An in-situ study on the effect of co-solvents on polymer solar cell morphology

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Award date:
2014

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An in-situ study on the effect of co-solvents on polymer solar cell morphology

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25-7-2014
Abstract

In optimized solution-processed bulk-heterojunction polymer solar cells, an extremely important facet is the morphology of the active layer. However, due to the formation of large donor and acceptor domains in the active layer, efficiency is often compromised. These large domains are caused by liquid-liquid phase separation, which occurs during processing of the cells. A well-known method to solve this problem is the use of co-solvents in solar cell processing.

This report describes three experiments that can be used to obtain insight in the role that these co-solvents play in preventing liquid-liquid phase separation. Laser-based thin-film interference is used to determine the thickness of the active layer during spincoating as a function of time. This experiment is performed in combination with either a scattering experiment or a transmission and absorption setup.

The scattering experiment is used to determine the onset of phase separation in the drying layer. For solar cells made with diketopyrrolopyrrole (DPP)-based polymers and a fullerene acceptor, liquid-liquid phase separation is found to occur at 83 ± 4% total solvent content when no co-solvents are used. This value is independent of spincoating speed, side chain-length and initial concentration of solids.

The transmission and absorption setup is used to determine when polymer aggregation starts. This experiment shows that, when processing without co-solvent, polymer aggregation occurs after liquid-liquid phase separation. However, when co-solvents are used, it is found that polymers aggregate before large scale liquid-liquid phase separation can occur. Hence, the formation of too large domains is prevented, leading to better solar cell performance.

Further research is necessary to explain why certain polymers perform best when processed with one co-solvent, whereas other polymers perform best when processed with a different co-solvent. It is found that the size of the fibers formed during aggregation differs between co-solvents. Experiments indicate that, in this process, the duration of polymer aggregation might play an important role.
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1 Introduction

In the ongoing pursuit of renewable energy sources, solar energy is an important contestant. Opposed to conventional silicon based solar cells, organic solar cells can be made on flexible substrates, which drastically widens the field of application for the devices and allows easier production methods\(^1\). Therefore a bright future may lie ahead for organic solar cells. With energy efficiencies already exceeding 9\% \(^2\) the scientific community is continuously improving organic solar cell technology.

It is already well known that morphology of the active layer, consisting of polymer donor and fullerene acceptor, is of vital importance to solar cell performance\(^3\). Thus, to achieve optimal efficiency, an optimised morphology is a necessity. A common problem is phase separation of the polymer:fullerene blend during processing, resulting in large domains of polymer and fullerene. These large domains have a negative influence on solar cell performance\(^4\).

A widely used method to solve this problem is the use of a co-solvent during processing \(^5\). Even though this method works, the exact process that underlies the improvement of the morphology remains poorly understood. In order to truly optimise morphology, a thorough understanding of the drying process is needed.

Some research has already been done on this subject. J. J. van Franeker et al. performed a study on the role of co-solvents during the processing of solar cells made with a low-bandgap diketopyrrolopyrrole (DPP-)based polymer\(^6\). This led to some interesting new insights on the role that these co-solvents play in the prevention of large scale phase separation.

A first objective of this experiment is to gain a wider understanding of the role of co-solvents during solar cell production. Therefore a similar study was performed with a different DPP-based polymer\(^7,8\). To be able to study the role of solubility of the polymers as well, two different side chains were chosen.

The second objective is to obtain insight in why certain polymers perform better when processed with one co-solvent, while others perform better when a different co-solvent is used. Therefore two different co-solvents were used in this experiment.
2 Theory

2.1 Solution-processed bulk-heterojunction polymer solar cells

The active layer of polymer solar cells generally consists of a donor material (often polymer) and an acceptor material (often fullerene). When light is absorbed in this layer, a bound electron-hole pair (exciton) is generated. To prevent the Coulomb attraction from recombining the electron and hole, they have to be separated as quickly as possible. Since this separation only occurs at the interface between donor and acceptor, an ultra-fine dispersion of these materials is optimal for charge generation. But since continuous pathways of donor and acceptor are needed to transport the charges to the electrodes, it will lead to very poor charge transport as many acceptor and donor domains lie isolated\cite{9}.

Consequently, the morphology plays a very important role in solar cell efficiency. According to literature a domain size of around 10 nm\cite{9} and a layer thickness of around 100 nm\cite{10} are optimal. In solution-processed polymer solar cells, donor and acceptor are stirred in a single solution. During layer formation, a bulk heterojunction (BHJ) structure, as sketched in Figure 1, is formed.

