MASTER

Towards stable organic photovoltaics
investigation of temperature induced degradation and characterization of High-Tg-PPV

Conings, B.S.T.

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Towards stable organic photovoltaics: 
Investigation of temperature induced 
degradation and characterization 
of High-$T_g$-PPV

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June 2008

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Abstract

With the discovery of semiconducting polymers, a new class of solar cells was born: the organic solar cell, which is fairly easy to produce and can be made flexible. The two main inadequacies of organic solar cells are their relatively low photovoltaic conversion efficiency (up to 5%) and their poor stability compared to traditional silicon solar cells. Stability issues occur a.o. due to the influence of light, oxygen and temperature. This thesis focuses on the latter. In current organic solar cells, the active layer is a blend that consists of two components, an electron donor polymer and an electron acceptor material, PCBM, a C_{60} derivative. Elevated operating temperatures (up to 70°C) induce a phase separation in the blend: PCBM molecules form large clusters, causing an inferior charge separation and transport. The physical processes governing this behavior are investigated in this work by means of electrical and morphological methods. The degradation of MDMO-PPV:PCBM solar cells, submitted to a set of temperatures, was fitted with a mono-model, yielding an activation energy of $E_a = 0.85$ eV. TEM and AFM investigation revealed that the total surface of the PCBM clusters, within as well as next to the device, evolves on the same time scale. The clustering was attributed to the Ostwald ripening process, where larger cluster grow at the expense of small particles. The clusters’ final fractal dimension was calculated to be $D \sim 1.85$. Using a fixed concentration profile, evidence was found that, as long as the system does not run out of dispersed PCBM, the growth of individual clusters follows a known diffusion model. Measurements of the generation rate of the MDMO-PPV:PCBM blend implied that annealing only affects the transport and recombination mechanisms, not the e-h pair generation. Furthermore, an electro-optical and morphological characterization was performed on a new polymer with great potential concerning stability: High-T_{g}-PPV. Thanks to its high glass transition temperature (measured 138°C), the polymer matrix stays rigid at normal operating temperatures (~70°C), impeding the clustering of PCBM in the High-T_{g}-PPV:PCBM blend. Several solvents, High-T_{g}-PPV:PCBM ratios, and active layer thicknesses were tested, and the blend performs optimally for 75-90 nm thick layers of ratio 1:6, spincoated from o-xylene. The charge carrier mobility of High-T_{g}-PPV:PCBM as a function of PCBM content is comparable to MDMO-PPV:PCBM. The absorption spectrum and external quantum efficiency High-T_{g}-PPV:PCBM thin films is comparable to MDMO-PPV:PCBM, and somewhat less favorable than P3HT:PCBM.
As opposed to MDMO-PPV:PCBM, no small scale phase separation was observed for High-T$_g$-PPV:PCBM thin films. In contrast to High-T$_g$-PPV’s abundant similarities to MDMO-PPV, this lack of phase separation was thought to be the reason for High-T$_g$-PPV:PCBM’s lower photovoltaic performance. In accelerated ageing experiments, however, High-T$_g$-PPV:PCBM solar cells demonstrate the highest stability and therefore prove that polymers with a high T$_g$ can be a viable route towards stable organic photovoltaics.
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1 Introduction

The world energy consumption in 1980 was 283 EJ (283·10^{18} J). In 2004 it was 447 EJ, of which 86.5% was generated by fossil fuels. Assuming a "business as usual" scenario, the global energy consumption will grow to over 700 EJ by 2030 [1]. The question of how much longer fossil fuels will be able to redeem the world's addiction to energy is ubiquitous nowadays. People have grown accustomed to using easy energy, but fossil fuel reserves are shrinking severely. Nuclear power has been around for some time, but stays controversial because of safety issues. Sustainable alternatives such as wind energy, biomass, and solar energy are gaining field, though at a slow pace. One of the major drawbacks of these renewables is their cost. This is especially true for photovoltaic (PV) energy. In 2006, the average PV system price was €8.31 per watt peak for off-grid systems, and €4.61 for grid-connected systems [2]. This results in a price of €0.55/kWh in the Netherlands, where "grey" electricity from fossil fuels costs €0.22 at this time [3]. In Southern Europe there is more solar yield and the difference is smaller with €0.30/kWh for solar power and €0.17/kWh for grey electricity [3, 4]. Nonetheless, the price of PV-technology is still too high to compete with conventional electricity. A comparable price would mean that PV technology could become a valuable asset in the energy business and flourish to its full potential as decentralized energy resource. The production process of silicon-based solar cells (by far the most popular ones) is intricate though, and moreover, keeping up the silicon feedstock requires careful production and recycling management [5]. Silicon solar cells have been around since the 1950's, with conversion efficiencies of about 6% [6]. Today, silicon technology can yield up to 25% cell efficiency and 23% module efficiency (single crystalline Si) [7]. Silicon solar cells are also heavy and stiff. With the discovery of semiconducting polymers in 1977 [8], a new class of solar cells was born: the organic solar cell, flexible and fairly easy to produce. Much effort was put into increasing the charge carrier mobility, improving the device parameters and understanding the physical background, such that nowadays devices with an efficiency up to 5% are feasible [9]. This fact reveals the first major downside of polymer-based solar cells: much work still needs to be done to increase the conversion efficiency. Another inadequacy is the fact that polymer solar cells have a strong tendency to degrade under the influence of oxygen [10], light [11] and temperature [12]. In this thesis, the temperature dependent degradation
is addressed for three polymers: MDMO-PPV, High-$T_g$-PPV and P3HT. By means of ageing experiments and theoretical modeling, an effort was made to reveal the physical background behind the degradation process, and to relate stability to morphology. In the first part, the degradation process is investigated and modeled, and in the second part, more knowledge is gained about a polymer with great potential concerning stability, through an electro-optical characterization and morphological examination.
2 Theory

Semiconducting polymers are the basis of the organic solar cell. In this chapter, their physical background is therefore introduced. Furthermore, their application in solar cells is clarified by means of a short historical sketch, and the relevance of the active layer morphology is explained. Finally, the most basic solar cell characterization tool is addressed: the current-voltage characteristic.

2.1 Conjugated polymers as semiconductors

The distinguishing property of conjugated polymers is the carbon-based alternating single and double bond structure. The simplest conjugated polymer, trans-polyacetylene, is used as an example (Fig. 1). σ-bonds, formed by the head-to-head overlapping of each carbon atom’s sp$^2$-orbitals, create the backbone of the polymer (Fig. 2). Bonding sp$^2$-orbitals have negligible overlap with others, so they are highly localized. Every remaining out-of-plane p$_z$ orbital can overlap with two neighboring p$_z$ orbitals. The electron states are therefore delocalized, and charge can be transferred along the polymer chain.

The molecular orbital theory dictates that the overlap of p$_z$ orbitals yields lower energy bonding (\(\pi\)) and higher energy anti-bonding (\(\pi^*\)) molecular orbitals (see Fig. 2). As more carbon atoms get involved, the number of available energy levels rises. The exact positioning of these energy levels is determined by solving the Schrödinger equation. Fig. 3 illustrates that for chain lengths approaching infinity, the abundance of energy levels forms bands, rather than discrete levels. If the bond lengths between the carbon atoms would be equal, the energy bands would coalesce and a metallic, instead of a semiconducting behavior, would be expected. It has been experimentally observed, however, that it is energetically more favorable if single bonds are longer, whereas double bonds are shorter \cite{13, 14}. This is referred to as the Peierls distortion.

\[\text{Fig. 1: A segment of trans-polyacetylene.}\]
2.2 Organic solar cells

2.2.1 Working principle and single layer devices

Almost all organic solar cells have a planar-layered structure, where the organic light-absorbing layer is sandwiched between two different electrodes. As light has to be able to penetrate the solar cell, one of the electrodes must be transparent. Indium-tin-oxide (ITO) is often used for this purpose. The other
2.2 Organic solar cells

The underlying principle of a light-harvesting organic PV cell (sometimes referred to as photodetecting diodes) is the reverse of the principle in light emitting diodes (LEDs). In LEDs an electron is introduced at the low-workfunction electrode (cathode) with the balanced introduction of a hole at the high-workfunction electrode (anode). At some point the electron and the hole meet, and upon recombination light is emitted. In the case of a photovoltaic device: when light is absorbed, an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), forming an exciton (bound electron-hole pair). In order to harvest energy, this process must be followed by exciton dissociation: the electron must reach one electrode while the hole must reach the other electrode. To achieve this charge separation, an electrical field is needed, which is provided by the the asymmetrical work functions of the electrodes.

![Diagram](image)

**Fig. 4:** Upon irradiation an electron is promoted to the LUMO leaving a hole behind in the HOMO. Electrons are collected at the Al electrode and holes at the ITO electrode. Φ: workfunction, χ: electron affinity, IP: ionisation potential, E_g: optical band gap [19].

To illustrate this, the single layer model from Fig. 5 is useful. The metal electrodes are represented by their Fermi levels, whereas for the organic active region the HOMO and LUMO-levels are shown. In Fig. 5a, the cell is short-circuited, and hence the electrode’s Fermi levels align, causing the HOMO and LUMO levels of the active layer to be pulled skew. These skew levels constitute an electric field in which (under illumination) separated charge carriers can drift towards the respective contacts. In Fig. 5b, the open circuit situation is shown. The open circuit voltage \( V_{oc} \) corresponds to the difference
2.2 Organic solar cells

in the electrode’s work functions and balances the built-in field. HOMO and LUMO levels are flat, meaning there is no driving force for mobile charge carriers, so the current is zero.

![Energy band diagram](image)

**Fig. 5:** Energy band diagram for (a) short circuit conditions and (b) open circuit conditions.

### 2.2.2 Bilayer and bulk heterojunction solar cells

For simplicity, the explanation given in section 2.1 is based on single layer devices. These were actually the first type of organic solar cells, and they do suffer some flaws. The electric field provided by the difference in their electrode’s work functions is insufficient to break up most of the photogenerated excitons, and only those excitons that are generated within a diffusion length (∼10 nm) from the contacts can contribute to the photocurrent. This kind of solar cells, made with PPV, delivered conversion efficiencies of less than 0.1% under white light illumination [20].

