

Electron microscopy and spectroscopy
of all-polymer solar cell active films
Correlating fabrication parameters to microstructure

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Cover:

Bright field TEM image at $-10\mu\text{m}$ defocus of a film of TQ1:N2200 in a ratio of 1:1 spin coated using o-DCB, showing fibrillar structures in the film.

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Abstract

This work concerns the microstructure of all-polymer solar cell active films, where the active film of an all-polymer solar cell is the photoactive polymer layer used to harvest light. The morphology of the active film is important for the efficiency of the solar cells. Both charge separation, facilitated by smaller domains with more interfaces, and charge carrier mobility, improved by crystalline domains in the material, are of importance.

The films in this work consist of the two polymers TQ1 and N2200. Active films spin coated from different solvents are compared as well as films with or without thermal annealing. The active films containing both polymers in a bulk heterojunction are also compared to films of a single polymer spin coated from the same solvents.

The films were studied by transmission electron microscopy using bright field imaging and electron diffraction. Scanning electron microscopy and atomic force microscopy were also used to image the surface structure of the films.

It was found that films of pure N2200 spin coated using ortho-dichlorobenzene or chloroform were crystalline as evidenced by electron diffraction. The films spin coated with ortho-dichlorobenzene showed a fibrillar structure on the surface. This was in agreement with what was previously known about solution processed films of N2200.

For the bulk heterojunctions it was found that films spin coated with chloroform crystallised during thermal annealing whereas thermal annealing did not seem to affect the films spin coated with ortho-dichlorobenzene which showed crystalline order in both as-spun and annealed films.

The data from the bulk heterojunctions showed that the morphology of the films spin coated with chloroform had features on a smaller length scale when compared to films spin coated with ortho-dichlorobenzene. This will affect the power conversion efficiency of devices made of these films, as both features on a smaller length scale and crystalline domains are favourable.

Keywords: All-polymer solar cells, TQ1, N2200, bulk heterojunction, spin coating, TEM, SEM.

Contents

1	Introduction	1
1.1	Background	1
1.1.1	Solar cells	1
1.1.2	Organic photovoltaics	2
1.1.3	Organic solar cells	3
1.2	Scope	6
1.3	Purpose	6
2	Experimental section	9
2.1	Materials	9
2.1.1	TQ1	9
2.1.2	N2200	10
2.2	TQ1:N2200 based solar cells	12
2.2.1	Film manufacturing	13
2.3	Techniques for imaging	14
2.3.1	Electron microscopy	14
2.3.2	Transmission electron microscopy (TEM)	15
2.3.3	Scanning electron microscopy (SEM)	17
2.3.4	Atomic force microscopy (AFM)	17
3	Single polymer films	19
3.1	Film morphology	19
3.2	Crystalline order	23
3.3	Electron energy loss spectroscopy	29
4	Bulk heterojunctions	31
4.1	Film morphology	31
4.1.1	Chloroform	31
4.1.2	o-DCB	32
4.1.3	p-Xylene	39
4.2	Crystalline order	42
4.2.1	Chloroform	42
4.2.2	o-DCB	42
5	Beam induced effects	47
5.1	The effect of the electron beam on N2200	47
5.2	Bulk heterojunctions	47

6	Discussion	53
6.1	Conclusions	53
6.2	Outlook	54
7	Acknowledgements	57
A	List of samples	61
B	Polymers	63
B.1	Crystalline polymers	64
B.2	The glass transition	64

List of abbreviations

AFM	Atomic force microscopy
DCBM	Dichlorobromomethane
DP	Diffraction pattern
EELS	Electron energy loss spectroscopy
EF-TEM	Energy filtered transmission electron microscopy
FEG	Field emission gun
FET	Field effect transistor
o-DCB	ortho-Dichlorobenzene
PCE	Power conversion efficiency
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy

Chapter 1

Introduction

The worldwide energy consumption continues to rise, leading to an increased exploitation of available energy sources. In 2011, 22 126 TWh worth of electricity was generated in the world, an increase with approximately 260% from 1973 [2]. 68% of this electricity was produced from fossil fuels (coal, oil and natural gas), the remaining electricity was produced by nuclear power (11.7%), hydro power (15.8%) and other sources (4.5%, including among others wind energy and solar energy) [2].

The amount of electricity produced by renewable or non-fossil fuels has increased during the last decades, but the share of electricity produced by these fuels decreased between 1995 and 2011 mainly due to increased use of coal for energy production [1].

Coal and other fossil fuels are non-renewable sources of energy and a finite resource. It is therefore necessary to increase the amount of energy produced from renewable sources. One such renewable energy source for producing electricity is solar cells that use energy extracted from solar radiation. Solar cell technology is responsible for an increasing portion of the generated electricity and was the fastest growing renewable energy technology in the world between 2000 and 2011 [3].

It is possible to further increase the amount of energy produced by solar cells, especially if it is possible to produce cheaper and more efficient devices. For cheap devices, organic solar cells based on semiconducting molecules are an interesting option. This work is focused on a specific type of organic all-polymer solar cell.

1.1 Background

Here follows a description of solar cells in general and organic solar cells in particular.

1.1.1 Solar cells

Solar cells use the electromagnetic radiation from the sun to produce electricity. Conventional solar cells have a photoactive layer of inorganic material, commonly semiconducting silicon. These inorganic solar cells can reach efficiencies above 40% in state of the art multijunction devices, and above 20% for silicon based devices with a simpler geometry [21]. Commercial devices are generally in the range of 10 to 20% efficiency.

The power conversion efficiency, PCE, of a solar cell is calculated as the ratio

between the produced electrical energy and the energy of the incoming solar radiation.

Inorganic solar cell technology faces problems with manufacturing of materials and exhaustion of scarce natural elements. The energy required to produce many of the semiconducting materials used in inorganic solar cells is significantly larger than the energy required to produce metallic materials or plastics. This along with the fact that the sources of gallium and indium, two common components in semiconductor technology, have been estimated to run out in 20 years [13] gives a strong driving force for the development of new technologies that eliminate or minimise the need for inorganic semiconducting materials.

1.1.2 Organic photovoltaics

Organic photovoltaics are based on organic materials with optoelectronic properties and include for example organic solar cells and organic light emitting diodes (OLEDs).

Conducting polymers

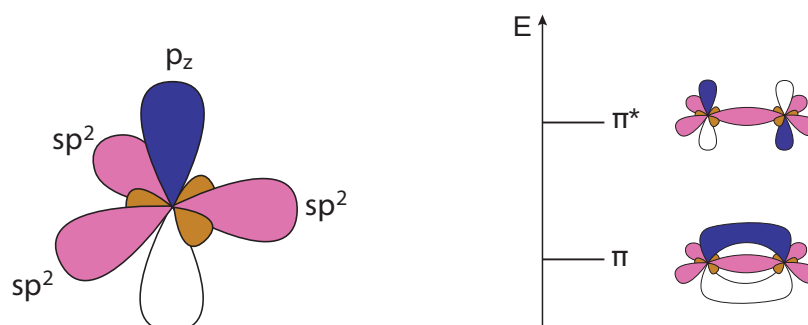
A brief introduction to polymers and polymeric materials can be found in Appendix B.

Polymers are molecular compounds and most of them are therefore electrical insulators [5]. This can be attributed to the fact that the valence electrons in the majority of covalently bonded molecular materials are localised at a specific bond and are therefore not free to conduct electricity [5]. However, there are exceptions. In 2000, the Nobel Prize in chemistry was given to Heeger, MacDiarmid and Shirakawa "for the discovery and development of conducting polymers" [12].

For it to be possible for a molecular compound to conduct electricity there must be delocalised electrons in the molecules. Common for most conducting polymers are sp^2 -hybridised carbon atoms, see Figure 1.1a, along the backbone of the chain. This is often seen as a structure of alternating single and double bonds along the chain. In reality the unhybridised p_z -orbital on one carbon atom does not simply form a bond with the p_z -orbital on one of the adjacent carbon atoms. The p_z -orbital interacts with all adjacent p_z -orbitals forming a bonding π -orbital, allowing electrons to be delocalised over the entire chain of sp^2 -hybridised atoms[5], or an anti-bonding π^* -orbital, see Figure 1.1b. The sp^2 -hybridised carbon atoms are commonly mixed with sulphur and nitrogen atoms in the chain [5].

Upon absorption of energy, electrons may be excited from the the bonding π -orbital, which forms the HOMO-level of the polymer, to the anti-bonding π^* -orbital, which forms the LUMO level of the polymer [12]. In this way energy can be harvested from the incoming solar radiation.

One clear advantage of using organic material in photovoltaics, or organic electronics in general, is the possibility to tune electronic properties by mixing materials [19].



(a) Orbitals of an sp^2 -hybridised carbon atom. (b) Energy diagram with the bonding π -orbital and the anti-bonding π^* -orbital.

Figure 1.1: Orbitals of the sp^2 -hybridised carbon and a sketch of an energy diagram showing the bonding π -orbital and the anti-bonding π^* -orbital. Note that in a polymer the π -orbital is extended over the entire conjugated backbone.

1.1.3 Organic solar cells

Organic solar cells have a photoactive layer of organic semiconductors, also known as the active layer or active film of the device, that is used for harvesting solar energy.

Organic solar cells have several advantages when compared to inorganic ones. One of these is the low production cost because of the possibility to use solution processing at room temperature for manufacturing of the active film [18]. Depending on substrates and electrodes they may also be lightweight and flexible [9]. Organic solar cells also don't require sparse elements in the same way that inorganic solar cells do.

Organic semiconductors have high extinction coefficients allowing thin active films of about 100-200 nm because of the relatively high absorption of solar radiation [18]. Thin films are also required because of the low electron mobility of organic materials, generally on the order of 10^{-4} cm²/Vs [12], which is one of the limiting factors in organic solar cells.

Organic solar cells absorb light by creating a bound electron-hole pair, a Frenkel exciton. Excitons in organic semiconductors usually have a binding energy that exceeds the thermal energy by one order of magnitude [26]. This means that the thermal energy of the material will not be enough to separate the electron and hole.

Once an exciton has been created there are several different possible scenarios [19]:

- Transfer of charge between a donor material and an acceptor material. Dissociation of the exciton into free carriers, an electron and a hole.
- Transfer of energy to the lower band gap material in a blend and radiative recombination.
- Non-radiative recombination.

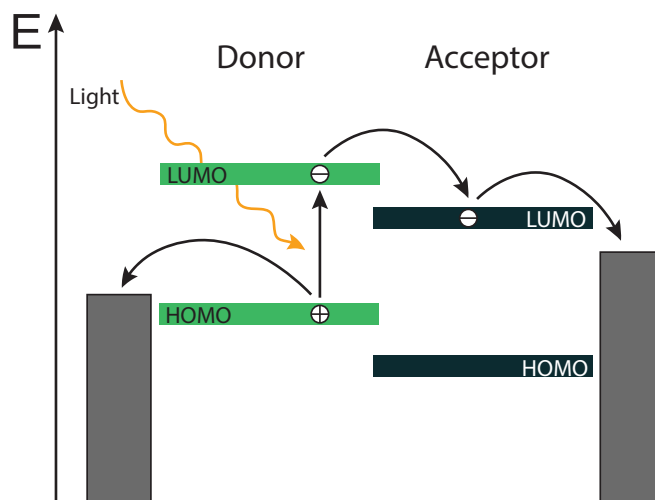


Figure 1.2: Sketch of the creation of a free electron and a hole and the successful separation of these and transport to the electrodes. The image shows absorption in the donor, but absorption may also occur in the acceptor with hole transfer to the donor.

Only the first scenario is desired in solar cell applications. Large differences in band gap favours energy transfer whereas smaller differences favour charge transfer [19].

Exciton dissociation in organic solar cells is achieved by transfer of an electron from a donor molecule with low ionization potential to an acceptor molecule with high electron affinity [26], see Figure 1.2. When the differences in ionization energy and electron affinity between donor and acceptor is larger than the exciton binding energy, which generally ranges between 0.1 and 1 eV [12], exciton dissociation is energetically favourable at the interface [19].

The further separation of charge carriers after exciton dissociation is driven by the difference in work function between the anode and cathode giving an internal electric field across the photoactive organic layer [12].

To get a functioning solar cell, excitons must be able to reach a donor-acceptor interface before the charge carriers recombine. Since the exciton diffusion length is commonly in the range of 5 to 20 nm in organic semiconductors [12], there must be an interface within 5 to 20 nm from the position where the exciton is created. The free charge carriers must also have continuous percolation paths to the relevant electrode to avoid trapping of charges on isolated domains [12]. Charge recombination and trapping leads to losses in solar cell efficiency. Therefore the microstructure on a nanoscale of the active film is very important for the power conversion efficiency of the organic solar cell.

A common way to achieve a favourable morphology is to use a bulk heterojunction, which contains random domains of the two polymers throughout the whole structure, see Figure 1.3.

Several parameters affect the microstructure of an organic film. Some of them are [26]:

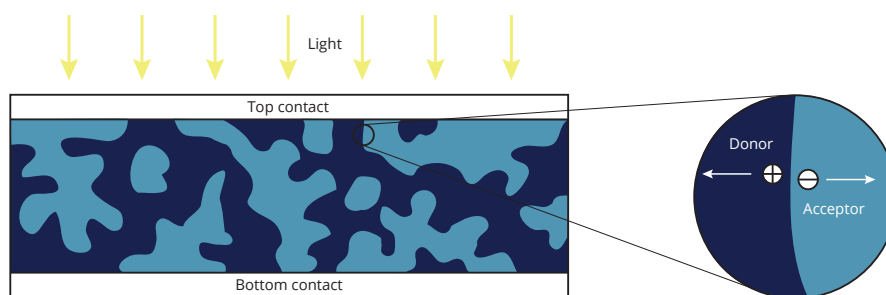


Figure 1.3: Sketch of a device with bulk heterojunctions, showing the charge separation that occurs at the interface between donor and acceptor. The top contact is transparent to allow light to reach the active layer.

