

Charge carrier mobility in poly(p-phenylenevinylene)

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ABSTRACT

The charge carrier mobility in unsubstituted poly(p-phenylenevinylene) (PPV) is investigated by the time-of-flight (TOF) method and by the space-charge limited current transient (SCLCT) technique. Both methods are performed on devices with the configuration indium-tin-oxide/PPV/Al, which is typically used in light-emitting diodes. Hole mobilities in the range of 10^{-5} cm²/Vs at room temperature for an electric field of about 10^5 V/cm are obtained. Field and temperature dependent TOF measurements yield an exponential increase of the mobility with the applied field and thermally activated behaviour with activation energies between 0.4 and 0.7 eV on different samples. The values of the mobility at room temperature are consistent with steady-state space-charge limited currents, but considerably larger than the data from transient electroluminescence measurements. This indicates that the transit times obtained by the latter method are dominated by the much lower electron mobility rather than by the hole mobility. Assuming luminescence quenching within a distance of 20 nm to the Al contact, an electron mobility of some 10^{-9} cm²/Vs can be estimated at room temperature and fields in the range of 10^5 V/cm.

Keywords: charge carrier mobility, poly(p-phenylenevinylene), light-emitting devices

1. INTRODUCTION

In the last ten years the semiconducting properties of conjugated polymers have been intensively studied because of their potential applications in electronics. Field effect transistors and Schottky diodes have been fabricated from a variety of materials.¹ More recently light-emitting diodes based on conjugated polymers have attracted considerable interest for large area displays.² Despite of the great progress in this field, the elementary charge transport mechanisms in the polymer layer and especially the magnitude, as well as the field and temperature dependence of the charge carrier mobility are not very well-known in most of these materials. Thus a direct determination of this quantity would be helpful for both an improvement of efficiency and a better quantitative description of device characteristics.

Transport properties were studied by the time-of-flight (TOF) technique for two soluble poly(p-phenylenevinylene) (PPV) derivatives.^{3,4} However, up to now the drift mobility could not be directly measured in unsubstituted PPV because of a featureless photocurrent decay. From their data Meyer et al. could only estimate an upper limit for the hole mobility of less than 10^{-8} cm²/Vs.⁴ Therefore, our work was aimed primarily at the direct determination of the drift mobility of carriers in PPV and the investigation of the temperature and field dependent characteristics of the mobility. In this paper, we present results on the hole mobility in unsubstituted PPV obtained by two different experimental techniques: one is the classical TOF method and the other one are space-charge limited dark current transients. We compare these results with other indirect methods like steady-state space-charge limited currents and transient electroluminescence measurements.

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2. EXPERIMENTAL

Devices consisted of indium-tin-oxide (ITO) coated glass substrates (Flachglas, $20 \Omega/\square$) on which the tetrahydrothiophene leaving group precursor PPV (synthesized by our group as described in Ref. 5) was deposited by a precision doctor blade-technique as several hundred μm thick liquid films. After drying and conversion (2-3 hours in a vacuum of 10^{-2} mbar at 170 to 190°C) films of some hundred nm thickness were obtained. Subsequently an Al electrode was vacuum evaporated at 10^{-5} mbar in a thickness of about 10 to 20 nm to get a semitransparent contact for the TOF measurements and about 100 nm for the SCLCT measurements. Several devices with thickness ranging from 700 to 1500 nm with active areas of 12 mm^2 were investigated. Thicknesses of the polymer films were determined using a Dektak surface profilometer.

During the thermal conversion, the elimination products HCl and tetrahydrothiophene can undergo chemical reactions with the ITO substrate leading to doping of PPV by InCl_3 ⁶ and to the formation of defects at the ITO/PPV interface,⁷ which becomes the more important the thicker the converting PPV film is. For film thicknesses exceeding about 500 nm already a partial destruction of the ITO substrate could be observed. Additionally, due to the rather bulky leaving groups a considerable fraction of them may stay in the film for larger thickness, leading to defects which can act as charge carrier traps. To avoid the enrichment of leaving groups in the film and thus to reduce their reaction with the ITO we subsequently casted and converted several PPV layers of about 150 to 200 nm thickness each. Additionally, due to the high optical absorption coefficient the total thickness of the PPV layers could be chosen rather thin as compared to usual TOF measurements on polymers with typical layer thickness of about 10 μm .

