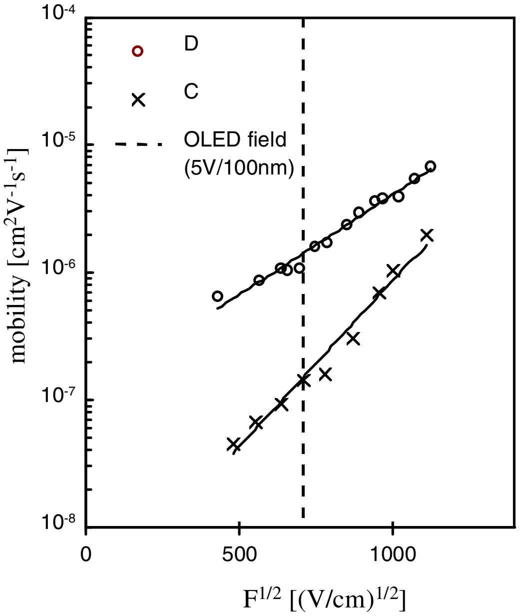
Figure 5. TOF transients in polymer B (upper curve) and polymer A (lower curve) at 220 kV/cm. The horizontal scale is 500μs/division

Precise, quantitative comparison of carrier lifetimes is difficult, but polymer A also exhibited more charge accumulation at repeated transients. This normally manifests as the signal becoming more and more square due to the trapped positive charge in the bulk modifying the internal field distribution. The TBB content in A is ~5% compared to 4.5% in polymer B. TBB is a possible reason for the increased trapping, especially if one examines greater differences of defect concentrations.

The orange compounds C1, C2 and D1-4 are also unipolar hole transporters. Mobilities are compared for C1 and D1 in Figure 6. The hole mobility of type C is significantly higher than that found in D. The TBB content is twice as high in D, which, in theory could account for this, providing that some TBB sites are "shallow traps". Intuitively, however, we expected that TBB was a deep trap accumulating space charge. We would like to extend our experiments to higher and lower defect concentrations to prove that TBB is causing the mobility reduction. After all, polymers of type C and type D are slightly different chemically.

PPV derivatives normally exhibit only hole transport. The mobilities observed by various workers[11-14], are in the range of 10^{-8} to 10^{-5} cm^{2}V^{-1}s^{-1}. Dispersive signals are often characteristic of PPVs[11,12,13]. We suspect that purity and polymer regularity plays great role in this. Lowering the TBB defect content just by 0.5% the trapping was visibly reduced in some of our PPV films. In good quality polymers we estimate the hole lifetime to be at least in the order of several ms. Signals do not indicate charge accumulation up to 100 Hz repetition rate of transients.

We have seen the apparent increase of mobility in PPVs with lower TBB content. Hoofman et al.[15] estimated the in-chain mobility in MEH-PPV to be around 0.1 cm^{2}V^{-1}s^{-1} by microwave techniques. No doubt interchain transitions and disorder should lower this figure for the bulk. However, amorphous layers of small molecules can easily yield 10^{-3} $cm^2V^{-1}s^{-1}$. One would expect highly conjugated materials like PPVs to reach the same speed of carrier transport. Defects such as TBB may well control the hole mobility in our PPVs. There are examples of ladder-type poly(para-phenylene)[16] and phenylamino-substituted PPVs with hole mobilities reaching 10^{-3} $cm^2V^{-1}s^{-1}$.



Fiure 6. Hole mobilities in orange PPVs type C (~8% TBB) and D (~4%TBB)

Electron mobilities can normally be estimated only by alternative methods, e.g. the analysis of I-V characteristics in ohmic or space charge limited current (SCLC) regimes[17-19]. Unfortunately, it is always difficult to distinguish between mobility and deep trapping. The product of the mobility and carrier lifetime called “carrier range” ($\mu\tau$) is a more accessible parameter. From what is seen in our TOF experiments, $\mu\tau$ must be much shorter than the device thickness at the applied fields, i.e. $\mu\tau < 5 \times 10^{-12}$ cm^2/V, which is about the same as measured by Antoniadis et al[17]. While the electron mobility may be high, severe trapping is probably responsible for reducing transport. We are currently working on determining the electron mobility independently.

We have also investigated the lifetime of devices prepared from the different polymers. Figure 7 illustrates device degradation in polymers samples C1, C2 and D1-D4. The curves are for different polymers of types **3** and **5** in Figure 1. The enhancement in lifetime is evident from this plot. TBB values are about 8% “wrong bonds” for **3** and 4% for **5**.

The impact of TBB content on the initial properties is weak, with the exemption of the drive voltage needed for the same brightness, which is an indication of the lower mobility. During the course of the lifetime test drive voltages increase faster for **3** to maintain a constant current. This increase is due to a bulk effect, the reduction of the carrier mobility or trapping. This is evident from the rate of drive voltage increase as a function of thickness.

Parker et al.[10] have shown that the major cause of device degradation is the passage of electrons through the device. In their work, both drive voltages and luminescence were only affected by electron injection only. It was suggested that electron mobility was reduced during degradation. In our case, it is likely that TBB is leading to electron trapping, although we cannot detect it directly from transient measurements. On the other hand, while hole transport alone does not lead to device degradation, it appears that some irregular bonds also manifest themselves as hole traps.