![Figure 1: Schematic cross-section of typical solution-processed bulk-heterojunction polymer solar cell. Figure taken from [11].](image)

A popular technique to apply such thin layers on the substrate is by spincoating the material\cite{12}. Spincoating consists of multiple phases, which are described in Figure 2.

![Figure 2: Phases of spincoating: 1) Material is placed in the center of the spincoater. 2) Radial flow of material. 3) Evaporation of the solvents.](image)

First, the solution is placed on the substrate in the center of the spincoater. As the spincoater is started, there is a radial flow of the material due to centrifugal force (phase 2)\cite{12}. This rapidly decreases layer thickness. In phase 3 the solvents evaporate (also referred to as ‘drying’)\cite{12}.
A problem that is often encountered, is that during the drying of the active layer (phase 3) liquid-liquid phase separation occurs \[^4\] , which leads to much larger domains of donor and acceptor and therefore lower solar cell performance. A common remedy for this problem is the use of an extra solvent (usually named co-solvent) during solar cell production \[^5\].

These co-solvents must have two important properties: they should evaporate slower than the main solvent and they should (ideally) only dissolve the acceptor material, contrary to the main solvent which dissolves both materials. The role these co-solvents play can then be explained with Figure 3.

\[\text{Figure 3: Schematic view of the drying of bulk heterojunction polymer solar cells. The orange arrow on the left corresponds to the process when no co-solvent is used. The purple arrow on the right corresponds to the process with co-solvent. Figure taken from [6].}\]

Without co-solvent the process is explained by the orange arrow on the left. In stage (1) the volume fraction of main solvent decreases due to evaporation. Around ~80% solvent content liquid-liquid phase separation occurs (stage (2)), causing large droplets of acceptor material. In stage (3) the polymers aggregate around ~50% solvent content.

The purple arrow on the right indicates the process with co-solvent. In stage (1) the solvents evaporate. Due to its faster evaporation, this is primarily the main solvent. Since the polymer hardly dissolves in the co-solvent, it starts aggregating around ~80-95% solvent content in stage (2). Because the donor already aggregated before liquid-liquid phase separation can occur, the formation of large domains is prevented during the final drying in stage 3 \[^6\].
2.2 Materials used in solar cell production

Various materials are used in polymer solar cell production. Those used in this experiment are described below. Structural formulas can be found in Figure 4.

Two donor polymers were used in this experiment. Both are DPPTPT (2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl)-alt-{(2,2’-(1,4-phenylene) bisthiophene)-5,5’-diyl}) polymers [7], [8]. The difference is in the length of the side chains of the polymers. The shorter-side chain-polymer has two hexyldecyl side chains, which results in limited solubility [8]. This polymer is referred to as HD-P17.

The other polymer (DT-P17) has two longer decyltetradecyl (DT) side chains. These longer side chains provide better solubility [8]. It does, however, limit solar cell performance due to the formation of too large domains [8].

In all experiments the fullerene-based [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM) is used as an acceptor. Chloroform is used as a main solvent.

As co-solvents, both 1,2-dichlorobenzene (oDCB) and 1,8-diiodooctane (DIO) are used. Due to its lower boiling point (179°C [13] vs 365°C [14] at 760 mmHg) oDCB evaporates much faster than DIO. As explained in paragraph 2.1, both evaporate more slowly than chloroform (boiling point of 61°C at 760 mmHg [15]) and mainly dissolve [70]PCBM.

![Structural formulas of materials used in this experiment.](image)

Figure 4: Structural formulas of materials used in this experiment.
2.3 Thin film interference

When light is directed at a (liquid) thin film, a part of the light is reflected at the top surface of the film. The other part is refracted into the material and then reflected at the bottom surface of the film, as shown in Figure 5.

![Figure 5: Thin film interference. Angle of incidence $\theta_i$, angle of refraction $\theta_r$, and film thickness $d$ as indicated.](image)

When multiple wavelengths are present in the incident light beam, the reflected beams can interfere constructively or destructively depending on wavelength. As a result certain wavelengths are amplified, while others are cancelled out. This is thin film interference.