TOF measurements were performed on ITO/PPV/Al sandwich structures with a conventional experimental setup.⁸ The excess carriers were generated by illumination with pulses of a N_2 laser (wavelength 337 nm, pulse duration 0.3 ns) through the semitransparent Al electrode, which forms a non-injecting contact for holes with PPV. The excitation intensity was chosen well below the level for space charge distortion of the applied electric field. The electric field was applied for a duration between 1 and 10 ms and the delay time of the laser pulse was 0.1 ms.

Space-charge limited current transients were measured on PPV films from the same substrate, which were prepared identically to the TOF samples, except for the thicker Al electrode ($\approx 100 \text{ nm}$). To obtain the dark current transients of holes a rectangular voltage pulse was applied to the device with the positive voltage at the ITO (forward direction). The current was monitored as a function of time with a 400 MHz digitizing oscilloscope via the voltage drop at a small resistance (as compared to the total device resistance) in series with the device.

3. RESULTS AND DISCUSSION

3.1. Time-of-flight measurements

The standard method to obtain charge carrier mobilities in insulating materials is to measure the transit time of excess carriers generated close to one electrode to reach the counterelectrode. In the conventional time-of-flight method these carriers are generated by illumination with a short ultra-violet light pulse. (The case of carrier generation by injection from electrical contacts will be discussed in the next subsection.) Depending on the polarity of the electric field only one type of carriers will be accelerated towards the counterelectrode. Electrical injection by the contacts has to be excluded in this experiment. For ITO/PPV/Al devices this has for the consequence that the illumination through the transparent ITO contact is not possible when the hole mobility is to be determined. Instead, a semitransparent Al contact has to be used.

In the following we only briefly discuss the results on the hole mobility in PPV obtained by TOF, since a detailed analysis has been published recently.⁹ Figure 1 shows a typical photocurrent transient of holes in PPV. The structureless decay in a linear representation (see the inset) is typical for dispersive transport in a large class of amorphous polymers.¹⁰ The transit time t_T can only be obtained from the change of slope in a double logarithmic plot. The drift mobility can then be calculated as:

$$\mu = \frac{d^2}{t_T V} \quad (1)$$

where d is the thickness of the sample and V the applied voltage. The value calculated from the data in the figure is $\mu = 1.4 \times 10^{-5} \text{ cm}^2/\text{Vs}$. We note that photocurrent transients with a clearly detectable transit time could only be observed on samples, where the film casting and thermal conversion was performed in several steps as