- The chemical structure of the donor and the acceptor.
- The solvent that is used to dissolve the materials for processing.
- The concentration of the materials in solution during the processing.
- The donor/acceptor ratio.
- The choice of post production treatments, such as thermal annealing at different conditions and exposing the resulting film to different solvents.

The three most common types of organic (or semiorganic) solar cells are:

- **All-polymer solar cells:** Both donor and acceptor are polymers, see more in Section 1.1.3.
- **Polymer/fullerene solar cells:** A polymer is used for donor material and a buckminsterfullerene, or more commonly a derivative commonly known as PCBM, or [6,6]-phenyl-C61-butyric acid methyl ester, is used as the electron acceptor. PCBM is more widely used because it is easier to dissolve in common organic solvents [12].
- **Polymer/nanoparticle solar cells:** A polymer is used as a donor material and inorganic nanoparticles are used as acceptor material.

So far the polymer/fullerene system has reached the highest power conversion efficiencies of approximately 8% [18]. All-polymer systems can have power conversion efficiencies of about 2% and polymer/nanoparticle systems have shown efficiencies of about 3% (numbers from 2012) [18]. It is estimated that power conversion efficiencies of about 10% should be reachable for materials with optimised energy levels, charge carrier mobilities and morphology [26].

All-polymer solar cells

Despite the lower power conversion efficiencies, all-polymer solar cell still have some advantages over polymer/fullerene systems.

One such advantage is the possibility to improve absorption by tuning the polymers to absorb in different parts of the solar spectrum, whereas fullerenes generally absorb poorly [26]. Solution processability may also be easier with all-polymer systems because of the possibilities to easily change the solution viscosity [9].

One of the problems that all-polymer solar cells face is low electron mobilities due to, for example, large portions of amorphous material. By using polymers and conditions such that crystalline structures may be formed in the film the mobility may be increased, but the mobility may also get anisotropic, which is why the orientation of crystalline regions may become important.

Morphology of all-polymer solar cell films

Long polymer chains do not normally gain enough entropy by mixing for a homogeneously mixed phase to be energetically favourable [19], therefore the thermodynamically stable situation should involve a phase separation.

The kinetics of film manufacturing may, however, not allow for thermodynamic equilibrium to be reached. If the solvents evaporate fast enough the polymer chains may be frozen in a morphology that does not correspond to thermodynamic equilibrium [18]. Annealing may then give the film opportunity to approach a more thermodynamically favourable morphology [26]. Thermal annealing is also good for mimicking conditions under which the device may have to operate [26].

It is believed that an ordered structure of the film is favourable. An ordered structure is assumed to give better charge transport and larger delocalisation of charge carriers [24]. There have been indications that also the relative direction of the crystallites in donor and acceptor is important for the efficiency. In a system of the two polymers P3HT (donor) and N2200 (acceptor) it was found that the charge dissociation was more efficient if the polymer chains in the crystal grains on adjacent sides were parallel at the interface between donor and acceptor [24].

1.2 Scope

In this work one specific type of all-polymer solar cell active film is investigated focusing on the microstructure of the film.

The specific films were spin coated with the polymer TQ1 as donor material and the polymer N2200 as acceptor material. Several parameters from the manufacturing of the films may affect the microstructure, including solvent, polymer concentration, spin speed and post production treatments. This work focuses on studying the effects of different solvents and thermal annealing.

The investigations were carried out mainly by transmission electron microscopy (TEM) using imaging and electron diffraction. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) was used for studies of the surface structure of the films.

1.3 Purpose

The purpose of this work is to investigate the microstructure of spin coated all-polymer solar cell active films consisting of TQ1 and N2200. The effect of the

solvent used for spin coating and the post production thermal annealing on the microstructure is studied. An important factor for the solar cell performance is the length scale of the microstructural domains rich in TQ1 or N2200 where a small scale is preferable to achieve a more efficient separation of the charge carriers excited by the incoming solar radiation. Particular attention is paid to the possibility to control the characteristic length scale by varying the solvent and by post production thermal annealing.

Chapter 2

Experimental section

This chapter focuses on the materials and experimental techniques that were used to study the solar cell films.

2.1 Materials

Here follows a description of the two polymers used for the bulk heterojunctions in this work. Both TQ1 and N2200 have previously been successfully used in combination with other organic semiconductors in solar cells.

2.1.1 TQ1

The polymer TQ1, or poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] is a semiconducting polymer [11] whose backbone consists of alternating thiophene and quinoxaline groups, see Figure 2.1. It is possible for thiophene to donate an electron to quinoxaline during excitation [10], allowing for absorption of low energy photons [11]. Some data on TQ1 is found in Table 2.1.

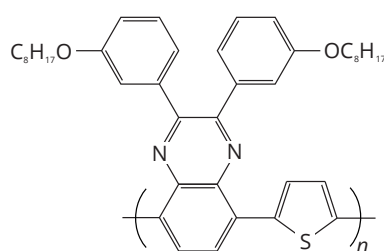


Figure 2.1: Structure of one monomer unit of TQ1 with the alternating quinoxaline and thiophene groups.

In its reduced state, TQ1 absorbs in two regions of the solar spectrum of electromagnetic radiation. The first absorption region is in the UV-part of the spectrum with only minor tailing into the visible region, the second absorption region is at lower energy and centred around the red region [11]. In Figure 2.2 the absorbance of

Table 2.1: Data on the TQ1 polymer.

Optical band gap:	1.8 eV
Charge carrier mobility (holes):	$10^{-5} \text{ cm}^2/\text{Vs}$ [4] (FET)
Monomer molecular weight:	618.9 g/mol

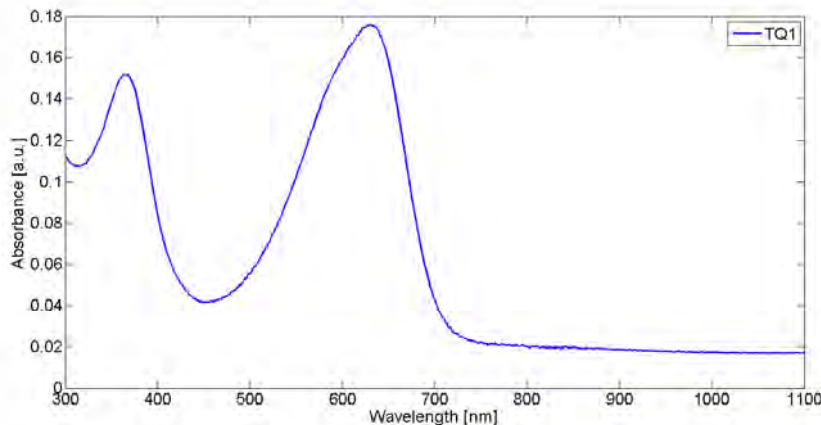


Figure 2.2: Absorbance spectrum of TQ1.

TQ1 is shown¹. TQ1 absorbs light at longer wavelengths than many other polymers used for photovoltaics [10]. The state of the polymer is easily detected optically since the reduced state has an intense blue color [11].

The TQ1 used in this work was synthesised at Polymer Tecnology, Chalmers university of Technology. It had a number-average molecular weight of 76 kg/mol and a polydispersity index of 2.6².

2.1.2 N2200

Polyera ActivInkTMN2200, or poly(N,N-bis-2-octyldodecyl-naphtalene-1,4,5,8-bis-dicarboximide-2,6-diyl-alt-5,5'-2,2'-bithiophene), is also known as P(NDI2OD-T2)³. For a semiconducting polymer, N2200 has a high electron mobility [25], and is therefore expected to perform well in organic photovoltaics. It is one of the few acceptor or electron conducting polymers with good performance in ambient conditions [7]. Some data on N2200 is found in Table 2.2.

The polymer backbone consists of the co-monomer NDIR, N,N'-dialkylnaphtalene-dicarboximide, and two connected thiophene groups. The NDIR co-monomer has a high electron affinity [7] and ensures an electron depleted electronic structure of the polymer [28].

Thin polymer films of N2200 have their main absorption of light at a wavelength

¹Measured by Amaia Diaz de Zerio Mendaza at Polymer Technology, Department of Chemical and Biological Engineering, Chalmers University of Technology.

²Values measured by Amaia Diaz de Zerio Mendaza at Polymer Technology, Department of Chemical and Biological Engineering, Chalmers University of Technology. The molecular weight was determined by size exclusion chromatography (SEC) with an Agilent PL-GPC220 instrument calibrated relative to polystyrene.

³Hereafter known as N2200

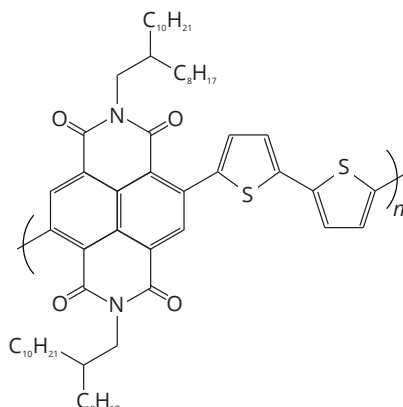


Figure 2.3: Structure of one monomer unit of N2200.

Table 2.2: Data on the N2200 polymer.

Optical band gap:	1.45 eV [7]
Charge carrier mobility (electrons):	0.85 cm ² /Vs [6] (FET)
Monomer molecular weight:	989.4 g/mol
Electron affinity:	-4 eV [24]

of 391 nm, in the violet region of visible light, and 697 nm, in the red region of visible light [7].

The N2200 used in this work was purchased from Polyera Corporation and had a number-average molecular weight of 33 kg/mol⁴.

Morphology of films of N2200

Previous studies of the morphology of N2200 films made use of both atomic force microscopy and x-ray diffraction. Atomic force microscopy have shown the presence of fibrillar structures at the film surface [28].

Studies using both grazing incidence x-ray diffraction and specular x-ray diffraction have shown that films of N2200 mainly have face-on packing⁵ [23]. This makes N2200 unique among polymers with high mobility where it is more common with edge-on packing⁶.

Several different diffraction peaks were found using high resolution grazing in-

⁴Value measured by Amaia Diaz de Zerio Mendaza at Polymer Technology, Department of Chemical and Biological Engineering, Chalmers University of Technology. The molecular weight was determined by size exclusion chromatography (SEC) with an Agilent PL-GPC220 instrument calibrated relative to polystyrene.

⁵Face-on orientation corresponds to the situation where the polymer backbone is oriented parallel to the substrate plane and the π - π -stacking is perpendicular to the substrate plane.

⁶Edge-on oriented crystal domains corresponds to the situation where the polymer backbone is oriented perpendicular to the substrate plane and the π - π -stacking is parallel to the substrate plane.

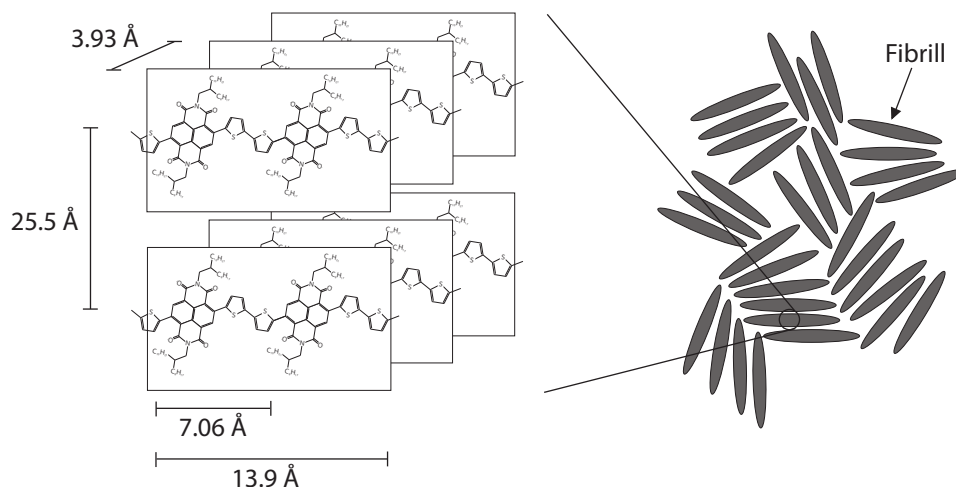


Figure 2.4: The different crystal planes in N2200 crystal structures and a schematic sketch of the fibrils in an isotropic film [23]. The π - π -stacking is the distance that measures 3.93 Å.

cidence x-ray diffraction on spin coated films of N2200 with ortho-dichlorobenzene (o-DCB), some of which are represented as distances in the polymer crystal in Figure 2.4 [23]. The π - π -stacking reflection was determined to be 3.93 Å. Depending on whether the incident x-ray beam was parallel with or perpendicular to the long axis of the fibrills, different scattering peaks were observed [23].

The diffraction data obtained when the incident x-ray beam was parallel with the fibrillar structures show diffraction from the backbone repeat of the chain. These lengths were found to be 13.9 Å and 7.06 Å [23]. For the situation when the incident x-ray beam was perpendicular to the fibrillar structures, peaks that correspond to the stacking of chains were found, giving a chain stacking distance of 25.5 Å [23].

Both from atomic force microscopy and analysis of x-ray diffraction patterns the short axis of the fibrills was found to be 10-30 nm [23].