When monochromatic light is used, this same phenomenon can be used to determine changes in film thickness $d$. As the film thickness changes, alternately constructive and destructive interference occurs at the top surface with known wavelength $\lambda$. This results in alternating light intensity of the reflected beam. In thin film interference all maxima are described by Equation (1):\[d \cos \theta_r = (2m + 1) \frac{\lambda}{4n}\] All minima are described by Equation (2):\[d \cos \theta_r = 2m \frac{\lambda}{4n}\] Here, $\theta_i$ is the angle of incidence, $\theta_r$ is the angle of refraction, $n$ is the refractive index of the material, $d$ is the film thickness and $m = 0,1,2,3\ldots$

When this method is used to monitor a decreasing film thickness and final thickness $d_{end}$ is known (as in this experiment), these can be rewritten to Equation (3):\[d = d_{end} + k \frac{\lambda}{4n \cos \theta_r}, \text{ with } \sin \theta_r = \frac{\sin \theta_i}{n}.\] Where $k$ is the number of minima and maxima in light intensity counted back from the end.

Since final thickness is reached when all solvent has evaporated, total solvent content is known to be zero in this situation. Therefore total solvent fraction $\phi$ at given film thickness $d$ can be calculated by:\[\phi = 100 \times \left(1 - \frac{d_{end}}{d}\right).\]
2.4 Light scattering

The law of reflection states that when a light ray is reflected by a surface, the angle of incidence equals the angle of reflection \[16\]. As long as polymer and PCBM are still dissolved, particles remain very small. Therefore they hardly alter the path of the light rays in the solution \[16\]. This can be seen in Figure 5.

However, when phase separation occurs, large structures are formed. As soon as these structures reach an order of magnitude similar to the wavelength (~100 nm) they start scattering light \[16\]. This is sketched in Figure 6. As the size of particles increases, the scattering of the longer wavelengths increases proportionally \[16\].

![Figure 6: Light will get scattered at the moment phase separation occurs.](image)

Because the rays will only be scattered significantly after phase separation sets in, this effect can be used to determine the onset of phase separation.
2.5 Absorption

Absorption is the phenomenon of matter taking over (absorbing) the energy of certain photons. As these photons are absorbed, electromagnetic energy is transformed to internal energy of the material and therefore the intensity of the transmitted light decreases.

A common way to quantize this effect is with absorbance $A$. The absorbance at given wavelength $\lambda$ is defined as:

$$ A(\lambda) = -\log_{10}\left(\frac{I_t(\lambda)}{I_o(\lambda)}\right). \quad (5) $$

Here, $I_t(\lambda)$ is the intensity of light at certain wavelength transmitted through the material and $I_o(\lambda)$ is the intensity of incident light at given wavelength.

When measuring with a spectrometer, Equation (5) changes slightly into:

$$ A(\lambda) = -\log_{10}\left(\frac{I_m(\lambda)-I_{m,dark}(\lambda)}{I_{m,light}(\lambda)-I_{m,dark}(\lambda)}\right). \quad (6) $$

Where $I_m(\lambda)$ indicates the measured amount of counts at given wavelength. $I_{m,dark}(\lambda)$ is a dark measurement performed to determine background noise and $I_{m,light}(\lambda)$ is a light measurement without the absorbing material to determine the incident light intensity.

The measured absorbance spectra of both HD-P17 and DT-P17 dissolved in chloroform and as a solid film are given in Figure 7.

![Figure 7: Absorbance spectra of HD-P17 (a) and DT-P17 (b), dissolved in chloroform (CF) and as film. Measured by dr. W. Li.](image)

From Figure 7 it becomes clear that as the polymers change from dissolved to solid state (when they aggregate), the main absorbance peak (around 800 nm) shifts to the red. This so-called redshift can be used to determine when polymer aggregation occurs.

At the moment absorbance starts shifting to the longer wavelengths, or equivalently, when transmission around 800 nm decreases, the polymers are aggregating.
3 Experimental setup

3.1 Solar cell production

The solar cells are made on glass substrates, prepared with an indium-tin-oxide (ITO) layer (supplied by Naranjo Substrates). Before further processing the substrates were cleaned. This cleaning process consists of several steps:

- 15 min sonication in acetone.
- Scrubbing and 15 min sonication in sodium dodecyl sulphate solution (99%, Acros).
- Rinsing with deionized water.
- 15 min sonication in 2-propanol.
- 30 min UV-ozone treatment.

Then, a poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Heraeus Clevios PVP Al 4083) layer is spincoated at 3000 RPM.

For producing the active layer either HD-P17 or DT-P17 (synthesized by dr. W. Li as described in [8]) was mixed in a 1:2 weight ratio with [70]PCBM (Solenne BV, 90-95%). This is dissolved, in a concentration of 5 mg/mL P17, in chloroform (>99.9%, supplied by Bisolve) with or without co-solvents and stirred for 2 to 3 hours at 90°C. The co-solvents (oDCB (99%) and DIO (98%)) were both supplied by Sigma-Aldrich. Finally, a Lithium-Fluoride (LiF) layer of 1 nm and an aluminum (Al) layer of 100 nm were evaporated as a back electrode.