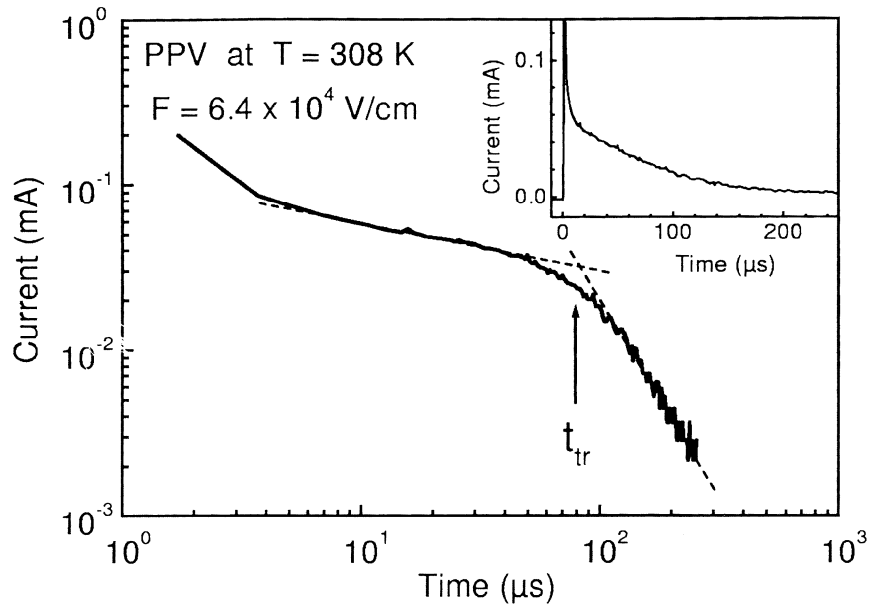


Figure 1. Photocurrent transient of holes in an ITO/PPV/Al device at a temperature $T = 308$ K and an electric field $F = 6.4 \times 10^4$ V/cm in a linear (inset) and in a double logarithmic representation. The PPV thickness was $0.7 \mu\text{m}$. (Reprinted from Ref. 9.)

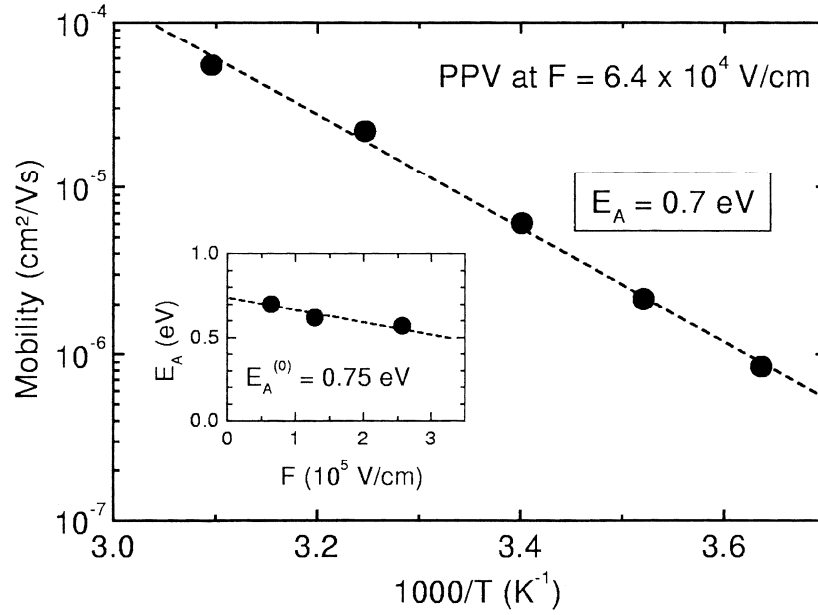


Figure 2. Temperature dependence of the drift mobility in PPV at $F = 6.4 \times 10^4$ V/cm in Arrhenius representation. The inset shows the field dependent activation energy of the drift mobility with an extrapolation to zero field. (Reprinted from Ref. 9.)

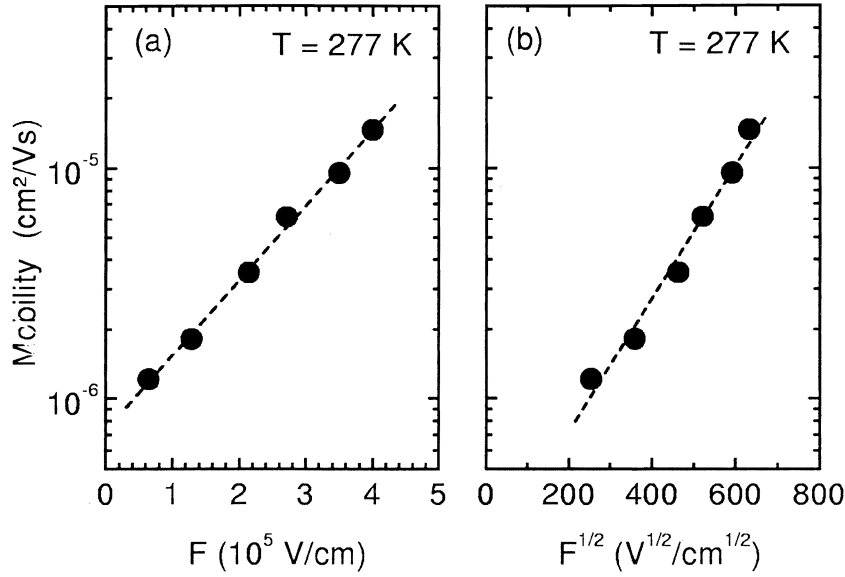


Figure 3. Dependence of the drift mobility in PPV at $T = 277$ K on the electric field (a) (polaron hopping model) and on the square root of the electric field (b) (Poole-Frenkel model). (Reprinted from Ref. 9.)