The idea behind a bilayer device (or: heterojunction) is that the active layer consists of two planar interface materials with different electron affinities and ionization potentials. This favors exciton dissociation: the electron will be accepted by the materials with the larger electron affinity (the acceptor) and the hole by the material with the lower ionization potential (the donor) (see also Fig. 4 and 7). The electrodes more or less match the donor’s HOMO level and the acceptor’s LUMO level (Fig. 7). Here, $V_{oc}$ corresponds to the energetic difference between the donor’s HOMO and the acceptor’s LUMO, assuming ohmic contacts[21]. Bilayer devices are still exciton diffusion limited though, as photogenerated excitons can only be dissociated in a thin layer at the junction. To overcome this, the bulk heterojunction structure was introduced. Its principle is similar to the bilayer structure, but the major difference is the intimate mixing of donor and acceptor components (interpenetrating network).
in a bulk volume (see Fig. 6) so that the major fraction of donor-acceptor interface is within a distance less than the exciton diffusion length of each absorbing site. There is a largely increased interfacial area where charge separation occurs and as the interface is dispersed through the bulk, no loss due to small exciton diffusion lengths is expected because ideally all excitons will be dissociated within their lifetime. The overlapping of HOMO and LUMO-levels of both materials that reach throughout the entire active layer (Fig. 8) also illustrates this [19, 22, 23, 24]. To conclude this section, the whole energy conversion in a solar cell is described in five steps. First, a photon is absorbed in the active layer, creating an exciton (1), after which the exciton diffuses to a donor-acceptor interface (2). Once at the interface, the electron is on its acceptor side and the hole is in the donor side, but they are still bounded (3). Next, the electron and hole are separated (4) and transported to their respective electrodes (5). Note that losses occur in each of these steps.
2.2 Organic solar cells 2 THEORY

2.2.3 Importance of morphology in bulk heterojunction solar cells

As mentioned in the previous section, the active layer of an organic solar cell consists of an interpenetrating network of electron donor and acceptor material. When an exciton is created after absorption of a photon, it diffuses towards a donor-acceptor interface to be split. A phase separation of the two blended materials at the length scale of the exciton diffusion length is therefore beneficial, though it cannot be too fine. It still has to allow for efficient charge percolation, so both donor and acceptor phases have to consist of pathways that are large enough such that electron-hole pairs (or: e-h pairs), once they have been separated, can easily escape from the donor-acceptor interface [25] to be transported to their respective electrodes. Fig. 9c shows an image of this requirement for MDMO-PPV:PCBM(1:4). Besides annealing treatment, the extent of the phase separation is influenced mainly by two parameters: the choice of solvent and ratio of donor and acceptor material. If toluene is used as solvent for the active layer blend, the resulting phase separation is very coarse (Fig. 10a), compared to the length scale of the exciton diffusion length. Using this solvent, the efficiency of MDMO-PPV:PCBM(1:4) is up to 0.9%. When chlorobenzene is used instead, the phase separation is much finer, at the length scale of the exciton diffusion length (Fig. 10b). The associated efficiency is 2.5% [23]. This clearly illustrated the importance of the solvent. The ratio of electron donor and acceptor material also has a great influence on the resulting morphology. Fig. 9 shows the morphology for different donor:acceptor ratios. 1:1 and 1:2 show a homogeneous film, but 1:4 results in a fine phase separation. As expected, this results in the optimal efficiency [25]. These examples make the importance of morphology intelligible.
2.3 Solar cell characterization

In this thesis, the emphasis concerning morphology lies in post-production annealing treatment or, more practically put: ageing experiments.

![Fig. 9: Transmission electron microscopy images of MDMO-PPV:PCBM thin film in ratios 1:1 (a), 1:2 (b) and 1:4 (c). Reprinted from [26].](image)

![Fig. 10: Scanning electron measurement of break sections of MDMO-PPV:PCBM blend films spin-cast from two different solvents onto ITO/(PEDOT:PSS) covered glass. Reprinted from [22].](image)

2.3 Solar cell characterization

The current-voltage characteristic (or: IV-characteristic) of a solar cell under illumination (see Fig.11) contains most of the ingredients needed to calculate what is probably the most popular and most easy-to-judge quantity to characterize the performance of a solar cell: the photovoltaic conversion efficiency
2.3 Solar cell characterization

η (Eq. 1). It indicates the fraction of the incident solar power that is absorbed and used for current generation.

\[
\eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \quad (1)
\]

\[
FF = \frac{I_{mpp}V_{mpp}}{I_{sc}V_{oc}} \quad (2)
\]

\(V_{oc}\) is the open circuit voltage, \(I_{sc}\) the short circuit current, FF is the fill factor and \(P_{in}\) is the incident light power density. In the so-called AM1.5 illumination, this light intensity is taken 1000 W/m\(^2\), corresponding to the sun being at an angle of elevation of 42°, according to the Standard Test Condition (STC) for solar cells. \(I_{mpp}\) and \(V_{mpp}\) are the current and voltage at the point where the solar cell produces its highest power. In the commonly used metal-insulator-metal (MIM) model, the open circuit voltage \(V_{oc}\) (point a in Fig. 11, a material parameter) is in first order approximation determined by the difference in work functions of the two metal contacts. This holds at least for the case where the Fermi levels of the contacts are within the bandgap of the insulator, and sufficiently far away from its HOMO and LUMO levels. Otherwise, with Ohmic contacts, \(V_{oc}\) is also governed by the energy level of the HOMO of the acceptor and the HOMO of the donor. Considering ideal, loss free contacts, the short circuit current \(I_{sc}\) (point b in Fig. 11, a device parameter) is a function of \(G\) (generation rate of free charge carriers), \(\mu\) (charge carrier mobility) and \(E\) (internal electric field). It is highly sensitive to nanoscale morphology. The indicated points a and b on the IV-curve in Fig 11 correspond to the illustrated situations in Fig. 5a and b. Only in the voltage range delimited by these points does the device exert a photovoltaic behavior. An external voltage source would be needed to get to voltages below zero (c) and higher than \(V_{oc}\) (d). The fill factor is the ratio of the full rectangle’s and the dashed rectangle’s areas in Fig. 11. In order to maximize \(\eta\), this ratio should be as close to 1 as possible. In the ideal case, the IV-curve is square-shaped and FF = 1. The behavior of an IV curve’s horizontal and vertical asymptotes reflect the parasitic series resistances \(R_s\) and parallel resistances \(R_p\): as \(R_s\) decreases and \(R_p\) increases, FF increases [6, 27, 28, 23].
2.3 Solar cell characterization

Fig. 11: IV-curves of a solar cell (dark: dashed curve, illumination: full curve).
3 Preparation of solar cells

In this chapter, the materials and methods are described to prepare bulk heterojunction solar cells, as represented in (Fig. 12). Their most critical component is the light-absorbing active layer. This is a blend of an electron donor (strings in Fig. 12) and an electron acceptor material (beads). In the simplest arrangement, this blend is sandwiched between two electrodes, and this whole sits on a glass substrate.

![Fig. 12: Basic setup of a bulk heterojunction solar cell.](image)

3.1 Acceptor material

1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C$_{60}$, or PCBM (Fig. 13a) was always used as the acceptor material. It is a soluble derivative of C$_{60}$ with a HOMO of 6 eV and LUMO of 4.5 eV, purchased from Solenne.

3.2 Donor materials

The three used polymers were purchased from Merck.

- MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]1,4-phenylenevinylene)
- P3HT (poly(3-hexylthiophene-2,5diyl)
- High-T$_g$-PPV

The chemical structure of these polymers is found in Fig. 13.
3.3 Solutions

As the active layer is spincoated on the substrate, it has to be in liquid form. Unless stated otherwise, chlorobenzene was used as the solvent. MDMO-PPV based solar cells were made with a 0.5 wt% solution (with respect to the polymer) of MDMO-PPV:PCBM (1:4). P3HT:PCBM devices were prepared in a 1:1 ratio with 1 wt% P3HT. For the optimal active layer thickness of High-Tg-PPV solar cells, solutions with 0.2, 0.3 and 0.4 wt% HTg-PPV:PCBM (1:4) were prepared. 1:3, 1:4, 1:5 and 1:6 solutions were used for the optimal High-Tg-PPV:PCBM ratio. The solutions were stirred at 50°C, 1 day for MDMO-PPV:PCBM and P3HT:PCBM solutions, and three days for HTg-PPV:PCBM solutions.

![Chemical structure of acceptor (a) and donor (b,c,d) materials. High-Tg-PPV is a copolymer with components x, y and z.](image)

3.4 Substrate

The samples used to prepare solar cells are glass substrates with an indium tin oxide (ITO) pattern (thickness ~100 nm): in every corner of the substrate
there is a 10x10 mm ITO square (see also Fig. 16a). The samples are cleaned in an ultrasonic bath with a soap solution, demineralized water and acetone, for 20 minutes, 2 x 10 minutes and 15 minutes, respectively, and finally, they are put in boiling isopropanol for 10 minutes. The last step is 15 minutes of ozone cleaning under UV-lighting.

3.5 Deposition techniques

3.5.1 Spincoating

Spincoating is a process for depositing a film of solvable material on single samples. The technique is shown in Fig. 14. A certain amount of solution is pipetted on the substrate. The substrate is rotated, and because of this rotation the solution spreads and forms a homogeneous film on the substrate. Both during and after spincoating the solvent is evaporated. Key parameters of this technique are the rotation speed, time and acceleration. Apart from these parameters, the film thickness can be tuned by using solution of different concentration as well. Thicknesses were measured with a Dektak-ST profilometer.