Solar cell performance is often characterized using a $J$-$V$ curve. An example is given in Figure 8.

![Figure 8: Schematic $J$-$V$ curve. $J_{sc}$, $V_{oc}$ and MPP are indicated. Solid curve is a light measurement, dashed curve is a dark measurement.](image-url)
A $J$-$V$ curve shows how current density $J$ depends on bias voltage. Short circuit current $J_{sc}$ and open circuit voltage $V_{oc}$ are the axes-intercepts as indicated in Figure 8. Since power equals current times voltage, solar cell power is maximized when bias voltage is set at maximum area of the solid square. This is called the maximum power point $MPP$. Fill factor $FF$ is then defined as Equation (7):

$$FF = \frac{MPP}{J_{sc}V_{oc}}$$  \hspace{1cm} (7)

The dark measurement, given by the dashed line, is measured when no light reaches the solar cell.

While measuring these solar cell characteristics the cells were kept in a nitrogen environment. To simulate the solar spectrum, a tungsten halogen lamp was used together with a Hoya LB120 daylight filter. Total light intensity on the solar cell was checked to be $\sim 100$ mW/cm$^2$ with a calibrated Si reference cell. To measure the $J$-$V$ curves, the bias voltage was swept from -2V to +2V using a Keithley 2400 sourcemeter. Since the total light intensity that reaches the cell is known to be about 100 mW/cm$^2$, the calculated maximum power point (MPP) is now more or less equal to the power conversion efficiency (PCE).

To determine layer thickness, first a knife was used to remove a stripe of material. Then, the dry-layer thickness was measured with a Veeco Dektak 150.

### 3.2 Interference and scattering experiments

The interference and scattering experiments were always performed simultaneously. A schematic view of the basic interference setup can be found in the Figure 9.

A 632.8 nm HeNe laser (5 mW, Melles-Griot) was pointed at the substrate at a 15° angle. The beam was slightly spread using a biconvex lens to decrease the influence of impurities present on the spinning substrate as the signal is now averaged over a larger area. A Si photodiode (Thor Labs SM1PD1A) was used to collect the light reflected by the substrate. To filter out variations caused by a not perfectly flat spinning substrate, a white piece of paper was used as a diffuser. The photodiode was connected to
a current preamplifier (Stanford Research System Model SR570) operating in high bandwidth mode.

In addition to this setup a second photodiode (Hamatsu S2281) was added to collect the light scattered by the spinning layer. This is displayed in Figure 10.

Figure 10: Schematic view of the scattering setup.

This extra photodiode was connected to an extra Stanford current amplifier. A single Keithley 2636A was used to collect the voltages coming from both preamps simultaneously. A schematic view of the interference and scattering on the sample is displayed in Figure 11a.

Figure 11: Schematic view of substrates during optical experiments. a) setup for interference and scattering experiment. b), setup for interference and absorption/transmission experiment. Figure taken from [6].

Through Equation (3) the thickness can now be calculated from the minima and maxima in the measured interference pattern. A Wolfram Mathematica 9.0 script was used to do this automatically. All were manually checked. Some input was needed for this calculation. The angle of incidence $\theta_i$ is the angle of the laser on the drying layer.
(15°). To estimate the refractive index $n$ of the drying layer, volume fractions of all components were used in combination with their respective refractive indices. The drying layer thickness $d_{end}$ was measured with a Veeco Dektak 150.

To get proper light reflection at the back of the substrate, silicon substrates (Si-Mat, 525 μm thickness with 200 nm SiO₂ layer) were used as can be seen in Figure 11a. Cleaning process and “cell production” were performed exactly the same as described in paragraph 3.1. However, to improve wetting of the PEDOT:PSS, the UV-ozone treatment was replaced with 15 min air plasma treatment in a Diener Femto PCCE operating at full power.

### 3.3 Interference and transmission experiments

For these measurements glass substrates were used, as indicated in Figure 11b. These were cleaned similar to the process described in paragraph 3.1. To have a reflecting layer for the laser, a titanium oxide layer was prepared using a sol-gel method. A mixture of 75 μL acetylacetone (99+%, Acros), 217.5 μL titanium(IV) isopropoxide (97%, Aldrich) and 3.0 mL 2-propanol was spincoated at 2000 RPM and then baked at 400°C for 1 hour. Then, a latex-based white paint was spincoated on the back of the substrate at 800-1000 RPM. The purpose of this white paint is to reflect and scatter the light from an added halogen lamp.