described before. Thick films converted in only one conversion step did not show this feature. Thus our improved film preparation technique is necessary for obtaining hole mobilities in PPV directly by TOF. But even with this improved preparation method we have not been able to determine transit times of electrons in PPV. This is probably due to severe trapping observed before by measuring $\mu\tau$ products with TOF¹¹ and also from trap limited conduction seen in the current-voltage characteristics of Ca/dialkoxy-PPV/Ca electron-only devices.¹²

TOF measurements were performed in the temperature range between 275 and 320 K and applied electric fields between 6.4×10^4 and $4 \times 10^5 \text{ V/cm}$. The obtained mobility follows an Arrhenius law with a field dependent activation energy as shown in figure 2. The activation energy E_A decreases with increasing field and the extrapolation gives a rough estimate of $E_A^{(0)} = 0.75 \text{ eV}$ at zero field (inset in figure 2). This value is in the same range as the measured activation energy of the d.c. conductivity of PPV ($E_A^{d.c.} \approx 0.6 \text{ eV}$).¹³ We note that the activation energy varies from sample to sample between 0.4 and 0.7 eV. However, as impedance spectroscopic investigations¹⁴ and thermally stimulated currents¹⁵ indicate, in PPV there are at least two sets of gap states with energies in the range 0.05-0.2 eV and 0.6-1 eV, respectively. The combination of these different states with varying density may explain the variations of the activation energy from sample to sample. This is subject of further investigations.

The field dependence of the drift mobility at $T = 277$ K is presented in figure 3. The drift mobility of the positive charge carriers increases with increasing electric field. In both representations linear regressions yield satisfactory fits of the experimental data. It is therefore hard to distinguish whether a polaron hopping model¹⁶ (case (a)) or a Poole-Frenkel mechanism (case (b)) is more appropriate to describe the measured mobility of PPV.

As compared to the soluble PPV derivatives, the mobility data of PPV are in the same order of magnitude as with a phenyl-substituted PPV (PPP)³ and only about a factor of 10 lower than in diphenoxyphenyl-PfV (DPOP-PPV),⁴ indicating that the precursor route to PPV does not necessarily produce films with higher defect concentration and reduced carrier mobility.

3.2. Space-charge limited current transients

The second method to obtain charge carrier mobilities in PPV is the so-called space-charge limited current transient (SCLCT) technique, where the transit time of a carrier species injected electrically from one electrode is measured.