![Fig. 14: Working principle of the spincoating technique](image)

3.5.2 Evaporation

All top electrodes of the prepared devices were deposited by evaporating one or more metals. The schematic in Fig. 15 depicts the working principle. The samples are placed on a rotatable disc (faced down) with weights keeping them in place. Metal pellets (e.a. aluminum) are put on a conductive crucible
which is held in place by two terminals that are connected to a current source. After the vacuum chamber is brought to a pressure of typically $1 \cdot 10^{-6}$ mbar, a very high current (e.g. $\sim 60$ A for Al) is sent through the crucible, which makes the pellets evaporate. The emerging metallic fume rises gently and the incorporated atoms stick to the samples such that a layer is grown at a rate of 0.1-0.2 nm/s. The rotation of the disc makes sure that every sample catches the same amount of fume and the grown layer is homogeneous.

Fig. 15: Schematic of the evaporator.

3.6 Device layout

The mentioned ozone cleaning renders the ITO-layer more hydrophilic, which favors the adhesion of the next layer, water-solved poly-3,4-ethylenedioxythiophene (PEDOT:PSS, Bayer), which was spincoated with a thickness of $\sim 25$ nm. The purpose of this hole-transporting layer is twofold: prevention of indium and oxygen diffusion into the active layer and smoothing out the uneven surface of the ITO [19]. The samples were dried on a hotplate at 120°C for 15 minutes. From then on, the process was continued in a glovebox with nitrogen atmosphere. The active layer (the polymer blend at hand for the experiment) was spincoated (typically 100-120 nm optimal thickness) on top of the PEDOT layer from the solutions mentioned in section 3.3. Then the top contact ($15 \times 15$ mm) was evaporated. This is typically an aluminum or "calcium + aluminum" contact for regular solar cells, or Pd or CsCO$_3$ for hole-only and electron-only devices, respectively. In some cases lithium fluoride
3.6 Device layout  

was evaporated between the active layer and the top contact for a better contact efficiency [22]. Fig. 16a and b give a schematic representation of a finished device. Because of the pattern in the ITO and the layers of different area, there are four identical solar cells on one sample (see shaded area).

Fig. 16: Top and side view of a solar cell. The actual active area is shaded in the top view.
4 Stability

Organic solar cells degrade easily under the influence of oxygen [10], light [11] and temperature [12]. In this thesis, the emphasis is on temperature dependent degradation. Section 2.2.3 explains the need for a certain extent of phase separation in the active layer. As polymer chains become mobile above the glass transition temperature $T_g$ ($\sim 45^\circ$C for MDMO-PPV), elevated temperatures allow PCBM molecules to move freely through the polymer matrix and so a further phase separation is induced, producing clusters of PCBM, rather than the original small scale pathways. This reduces the interfacial area between polymer and PCBM tremendously, resulting in a far less efficient device [12]. Fig. 17 shows the clustering at different annealing times for MDMO-PPV:PCBM(1:4). For P3HT, the effect is similar except that the clusters have needle-like features [29]. One of the major goals in organic photovoltaics is developing stable solar cells that do not exhibit such phase separation.

![Fig. 17: Morphology of MDMO-PPV:PCBM(1:4) thin film, annealed at 110°C, for different times. $T_g$(MDMO-PPV) = 45°C.](image)

4.1 Accelerated lifetime modeling

4.1.1 Modeling measured data

To determine the lifetime of a device, a life test model is needed to correlate the accelerating stress (in this case: temperature) to a device or material parameter. The short-circuit current $J_{sc}$ is considered the most decisive parameter with respect to the degradation of the solar cell, since it is strongly material related [12, 30]. Therefore, IV-characteristics were measured as a
function of time, for a set of temperatures. One of the most popular models for accelerated lifetime tests is the Arrhenius model. The degradation constant $k_{\text{deg}}$ is a quantity that indicates how fast the degradation is evolving. For this model it is given by:

$$k_{\text{deg}} = A \exp \left( \frac{-E_a}{k_B T} \right)$$

(3)

Where $E_a$ is the activation energy in eV, $k_B$ the Boltzmann constant (8.62·10^{-5} eV/K) and $A$ is a constant that depends on the degradation mechanisms and the experimental conditions. A higher $E_a$ for degradation means a higher barrier to overcome for the system to degrade, so this characterizes a stabler device. The simple Arrhenius model can be extended to account for additional stresses, but this is not necessary as they were prevented. In order to determine a degradation constant from experimental data, a mathematical model for its time dependence has to be assumed. Commonly used are linear and first order exponential models. In this work, the model in equation 4 was used as a starting point [31], and a modification was introduced (equation 5).

$$J_{\text{sc}}(t) = J_{\text{sc}}(\infty) + J_{\text{sc}}(0) \exp(-k_{\text{deg}} t)$$

(4)

$$J_{\text{sc}}(t) = J_{\text{sc}}(\infty) + J_{\text{sc}}(0) \exp(-k_{\text{deg}} \sqrt{t})$$

(5)

When performing an accelerated experiment at a number of different test temperatures $T'$, and taking one temperature $T$ as reference temperature, the acceleration factor $K$ can be calculated for all $T'$ according to:

$$K = \frac{k_{\text{deg}}(T')}{k_{\text{deg}}(T)} = \exp \left[ \frac{E_a}{k_B} \left( \frac{1}{T} - \frac{1}{T'} \right) \right]$$

(6)

From a fit through the $K(T')$-curve, the activation energy $E_a$ can be extracted.

4.1.2 Experimental details

For these degradation experiments, solar cells with MDMO-PPV:PCBM (1:4) as active layer ($\sim 110$ nm) and LiF (1 nm) and aluminum (60 nm) as contact were prepared. They were put in an in-situ chamber at temperatures from 50°C to 90°C. A Keithley 2400 SourceMeter was used for measuring. For 50 and 60°C, a measurement was taken every 30 minutes for the first 16 hours, and then every hour. For 70, 80 and 90°C, a measurement was taken every 15 minutes for the first 2 hours, every 30 minutes for the remaining day, and then every hour. White light illumination with an intensity of $\sim 1$ sun was only switched on at times when a characteristic was measured.
4.1.3 Results

The degradation of the short circuit current of the solar cells is found in Fig. 18. The values were normalized in order to compare the different curves. Because of practical reasons, the curves for 80°C and 90°C were obtained from solar cells that originate from another batch. Their degradation curve stabilized on a lower value than the curves for the other three temperatures. The shape was the same though, and there was no evidence of time dilatation or acceleration. The difference in stabilization current was attributed to slightly different layer thicknesses and impurity levels for both batches of solar cells. Therefore, the data was scaled such that the stabilization value was the same for each curve. All curves were fit simultaneously to the Arrhenius model, described in section 4.1. Using equations 4 and 5 to mimic the J_{sc} degradation, it is seen from the result in Fig. 19 that the fits match the measured data better for equation 5. Each fitted curve possesses a specific degradation constant k_{deg}. When this constant is plotted on a logarithmic scale against $\frac{1}{k_{BT}}$, the activation energy can be calculated from the slope, formed by the k_{deg}-values. Fig. 20 shows the slopes that correspond with Fig. 19a and b. The more successful fitting result for the eq. 5 model is reflected in the activation energy calculation: it yields a more consistent slope with a higher R² (0.9986) as opposed to the eq. 4 model (0.9574). The resulting activation energies are 0.85 eV and 1.19 eV, respectively. Previously reported for a MDMO-PPV:PCBM material system (though with a 1:3 ratio, Ca/Ag electrode and constant illumination under 1/3 sun) was an Eₐ of 0.35 eV [31]. The lower Eₐ-value is to all likelihood a consequence of the additional degradation due to the continuous illumination.
4.1 Accelerated lifetime modeling

Fig. 18: Degradation of the short circuit current as a consequence of temperature.

Fig. 19: Degradation of the short circuit current, fitted with models from eq. 4 (a) and eq. 5 (b).
4.1 Accelerated lifetime modeling

The activation energy is determined from the slope of the degradation constant’s log-plot. (a) with model from eq. 4, (b) with model from eq. 5.

Fig. 20:
4.2 Morphological analysis

This section deals with the morphological analysis of an MDMO-PPV:PCBM thin film upon annealing, both beside and under the top electrode, and a comparison is made. The structure of the formed clusters is analyzed by looking into the fractal dimension and the cluster growth is linked to a diffusion model. The study was conducted by means of transmission electron microscopy and atomic force microscopy.

4.2.1 Transmission electron microscopy (TEM)

Fig. 21 shows a (rotated) schematic representation of the TEM used in this thesis (Philips CM12-STEM). The tungsten coil at the top produces a stream of electrons. The stream passes through two magnetic lenses (the first and second condenser lenses) that focus it into a small, coherent beam. The condenser aperture blocks the high angle electrons before the beam strikes the sample. The transmitted part of the beam is focused into an image by the objective lens. The objective aperture, which blocks the high-angle diffracted electrons, enhances the contrast of the image.

![Schematic of a TEM](image)

Fig. 21: Schematic of a TEM.
4.2 Morphological analysis

4.2.2 Atomic force microscopy (AFM)

Fig. 22 shows a typical setup of an AFM system (in this thesis: a Veeco Multimode V). The main component of the microscope is a sharp tip of a few microns wide, located at the end of a cantilever with a length of 100 to 200 µm. As the tip scans the surface of the sample, the topology of the sample causes the cantilever to bend. A laser is directed towards the tip at all times, and a photodetector detects any deflections of the laser beam, caused by the bending of the cantilever, thus revealing the topology of the sample.

Fig. 22: Schematic of an AFM system.

4.2.3 Sample preparation

For beside-electrode analysis, active layer solution was spincoated on silicon substrates, for under-electrode analysis, solar cells were made as described in section 3. The substrates/solar cells were annealed at different temperatures and for different times, and were then cut into smaller pieces. These could be used as AFM samples. To make TEM-samples, the small cut samples were put in hydrofluoric acid (HF). This way, the annealed thin film comes off the substrate and could be picked up by a 200-mesh copper TEM grid.