Apart from the halogen lamp, a lens, fiber optic cable and extra photodiode with filter were then added to the interference setup in Figure 9. Because of the extra light from the halogen lamp, a diffuser was now attached directly to the interference photodiode to increase the signal-to-noise ratio of the collected light.

![Figure 12: Schematic view of the transmission and absorption setup.](image)

As seen in Figure 12, a lens was used to focus the light from the halogen bulb on the same area as the laser spot. To avoid influencing the measurement by heating the illuminated area, a low light intensity is to be used.
The fiber optic cable was connected to a spectrometer (Avantes Avaspec-2048x14) set to store-to-RAM mode. From the measured data an absorbance spectrum can be calculated using Equation (6). Since there is no absolute time reference during the measurement, these results cannot be linked precisely to the results of the interference measurement.

Therefore a band pass filter (800 nm, FWHM 40 nm) was placed in front of a third photodiode (Thor Labs SM1PD1A). Similar to the scattering diode in the previous experiment, this signal was amplified by a preamp and then measured by the sourcemeter. Since this diode collects light transmitted through the active layer, the decrease in this signal can be used to determine the polymer aggregation (see paragraph 2.5).

In the resulting transmission graphs the duration of polymer aggregation can be estimated as well. This is done by fitting a line through the decrease in transmission as shown in Figure 13.

![Figure 13: Example of an estimated polymer aggregation duration calculation.](image)

Estimated polymer aggregation duration $t_{agg}$ can then be calculated by:

$$t_{agg} = \frac{\Delta I}{\text{slope}}.$$  (#)

Here, $\Delta I$ is the decrease in intensity measured by the transmission photodiode. $\text{slope}$ is the slope of the linear fit.
4 Results and discussion

4.1 Solar cells

To obtain insight in the effectiveness of adding co-solvents during solar cell production, a batch of cells with various co-solvent fractions was made. The characteristics of these cells can be found in the table below. The J-V curves can be found in Figure 14.

Table 1: Characteristics of solar cells made with HD-P17 and [70]PCBM (1:2 weight ratio) at different initial oDCB concentrations. The active layers were spincoated at 2000 RPM.

<table>
<thead>
<tr>
<th>Co-solvent</th>
<th>d (nm)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% oDCB</td>
<td>119</td>
<td>2.34</td>
<td>0.82</td>
<td>0.68</td>
<td>1.31</td>
</tr>
<tr>
<td>1% oDCB</td>
<td>117</td>
<td>5.66</td>
<td>0.81</td>
<td>0.62</td>
<td>2.75</td>
</tr>
<tr>
<td>2% oDCB</td>
<td>213</td>
<td>5.01</td>
<td>0.79</td>
<td>0.49</td>
<td>1.95</td>
</tr>
<tr>
<td>5% oDCB</td>
<td>222</td>
<td>10.2</td>
<td>0.77</td>
<td>0.45</td>
<td>3.54</td>
</tr>
</tbody>
</table>

A first thing that can be noticed is the poor performance of both the 2% oDCB and the 5% oDCB solar cell. Both have a very low fill factor FF, as can be seen in Table 1 and the respective J-V curves in Figure 14. The 2% cell also has a short circuit current Jsc lower than the 1% cell.

Since the 0% and 1% oDCB cell do behave as expected, it is quite clear there are no systematic flaws in the production process described in paragraph 3.1. And as all dark
measurements in Figure 14 look normal, there is no physical defect in the malfunctioning solar cells.

The answer can probably be found in the large layer thickness $d$ of both cells (over 200 nm). As stated in paragraph 2.1 a layer thickness around 100 nm is optimal. Since all four solar cells were spincoated at the same speed, something must have gone wrong before this stage. The vials with the 2% and the 5% oDCB solutions were probably not properly closed during stirring. In this case part of the solvent already evaporated, resulting in a higher polymer/PCBM and co-solvent concentration. This explains the large layer thickness, and therefore, the low efficiency of both cells.

To investigate the influence of layer thickness on solar cell performance another batch of solar cells was made with various spincoating speeds. This time an oDCB concentration of 6% was used. According to literature this is the optimal value for HD-P17:[70]PCBM solar cells. Special care was taken of properly closing the vials. The results can be found in Table 2 and Figure 15.

Table 2: Characteristics of solar cells made with HD-P17 and [70]PCBM (1:2 weight ratio) at different spincoating speeds. With all cells an initial co-solvent concentration of 6% oDCB was used.