2.2 TQ1:N2200 based solar cells

Solar cells fabricated from TQ1:N2200 blends in a 7:3 ratio dissolved in a chloroform solution and spin coated have been found to have power conversion efficiencies of up to 4.1% [20], for an all-polymer active film this is a very high value.

The ratio between the two polymers in the active layer has been found to play an important role in the performance of the solar cell. For a ratio of 1:1 the PCE is reduced to 3.4%, which is still a high value for an all-polymer system [20].

Atomic force microscopy has previously been performed on spin coated films of TQ1:N2200 with chloroform in a 1:1 ratio, where no distinct phase separation was observed[20].

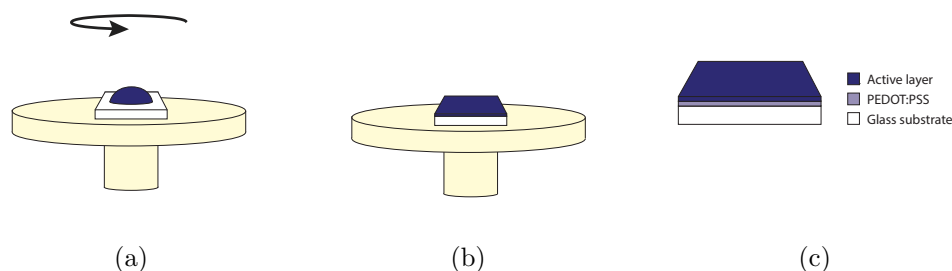


Figure 2.5: The principle of spin coating showing (a) the drop of solution on the substrate before the spinning starts and (b) the resulting thin film. Finally the sample with the PEDOT:PSS and the active layer of polymer in (c).

2.2.1 Film manufacturing

Films from TQ1 and N2200 are spin coated on glass substrates having a spin-coated buffer layer of poly(3,4-ethylenedioxy-thiophene):poly-(styrene-sulfonate), PEDOT:PSS.

The layer of PEDOT:PSS is usually inserted between the active layer of polymers and the transparent electrode. This water soluble buffer layer is included because it has been found to increase the overall PCE of the solar cell device by modifying the interface to the active layer [15].

Before spin coating, the glass substrates are cut in pieces and washed by ultrasonication for 5 minutes in acetone followed by 5 minutes in iso-propanol. The substrates are thereafter rinsed individually in (one by one): distilled water, acetone, DCBM and iso-propanol, and thereafter dried in air. The substrates are placed in an oven for 10 minutes to dry completely.

The PEDOT:PSS-layer is spun by placing 100 or 200 μL of PEDOT:PSS in solution on the substrate followed by spin-coating at a speed of 3000 rpm for 1 minute. The PEDOT:PSS coated substrates are then annealed on a hot-plate at 140°C for 20 minutes and allowed to cool before the polymer layer is spun.

Spin coating is used to obtain a thin film by rapid rotation of the substrate with solution on it, see Figure 2.5. The rapid rotation leads to disposal of excess solution, reducing the thickness of the film, and evaporation of the remaining solvent due to convective mass transport. When the solvent evaporates the viscosity of the film increases and this hinders the thinning process and also locks the polymers in a non-equilibrium morphology once all solvent has evaporated, known as solvent quenching [8].

For dissolving the polymers into solution either of three different solvents are used: chloroform, ortho-dichlorobenzene (o-DCB) or para-xylene (p-xylene). The molecular structure for each solvent can be seen in Figure 2.6. Chloroform and o-DCB were the main solvents used in this work, they were chosen because they are both common solvent used in organic solar cell manufacturing. Chloroform was particularly interesting since films spin coated from solution in chloroform have previously reached relatively high power conversion efficiencies.

The polymers are dissolved in the chosen solvent in total polymer concentrations ranging from 5 mg/mL to 12 mg/mL. The solutions are kept at 60°C prior to spin-

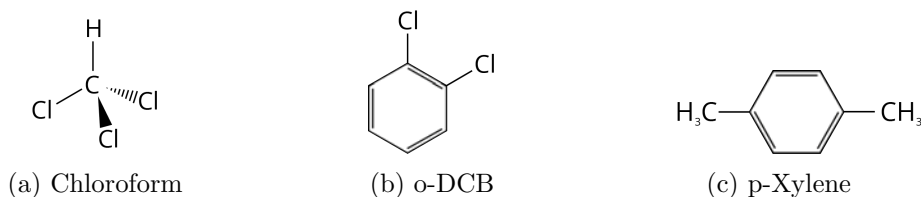


Figure 2.6: Solvents used.

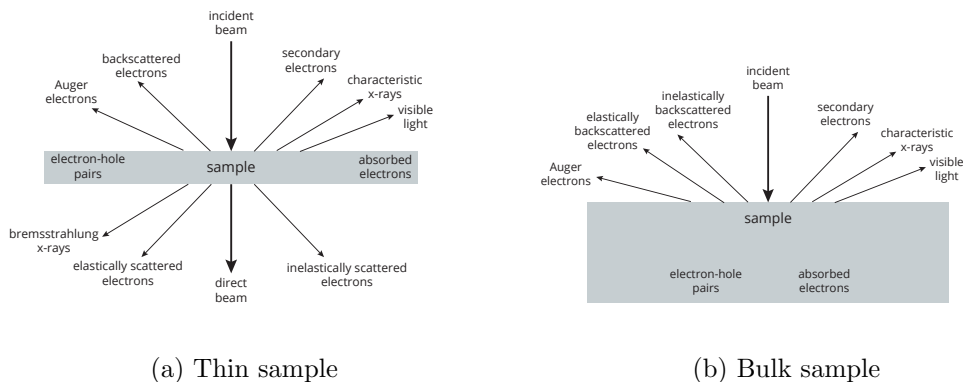


Figure 2.7: The signals produced when hitting a sample with electrons.

coating to ensure that all of the polymer dissolves.

An amount ranging between 80 and 200 μL of the polymer solution is placed upon the glass substrate on the PEDOT:PSS coated side and spin coated. The parameters of the spin coating differ depending on the solvent because of the difference in viscosity of the solutions. The spin speed is also varied depending on the intended thickness of the film, where a larger number of rotations per minute give a thinner film. A full list of samples with spin speeds and spin times can be found in Appendix A.

The film is stored on the substrate and out of reach for sunlight to avoid degradation.

2.3 Techniques for imaging

Different imaging techniques provide different information about the structure of the sample. In this work the major technique used has been transmission electron microscopy, TEM. Scanning electron microscopy, SEM, and atomic force microscopy, AFM, have been used as complementary techniques providing information about the surface structure of the films.

2.3.1 Electron microscopy

In electron microscopy electrons are emitted from an electron gun and accelerated towards a sample. Depending on the nature of the sample it is possible to observe and record different signals, see Figure 2.7.

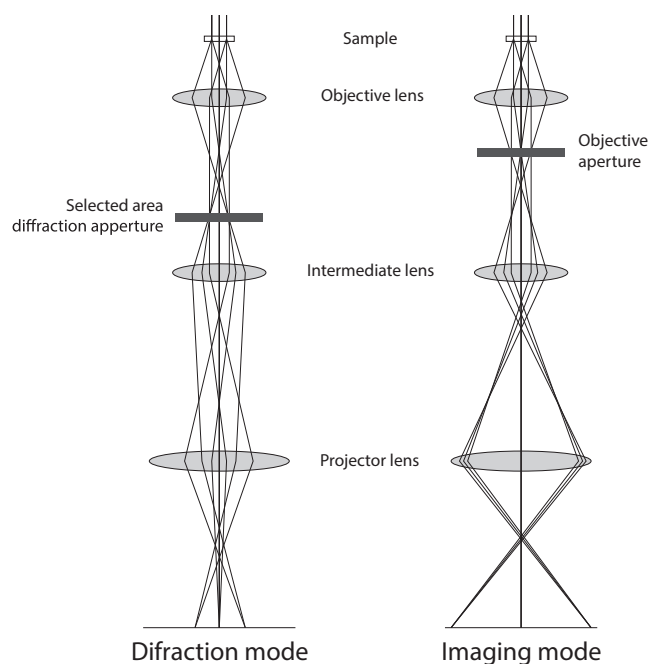


Figure 2.8: The set-up of a transmission electron microscope from the sample to the viewing screen or camera. Both diffraction and imaging mode are shown. Also, the placement of the selected area diffraction aperture and the objective aperture, both of which can be removed, are shown.

2.3.2 Transmission electron microscopy (TEM)

In transmission electron microscopy, TEM, the sample is thin enough to allow for electrons to travel through the sample. Some electrons will travel straight through while others will be scattered or absorbed in the sample. By choosing which signal that is measured and how the signal is projected to an image by the lenses, different information about the sample can be obtained.

The chosen thickness of a "thin sample" may vary with the material of the sample and the resolution that is strived for, but generally one would wish for a sample thickness of the order of 100 nm or thinner [27]. The samples used in this work generally had thicknesses between 100 and 300 nm, see Appendix A.

For imaging it is mainly the electrons that do not deviate far from their original trajectory that are interesting. These give information about the structure of the sample and also the chemistry [27]. One main source of contrast in TEM images is the elastically scattered electrons, and it is also these that give information about the crystal structure of the sample through the diffraction pattern [27]. How different lenses and strengths of lenses are used for imaging the structure and for obtaining the diffraction pattern is presented in Figure 2.8.

Bright field imaging

To enhance the contrast from the film structure, bright field imaging was used in this work.

In bright field imaging only the forwardly scattered electrons of the direct beam

are used to form an image. This is achieved by inserting the objective aperture which blocks all electrons except for a portion of choice, for bright field imaging this portion is the direct beam. It is also possible to perform dark field imaging where the objective aperture is placed at locations corresponding to diffracted electrons such that only electrons not in the direct beam can reach the detector.

Selected area diffraction

When acquiring the diffraction patterns it is sometimes desired to get only the signal from a small area of the sample. This is obtained by inserting the selected area aperture that only allows electrons from a small circular area to contribute to the diffraction pattern. In this work, selected area apertures with diameters of 200 and 750 nm were used.

Electron energy loss spectroscopy (EELS)

By measuring the energy distribution of the transmitted electrons, specifically the inelastically scattered, and plotting the number of counts at each energy it is possible to achieve information about the origins of inelastic scattering in the material.

Energy filtered TEM (EF-TEM) and thickness mapping

Energy filtered TEM can be used to form an image of electrons with a specific energy. It can be used to separate between different material phases from which the number of inelastically scattered electrons with a specific energy loss may differ.

Another possibility with EF-TEM is to do so-called thickness mapping, because the probability that an electron will loose energy while travelling through the sample increases with sample thickness. By forming an image of the electrons without energy loss, electrons from the zero-loss peak in the energy loss spectrum, and comparing this to a TEM image of the same area but including electrons of all energies a thickness map in units of electron mean free path of the sample is obtained. The thickness map is described by the formula [17]

$$\frac{t}{\lambda} = \ln \left(\frac{I_{unfiltered}}{I_{zero-loss}} \right), \quad (2.1)$$

where t is the thickness, λ is the mean free path of an electron in the material, $I_{unfiltered}$ is the intensity in a pixel in the unfiltered image and $I_{zero-loss}$ is the intensity of a pixel in the filtered zero-loss image. Without knowing the electron mean free path in the material it is not possible to tell if the obtained contrast comes from variations in thickness or variations in electron mean free path.

In this work, a FEI Tecnai T20 LaB₆ is used for bright field images and diffraction patterns, if nothing else is stated. The acceleration voltage used for the electrons was 200 kV. For EELS and EF-TEM a FEI Titan 80-300 and a Phillips CM200 FEG TEM are used.

Applications for polymeric materials

Different phases in all-polymer films may be difficult to distinguish using TEM since they may have very similar electron densities and chemical composition [18]. It is

possible to get some contrast at sufficient defocus, but this may also lead to artefacts and misinterpretation of the data [18].

Sometimes lower acceleration voltage may also be used to enhance the contrast between polymers.

Because the electrons in a TEM can break covalent bonds in molecules, polymers may be extra sensitive to beam damage. Common beam damage effects are broken polymer backbones or broken off side chains [27]. Crystalline phases may also transform to amorphous phases.

Sample preparation

To be able to study the films using TEM they must first be removed from the substrate and transferred to a copper TEM-grid (here Polaron, 3.05 mm).

Since the PEDOT:PSS buffer layer is water soluble while the film does not dissolve in water, the film may be easily removed from the substrate by "floating off" in water. A scalpel is used to cut squares with a side of approximately 2.5 mm of the polymer films on the glass substrate. Once the substrate is put under water the PEDOT:PSS layer starts dissolving and the pieces of film will float on the water surface where they may be picked up directly using a TEM-grid.

To avoid effects caused by the edge of the substrate all films cut and placed on TEM-grids originally had a minimum of 1 millimeter to the closest substrate edge. The part of the film that was located at the rotation center during spin coating was also avoided.

The TEM-grids with polymer films are stored in plastic containers wrapped in aluminium foil to avoid degradation by sunlight.

Some samples were plasma cleaned on the TEM grid. The plasma cleaner uses a plasma, in this case air, to remove material from the surfaces of the film. It is generally used to remove contamination, but for these polymer films, material is also removed from the actual film. All samples that were plasma cleaned were run for 20 seconds in the plasma inside a shield for TEM samples. The shield protects the film such that the amount of material removed is minimised.

2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy is used to image the surface of a sample. The signal that is measured is generally the number of backscattered or secondary electrons, both of which depend on the local composition and surface topography of the sample [16]. The scanning electron microscope focuses the electron beam and measures the signal as a function of the location of the electron beam, building the image pixel by pixel.