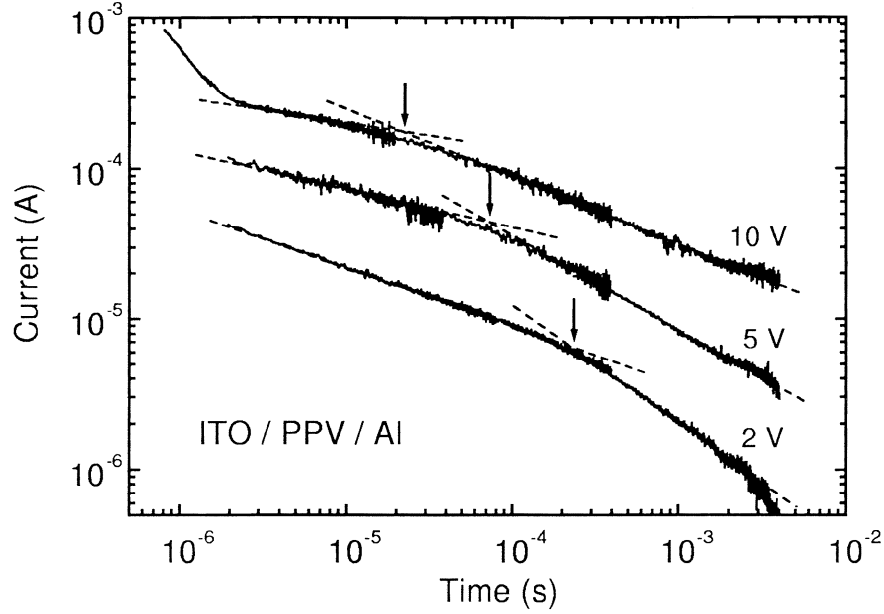


Figure 4. Dark current transients at room temperature of an ITO/PPV/Al device with a PPV thickness of 1100 nm for different pulse amplitudes in forward direction. Dashed lines indicate the asymptotic power law dependence $I(t) \propto t^{-\beta}$ with different exponents $\beta_{i,f}$. The arrows mark the determined transit time t_T^* .

In the ideal case of non-dispersive trap-free transport the current shows a sharp maximum at the characteristic time t_T^* required for the injected carriers to reach the counterelectrode. If injection is high enough to achieve space-charge limitation, it can be shown¹⁷ that the transit time t_T^* is equal to $0.786 \cdot t_T$ (t_T being the space-charge free transit time obtained e.g. by the TOF technique). t_T^* is shorter than t_T , because the formation of the space-charge reduces the electric field at the injecting electrode and leads to a field enhancement between the leading front of carriers and the counterelectrode (as compared to the uniform field V/d in the TOF experiment). The mobility is then given by¹⁷:

$$\mu = 0.786 \frac{d^2}{t_T^* V} \quad (2)$$

The SCLCT technique is well-established for the determination of charge carrier mobilities in a variety of organic and inorganic crystalline materials¹⁷ and certain organic photoconductors,¹⁸ where transport is found to be non-dispersive. Despite of the great progress in the theoretical description of dispersive transport in amorphous materials like polymeric photoconductors and amorphous silicon (a-Si:H) and the vast number of successful TOF measurements on these materials, the use of the SCLCT technique is not very common in this field. There has been some work on a-Si:H,¹⁹ but to our knowledge no application to polymeric materials (in Ref. 20 only space-charge limited photocurrent transients were measured on poly(methylphenylsilylene)). This may be partly due to the requirement of a very good injecting contact in order to reach the space-charge limit, which is sometimes difficult to achieve with polymers.

In the case of PPV, we know from our studies of current-voltage and capacitance-voltage measurements^{21,22,6} that due to the doping reaction at the interface ITO forms quite good hole injecting contacts to PPV. Thus we have used the same device configuration (ITO/PPV/Al) as with the TOF experiments to study the transient behaviour of the current during application of a rectangular voltage pulse in forward bias direction. Figure 4 shows the current transients at room temperature for different pulse amplitudes obtained on a device with a polymer thickness of $d = 1100$ nm and an active area of 0.12 cm^2 in a double logarithmic representation. We note that due to the small sampling depth of our oscilloscope (2000 points) 3 curves with different time base had to be measured and matched together in order to cover the displayed 3.5 orders of magnitude in time with a sufficient number of points per