<table>
<thead>
<tr>
<th>Spincoating speed (RPM)</th>
<th>d (nm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>239</td>
<td>12.8</td>
<td>0.77</td>
<td>0.58</td>
<td>5.65</td>
</tr>
<tr>
<td>1000</td>
<td>160</td>
<td>12.4</td>
<td>0.78</td>
<td>0.64</td>
<td>6.23</td>
</tr>
<tr>
<td>2000</td>
<td>106</td>
<td>12.6</td>
<td>0.79</td>
<td>0.66</td>
<td>6.59</td>
</tr>
<tr>
<td>4000</td>
<td>76</td>
<td>12</td>
<td>0.8</td>
<td>0.64</td>
<td>6.18</td>
</tr>
</tbody>
</table>

Figure 15: $J$-$V$ curves of solar cells made with HD-P17 and [70]PCBM (1:2 weight ratio) at various spincoating speeds. With all cells an initial co-solvent concentration of 6% oDCB was used.
As final layer thickness $d$ depends heavily on spincoating speed, the measured layer thicknesses vary widely between cells. The optimal spincoating speed was found to be 2000 RPM. This is in line with literature\cite{8}.

It is surprising to find that the 500 RPM cell (over 200 nm layer thickness) is not greatly outperformed by the other solar cells. It does have a lower fill factor, just like the malfunctioning cells in the previous experiment. But the measured short circuit current is highest on this thickest solar cell, which is certainly not in accordance with the previous experiment. So the thicker layers do partly explain the lower fill factors measured on the 2% and 5% cell. Another explanation needs to be found for the lower short circuit current.

Since it is unknown how much chloroform and oDCB evaporated while stirring the solutions in the first batch of cells, one can only guess the fractions of main solvent, co-solvent and polymer/PCBM present in the solutions used during spincoating. This might have had an influence on the morphology of the final product. As stated in paragraph 2.1 morphology is very important for solar cell efficiency.
4.2 Interference and scattering

As explained in paragraph 2.3, an interference measurement is used to determine the layer thickness at a given point in time. Examples of interference measurements can be found in the two middle graphs in Figure 16. For these measurements the interference setup described in paragraph 3.2 was used.

![Figure 16](image.png)

*Figure 16: Examples of interference and scattering measurements as a function of time. From the interference measurement the thickness curve can be calculated. Measured while spincoating a HD-P17 solution in 1:2 weight ratio with [70]PCBM at 2000 RPM. In graph a with pure chloroform as a solvent, in graph b chloroform with 6% oDCB. Note the difference in timescale between a and b.*

Each maximum and minimum in the interference pattern in Figure 16 corresponds to either a full or a half wavelength fitting inside the spincoated layer, respectively. Through Equation (3) the layer thickness can be calculated, as shown in the upper plots in Figure 16. Two different stages of spincoating can be seen in this thickness graph (see paragraph 2.1). The curved segment of the graph corresponds to radial flow of material. The linear section that follows corresponds to the solvent evaporation phase.

The first 1.5 seconds of the interference graph in Figure 16b (with 6% oDCB) look similar to the measurement without oDCB. During this time both chloroform and oDCB evaporate. It is assumed that after this time all chloroform has evaporated and only oDCB remains to evaporate. Since oDCB evaporates more slowly than
chloroform (see paragraph 2.2), layer thickness will decrease more gently in this stage. This explains the sudden increase in time between the interference peaks and therefore the decrease in slope in the thickness graph.

The scattering graphs with and without co-solvent are shown on the bottom in Figure 16. Note the clear difference in scattering voltage measured with and without co-solvent. It must be said these two measurements were not performed on the same day, so the setup may have been altered slightly. This does, however, not explain an entire order of magnitude difference between the measurements. And since both measurements had the preamp set to the same amplification, it is concluded that the sample without co-solvent scatters much more light than the sample with co-solvent. This is due to the large domains of donor and acceptor that are formed when no co-solvent is added and liquid-liquid phase separation occurs (see paragraph 2.1).

Because layer thickness still decreases during oDCB evaporation, the scattered light beams interfere with each other. Therefore an interference pattern arises in the scattering voltage measured when spincoating with oDCB (bottom-right graph).

The precise onset of scattering can now be taken from the scattering graphs. Then, through Equation (4) and an interpolation of the thickness curve, the volume fraction of solvent (note this is both main solvent and co-solvent) is calculated.