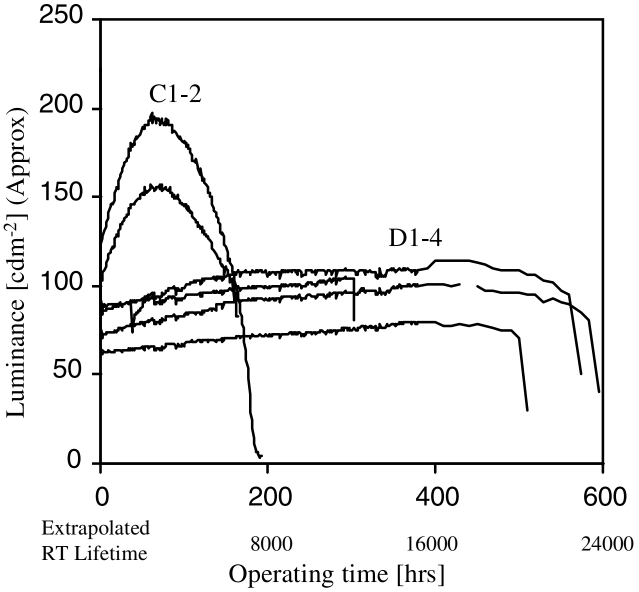


Figure 7. Degradation of PLEDs prepared from orange PPVs with different defect contents. The polymers used were C1,C2 (~8% TBB) and D1-D4 (~4% TBB). Courtesy of UNIAX, Santa Barbara, USA.

It is clear that the device lifetime is influenced by the polymer and by the amount of defects, but it is also clear that only with optimization and strong cooperation between material synthesis and device preparation improvements are achievable. The data presented show that the improved polymers are certainly useful for a wide range of applications because almost 3 years (24000 h) of continuous operational lifetime (the acceleration factor 40 is taken from literature[10]) are already satisfying a large variety of customer specifications.

Conclusions

We have investigated carrier transport in some novel PPV derivatives. The polymers were found to be unipolar hole conductors, with hole mobilities around 10^{-6}-10^{-7} $cm^2V^{-1}s^{-1}$ at fields typical in PLED structures. We have reported on the effect of a major defect in PPVs, TBB. Polymers with irregular vinylene bonds exhibit hole transport hindered by trapping. In some cases by reducing the defect content increased carrier mobility has been achieved. It is possible that some of the irregular bonds are shallow traps influencing the mobility itself.

Materials with low TBB content have also shown drastically increased device lifetime. The increase of lifetime may be due to reduced electron trapping. Unfortunately, the electron range remains still too short to observe electron transients directly by TOF. The new PPV polymers illustrate that defect concentration can be reduced by the choice of specially designed monomers favouring head-to-tail links during polymerisation.

References

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature*, **347**, 539. (1990).
2. http://www.research.philips.com/pressmedia /releases/9802e.html. (March 1998).
3 H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H.Schenk, R. Demandt, H. Schoo, *Adv. Mater*, **10**, 1340. (1998).
4. P.K.H. Ho, J.-S. Kim, J.H. Burroughes, H. Becker, S.F.Y. Li, T.M. Brown, F. Cacialli, R.H. Friend, *Nature,* **404**, 481 (2000).
5. H. Becker, H. Spreitzer, K. Ibrom, W. Kreuder, *Macromolecules*, **32**, 4925, (1999).
6 H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker, Y. Cao, *Adv. Mater*, **12**, 42, (2000).
7. H. Sixl, H. Schenk, N. Yu, *Phys. Bl.*, **54**, 225, (1998).
8. H. G. Gilch, W. L Wheelwright, *J. Polym. Sci.*, Part A: Polym Chem., **4**, 1337, (1966).
9. K. Ziemelis, *Nature*, **399**, 408, (1999).
10. I. D. Parker, Y. Cao, C. Y. Yang, *J. Appl. Phys.*, **85**, 2441, (1999).
11. M. Gailberger and H. Bässler, The American Physical Society, 44, 8643, (1991).
12. H. Meyer, D. Haarer, H. Naarmann and H.H. Hörhold, *Physical Rev. B*, **52**, 2587, (1995).
13. E. Lebedev, T. Dittrich, V. Petrova-Koch, S. Karg and W. Brütting, *Appl. Phys. Lett.*, **71**, 2686, (1997).
14. W. Brütting, E. Lebedev, S. Karg, T. Dittrich, V. Petrova-Koch and M. Schwoerer, Proc. SPIE, vol 3281, pg 257.
15. R.J.O. Hoofman, M.P De Haas, L.D.A. Siebbeles and J.M. Warman, *Nature*, 392, 54 (1998).
16. D. Hertel, H. Bässler, U. Scherf and H.H. Hörhold, *J. Chem. Phys.*, 110, 9214, (1999).
17. H. Antoniadis, M.A. Abkowitz and B.R. Hsieh, *Appl. Phys. Lett.*, 65, 2030 (1994).
18. P.W.M. Blom, M.J.M. de Long and J.J.M. Vleggaar, *Appl. Phys. Lett.*, **68**, 3308, (1996).
19. S. Forero, P.H. Nguyen, W. Brütting and M. Schwoerer, *Phys. Chem. Chem. Phys.*, 1, 1769, (1999).

Biography

János Veres received his MSc from the Faculty of Electrophysics of Lviv University, USSR in 1990. He earned his PhD from Imperial College, London in 1995 in solid state electronics studying Organic Photoreceptors (OPC). He worked in R&D and manufacturing of photoconductors for three years at Gestetner Byfleet Ltd. (GBL). Since 1998 he has been a Senior Scientist at Avecia (formerly Zeneca Specialties) leading the Physics and Characterisation of OPC chemicals and organic electronic materials. e-mail: janos.veres@avecia.com