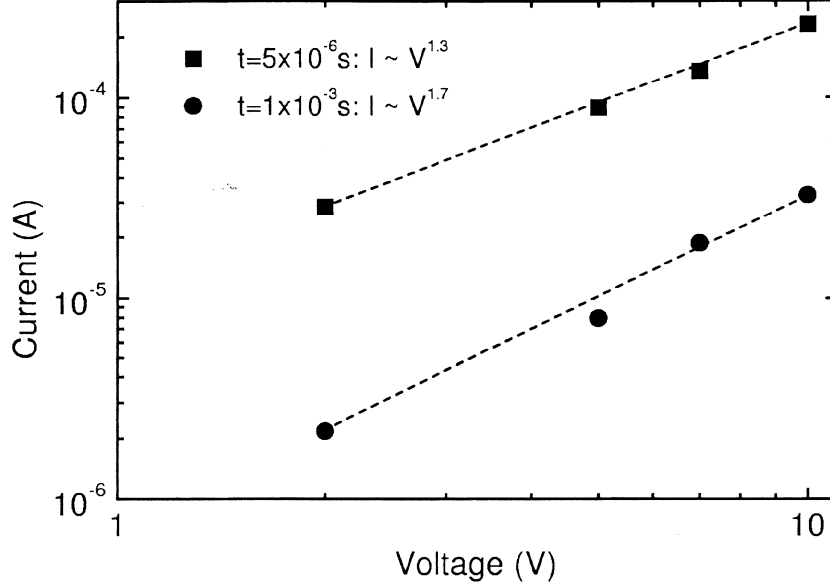


Figure 5. Current-voltage dependence obtained from Fig. 4 at two different times. Dashed lines indicate power laws $I(V) \propto V^n$.

decade. Nevertheless, a similar behaviour as in the afore described TOF measurements is observed. The asymptotic behaviour of the transients follows power laws $I(t) \propto t^{-\beta}$ with different exponents β for short and long times (dashed lines in Fig. 4). From the intersections of the asymptotic straight lines the transit time t_T^* can be determined and the mobility calculated according to equation (2). In table 1 we have given the parameter values obtained from the data in Fig. 4.

Table 1. Parameter values obtained from the analysis of the data shown in Fig. 4.

Pulse height (V)	Field (10^5 V/cm)	Transit time (10^{-6} s)	Mobility (10^{-5} cm ² /Vs)	β_i	β_f
2	1.8	220	2.1	0.39	0.78
5	4.5	73	2.6	0.25	0.63
10	9.1	21	4.5	0.17	0.45

We note that the absolute numbers of the hole mobilities obtained from SCLCT and TOF at room temperature are in good agreement. Nevertheless, there remain some open questions. First, one has to check whether space-charge limited conduction is in fact achieved in our experiments. For this purpose we have plotted in figure 5 the magnitude of the current as a function of voltage at two different times (one before and one after the transit time) on a double logarithmic scale. The data can be fitted by power laws with reasonable agreement yielding exponents of 1.3 for $t = 5 \times 10^{-6}$ s and 1.7 for $t = 1 \times 10^{-3}$ s. These numbers suggest that the SCLC limit is not yet achieved at short time scales, but approaches this limit with increasing time. To prove this, however, further measurements on a much longer time scale are necessary and also the steady state SCL current has to be studied.

Next are the exponents β_i and β_f of the asymptotic behaviour before and after the transit time. For the space-charge free transients they can be identified as $\beta_i = 1 - \alpha_i$ and $\beta_f = 1 + \alpha_f$ with $0 < \alpha_{i,f} < 1$.²³ Thus β_i should be smaller and β_f larger than unity. This is obviously not the case for β_f . Additionally, β_i decreases with increasing

field, while the opposite behaviour was observed for $1 - \alpha_i$ in the TOF experiments.⁹ However, one has to note that the correlation between the dispersion parameters in the space-charge free and space-charge limited case may not be a straight-forward one-to-one correspondance.

Finally, the field dependence of the mobility from SCLCT is very weak. It changes only by a factor of 2 with a 5-fold increase in the field. This is in clear contrast to the TOF results, where an exponential field dependence is observed, which would expect an increase in mobility by roughly one order of magnitude with the given field range. Once again one has to note that the situation with the SCLC transients is much more complicated than with TOF. Since the field distribution inside the device is not homogeneous – neither spatially nor in time – and the mobility itself is field-dependent, the evaluation of the observed transit times in SCLCT may be more complicated than given by equation (2). Even the expression

$$\mu = (0.786)^{(1/\alpha)} \frac{d^2}{t_T^* V} \quad (3)$$

with a field-dependent dispersion parameter α suggested by Silver et al.²⁴ for dispersive transport in a-Si:H still leads to a discrepancy between SCLCT and TOF data.