4.2.4 Morphology under and beside electrode

Morphological analysis of annealed active layer thin films are very often performed on samples without top electrode. The relevant location of interest, however, is under the electrode as this is where the active layer is operative. The question is therefore: to what extent are conclusions based on investigation beside the electrode still valid under the electrode. Fig. 23 shows an
array of annealed films, beside and under the electrode, annealed for different
times. The PCBM clusters formed beside the contact are sharply defined and
in the first stages of annealing the diffusion fronts are even visible (Fig. 23a
and b). Under the contact, the clusters are less pronounced and fuse into each
other. To quantify the comparison between the clusters under and beside the
electrode, the total cluster surface at every temperature was calculated with
the program ImageJ. The resulting values are depicted in Fig. 24. A logistic
fit was made of the total cluster surface \( A \), according to the formula:

\[
A = A_1 + \frac{A_1 - A_2}{1 + \left( \frac{t}{t_0} \right)^\rho}
\]

(7)

where \( A_1 \) is the initial value of \( A \), \( A_2 \) the final value of \( A \), and the power \( \rho \)
represents how fast the transition from low to high surface occurs. Finally,
the most important parameter in the context of this section is \( t_0 \). It indi-
cates when exactly the transition takes place. In the framework of this thesis,
the time scale of the morphological change is at least as important as how
the change comes to expression. After all, one of the goals is to relate the
morphology to the performance of the solar cell and the corresponding key
parameter is the time in which changes are detected in both fields. Beside the
electrode, \( t_0 \) was calculated to be \( t_{0,\text{beside}} = 1 \text{ h 25 min} \), and under the electrode
\( t_{0,\text{under}} = 1 \text{ h 21 min} \). Taking into account an error margin of 5%, \( t_{0,\text{beside}} = t_{0,\text{under}} \),
which means that though a different morphology is found beside versus under
the electrode, both cases do occur on the same time scale. It can be con-
cluded that time scale dependent interpretations from previous morphological
research on beside-electrode thin films are still valid under the electrode.

Fig. 25 shows Atomic Force Microscopy images of the morphology of an-
nealed MDMO-PPV:PCBM thin films under the electrode. The time course
of the morphology was studied by taking a height histogram of each image.
For a total of 512 x 512 pixels in each image, each pixel was indexed in its
corresponding height range. The result is in Fig. 26, where the heights are
considered as deviations from the average height. For short annealing times
(0.5 h and 1 h), the histogram is sharp and close to the average, indicating a
rather even surface. Starting from 2 h, the histogram it is very wide, so a wide
range of heights is present in the topography. It is notable that after 2 h of
annealing, the histogram does not really change anymore. Hence, somewhere
between 1 and 2 h, the vertical growth of the clusters stagnates, indicating
that when the lateral growth has ceased (after 80–85 minutes, as mentioned
Fig. 23: Annealed thin films of MDMO-PPV:PCBM(1:4) at $110^\circ$C for several times (0.5 h (a,f), 1 h (b,g), 2 h (c,h)), 7h (d,i), 15.5h (e,j)), beside (a-e) and under (f-j) the top electrode. Scale bar = 2 $\mu$m.

Fig. 24: Logistic fit of the relative total cluster surface for clusters under and beside the top electrode, upon annealing at $110^\circ$C.
before), the vertical growth also stops, so lateral and vertical growth follow the same time scale.

Fig. 25: 10x10 μm AFM images of annealed MDMO-PPV:PCBM(1:4) thin film at 110°C under the electrode, for different annealing times.

Fig. 26: Height histogram under the electrode for different annealing times at 110°C.
4.2 Morphological analysis

4.2.5 Clustering process

Consider images Fig. 23a to e. In the first two images, it is clearly visible that small nuclei of PCBM are formed. Each nucleus is surrounded by a PCBM-depleted zone. Once a nucleus is formed, it grows by adsorption of new PCBM molecules that are drawn from the PCBM network that is originally dispersed throughout the polymer matrix. At some point, the clusters touch because of their growing number and size. One could say that they aggregate, though this is only a consequence of the fact that they grow into each other due to lack of space; the clusters do not move as a whole [32]. This clustering behavior, that starts from nuclei (which can form under the presumption that the system is sufficiently saturated with its dispersed phase) and grows clusters without them having to make contact, fits into the theory of the Ostwald ripening process. The spontaneous process occurs because larger particles are energetically more favorable than smaller ones. The larger particles’ lower surface to volume ratio results in a lower surface energy. As the system tries to lower its overall energy, the smallest occurring particles will tend to diffuse towards the larger clusters, and add to them [33, 34]. In the context of the polymer:PCBM system, the smallest occurring particles refer to the PCBM network (domains of 50-100 nm), with its very large surface area (Fig. 27). Evidently, the larger particles are the ones as in Fig. 23. There is a limited amount of PCBM in the system, so when all PCBM is assembled in the clusters, they stop growing. The same process is believed to happen under the electrode, though the electrode itself impedes the proper clustering, resulting in blurry clusters.

Fig. 27: PCBM network (dark domains) in the MDMO-PPV matrix. Scale bar = 100 nm.
4.2.6 Fractal dimension of PCBM clusters

**Introduction** Fractal dimension analysis is a regularly used tool in various kinds of structural research [35, 36, 37]. It is a statistical quantity that gives an indication of how completely a structure appears to fill space, as one zooms in to finer and finer scales. In this thesis, the fractal dimension of the PCBM clusters in the MDMO-PPV matrix upon thermal treatment was calculated.

**Definition** The fractal dimension of a phase A in Euclidean space is defined as:

\[
D = \lim_{r \to 0} \frac{\log(N_r)}{\log(1/r)}
\]

where \(N_r\) is the least number of distinct copies of a unit object with characteristic length scale \(r\) that is needed to cover A perfectly [38]. D was determined from the TEM images in the previous section (beside electrode) using the so-called box counting method.

**Box counting method** The aforementioned unit object is taken to be a square. Initially, it is one by one pixel wide (\(r = 1\) pixel). The square side is then increased to 2, 3, 4, 6, 8, 12, 16, 32 and 64 pixels. For each size, the number of corresponding squares that is needed to cover all of the (in this case PCBM-) phase is measured. A plot of the log of the square count versus the log of the square size is made and is fitted with a straight line. According to equation 8, D is then given by \(-S\), with S the slope of the line [39]. To clarify this, Fig. 28 shows a graph of such a fit. In that particular case, \(D = 1.86\). \(R^2\) is close to 1, indicating a good fit, which means that the fractal dimension is consistent for different square sizes, so it is reliable.

**Result** In Fig. 29, D of the annealed MDMO-PPV:PCBM thin films is presented for different temperatures and annealing times. All fits had an \(R^2\) higher than 0.999 so error bars were left aside, though this does not mean that the accuracy is very high. After all, the measurements were performed on a limited amount of images. As is apparent from the graph, D starts at \(\sim 1\) when the clusters have just begun to grow, and gradually rises to a final value of \(D \sim 1.85\).
4.2 Morphological analysis

Fig. 28: Fractal dimension fit of the PCBM clusters after 2 h of annealing at 110°C.

\[ y = -1.8576x + 14.529 \]
\[ R^2 = 0.9993 \]

Fig. 29: Fractal dimension of PCBM clusters as a function of annealing time, at different temperatures.
4.2 Morphological analysis

4.2.7 Link to theoretical model

While the previous section dealt with all clusters as a whole, now the clusters are treated more individually, in the sense that a general concentration gradient is supposed for each cluster. PCBM clusters are assumed roughly circular, and \( R \) is their radius. At a distance \( R \) from the center, a sudden drop in PCBM concentration is present that delimits the cluster. Fig. 30 illustrates this, together with an assumed concentration profile, based on the work of Zhong et al. [32]. The red line in the image represents the path along which the graph is taken. \( c_0 \) is the PCBM concentration at some distance from a cluster, \( c_\beta \) is the concentration in the cluster itself, and \( c_\alpha \) the lowest concentration in a zone around the cluster where the PCBM is depleted, as a consequence of clustering. If diffusive motion of clusters is assumed (\( \rightarrow \) random walk) and the depicted concentration gradient is used, the cluster radius as a function of time is governed by the formula [40]:

\[
R(t) = \left(2 D \frac{c_\beta - c_\alpha}{c_\beta - c_\alpha} \right)^{1/2} t^{1/2}
\]  

(9)

where \( D \) is the diffusion coefficient (full derivation in Appendix B). This means that for lateral diffusion, the area of the cluster is directly proportional to the time. Fig. 31 shows that this prediction is indeed observed in the first stages of clustering: the annealing time and the average cluster area are linked with a linear relation. Later on, the area starts to stagnate (inset of Fig. 31) because the polymer matrix is practically completely depleted of PCBM, and clusters may break up and recombine with other clusters (see previous section), so the
linear relation no longer holds.
Yang et. al. [41] observed a fast and a slow growth direction in the same material system. No such behavior was observed in this thesis. However, Yang’s one dimensional growth rate in their observed fast direction relates to $\sqrt{t}$. This implies an area growth directly proportional to time, assuming that no slow growth rate exists, which is the observation in this thesis.