For this work images were taken with secondary electrons using the InLens detector of a Zeiss Ultra 55 FEG SEM. The films were imaged on the same copper grids that were used for TEM imaging.

2.3.4 Atomic force microscopy (AFM)

In an atomic force microscope, AFM, a sharp tip is mounted at the end of a cantilever. The general set up is shown in Figure 2.9. The vertical displacement of

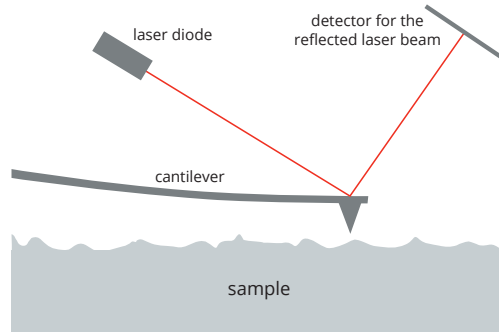


Figure 2.9: The setup of an AFM.

the cantilever, and thereby the force between the tip and the sample, is measured and plotted against the position of the tip in the sample plane [16]. The vertical displacement of the tip is commonly measured by a laser that is reflected at the back of the cantilever [16].

The deflection of the cantilever is influenced by all forces between the tip and the sample. This includes mainly van der Waals forces and contact forces [16]. Because the signal can be measured for forces of many different origins, AFM can be used to investigate the surface structure of many different materials, including non-conducting samples that may be difficult to image in electron microscopy [16].

For AFM imaging the films were imaged when still on the glass substrate. The AFM measurements were made with a NTEGRA Probe NanoLaboratory in tapping mode and in air using a NT-MDT golden silicon cantilever.

Chapter 3

Single polymer films

Films of the pure polymers were manufactured to study the morphology of each polymer individually. The pure films were investigated with respect to morphology, crystal structure, inelastic scattering of electrons and sensitivity to the electron beam. Both films spin coated with chloroform and with o-DCB were studied.

3.1 Film morphology

Spin coated films of the two polymers in chloroform and o-DCB were studied using bright field imaging.

Films of TQ1 were found to be more or less uniform without any distinct structure visible at scales ranging from 100 nm to 1 μ m, independent of solvent. Bright field images of spin coated films of TQ1 with chloroform and o-DCB are shown in Figure 3.1.

When studying the films of N2200 it was found that there is a difference in structure between films spin coated with chloroform and films with o-DCB, this can be seen in Figure 3.2. While films spin coated from chloroform appear to be more or less uniform, films with o-DCB have a quite distinct contrast variation over the film.

The contrast variations may have different origins, one of which may be thickness variations of the film. In order to further investigate the film of N2200 spin coated with o-DCB the surface of the film is imaged in the SEM. Both the side facing air during spin coating, called the top, and the side facing PEDOT:PSS during spin coating, called the bottom, were imaged while the film was on the TEM-grid. In Figure 3.3 the top and bottom as imaged in the SEM are shown. It is seen that there are surface structures on the top of the film. The same structures are not found on the bottom of the film, which indicates that there are thickness variations on the film.

The thickness variations seen in the SEM have similar size and shape to the contrast variations seen in the TEM images in Figure 3.2. It is therefore probable that it is thickness variations that give rise to the structures seen as contrast variations in the TEM.

The films were also imaged at higher magnification. At the higher magnification, using bright field imaging and defocusing of the images proved to be important for

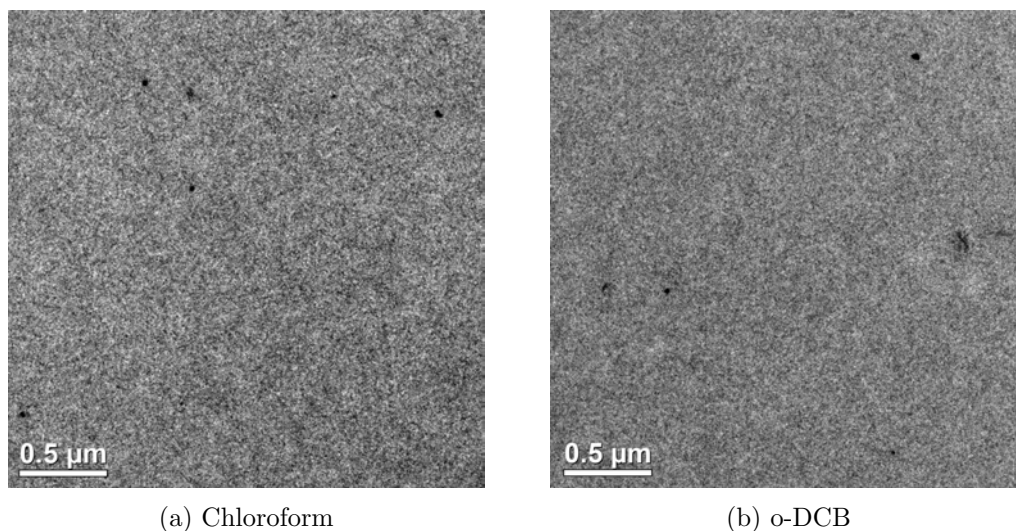


Figure 3.1: Spin coated films of pure TQ1 with different solvents imaged in bright field. The images show no distinct structure.

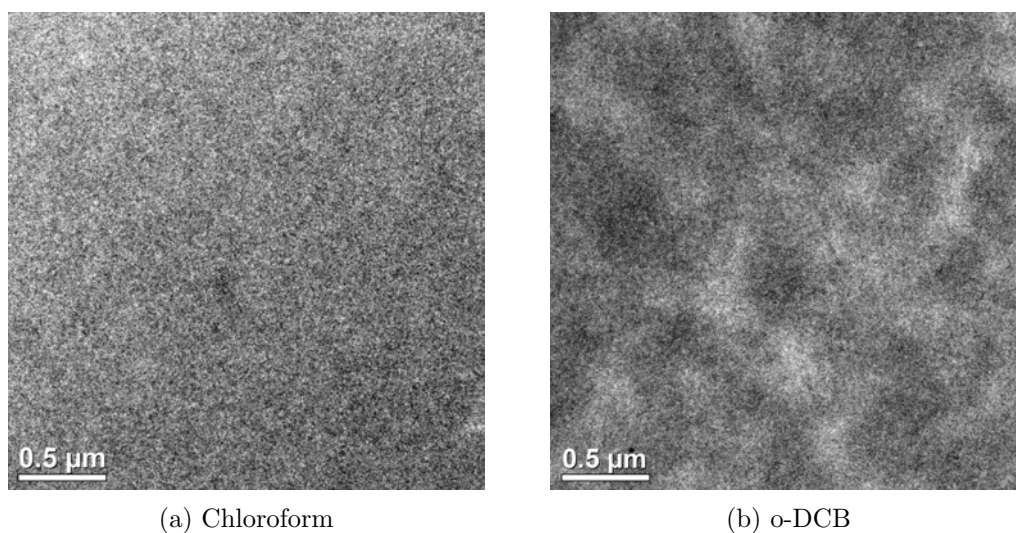


Figure 3.2: Spin coated films of pure N2200 with different solvents imaged in bright field. The films with chloroform showed no distinct structure while the films with o-DCB show contrast variations over the film.

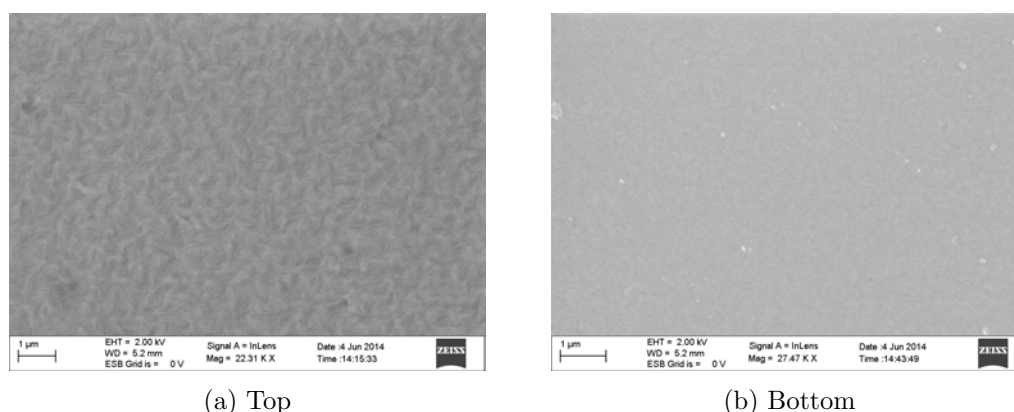


Figure 3.3: The top surface (the side facing air during spin coating) and the bottom surface (the side facing PEDOT:PSS during spin coating) of a film of N2200 with o-DCB imaged by SEM. The structures visible on the top are not visible on the bottom indicating thickness variations over the film.

seeing the structures of the films, this is illustrated in Figure 3.4. Figure 3.4 also shows fibrillar structures in the films of N2200 spin coated with o-DCB.

When looking at the films of TQ1 spin coated with chloroform and o-DCB at the higher magnification, both in focus and at $-10\text{ }\mu\text{m}$ defocus, no distinct structures were found on this scale either, see Figure 3.5.

For the films of N2200 there was a difference between different solvent also at the higher magnification. As was seen in Figure 3.4, there are fibrillar structures in films spin coated with o-DCB. In films spin coated from chloroform no distinct structures were found, see Figure 3.6.

It is interesting to try to figure out where in the films of N2200 spin coated from o-DCB the fibrillar structures are located. It is especially interesting to see if they are seen only on the surface or if they are also present in the bulk. To image only the bulk of the sample the top and bottom surface layers are removed by plasma cleaning and the film is imaged in the TEM again. In Figure 3.7 images of the film after plasma cleaning are shown. No distinct fibrillar structures were seen in the films after plasma cleaning, although some traces of them are still visible. This indicates that the fibrills that could be seen before plasma cleaning were in fact surface structures. This does not say anything about whether or not there are fibrills also in the bulk of the film. The fibrills on the surface can be seen because their long axes are oriented in parallel with the surface. There may be fibrillar structures also in the bulk that are oriented in different directions and may therefore not be seen in the images.

Once it is seen that the visible fibrillar structures are found on the surface it is also interesting to investigate if they can be found on the top surface or bottom surface, or both. To investigate this SEM is used once again to image both the top and bottom of the film on the TEM-grid. The SEM images are shown in Figure 3.8. The fibrillar structures are only seen on the top of the film in the SEM images, it is therefore assumed that the fibrills orient in the plane of the film only on the surface facing air during spin coating.

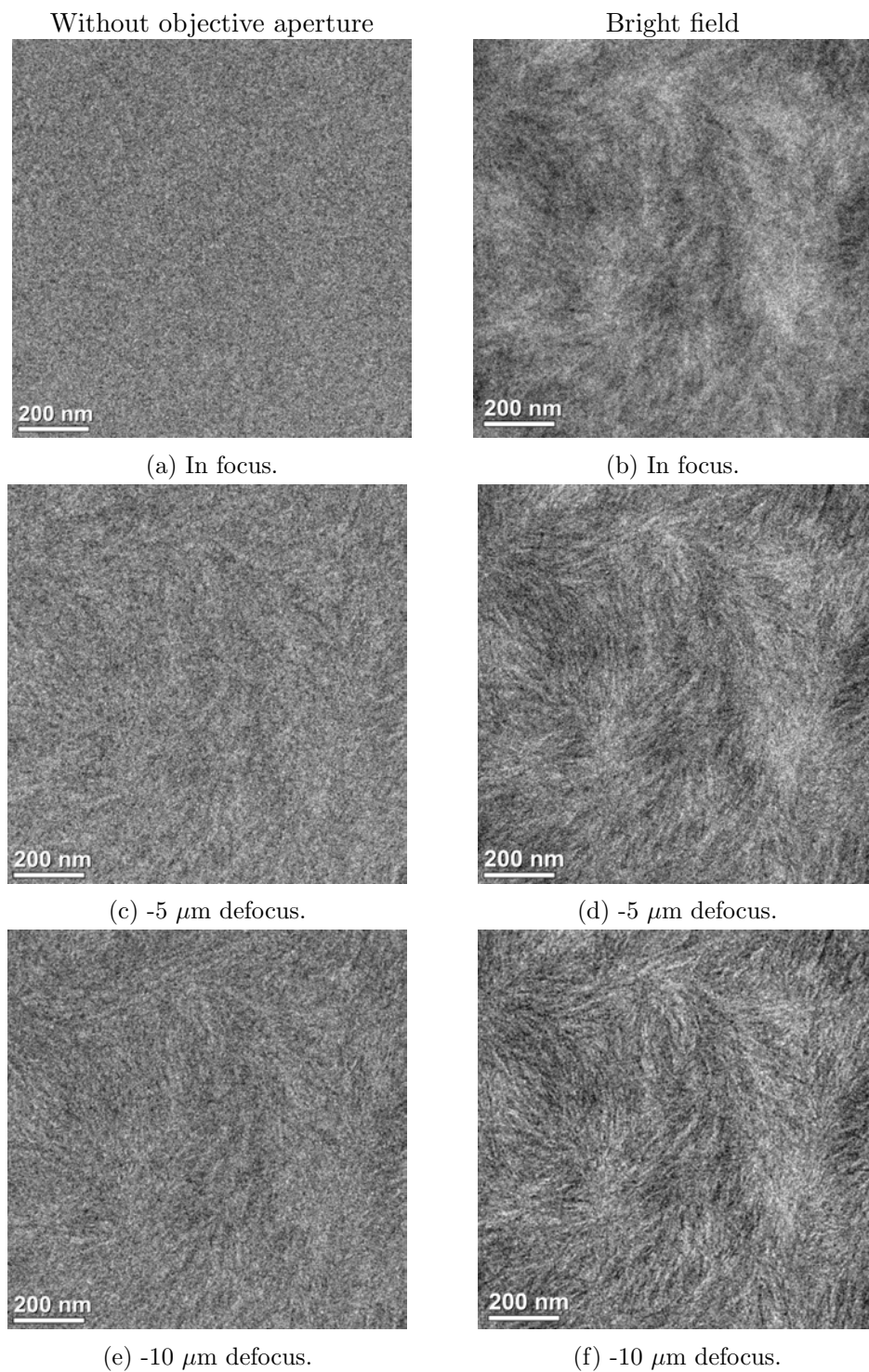


Figure 3.4: Spin coated films of N2200 with o-DCB imaged without objective aperture and by bright field imaging at different focus showing the importance of using bright field and defocus for seeing the structures of the film. The films showed fibrillar structures.