Thus we conclude that SCLCT on ITO/PPV/Al devices yields the correct order of magnitude of the mobility, however, further systematic studies varying the electric field, the temperature and other device relevant parameters are necessary to establish this technique for the determination of charge carrier mobilities in polymeric materials. The potential benefit of this method is that it can be performed on thin films with the typical thickness of light-emitting devices (≈ 100 nm) which is in the same range as the penetration depth of light and thus excludes the application of transient photoconductivity measurements to such thin structures. The measurement of the mobility on thin films is especially interesting, because in the case of unsubstituted PPV, due to the preparation by the tetrahydrothiophene leaving group precursor route, the properties of the films may depend in a non-linear manner on the film thickness. Additionally, for dispersive transport the experimentally obtained mobility values are found to be thickness dependent.¹⁹

3.3. Comparison with other methods for the determination of charge carrier mobilities in PPV

Already a couple of years ago it has been shown by Karg et al.²⁵ that the presence of a Schottky contact in our ITO/PPV/Al devices with a depletion layer of width between 50 and 100 nm can be utilized to obtain information on the charge carrier mobility from transient electroluminescence (EL) measurements. Assuming that the delay time between the rising edge of the voltage pulse and the first appearance of EL is solely determined by the transit of holes through the depletion layer at the Al contact, mobilities of about 10^{-7} cm²/Vs at a field of 2×10^5 V/cm have been obtained at room temperature. These values are about two orders of magnitude lower than the TOF results here. One important reason for this discrepancy is that the contribution of the electron motion to the delay time was neglected since the electron mobility in PPV and its derivatives was estimated to be several orders of magnitude lower than the hole mobility.^{11,12} This assumption implies that electron-hole or exciton recombination takes place directly at the Al contact. However, it is known from organic single crystals²⁶ and was recently also shown for polymeric light-emitting devices²⁷ that the presence of the metal electrode quenches EL within a distance of 15 to 20 nm from the electrode. Thus the contribution of electron motion to the transit time cannot be neglected (as already noticed by Redecker et al.²⁸). Assuming a minimum schubweg of $d = 20$ nm required for the electron to avoid EL quenching (instead of $d = 100$ nm for the drift of holes through the depletion layer) the data of Ref. 25 yield an electron mobility of about 4×10^{-9} cm²/Vs at the above mentioned field. This is not an unreasonable value since the electron mobility was estimated to be much lower than the hole mobility by other experiments.^{11,12} Thus, instead of the hole mobility, in transient EL measurements one gains information about the electron mobility in PPV. In order for the delay time of EL to be dominated by hole transport, the ratio between the width of the EL quenching zone and the depletion layer (or the sample thickness) had to be much larger than the ratio of the hole to the electron mobility.

Another method, which is frequently used to obtain charge carrier mobilities, is the observation of steady-state space-charge limited currents. In the trap-free case the current-voltage characteristics should follow Child's law with

$$j = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3} \quad (4)$$

which allows for a direct determination of the effective carrier mobility μ . This method has been successfully applied to hole transport in dialkoxy-PPV by Blom et al.^{12,29} Assuming a Poole-Frenkel-like field-dependence of the mobility they could fit their data at room temperature up to fields of 3×10^5 V/cm with a zero-field mobility of 5×10^{-7} cm²/Vs. From temperature dependent measurements an activation energy of about 0.5 eV was obtained. Although our devices are Schottky diodes, a quadratic dependence of the current on voltage can also be observed at high forward bias ($V > 2 - 4$ V) with current densities exceeding 1 mA/cm². Values of the hole mobility of about 10^{-5} cm²/Vs at room temperature were obtained in this way, which is in good agreement with the data given before.

4. CONCLUSION

The comparison of different experimental techniques shows that charge carrier mobilities in light-emitting diodes based on PPV (prepared by the precursor route on ITO substrates) can be determined with good agreement among the different techniques. Although the conventional TOF technique is still the most direct and easiest to interpret method, other less sophisticated methods like SCLCT can at least give the correct order of magnitude. Further systematic studies varying the electric field, the temperature and other device relevant parameters are necessary to establish this technique for the determination of charge carrier mobilities in polymeric materials.

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