Fig. 31: Average cluster area as a function of time for different temperatures

4.3 Generation rate

Notwithstanding the fact that a solar cell does not deliver energy at negative voltages, when the amplitude of the negative voltage is large enough, ideal solar cell features can be fulfilled (no recombination and space-charge formation), and interesting physical information can still be obtained: the produced photocurrent $I_{ph}$ (light current minus dark current) can be a direct measure of the photogeneration rate $G$ of free charge carriers, i.e. the number of excitons reaching an interface. Evidently, at short circuit and MPP, not all generated e-h pairs reach the electrodes as a consequence of geminate (from same pair) and non-geminate (from different pairs) recombination. At high negative voltages, however, the efficiency of interface exciton splitting and transport is assumed to be 1 [23]. Recalling the five steps of energy conversion, described in section 2.2.2, this means that only the first two remain: absorption and exciton diffusion. Applying a large negative bias is therefore a good method to study the maximum generation rate.
4.3 Generation rate

4.3.1 Theoretical basis

Goodman and Rose developed a model to derive an approximate theory of double extraction of uniformly generated electron-hole pairs from a photoconducting layer with non-injecting contacts [42]. It states that the extracted current \( J \) resulting from an applied voltage \( V \) is:

\[
J(V) = \frac{egL(1+b)(-b + \sqrt{b^2 + 4(1-b)V\mu_n\tau_n/L^2})}{2(1-b)}
\]

(10)

with \( \mu_n \) and \( \mu_p \) the electron and hole mobility, \( e \) the elementary charge, \( \tau_n \) and \( \tau_p \) the electron and hole lifetime, \( g \) the generation rate of electron-hole pairs and \( L \) the active layer thickness. In the normal operating voltage range, an appreciable fraction of electron-hole pairs will recombine before it can be split. Very high negative voltages, though, will force all photogenerated charges to leave the device before recombining. In that case, the charge carrier lifetime can be assumed equal to the transit time \( \tau_t = L^2/\mu V \) (time needed to reach the electrodes) [23]. Inserting this expression in equation 11 yields:

\[
b = \frac{\mu_n \mu_p}{\mu_p \mu_n} = 1
\]

(11)

This means that in the limit for high negative voltages:

\[
\lim_{b \rightarrow 1} J(V) = 2egL = eGL \quad \text{with} \quad G = 2g
\]

(13)

and \( G \) is the rate of generated free charge carriers. Concisely summarized, equation 13 gives the value that the photocurrent approaches in the limit of large negative applied voltages, and this value is independent of the mobility of neither electrons or holes and is a direct measure of \( G \). Fig. 32 gives the \( I_{ph} - V_{eff} \)-curve of pure PCBM, pure MDMO-PPV and MDMO-PPV:PCBM(1:4). At \( \sim -9V \) (as low as could be measured), the current of the pristine components has not reached their plateau yet, but for the blend it is plausible that the final current (thus indicating \( G \)) is about 30 A/m\(^2\). Owing to the intimate mixing of MDMO-PPV and PCBM in the blend, its generation rate is a lot higher than the sum of the generation rates of the separate components.
Upon annealing, the formation of PCBM clusters leads in time to a polymer matrix with discrete clusters of PCBM, and the interpenetrating network that was started off with has virtually vanished. The e-h pairs (almost all generated in the MDMO-PPV) must thereby be split without the help of the donor-acceptor interface before being forced to the electrodes. As a consequence, one would expect that the generation rate of an annealed MDMO-PPV:PCBM film falls back to the generation rate of the pristine polymer, as in Fig. 32. Fig. 33 shows the $J_{ph}$–$V_{eff}$-curve of an MDMO-PPV:PCBM(1:4) device, before and after two days of thermal treatment at 90°C. It is immediately obvious that nothing has changed for voltages below -1 V. The current stagnates at the same value, whether the device had been annealed or not, indicating a similar G. Since G at low voltages denotes the maximum number of excitons that can reach an interface for the particular morphology of the device at hand, it seems that thermal treatment only affects the transport and recombination mechanisms, but not the e-h pair generation.
4.3 Generation rate

Fig. 33: Graph of the photocurrent \( I_{\text{ph}} \) versus the effective voltage \( V_{\text{eff}} = V_{\text{oc}} - V \), before and after annealing.
4.4 Conclusion

The temperature induced degradation of MDMO-PPV:PCBM solar cells was investigated by means of several research routes. The short circuit current was chosen as the main parameter for the electrical measurements, and it was shown that its degradation upon thermal treatment is governed by an Arrhenius process. Using an exponential model based on $\sqrt{t}$, an activation energy of 0.85 eV was obtained.

Morphological investigation based on TEM images revealed that the total surface (lateral) of the clusters of PCBM that are formed upon annealing grow on the same time scale under and beside the electrode. Supplementary AFM measurements confirm that also the vertical growth stops within the same time range. The clustering is attributed to the Oswald ripening process, where larger clusters are formed at the expense of small particles. The clusters’ final fractal dimension $D$ was calculated using the box counting method and yielded $D \sim 1.85$. The average surface of individual clusters is linear in the first stages of clustering. This was explained by a diffusion model, assuming a general concentration profile that is applicable for each cluster. After some annealing time, the growth is no longer linear due to the limited amount of PCBM in the polymer matrix.

The generation rate $G$ of charge carriers at high negative voltages was used as a measure for the maximum number of excitons reaching a donor-acceptor interface. High negative voltages eliminate several loss mechanisms so that only absorption and exciton diffusion remain relevant. The maximal $G$ turned out to stay constant upon annealing, which implies that annealing only has an influence on the transport and recombination of charge carriers, not so much on the e–h pair generation.
5 Towards stable organic solar cells: High-$T_g$-PPV

It is obvious from the previous chapter that once a solar cell is developed that does not suffer from morphological instability anymore, a major step towards a wide array of practical organic solar cell applications will have been taken. A possible strategy towards this goal is to use polymers with a high glass transition temperature $T_g$ so that the polymer stays in its glassy state, even at outdoor service temperatures (up to 70°C), and consequently no clustering of PCBM through the polymer matrix occurs. A polymer that manifests this property is a copolymer that is informally called "High-$T_g$-PPV" (henceforth referred to as HT$_g$-PPV). Its chemical structure is depicted in Fig. 13d. It is already demonstrated that this polymer has potential concerning stability [43] (see Fig. 34), but in general not much is known about this polymer. Therefore, this chapter provides more knowledge about HT$_g$-PPV through an electrical, morphological and optical characterization.

![Fig. 34: Short circuit current as a function of time, for a HT$_g$-PPV:PCBM(1:4) solar cell at 110°C and an MDMO-PPV:PCBM(1:4) solar cell at 90°C. Even at such a high temperature, $I_{sc}$ will stabilize at 90% of its original value for HT$_g$-PPV:PCBM.](image)

5.1 Photovoltaic performance

A relatively easy way to tune the performance of a solar cell is to determine the optimal active layer thickness that allows for sufficient light absorption but at the same time contains as little charge traps as possible. This was done in section 5.1.1. As the solvent of the active layer material is determinative for the device morphology and performance (explained in section 2.2.3),
different solvents were tried (section 5.1.2). In order to obtain an efficient organic solar cell, it is also vital to organize its electron donor and acceptor materials such that their interface area is maximized, while the dimensions of phase separation are within the exciton diffusion range and continuous pathways for charge transport to the electrodes are ensured. A key feature to fulfill these requirements is an optimal ratio between electron donor and acceptor material (section 5.1.3). All measurements were performed under an AM1.5-like illumination.

5.1.1 Active layer thickness

Solar cells with layers ITO/PEDOT/HT$_g$-PPV:PCBM(1:4)/Ca/Al were prepared to determine the optimal active layer thickness $d$ for this blend. Fig. 35 shows the common characterization parameters of a solar cell as mentioned in section 2.3, for HT$_g$-PPV:PCBM devices. The short circuit current in part a shows a fluctuating behavior as a function of $d$, with an optimal value of 2.56 mA/cm$^2$ (at $d = 75$ nm), which is about 25% lower than the optimal value for MDMO-PPV:PCBM(1:4). One may argue that a thicker active layer should yield more current as a result of a larger absorption, however, this is only the electrical interpretation. Optical losses have to be considered simultaneously. Models that incorporate both electrical and optical effects have been developed [44, 45, 46]. Their predictions of the $J_{sc}(d)$ generate fluctuating results for MDMO-PPV:PCBM and P3HT:PCBM devices, very similar to the results that were measured for HT$_g$-PPV:PCBM, hence these results are perfectly viable. The open circuit voltage $V_{oc}$ as shown in Fig. 35b stays constant at 0.9 V over almost the entire thickness range. This makes perfect sense as $V_{oc}$ is a material parameter (see section 2.3). Only for thin devices a considerable reduction is detected. The same effect has been noticed before, and was associated with shorts [47]. For MDMO-PPV:PCBM(1:4), $V_{oc}$ is about 0.85 V and for P3HT:PCBM(1:1) up to 0.62 V, so HT$_g$-PPV:PCBM(1:4) displays a decent $V_{oc}$ as compared the workhorse material systems. The fill factor varies slightly from 0.36 to 0.41 along the measured thickness range (Fig. 35c). As a consequence of the before mentioned shorts at low thicknesses, the parallel resistance is lower and gives rise to a lower FF. This effect diminishes with thickness and a maximum is found at 90 nm. For devices > 90 nm the FF decreases again, caused by a higher risk of traps and space charges [47, 48]. The power conversion efficiency (Fig. 35d) is the combined effect of $I_{sc}$, $V_{oc}$ and FF.
5.1 Photovoltaic performance

The conclusion is that active layer thicknesses from 75 to 90 nm yield the optimum performance for HT$_g$-PPV:PCBM(1:4) devices. This is thinner than the optimal thickness for MDMO-PPV-based devices (110-120 nm) and comparable with P3HT-based devices [45]. The maximal HT$_g$-PPV:PCBM efficiency of 0.88% is somewhat disappointing, compared to values that were reached with the other two blends (1.5% for MDMO-PPV:PCBM and 2% for P3HT).

Fig. 35: Performance characteristics for HT$_g$-PPV:PCBM devices with varying active layer thickness.

5.1.2 Solvents

Devices were prepared from five common solvents: o-xylene, chlorobenzene, dichlorobenzene:chloroform(1:1), toluene and meta-dichlorobenzene. The results (Fig. 36) can be divided in two groups: o-xylene, CB and DCB:CHL (group 1) and toluene and meta-DCB (group 2). Group 2 is clearly unsuited for HT$_g$-PPV:PCBM solar cells as the low $V_{oc}$ indicates that a lot of short circuits are present and the low FF indicates a large parasitic resistance. Group 1 benefits from the higher $V_{oc}$ of $\sim$0.9 V and FF of 0.4. In the end, o-xylene is the best solvent, followed by chlorobenzene and DCB:CHL, though
the difference is very small.