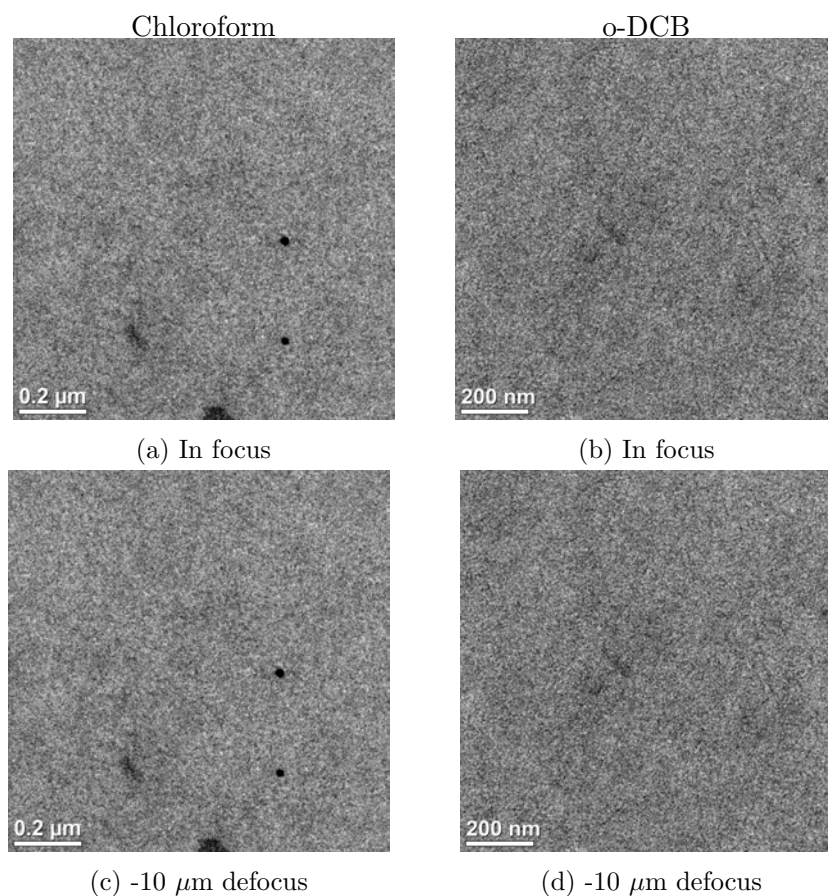


Figure 3.5: Films of TQ1 spin coated with different solvents and imaged in bright field at different defocus. No distinct structures were found.

3.2 Crystalline order

The samples were also investigated with respect to crystalline order via electron diffraction.

Examples of diffraction patterns acquired from films of TQ1 spin coated from chloroform and o-DCB can be seen in Figure 3.9. The diffraction patterns of films of TQ1 showed no indications of crystalline structures, which means that the films were amorphous.

The diffraction patterns of films of N2200 on the other hand, showed relatively sharp rings indicating crystalline structures in the film. These rings were found in films spin coated with both chloroform and o-DCB, which can be seen in Figures 3.10 and 3.11.

The distances corresponding to the rings in the diffraction patterns were measured and the values can be found in Table 3.1. The values are found to be very similar in films spin coated with the two different solvents, and also similar to the previously measured values by grazing incidence x-ray diffraction, see Section 2.1.2 [23].

The rings seen in Figures 3.10 and 3.11 are not homogeneous, but have an angular dependence in the intensity around the ring. The ring with the smallest diameter has its highest intensity at scattering angles that are perpendicular to the highest

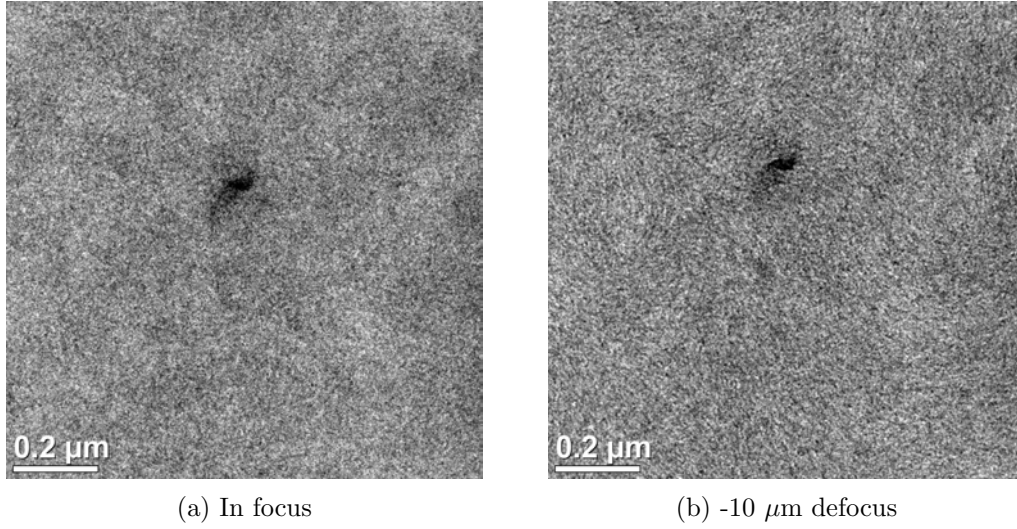


Figure 3.6: Films of N2200 spin coated with chloroform and imaged in bright field at different focus. No distinct structures were found.

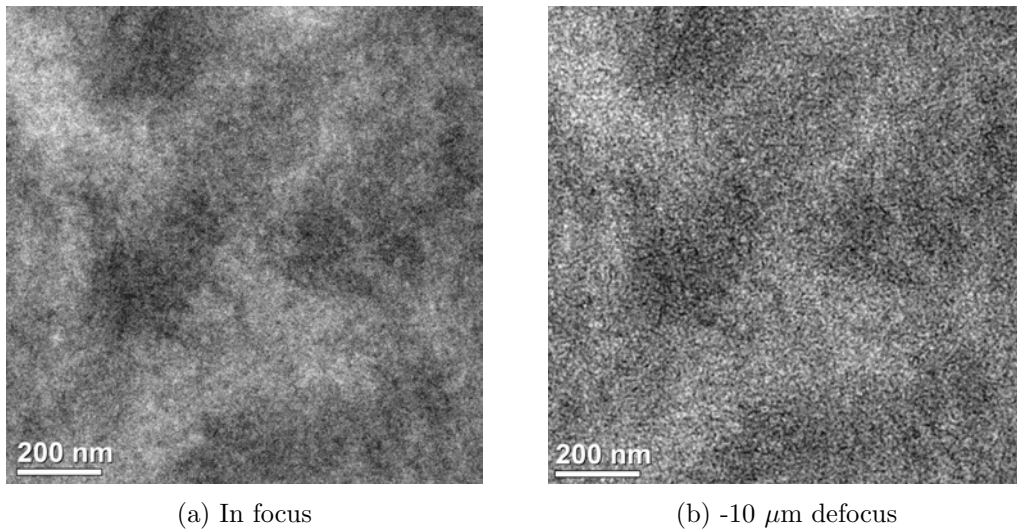


Figure 3.7: Plasma cleaned films of N2200 spin coated with o-DCB imaged in bright field at different focus. The film showed no distinct fibrillar structures after plasma cleaning.

intensity of the other three rings. This is in agreement with what was also found in previous grazing incidence x-ray measurements [23], where the peak corresponding to the distance between polymer chains, corresponding to the inmost ring in the electron diffraction patterns acquired in this study, was detected when the incident x-ray beam was perpendicular with the fibrillar structures. The other three peaks were detected when the x-ray beam was parallel with the fibrillar structures. The same effect with different peaks at different angles is here also seen in the electron diffraction patterns.

The fact that the angular dependence can be seen in the diffraction patterns

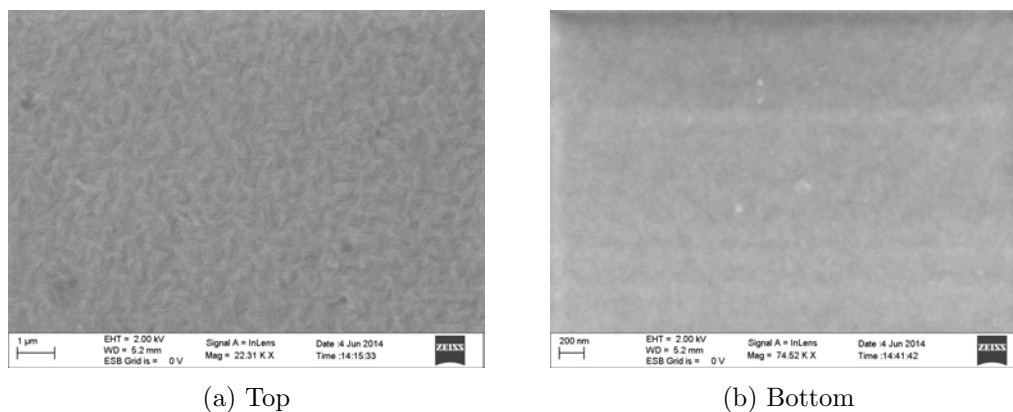


Figure 3.8: The top surface (the side facing air during spin coating) and the bottom surface (the side facing PEDOT:PSS during spin coating) of a film of N2200 spin coated with o-DCB imaged by SEM. The fibrillar structures are only visible on the top surface of the film.

means that the fraction of the area over which the crystallinities in the film have a preferred crystal orientation is large enough for there to be a resulting preferred orientation of the area that is used to collect the diffraction signal. In Figures 3.10 and 3.11 this area is the area of the selected area aperture used for the images, which was a circle with a diameter of 200 nm.

If the size of the selected area aperture is increased to 750 nm, the angular dependence in the rings of the diffraction pattern mostly disappears, see Figure 3.12. This means that over the larger area there is no resulting preferred direction and the average direction of crystallinities is random.

From this it is possible to deduce that the range over which the crystallinities orient along a preferred direction is of the order of 200 nm.

It is known from previous studies, see Section 2.1.2, that N2200 crystallise in fibrillar structures. In Section 3.1 it was seen that films of N2200 spin coated with o-DCB have fibrillar structures on the top surface of the film. The same type of clear fibrillar structures were not seen in the films spin coated with chloroform which can either mean that there are no fibrills in this type of films or that the fibrills are randomly oriented and can therefore not be seen as easily. Since these films show crystalline structure in the diffraction patterns it is the latter alternative that is most likely.

It was also found in Section 3.1 that most of the fibrillar surface structures that can be seen in films of N2200 spin coated with o-DCB was removed during plasma cleaning. By studying the diffraction patterns from a film after plasma cleaning, see Figure 3.13, it is seen that there are still rings and that the angular dependence remains. Thus there are fibrillar structures also in the bulk of the films and they have a preferred direction of the crystal structure over a range on the order of 200 nm.

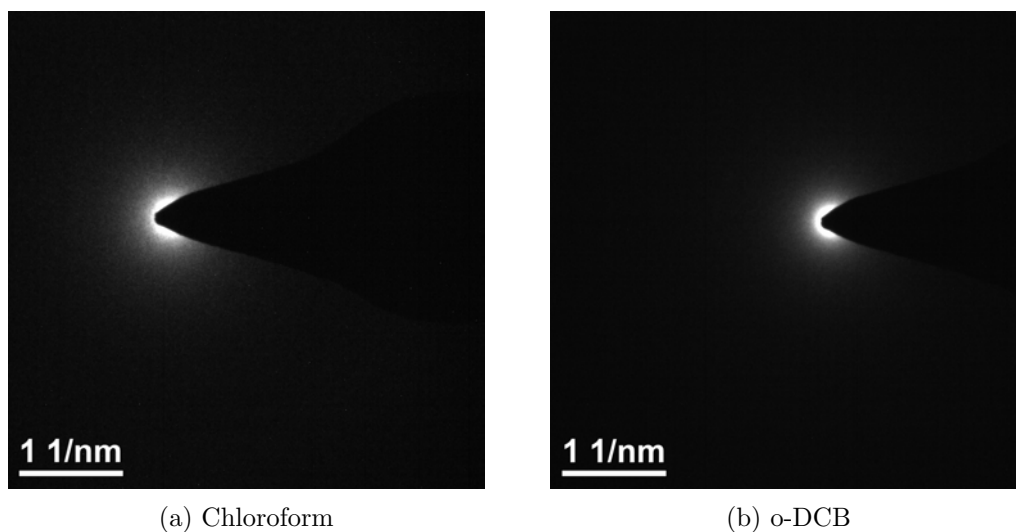


Figure 3.9: Diffraction patterns from films of TQ1 spin coated with different solvents. The images were acquired with a selected area aperture with a diameter of 200 nm. The diffraction patterns showed no indications of any crystalline structure.