First this was performed for both HD-P17 and DT-P17 in pure chloroform to determine the solvent content where liquid-liquid phase separation occurs. Various spincoating speeds and two different initial polymer/acceptor concentrations were used. The results are shown in the Figure 17.

![Figure 17](image)

**Figure 17:** Total solvent content at the onset of scattering when spincoating at various speeds and with different initial P17 concentrations, as indicated in legend. In graph a HD-P17 is used and the values have an average of 82 ± 4 %. In graph b DT-P17 is used. These values have an average total solvent content of 84 ± 2 %. All are mixed in a 1:2 weight ratio with [70]PCBM.

As can be seen in Figure 17, spincoating speed, initial concentration and polymer side chain length have no significant influence on the solvent fraction where liquid-liquid phase occurs. A combined average value of 83 ± 4 % is found, which is in accordance with literature on a different DPP-based polymer\(^6\).
4.3 Interference and transmission

To determine the onset of polymer aggregation, transmission measurements were performed (see paragraph 2.5 and paragraph 3.3). Again this was combined with interference measurements to determine the layer thickness as a function of time. Some exemplary results can be found in Figure 18.

Since DIO evaporates very slowly (see paragraph 2.2), hardly any DIO evaporated while spincoating. Therefore the final dry layer thickness is not reached during the
measurement. It is assumed no DIO evaporated in the chloroform evaporation stage. This means polymer/acceptor/DIO fraction in the last data point of the thickness curve is the same as the initial fraction.

The waves visible in both oDCB measurements are (just like in the previous paragraph) an interference pattern. Because layer thickness is still decreasing as oDCB is evaporating, interference occurs in the transmitted light. This effect cannot be seen in the DIO measurement, because of the slow evaporation of this co-solvent. The waves are too slow to be seen on this timescale.

What can be seen in the graph is that samples with HD-P17 generally have a larger relative decrease in transmission than DT-P17 (~20% vs ~10%). This difference was present in all measurements. As can be seen in Figure 7 HD-P17 has a slightly larger redshift in its absorbance spectrum. More absorbance means less transmission, which explains the larger decrease in transmission.

Because the decrease in transmission indicates polymer aggregation, Figure 18 already shows that polymers aggregate at higher layer thicknesses when co-solvents are used. Thicker layers indicate that more solvent is still present in the layer. To obtain more insight in what happens, both transmission and scattering are combined. The results can be found in Figure 19.
Figure 19: Total solvent content at the onset of scattering and during decrease in transmission. Determined for both HD-P17 and DT-P17 mixed with [70]PCBM (1:2 weight ratio) with various co-solvents.

In Figure 19 the red circles correspond the onset of scattering, which indicates phase separation. The black squares correspond to the decrease of transmission, which indicates polymer aggregation. Because pinpointing the exact onset of the decrease in transmission is difficult, the solvent content halfway during the decrease is used. The error bars of this so-called 50% point now indicate the area where polymer aggregation is clearly taking place.

The relatively large error bars in column 1 and 4 can be explained by the large layer thickness sensitivity in this area. During the last 100 nm decrease of layer thickness, the total solvent content drops from ~50% to 0%.

In both cases without co-solvent, scattering clearly occurs before the decrease in transmission. When a co-solvent is added, scattering and decrease in transmission occur at more or less the same time, as can be seen in column 2, 3 and 5. In all measurements the point of decrease in transmission lies slightly below the onset of scattering. This is because the 50% point described earlier is used, whereas the point of scattering is really taken at the onset.

This indicates that, when no co-solvent is used, liquid-liquid phase separation occurs before the polymers aggregate, resulting in large domains of polymer and PCBM. When a co-solvent is used, the polymers aggregate before this can happen. By doing so large scale liquid-liquid phase separation is prevented. Since polymer aggregation is phase separation as well, this is what causes the light to scatter. The smaller domains that arise this way explain the smaller scattering signals discussed in paragraph 4.2 and this confirms the model discussed in paragraph 2.1.
It does, however, not clarify why HD-P17 has optimal performance with oDCB and DT-P17 with DIO as a co-solvent \cite{8}. For further investigation atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used. The resulting images are presented in Figure 20.