![Graphs](image)

**Fig. 36:** Performance characteristics for HT$_g$-PPV:PCBM devices, with active layer spincoated from different solvents.

### 5.1.3 Donor:acceptor ratio

To determine the optimal ratio between HT$_g$-PPV (electron donor) and PCBM (electron acceptor), solar cells with layers ITO/PEDOT/HT$_g$-PPV:PCBM/ Ca/Al were prepared, with varying HT$_g$-PPV:PCBM ratio (1:3, 1:4, 1:5, 1:6 and 1:7), and constant thickness of 101 ± 3 nm, spincoated from chlorobenzene. Fig. 37a shows $J_{sc}$ versus the blend ratio. The 1:3 blend clearly performs worse than the other ratios. An improvement arises from adding more PCBM, giving a maximum at 1:6. At 1:7, $J_{sc}$ tends to drop again. $V_{oc}$ (Fig. 37b) decreases a little for rising PCBM concentrations, as predicted by [49]. Varying the ratio does not have a large effect on the fill factor either (Fig. 37c), though the maximum occurs at 1:4. The optimal efficiency is obtained with a 1:6 ratio of polymer and PCBM (Fig. 37d).
Fig. 37: Performance characteristics for HT_{g}\text{-}PPV:PCBM devices with varying donor:acceptor ratio.
5.2 Glass transition temperature determination

Many conjugated polymers have characterizing thermochromic properties. Here they were used to determine the $T_g$ of HT$_g$-PPV. This is possible because of the fact that these thermochromic effects are directly correlated with temperature dependent deviations from planarity of the conjugated system, which occur above $T_g$. Below $T_g$ the backbone conformation no longer changes and as a result no thermochromism, but only ground-state aggregation phenomena are observed. This suggests that $T_g$ can be determined from temperature dependent UV/VIS absorption spectra: the $\pi - \pi^*$ transition (so the band gap) of the polymer increases as a function of temperature, and the associated peak wavelength in the absorption spectrum shifts to the UV (technique formerly used in [50]). To guarantee reversibility, four cycles of heating and cooling were done. Fig. 38 shows the characteristic peak wavelength at half maximum for a range of temperatures. Two linear fits are obtained, and their intersection indicates $T_g$, which was determined to be 138°C [43].

![Fig. 38: Wavelength $\lambda$ at half maximum of the $\pi - \pi^*$ transition as a function of temperature. Reprinted from [43].](image)

5.3 Absorption spectrum

5.3.1 Measurement technique

An optical means of characterizing a photovoltaic blend is to determine what is its useful wavelength range for light absorption. The relative amount of absorbed light power $A$ by a certain material is represented as: $A = \log \frac{P_0}{P}$, where $P_0$ the incident light power, and $P$ the emergent light power. By means
of ultraviolet/visible absorption spectrometry (UV/VIS), one can determine the absorption of a material as a function of the incoming light’s wavelength. To this end, a Varian Cary absorption spectrometer was used. The measurable range of wavelengths is roughly 200 to 800 nm. A simple schematic of how this measurement is performed is shown in Fig. 39. Light of adjustable wavelength and power $P_0$ is sent through a glass plate with the polymer blend spincoated on top. Behind the glass plate a detector monitors the remaining light power after passing through the sample. Because not only the polymer blend, but also the glass on which it is spincoated has an absorption spectrum, this latter background spectrum is measured first, and compensated for in the actual measurement.

### 5.3.2 Spectra for three photovoltaic blends

The absorption spectrum of HT$_g$-PPV:PCBM(1:4) is depicted in Fig. 40, together with MDMO-PPV:PCBM(1:4), P3HT:PCBM(1:1) and the part of the irradiation spectrum of the sun that is relevant in relation to the spectra of the blends. The peaks around 330 and 700 nm belong to PBCM, all other peaks are polymer characteristics. In the wavelength region where the sun emits the most (>500 nm), P3HT:PCBM absorbs more than MDMO-PPV:PCBM and HT$_g$-PPV:PCBM. The absorption edges for MDMO-PPV:PCBM, P3HT:PCBM, and HT$_g$-PPV, are $\sim$ 560, 650, and 560 nm, respectively, which corresponds to band gaps of 2.2, 1.9 and 2.2 eV. Fig. 41 shows the absorption spectra of HT$_g$-PPV:PCBM of a new device and one that was annealed for one day at 130$^\circ$C. There is no appreciable difference between the two spectra, which gives rise to the assumption that no major morphological change occurs in the
blend upon thermal treatment.

Fig. 40: UV/VIS absorption spectrum of three polymer:PCBM blends, and the irradiation spectrum of the sun (AM1.5).

Fig. 41: UV/VIS spectrum of a HT$_2$-PPV:PCBM film, as produced and annealed for 24h at 130°C.
5.4 External quantum efficiency

5.4.1 Introduction

The external quantum efficiency (EQE) of a solar cell is a measure for its electrical sensitivity for light: it is the fraction of incoming photons that produces an electron-hole pair. The effect of optical losses is included herein. The EQE is given as a function of wavelength (or energy) to obtain a spectrum. For each wavelength, the following equation applies:

\[ EQE = \frac{\text{electrons out}}{\text{photons in}} = \frac{I/q}{P_{\text{ph}}/(hc/\lambda)} \]  

where \( I \) is the measured current, \( q \) the charge of one electron, \( P_{\text{ph}} \) the total power of photons colliding with solar cell’s active layer, and \( \frac{hc}{\lambda} \) is the energy of one photon, in which \( h \) is Planck’s constant, \( c \) the speed of light, and \( \lambda \) the photon’s wavelength. The ideal EQE spectrum is equal to 1 at all wavelengths. In reality, it is reduced as a consequence of recombination of charge carriers and reflection. This is clarified by Fig. 42.

![EQE Spectrum Diagram](image)

Fig. 42: Example of an EQE spectrum.

5.4.2 Measurement technique

The EQE measurements were performed with a Fourier Transform Infrared (FTIR) spectrometer (Thermo Electron Nicolet 8700 FTIR) in Fourier Trans-
5.4 External quantum efficiency

form Photocurrent Spectroscopy (FTPS) mode. As opposed to UV/VIS, where a wavelength sweep has to be performed to obtain a spectrum, in FTIR spectroscopy (FTPS mode) the sample is exposed to a single white light pulse with known Fourier spectrum that contains all wavelengths at a time ($\rightarrow$ fast). The main part of the FTPS setup is the FTIR spectrometer, which is a two beam interferometer as designed in 1891 by Michelson (see Fig. 43). A white light source (all wavelengths) is shone on the beamsplitter which partially reflects and partially transmits the incident light, thus creating two light beams. A path difference (or: retardation) $\delta = 2(om-\omega f)$ is created by moving one of the mirrors while the second mirror is fixed. Depending on the mirror position, this retardation creates constructive or destructive interference of the two reunited light beams, which is picked up by the detector. The detected interferogram $S$ is given by:

$$S(\delta) = \int_{0}^{\infty} B(\vec{k}) \cos \left( \frac{2\pi \delta}{\lambda} \right) d\vec{k} \quad (15)$$

where the cosine governs the retardation dependent interference, $B(\vec{k})$ is the spectral characteristic of the light source, and $k = \frac{1}{\lambda}$ is the wave number. Imposing a constant mirror speed, the retardation becomes $\delta = 2Vt$. Combining

Fig. 43: Michelson interferometer, where mirror $m$ moves at constant speed, while mirror $f$ is fixed, creating a retardation.
5.4 External quantum efficiency

This with eq. 15 yields:

\[ S(t) = \int_{0}^{\infty} B(\mathbf{k}) \cos(2\pi \mathbf{k} \cdot 2Vt) d\mathbf{k} \]  

(16)

\( S(t) \) is the cosine Fourier transform of \( B(\mathbf{k}) \), so an inverse Fourier transform yields \( B(\mathbf{k}) \), the spectral characteristic of the light source [51]. To obtain the EQE of a solar cell, \( B(\mathbf{k}) \) of the white light source is first determined by means of an Si-detector, as a calibration. Then \( B(\mathbf{k}) \) of the same white light source is measured, but first the Si-detector is replaced by the solar cell. In the end, the spectrum that was measured with the solar cell as detector is divided by the formerly measured spectrum (with Si-detector), resulting in the EQE of the solar cell.

5.4.3 Difference with absorbance

The absorption spectrum and the EQE spectrum seem alike but are actually complementary. The absorption spectrum indicates at what wavelengths a blend absorbs easily, though this does not necessarily mean that a great share of the generated current in the solar cell will originate from that specific wavelength range. This is because wavelengths with large optical absorption are not automatically the wavelengths at which there is an efficient charge separation to generate current. This latter feature is reflected in the EQE spectrum. (Wavelengths at which not much light is absorbed will obviously never generate an appreciable current.)

5.4.4 EQE for three photovoltaic blends

Fig. 44 compares the EQE for three common polymer:PCBM blends. All three blends are most efficient around a wavelength of 500 nm, while the sun emits the most photons around 700 nm (Fig. 40). HT<sub>0</sub>-PPV:PCBM has the lowest peak value, but behaves roughly the same way as MDMO-PPV:PCBM. P3HT is clearly the most efficient over a greater spectral range. Fig. 45 displays the EQE for a HT<sub>0</sub>-PPV:PCBM solar cell. Both spectra are from the same device, one before and the other after a thermal treatment of 24 h at 130°C. Annealing has a considerable effect on the EQE, and is definitely one of the major causes for the degradation of the device. The reason for the decrease in EQE is most likely manifold. The stiff HT<sub>0</sub>-PPV network cannot completely
impede clustering of PCBM (see next section), thus still inducing inferior percolation pathways for conduction. Chemical degradation can play a role as well. Moreover, after annealing at 130°C, the metal electrode of the solar cell has degraded to a certain extent as well.

Fig. 44: EQE for three polymer:PCBM blends.