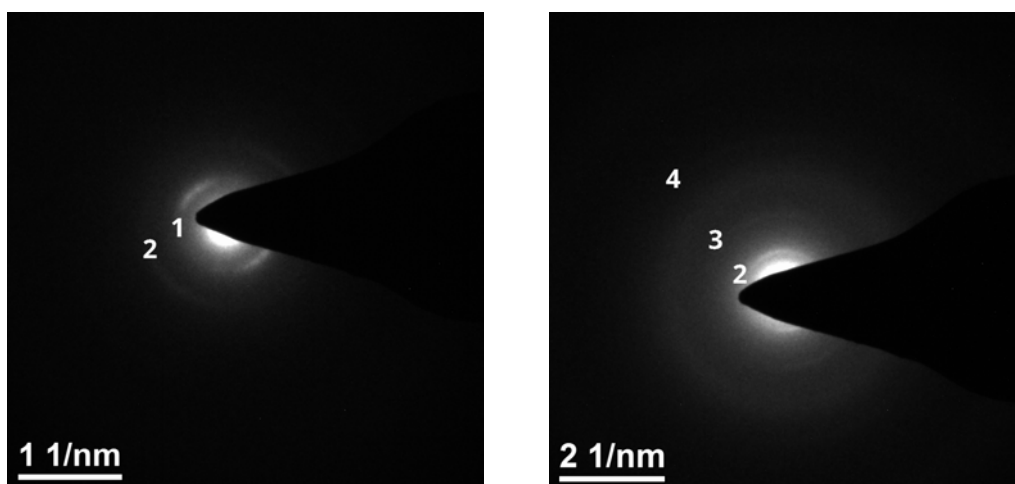


Figure 3.10: Diffraction patterns from films of N2200 spin coated with chloroform. The images were acquired with a selected area aperture with a diameter of 200 nm, at two different camera lengths to show the four detectable rings which are marked 1-4 in the images. The diffraction patterns show crystalline structure and also a preferred orientation of crystallinities.

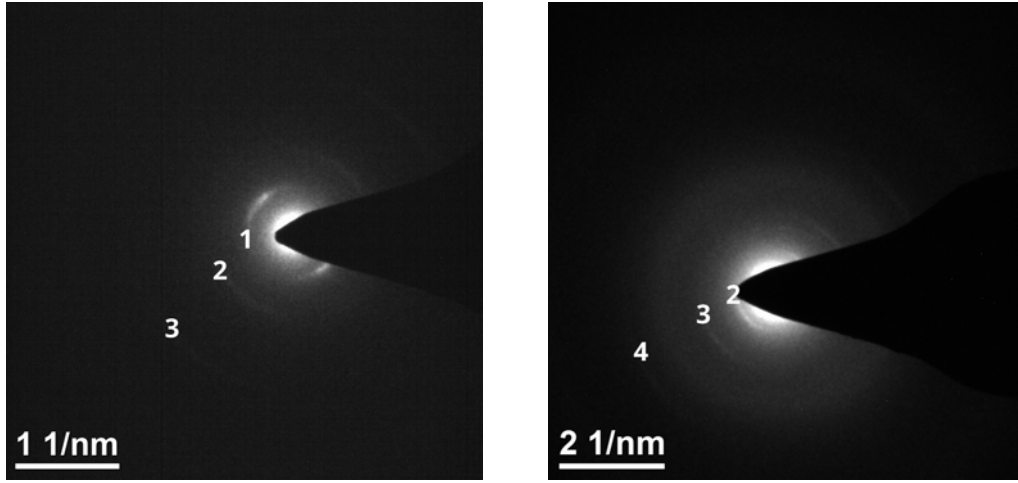


Figure 3.11: Diffraction patterns from films of N2200 spin coated with o-DCB. The images were acquired with a selected area aperture with a diameter of 200 nm, at two different camera lengths to show the four detectable rings which are marked 1-4 in the images. The diffraction patterns show crystalline structure and also a preferred orientation of crystallinities.

Table 3.1: Distances in the diffraction patterns (DP) and interplanar distances in the film for the four rings detectable in the diffraction patterns from films of N2200 spin coated with o-DCB, see Figure 3.11, and chloroform, see Figure 3.10. The values are calculated as the mean of the measured distances in 8 separate diffraction patterns for each ring, included is also the standard deviation. The 4th ring was difficult to distinguish in the acquired diffraction patterns from films spin coated with chloroform, hence the parentheses.

Ring	Distance in DP [nm^{-1}]	Interplanar distance [nm]
o-DCB		
1	0.43 ± 0.02	2.34 ± 0.08
2	0.73 ± 0.03	1.38 ± 0.05
3	1.44 ± 0.03	0.69 ± 0.02
4	2.87 ± 0.01	0.35 ± 0.004
Chloroform		
1	0.43 ± 0.01	2.32 ± 0.06
2	0.72 ± 0.03	1.40 ± 0.05
3	1.45 ± 0.01	0.69 ± 0.005
4	(2.82 ± 0.04)	(0.35 ± 0.004)

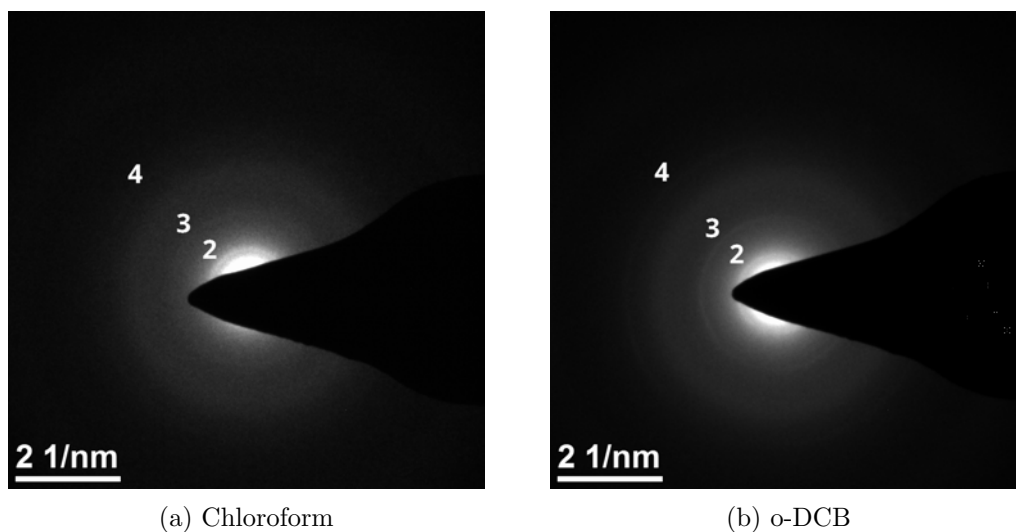


Figure 3.12: Diffraction patterns from films of N2200 spin coated with different solvents. The images were acquired with a selected area aperture with a diameter of 750 nm. The diffraction patterns show no angular dependence in the diffracted rings, showing that from larger areas the overall orientation of the crystallites in the film is random.

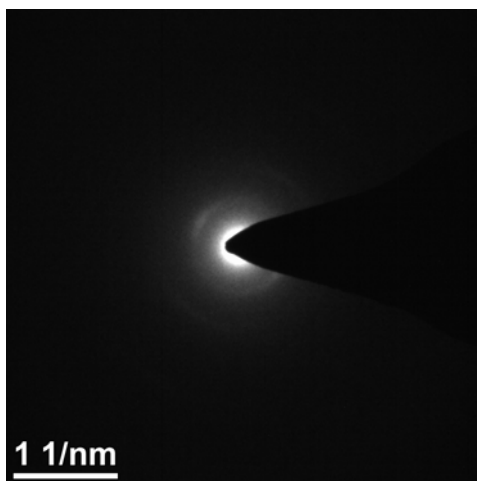


Figure 3.13: Diffraction pattern from a film of N2200 spin coated with o-DCB, acquired after the film has been plasma cleaned and with a selected area aperture of 200 nm in diameter. The rings are still present, and also the angular dependence of the intensity, indicating that there are crystals oriented with a preferred crystal orientation in the bulk of the sample.

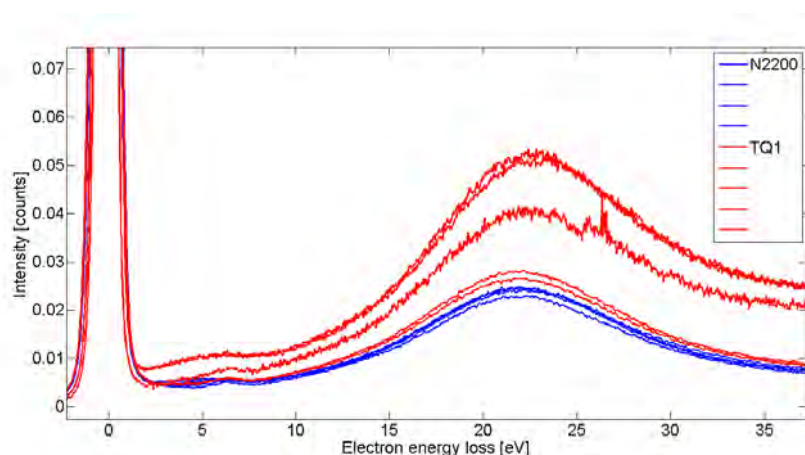


Figure 3.14: Electron energy loss spectrum showing the zero-loss peak and the plasmon region for films of the pure polymers spin coated with chloroform. The data are normalised with respect to the zero-loss peak. There are no distinct differences between the spectra of TQ1 and N2200.

3.3 Electron energy loss spectroscopy

In order to investigate if it is possible to do energy filtered TEM to distinguish between the two polymers in the mixed films electron energy loss spectroscopy was performed. The focus was on the plasmon region and the peaks from electron energy loss in sulphur and carbon atoms. In Figures 3.14 and 3.15 multiple spectra acquired from films of both polymers spin coated from chloroform are plotted. It can be seen that the spectra from the two polymers have no distinct differences, and the plasmon peaks appear to overlap.

Further electron energy loss spectra were acquired also from thinner films of the pure polymers spin coated with chloroform, but no distinct differences were found here either.

Because there were no useful differences between the electron energy loss spectra of the two polymers no attempts were made to perform energy filtered TEM to distinguish between the two polymers in the mixed films.

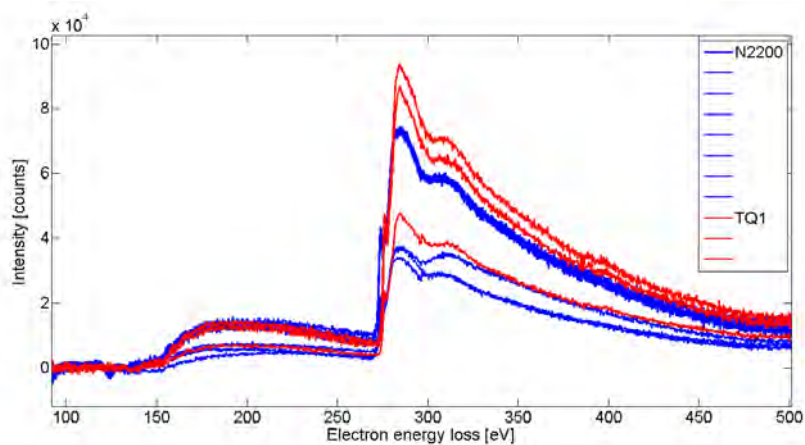


Figure 3.15: Electron energy loss spectrum showing the sulphur and carbon peaks for films of the pure polymers spin coated with chloroform. Also for this region, no distinct differences were found between the spectra from TQ1 and N2200.

Chapter 4

Bulk heterojunctions

This chapter presents the results from the investigations of the bulk heterojunction films, consisting of a mixture of the two polymers.

4.1 Film morphology

The spin coated films of the polymer blends were imaged with bright field imaging in the TEM, and also by SEM and AFM. The results below are presented for the different solvents.

4.1.1 Chloroform

The films spin coated with chloroform show no particular features when observed using bright field imaging, see Figure 4.1. This is true for both as-spun films and annealed films. When imaged at a higher magnification, see Figure 4.2, there are once again no distinct features seen in the images, both for as-spun and annealed films for any of the different values of the defocus used. Since there is so far no way to distinguish between the two polymers in the bright field images these images do not give any information about how the TQ1 and the N2200 are distributed in the films.

The effect of the ratios between the two polymers was studied but changing the ratio did not change the appearance of the film in bright field imaging.

Although energy filtered TEM was assumed to not be able to give contrast between the two polymers it was still used for thickness mapping of the mixed films, see Figure 4.3. For the annealed film of TQ1:N2200 in a ratio of 1:1 spin coated from chloroform the thickness mapping did not provide any additional information. The thickness map shows a more or less uniform structure, much like the bright field images.

To investigate if additional information can be extracted if the films were imaged at a lower acceleration voltage for the electron beam the films were imaged also in 80 kV acceleration voltage, as compared to the 200 kV which was the standard value used in this work. Images acquired at the lower acceleration voltage can be found in Figure 4.4. No additional information about the structure of the film was given by these images.