Figure 20: TEM (top) and AFM (bottom) images of samples with both HD-P17 and DT-P17 mixed with [70]PCBM (1:2 weight ratio). All were spincoated at 2000RPM. The bottom-right TEM-image shows a higher magnification of the sample with DT-P17 and 6% oDCB (top-right image). TEM done by J. J. van Franeker. In the AFM images the width is 5.0 μm and the vertical scale length is 80.0 nm.
The samples without co-solvent show the typical large domains of polymer and PCBM resulting from early liquid-liquid phase separation. In the images made from the samples with the optimally processed polymers (HD-P17 6% oDCB and DT-P17 5% DIO) one can immediately see the difference in size of the fibers. This explains the difference in efficiency between the two. When processing DT-P17 with 6% oDCB this leads to even bigger fibers, explaining the even lower performance. It is certain polymer aggregation did occur, as the lamellar stacking of the polymer can be seen clearly in the higher magnification (bottom-right image).

So from both Figure 19 and Figure 20 it can be concluded that by adding either oDCB or DIO, large scale liquid-liquid phase separation can be prevented. For some reason, however, the size of the fibers is quite different. Apparently something different happens during the drying of the spincoated layer. Some slight differences can be found in the measured absorbance spectra in Figure 21.

![Absorbance spectra of HD-P17 and DT-P17 with various co-solvents. Calculated at various times: before, during, just after and longer after polymer aggregation. Each line is an average of the five surrounding measurements at given time.](image)

Figure 21: Absorbance spectra of HD-P17 and DT-P17 with various co-solvents. Calculated at various times: before, during, just after and longer after polymer aggregation. Each line is an average of the five surrounding measurements at given time.

In all spectra similar behaviour occurs. As the polymers aggregate the absorbance spectrum shifts to the longer wavelengths. This is in accordance with literature [6] (see paragraph 2.5). The samples do differ, however, in the duration of this process (~0.22
s for DT-P17 in pure chloroform, ~0.87 s for 5% DIO and ~1.30 s for 6% oDCB). It seems that, without co-solvents, the duration of polymer aggregation is the shortest. This is probably because chloroform evaporates more rapidly than oDCB and DIO (see paragraph 2.2).

However, when co-solvents are used, faster polymer aggregation apparently leads to smaller fibers. But since there is no absolute time known during the absorbance measurement, this duration remains imprecise.

In an attempt to obtain some more accurate estimations of these values the polymer aggregation duration was calculated as described in paragraph 3.3. The results can be found in Figure 22.

![Figure 22: Calculated polymer aggregation duration $t_{agg}$ of HD-P17 and DT-P17 with various co-solvents. Calculated as described in paragraph 3.3.](image)

In Figure 22 a similar pattern to Figure 21 can be identified. The fastest polymer aggregation occurs without co-solvents. This is, as stated previously, most likely caused by the fast evaporation of chloroform. As before, with co-solvents it seems that as the duration of aggregation decreases, the fiber size decreases.

A possible explanation for the slower aggregation is that the polymer partly dissolves in the oDCB. This fragment of polymer will only aggregate during oDCB evaporation.

The clear mismatch between the two values found for DT-P17 in pure chloroform does, however, cause some doubt. Perhaps the method used is not ideal to calculate the polymer aggregation duration. Nevertheless, it is an indication towards the importance of the aggregation duration. To be able to give conclusive evidence on this subject, further research is needed.
5 Conclusion

For solution-processed bulk-heterojunction polymer solar cells, the morphology of the active layer is very important for optimal performance. To obtain optimal morphologies, co-solvents are often used.

To determine the role which these co-solvents play during the drying of the active layer, three relatively simple experiments can be used. A basic laser interference setup is used to determine the thickness of the active layer during spincoating as a function of time. This experiment is combined with a scattering experiment to determine the onset of phase separation. For DPPTPT polymers mixed with [70]PCBM in chloroform, the onset of liquid-liquid phase separation is found to be at 83 ± 4% total solvent content. This is independent of side chain length, spincoating speed and initial polymer concentration.

The onset of polymer aggregation is determined with a transmission and absorption setup. It is found that without co-solvent the polymer aggregation occurs after liquid-liquid phase separation, resulting in large domains and therefore low-efficiency solar cells. However, when co-solvents are used, polymer aggregation is found to occur before large scale liquid-liquid phase separation can occur. This is possibly due to the increased viscosity caused by the polymer aggregation. Since donor and acceptor domains are now smaller, more charge separation can take place. This explains the higher efficiencies of solar cells processed with co-solvent.

It is known that HD-P17 performs better with oDCB as a co-solvent, whereas DT-P17 is better when processed with DIO. The experiments show that the difference in efficiency follows from a difference in fiber size, which in turn might result from the duration of polymer aggregation. Therefore a possible important role for duration of aggregation is indicated. However, for a more thorough understanding on this subject, more research on the drying process is necessary.
6 References