Fig. 45: EQE of HT$_9$-PPV:PCBM before and after annealing.
5.5 Morphology

Fig. 46 shows TEM images of the morphology of a HT_g-PPV:PCBM thin film in several ratios, spincoated from chlorobenzene, on a scale that should reveal any relevant phase separation. Surprisingly, there is no phase separation to be found in any of the ratios. This indicates directly that the difference in performance between the different ratios, as seen in the previous section, is not ascribable to any morphological cause. The fact that HT_g-PPV:PCBM performs worse than MDMO-PPV:PCBM, despite that these blends display similar charge carrier mobility, absorption spectrum and EQE, could very well be a consequence of the absence of phase separation. Images of films spincoated from other solvents from group 1 were not made since no major morphological difference is expected. The justification for this is the similar photovoltaic performance. As an illustration of the stability of HT_g-PPV:PCBM as opposed to MDMO-PPV:PCBM, Fig. 47 shows a TEM image of the former blend, annealed for 16 hours at 110°C. Bertho et al. demonstrated that it is only after this time that one single PCBM cluster is detected on an entire TEM grid, whereas MDMO-PPV:PCBM starts forming clusters throughout the whole film in a matter of minutes at the same temperature. This clearly indicates the stability potential of HT_g-PPV.

Fig. 46: HT_g-PPV:PCBM(1:x) morphology for different values of x, spincoated from chlorobenzene

5.6 Charge carrier mobility

5.6.1 SCLC

Introduction Charge carrier mobility can also be determined by space charge limited current (SCLC) measurements. The SCL regime, in which there is a
5.6 Charge carrier mobility

Fig. 47: HT$_{g}$-PPV:PCBM thin film, annealed for 16 h at 110°C. Reprinted from [43].

A quadratic relation between current and voltage, occurs when the equilibrium charge concentration of a material (before charge injection) is negligible compared to the injected charge concentration. This contrast gives rise to a space charge cloud near the injecting electrode. Space charge occurs only in media with low dielectric constants (such as the polymers used in organic photovoltaics), because in a conductive medium the excess charge would be quickly neutralized. The SCL current in a plane-parallel dielectric sample with thickness L is given by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$  \hspace{1cm} (17)

where $I$ is the current density, $\varepsilon_0$ the vacuum permittivity, $\varepsilon_r$ the relative dielectric constant of the material, $V$ the applied potential, and $\mu$ the charge carrier mobility. The expression holds for both electron or hole currents. A full derivation is found in appendix A.

Device preparation In order to measure the mobility of only one type of charge carrier, adapted electrodes are necessary, otherwise holes as well as electrons will be measured and the difference cannot be told. To detect only holes, palladium (Pd, $\Phi=5.12$ eV) was used as top electrode, for electron-only measurements, Ca was used on both sides ($\Phi=2.87$ eV). Apart from the appropriate electrodes, the devices are prepared like a regular solar cell (see section 3).

Result The hole mobility of pure HT$_{g}$-PPV, measured by SCLC, is $\mu_h = (2.6 \pm 0.1) \cdot 10^{-10} \text{m}^2/\text{Vs}$, which is somewhat higher than $\mu_h = (5 \pm 0.1) \cdot 10^{-11} \text{m}^2/\text{Vs}$ for
5.6 Charge carrier mobility

pure MDMO-PPV [23]. Notice that SCLC determined mobility values are a lot lower than those measured by FET. This is because the mobility is a function of the charge carrier density, which is intrinsically a lot higher in a FET than in a solar cell [23]. Fig. 48 shows that the mobility trend of HT$_g$-PPV:PCBM (a) as a function of PCBM content exhibits the same behavior as for MDMO-PPV:PCBM (b). Though the formerly observed contra-intuitive increase of $\mu_h$ for higher PCBM concentrations in MDMO-PPV:PCBM ([52]) is also present in HT$_g$-PPV:PCBM, the effect is a lot smaller in the latter. In MDMO-PPV:PCBM, this odd behavior of $\mu_h$ was attributed to the influence of PCBM on the asymmetric side chains of MDMO-PPV that form ringlike features, thus inducing an enhanced intramolecular reaction and an improved charge transfer between adjacent polymer chains [53]. Unlike MDMO-PPV, HT$_g$-PPV is a copolymer (consisting of three different components), massively increasing its asymmetry, and most likely impeding the formation of any such ringlike features. This is a plausible explanation why in HT$_g$-PPV:PCBM, the charge carrier mobility for holes is not so strongly influenced by the fraction of PCBM in the blend. For electrons, on the other hand, the effect is not so pronounced either. Naturally, an increase of $\mu_e$ is to be expected for higher PCBM concentrations as PCBM is an electron acceptor, but considering the rather minor effect, perhaps also here the reason should be looked for at the molecular level.

![Graph](image)

*Fig. 48:* Electron and hole mobility of and HT$_g$-PPV and MDMO-PPV, measured by SCLC, as a function of PCBM content.
5.6.2 FET

**Working principle**  A Field Effect Transistor (FET) is a device in which a conducting channel between two electrodes (source and drain) is controlled by the voltage between the source and a third electrode, the gate. The transistor used for the mobility measurements in this work is the Thin Film Transistor (TFT). Its architecture is depicted in Fig. 49. From bottom to top, it consists of a silicon n+ doped gate, an SiO$_2$ insulator layer (~200 nm), a source and drain electrode (both 10 nm of titanium and 100 nm of gold). This is the transistor (apart from the channel), of which multiple are present on the FET samples, purchased from Philips Research. The (p-type) polymer of which the mobility is to be determined, forms the channel and is spincoated on top, with a thickness of about 60 nm, though the polymer thickness is not of the utmost importance since only a few monolayers suffice for proper transistor operation [54]. As a positive voltage $V_{gs}$ is applied between gate and the grounded source electrode, the channel is depleted of carriers since it is p-type, resulting in a very high resistivity. When a negative $V_{gs}$ is applied, holes from the channel accumulate near the interface with the insulator and, applying a small source-drain voltage $V_{sd}$, a current can now easily flow between source and drain (=accumulation mode or enhancement mode). If $V_{sd}$ is not too high, the output characteristic exhibits a linear behavior, otherwise it saturates (see Fig. 50). To sum up, the FET can be considered a voltage-controlled resistor because the amount of current that is allowed to flow through the channel can be controlled by $V_{gs}$.

![Fig. 49: Schematics of a field-effect transistor.](image)

For the experiments, the transistor was used in enhancement mode, in the linear regime, for which the following equation is valid [54]:

$$I_{sd} = \frac{W C_i \mu}{L} \left( V_{gs} - V_T - \frac{V_{sd}}{2} \right) V_{sd}$$  \hspace{1cm} (18)

where $L$ is the channel length (distance between S and D in Fig. 51), $W$
5.6 Charge carrier mobility

![Input characteristics of a p-type TFT in enhancement mode. Highlighted areas mark the linear regime (right) and the saturation regime (left) [55].](image)

\[ g_m = \left. \frac{\partial I_{sd}}{\partial V_{gs}} \right|_{V_{sd}=\text{const.}} = \frac{WC_i}{L} \mu V_{sd} \] (19)

**Measurement procedure**  After spincoating the polymer, the samples were left to dry in a nitrogen atmosphere for at least one night. For measurement, the transistors were contacted by needles (see Fig. 51). The FET current-voltage characteristics were measured using two Keithly 2400 multimeters. They are indicated on the current scheme of the transistor in Fig. 52. A \( V_{gs} \) sweep was carried out, whilst keeping the source-drain voltage \( V_{sd} \) constant at a sufficiently low value (in order to stay in the linear regime), and measuring \( I_{gs} \) and \( I_{sd} \). This latter current is actually a leakage current. Using Kirchhoff’s second law, the current that passes through the polymer is:

\[ I_{\text{polymer}} = \frac{I_{\text{leak}}}{2} - I_{sd} \] (20)

The dependence of the mobility on the electric field was avoided by adjusting \( V_{sd} \) such that the ratio \( V_{sd}/L \) stayed the same for each transistor.
5.6 Charge carrier mobility

**Fig. 51:** Layout of a TFT as used in this thesis. Source, drain and gate electrode are contacted by needles [55].

**Result** The hole mobility of pure HT$_g$-PPV, measured by FET is $(2.1 \pm 0.2) \times 10^{-9} \text{m}^2/\text{Vs}$. This is somewhat lower than for pure MDMO-PPV: $\mu_h = (4.4 \pm 0.4) \times 10^{-9} \text{m}^2/\text{Vs}$. Notice that FET determined mobility values are a lot higher than those measured by SCLC. This is because the mobility is a function of the charge carrier density, which is intrinsically a lot higher in a FET than in a solar cell [23]. Fig. 53 depicts the electron and hole mobility, $\mu_e$ and $\mu_h$, for HT$_g$-PPV:PCBM and MDMO-PPV:PCBM blends at several PCBM fractions. For both blends, $\mu_e$ increases several orders of magnitude as more PCBM is added. This is logical because PCBM is an electron acceptor material. $\mu_e$ is slightly higher for HT$_g$-PPV:PCBM than for MDMO-PPV:PCBM, though the difference shrinks as the PCBM content is higher. For 80% PCBM, which is relevant concerning performance, the difference is no longer present. $\mu_h$ is higher for MDMO-PPV:PCBM for all measured ratios, but still in the same order of magnitude. It has a slight increase for 50% PCBM and drops for higher concentrations, whereas HT$_g$-PPV:PCBM stays constant till 70% PCBM before decreasing. Overall, the charge carrier mobilities of the two blends show comparable magnitudes and trends.
Fig. 53: Electron and hole mobility of MDMO-PPV and HT$_{g}$-PPV, measured by FET, as a function of PCBM content.
5.7 Conclusion

HT\textsubscript{g}-PPV, a polymer with potential concerning stability due to its high glass transition temperature, was characterized by means of electrical, morphological and optical characterization.

HT\textsubscript{g}-PPV's glass transition temperature was determined to be 138°C, based on its thermochromic properties.