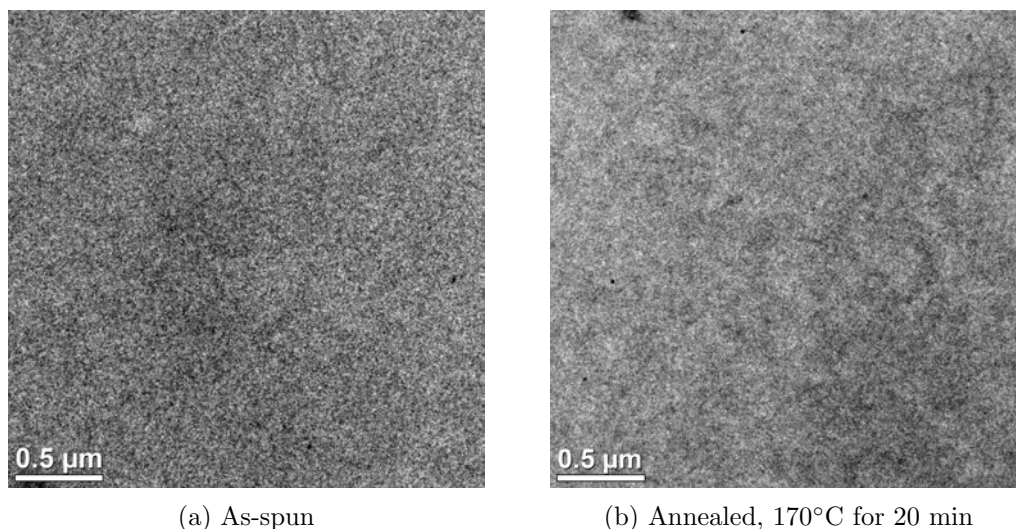


Figure 4.1: Films of TQ1:N2200, 1:1, spin coated with chloroform, both as-spun and annealed, imaged using bright field. There are no clear features detected in either as-spun or annealed films.

Annealed films of TQ1:N2200 at a ratio of 4:1 were imaged by AFM while still on their glass substrate, this can be seen in Figure 4.5. In the AFM, some height variations over the film were found but no other particular structures were observed.

4.1.2 o-DCB

While the films spin coated with chloroform did not show any particular structures in bright field imaging the films spin coated with o-DCB have structures similar to those of pure films of N2200 spin coated from the same solvent.

In Figure 4.6 films of TQ1:N2200 in a ratio of 1:1 are imaged in bright field. Both for the as-spun film and the annealed film similar contrast variations are found to those that were determined to be thickness variations in the pure N2200 film. When films of TQ1:N2200 with a ratio of 4:1 were imaged in bright field similar contrast variations were found over the film.

When the top and bottom of annealed films of TQ1:N2200 in a ratio of 1:1 spin coated with o-DCB were imaged in the SEM structures were found on the top surface, the side facing air during spin coating, but not on the bottom surface, the side facing PEDOT:PSS during spin coating. Just like in the case of the pure N2200 films spin coated with o-DCB, it is probable that the films have thickness variations and that it is these thickness variations that give the contrast variations seen in the bright field images.

Although no SEM imaging was done on the as-spun films it is probable that the contrast variations seen in the bright field images of Figure 4.6 have the same origin as the contrast variations in the annealed film. This is also indicated by the AFM images acquired for both as-spun and annealed films of TQ1:N2200 at a ratio of 4:1 which show height variations over the surface. Since the height profiles in the AFM were acquired when the film was still on the substrate it is not possible to claim that these height variations are thickness variations of the film, but combined with the

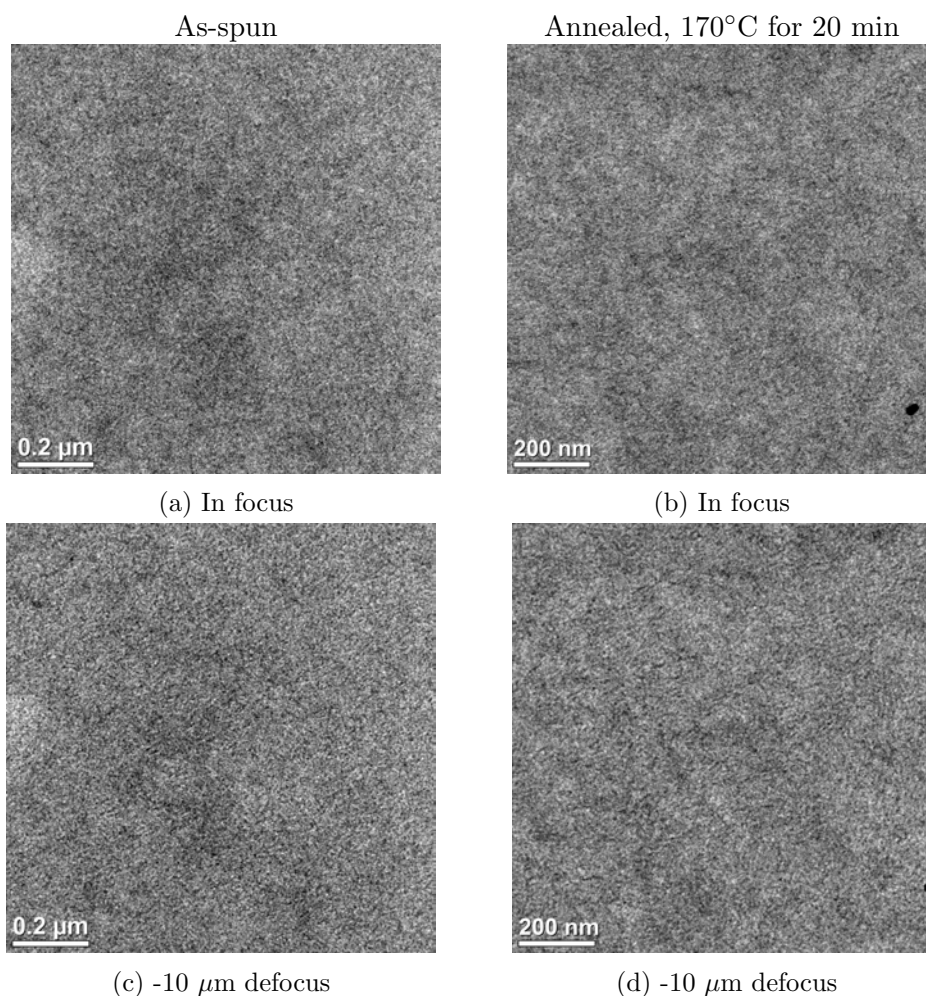


Figure 4.2: Films of TQ1:N2200, 1:1, spin coated with chloroform, both as-spun and annealed, imaged using bright field. These images are taken of the same films as the images in Figure 4.1, but taken at a larger magnification. There are no clear features detected at this magnification either.

previous information obtained from the SEM and TEM imaging is is probable that this is the case.

Thickness mapping via energy-filtered TEM was made also for an annealed film spin coated with o-DCB, with a ratio of 1:1 of TQ1:N2200. The images can be found in Figure 4.9 and show similar structures to what has previously been found by the other techniques.

Similar to the case of the pure N2200 film there are fibrillar structures that can be seen at higher magnification in bright field imaging also for the mixed films spin coated with o-DCB. In Figure 4.10c and 4.10d this is seen for films of TQ1:N2200 in a ratio of 1:1 for both as-spun and annealed films. Figure 4.10 also shows that defocus is needed for the fibrills to be clearly seen, much like the case of the pure films of N2200.

Also films spin coated with o-DCB are imaged at lower acceleration voltage to investigate if any additional information can be extracted. In Figure 4.11 images of

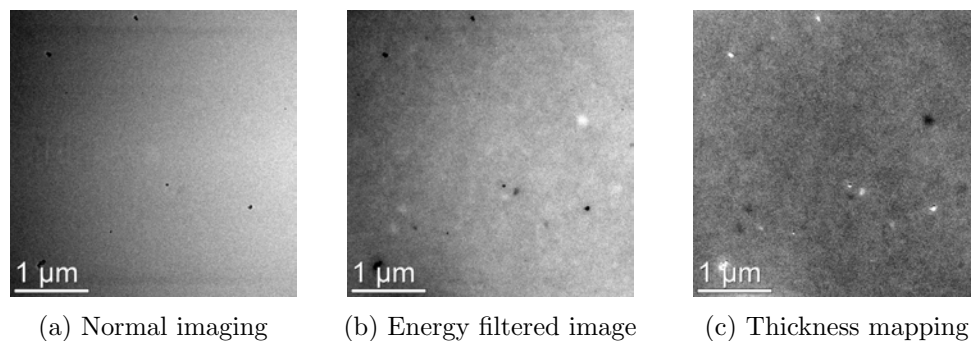


Figure 4.3: Thickness mapping performed on a film of TQ1:N2200, 1:1, spin coated with chloroform and annealed at 170°C for 20 minutes. The energy filtered image is obtained by filtering out all electrons except those within a 5 eV interval around the zero loss peak. The image in (c) is calculated using Equation 2.1 for the intensity of each pixel.

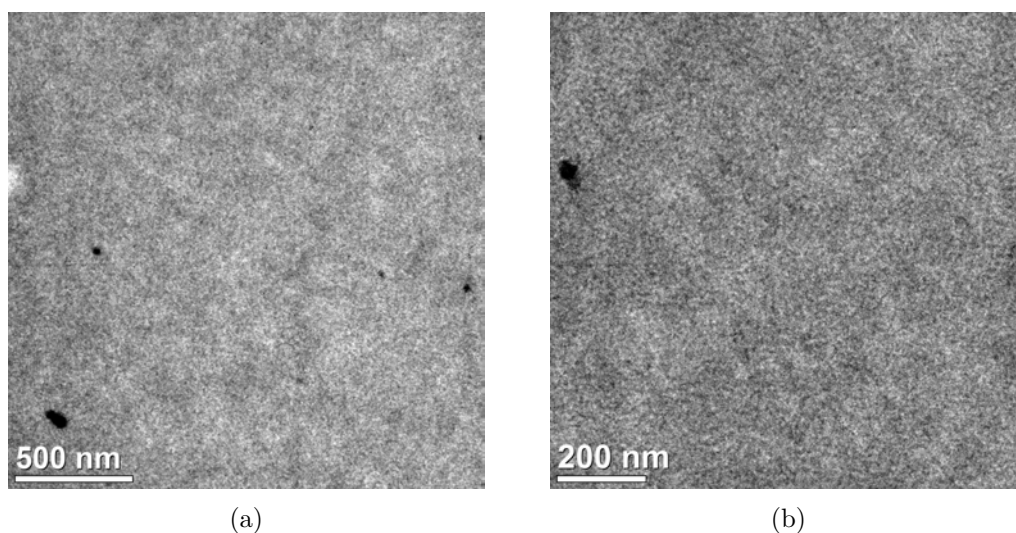


Figure 4.4: Film of TQ1:N2200, 1:1, spin coated with chloroform and annealed at 170°C for 20 min. Imaged in bright field at 80 kV acceleration voltage for the electrons. (a) was imaged in focus and (b) at -10 μm defocus. The morphology, lacking distinct features, seen in these images is similar to those seen at 200 kV.

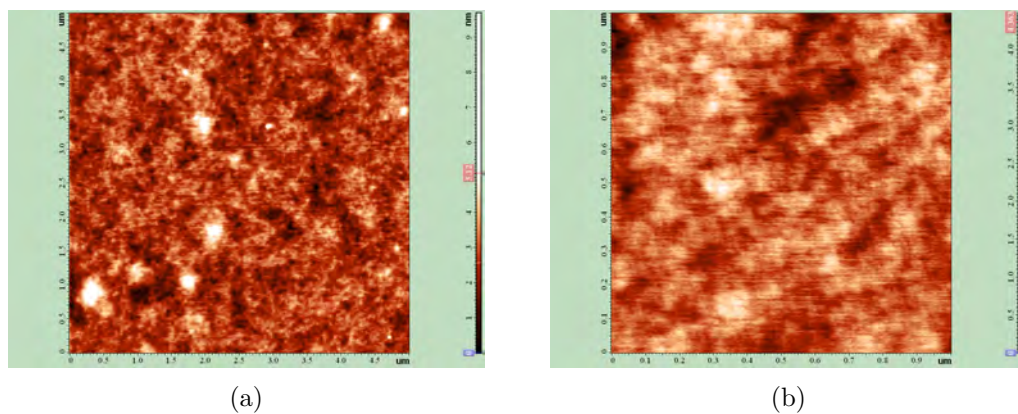


Figure 4.5: Film of TQ1:N2200, 4:1, spin coated with chloroform and annealed at 150°C for 20 min imaged as height profiles by AFM in tapping mode. The images show some height variations over the film.

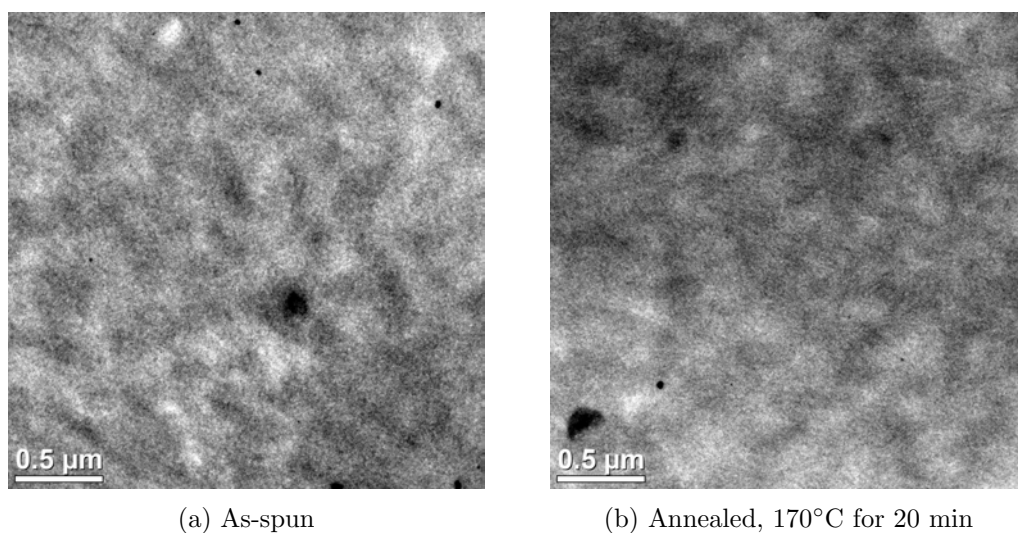


Figure 4.6: Films of TQ1:N2200, 1:1, spin coated with o-DCB and imaged using bright field for an as-spun film and an annealed film. Contrast variations similar to films of pure N2200 spin coated with the same solvent are seen.