Field effect transistor measurements pointed out that the hole mobility of HT\textsubscript{g}-PPV is $(2.1 \pm 0.2) \times 10^{-9} m^2/Vs$, somewhat lower than MDMO-PPV ($\mu_h = (4.4 \pm 0.4) \times 10^{-9} m^2/Vs$). In contrast to the FET result, the charge carrier mobility, as measured by space charge limited current, reveals a higher $\mu_h$ for HT\textsubscript{g}-PPV ($\mu_h = (2.6 \pm 0.1) \times 10^{-10} m^2/Vs$) than for MDMO-PPV ($\mu_h = (5 \pm 0.1) \times 10^{-11} m^2/Vs$). The trend of $\mu$ as a function of PCBM content is the same for both blends, but the effect is only one order of magnitude change for HT\textsubscript{g}-PPV:PCBM whereas it is known to be three orders of magnitude for MDMO-PPV:PCBM. This difference could be attributed to the complexity and asymmetry of the copolymer HT\textsubscript{g}-PPV and/or the different nanoscale mixing.

Concerning absorption spectrum and external quantum efficiency, HT\textsubscript{g}-PPV is comparable to MDMO-PPV. P3HT still absorbs the most of the three polymers and has the highest EQE. HT\textsubscript{g}-PPV's absorption spectrum is adequately resistant to thermal treatment, whereas under the same thermal stress its EQE drops considerably.

HT\textsubscript{g}-PPV's photovoltaic performance is rather low with a conversion efficiency of at most 0.9% under AM1.5-like illumination at an optimal active layer thickness of 75-90nm. The open circuit voltage of 0.9V is promising, but the reason for the low efficiency is the low fill factor of 0.41 and the relatively low short circuit current of 2.34mA/cm\textsuperscript{2}. A plausible explanation for the somewhat low performance was found in the morphology of the blend: while a small phase separation is necessary for an efficient solar cell, TEM images revealed a total lack of phase separation in the HT\textsubscript{g}-PPV:PCBM blend that was spincoated from chlorobenzene. Hence, the phase separation absence is held responsible for the low photovoltaic performance. This presumption is further confirmed by the fact that HT\textsubscript{g}-PPV exhibits features, other than morphology, that are very similar to MDMO-PPV (UV/VIS, EQE, $\mu$), so in theory should be able to yield much higher efficiencies than obtained here. Devices spincoated from other solvents did not yield appreciably better photovoltaic
results than chlorobenzene so no morphological difference is expected. Different donor:acceptor ratios were tried. For a 1:x ratio of HT$_g$-PPV:PCBM, devices with x < 4 clearly perform less. x $\geq$ 4 gives better results, with a slight maximum at 1:6.
References


[46] A.J. Moulé and K. Meerholz. Minimizing optical losses in bulk hetero-


[55] M. Breselje. *Electrical characterization of 2,5-substituted poly (p-
6 Publications and poster

- Sabine Bertho, Griet Janssen, Thomas J. Cleij, Bert Conings, Wouter Moons, Abay Gadisa, Jan D’Haen, Etienne Goovaerts, Laurence Lut- 
  sen, Jean Manca and Dirk Vanderzande, *Effect of temperature on the 
  morphological and photovoltaic stability of bulk heterojunction poly-
  753-760.

- *Fractal dimension of phase separated PCBM network in organic solar 
  cells*, manuscript of communication in preparation.

- *Arrhenius analysis of degradation kinetics in organic solar cells*, manuscript 
  of article in preparation.

- B. Conings, S. Bertho, K. Vandewal, I. Haeldermans, J. Manca, R. 
  Janssen, "Towards stable organic solar cells; degradation investigation 
  and characterization of a new polymer" (Poster).
  
  – RUG Groningen - UHasselt workshop, 20th May 2008
  – General Scientific Meeting of the Belgian Physical Society (Uni-
    versité Libre de Bruxelles), 21st May 2008
Towards stable organic solar cells
degradation investigation and characterization of a new polymer

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Organic solar cells have become a promising alternative for their classical semiconducting counterparts, perhaps their largest disadvantage is that they tend to degrade under the influence of elevated operating temperatures. A specific degradation mechanism is the thermally induced phase separation of the active layer components. The thermally induced electrical and morphological changes were investigated and modeled for MDMO-PPV:PCBM solar cells. A new polymer, High-Tg-PPV, was characterized that impedes degradation through its high glass transition temperature.

The degradation curves were modeled using the Arrhenius model, where
\[ k_{deg}(T) = K \exp\left(\frac{E_a}{RT}\right) \]
The graph below shows the value of K for different temperatures (Tg = 50°C). A reliable fit was made (R^2 = 0.9986). The exponent in the formula represents the activation energy E_a needed to initiate degradation (E_a = 0.85 eV).

**MORPHOLOGY and DEGRADATION**

In solar cells based on polymers with a low T_g, elevated operating temperatures (up to 70°C) induce clustering of the PCBM component, as a consequence of diffusion. The degradation of MDMO-PPV:PCBM (1:4) solar cells is governed by an activation energy of 0.85 eV. The total cluster area evolves at the same rate beside and under the electrode. It is plausible that the I_sc degradation stagnates as the clustering does so. High-Tg-PPV seriously diminishes clustering of PCBM, resulting in a far more stable device.

**Conclusion**
7 Acknowledgements

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Bert Conings
June 2008
A Space-charge-limited current — derivation

The space-charge-limited current equation is now derived for electrons. For holes it works exactly the same way. Assuming an undoped material, Poisson’s law dictates:

\[ \frac{\varepsilon_r \varepsilon_0 dE}{dx} = n \]  

(21)

where \( n \) is the electron concentration, \( E \) the electric field, \( \varepsilon_0 \) the vacuum permittivity, \( \varepsilon_r \) the relative permittivity and \( e \) the elementary charge [56]. With \( \mu_e \) the electron mobility, the drift current is defined as [56]:

\[ J = en\mu_e E \]  

(22)

Current diffusion was neglected because its effect is small compared to the drift current. Combining equations 21 and 22:

\[ J = \mu_e \varepsilon_r \varepsilon_0 \frac{dE}{dx} = \frac{1}{2} \mu_e \varepsilon_r \varepsilon_0 \frac{dE^2}{dx} \]  

(23)

The following boundary conditions are imposed:

\[ \begin{cases} J = \text{constant} \\ E(0) = 0 \end{cases} \]  

(24)

Integrating equation 23 then gives:

\[ Jx = \frac{1}{2} \mu_e \varepsilon_r \varepsilon_0 E^2 \]  

(25)

Solving to \( E \):

\[ E = \sqrt{\frac{2Jx}{\mu_e \varepsilon_r \varepsilon_0}} \]  

(26)

The voltage between two points with a distance \( d \) is:

\[ V = \int_0^d E \, dx \]  

(27)

Inserting equation 26:

\[ V = \sqrt{\frac{2J}{\mu_e \varepsilon_r \varepsilon_0}} \int_0^d \sqrt{x} \, dx = \sqrt{\frac{2J}{\mu_e \varepsilon_r \varepsilon_0}} \frac{2}{3} \sqrt{d} \]  

(28)
This works out to:

\[ J = \frac{9}{8} \mu_e \varepsilon_r \varepsilon_0 \frac{V^2}{d^3} \]  \hspace{1cm} (29)

For holes, the equation becomes:

\[ J = \frac{9}{8} \mu_h \varepsilon_r \varepsilon_0 \frac{V^2}{d^3} \]  \hspace{1cm} (30)
B Diffusion model — derivation

Presume that the PBCM is initially homogeneously dispersed throughout the polymer matrix. Assume that the smallest occurring units of PCBM are spherical and that cluster growth will result in spherical structures. $c_0$ is the PCBM concentration at an appreciable distance from the cluster. Let $c_\alpha$ be the lowest concentration in the zone around the cluster where the PCBM is depleted (confining the cluster), and $c_\beta$ be the concentration in the cluster itself, $J$ the PCBM-flux and $R$ the cluster radius, then:

$$4\pi R^2 \cdot (c_\beta - c_\alpha) \, dR = 4\pi R^2 \, |J| \, dt \quad (31)$$

Fick’s law dictates that the flux and the concentration gradient at the interface relate through diffusion constant $D$:

$$J = -D(\nabla c)_R \quad (32)$$

Combining the previous two equations gives:

$$\frac{dR}{dt} = \frac{D}{c_\beta - c_\alpha} (\nabla c)_R \quad (33)$$

The principle of continuity is governed by:

$$\nabla J = -\frac{\partial c}{\partial t} \quad (34)$$
Together with equation 32, this yields

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$  \hspace{1cm} (35)$$

In spherical coordinates, this is written as

$$\frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) = \frac{dc}{dt}$$  \hspace{1cm} (36)$$

For a constant regime,

$$r^2 \frac{dc}{dr} = \text{constant}$$  \hspace{1cm} (37)$$

Using the boundary conditions

$$\begin{cases} r = R & \rightarrow c = c_a \\
 r = R_\infty & \rightarrow c = c_0 \end{cases}$$  \hspace{1cm} (38)$$

equation 37 works out to

$$\frac{dc}{dr} = \frac{1}{r^2} \frac{c_0 - c_a}{R - R_\infty}$$  \hspace{1cm} (39)$$

Assuming that $R_\infty \gg R$, this shows that the concentration profile is

$$c(r) - c_0 = (c_a - c_0) \cdot \frac{R}{r}$$  \hspace{1cm} (40)$$

and at $r = R$:

$$\left( \frac{dc}{dr} \right)_R = \frac{c_0 - c_a}{R}$$  \hspace{1cm} (41)$$

Inserting this in equation 33 yields

$$\frac{dR}{dt} = D \frac{c_0 - c_a}{c_\beta - c_a} \frac{1}{R}$$  \hspace{1cm} (42)$$

and by integration:

$$R(t) = \left( 2D \frac{c_0 - c_a}{c_\beta - c_a} \right)^{1/2} t^{1/2}$$  \hspace{1cm} (43)$$

Based on [40].