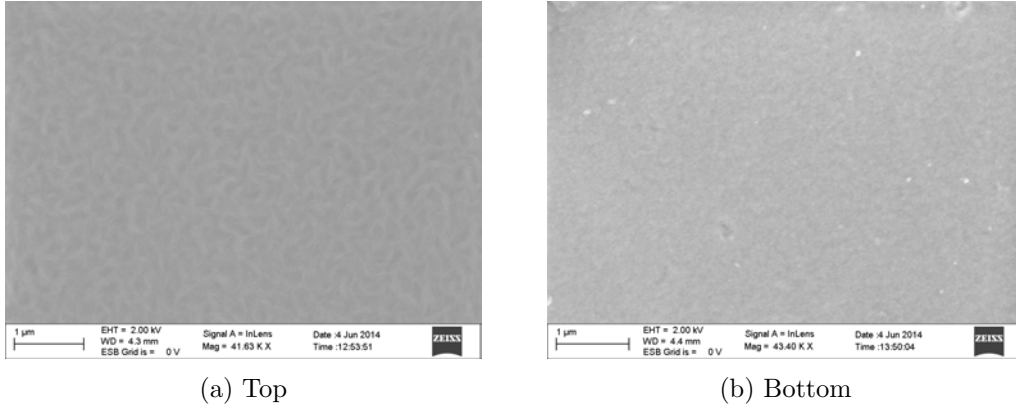


Figure 4.7: Film of TQ1:N2200, 1:1, spin coated with o-DCB and annealed at 170°C for 20 min imaged by SEM. The images show similar thickness variations to the ones found in the SEM images of pure N2200 films spin coated from o-DCB.

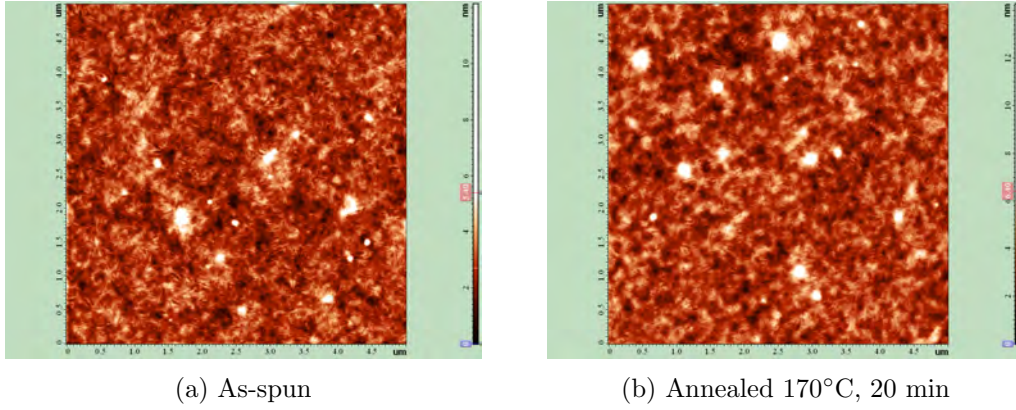


Figure 4.8: Film of TQ1:N2200, 4:1, spin coated with o-DCB imaged as height profiles by AFM in tapping mode. The images show height variations over the film similar to those seen in the SEM images.

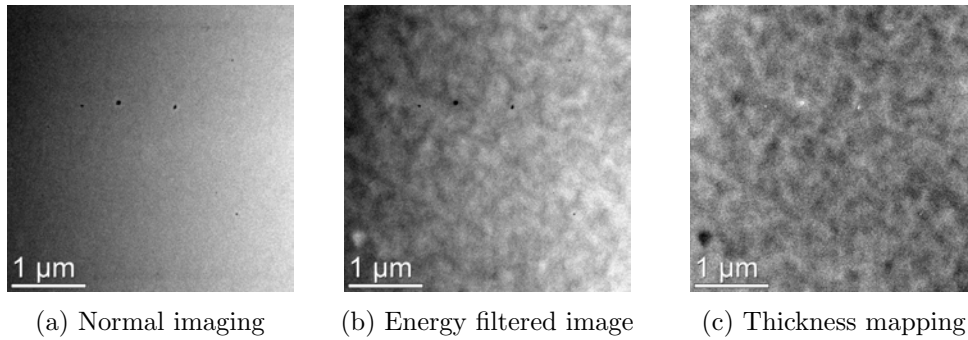


Figure 4.9: Thickness mapping performed on a film of TQ1:N2200, 1:1, spun with o-DCB and annealed at 170°C for 20 minutes. The energy filtered image is obtained by filtering out all electrons except those within a 5 eV interval around the zero loss peak. The image in (c) is calculated using equation 2.1 for the intensity of each pixel.

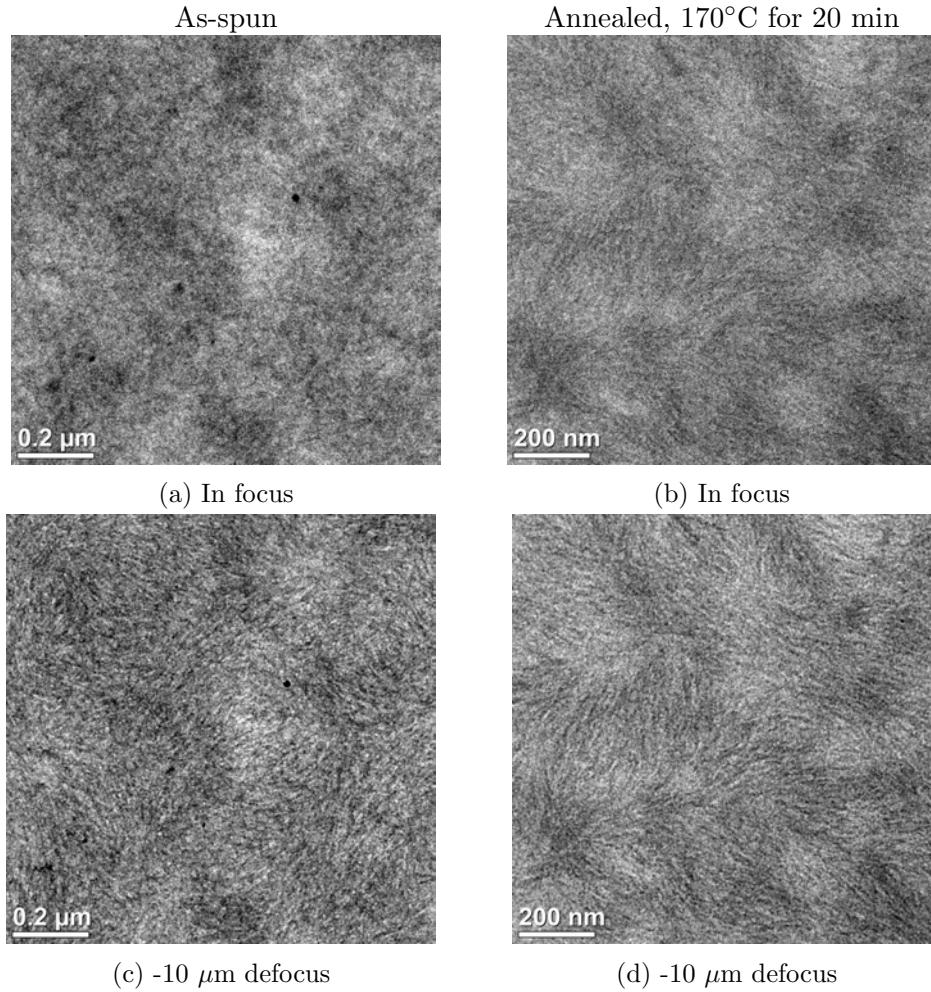


Figure 4.10: Annealed and as-spun films of TQ1:N2200, 1:1, spin coated from o-DCB, imaged by bright field imaging. There are fibrillar structures visible in the defocused images from both as-spun and annealed films.

TQ1:N2200 films with a ratio of 1:1 spin coated with o-DCB and annealed at 170°C for 20 min acquired at an acceleration voltage of 80 kV are shown. The same types of structures as were seen on 200 kV acceleration voltage are seen, including both larger contrast variation and fibrillar structures. It is possible that the contrast is slightly increased at 80 kV acceleration voltage.

When the mixed films are plasma cleaned, the fibrillar structures are no longer visible in bright field imaging, see Figure 4.12. This is once again in agreement with the films of pure N2200 spin coated with o-DCB.

To investigate if the fibrills in the mixed films are only visible on the top surface like in the case of the pure film, also in annealed films of TQ1:N2200 in a ratio of 1:1 spin coated with o-DCB is imaged in the SEM. In Figure 4.13 the film is imaged at both top and bottom, and similarly to the pure film the fibrills are only visible on the top surface.

These results show that the fibrills are only visible on the top surface, meaning that on the top surface they arrange themselves in parallel with the surface plane. It

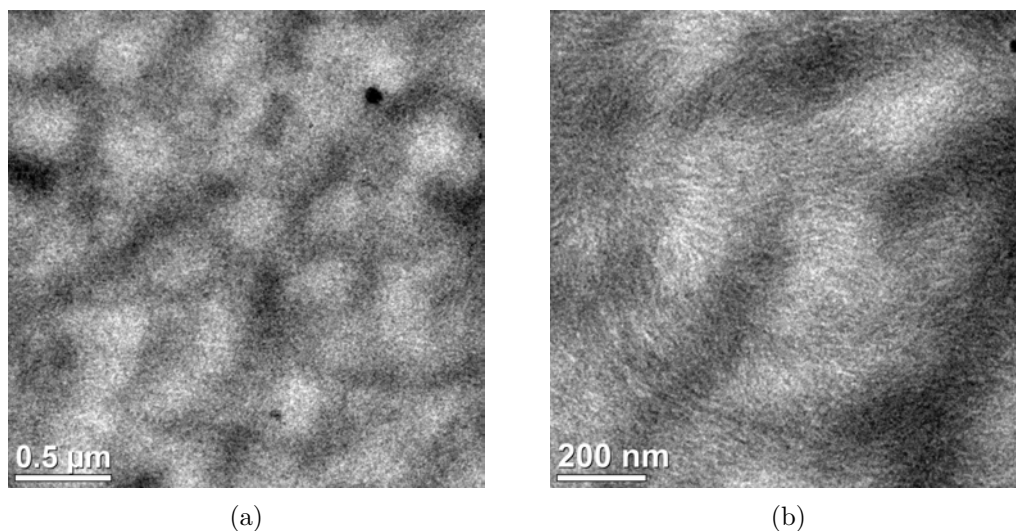


Figure 4.11: Film of TQ1:N2200, 1:1, spin coated with o-DCB and annealed at 170°C for 20 min. Imaged in bright field at 80 kV acceleration voltage for the electrons. (a) was imaged in focus and (b) at $-10\ \mu\text{m}$ defocus. The structures, larger contrast variations in (a) and fibrills in (b), seen in these images are similar to those seen at 200 kV.

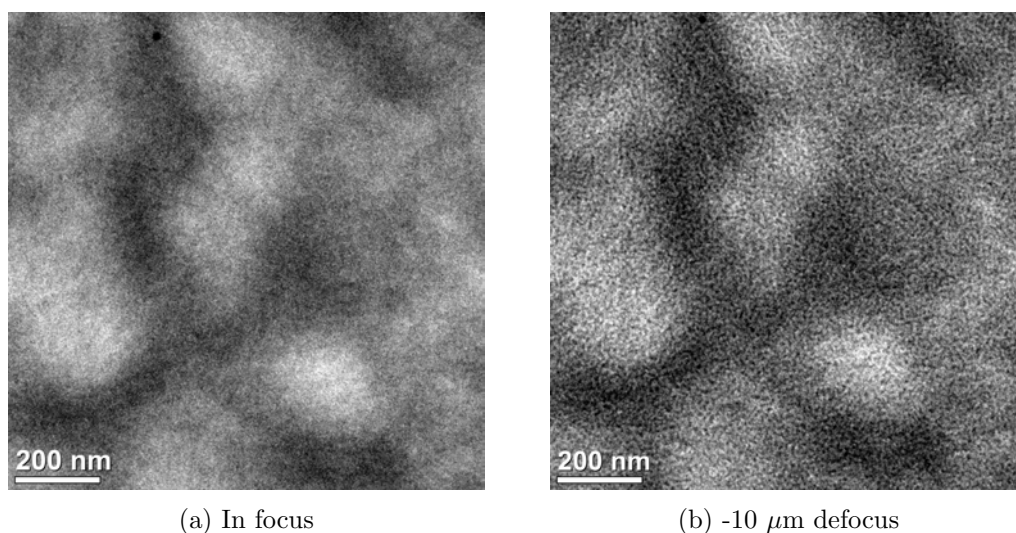


Figure 4.12: Plasma cleaned film of TQ1:N2200, 1:1, spin coated with o-DCB and annealed at 170°C for 20 min, imaged using bright field at different defocus. The fibrillar structures seen in the film before plasma cleaning are no longer visible.

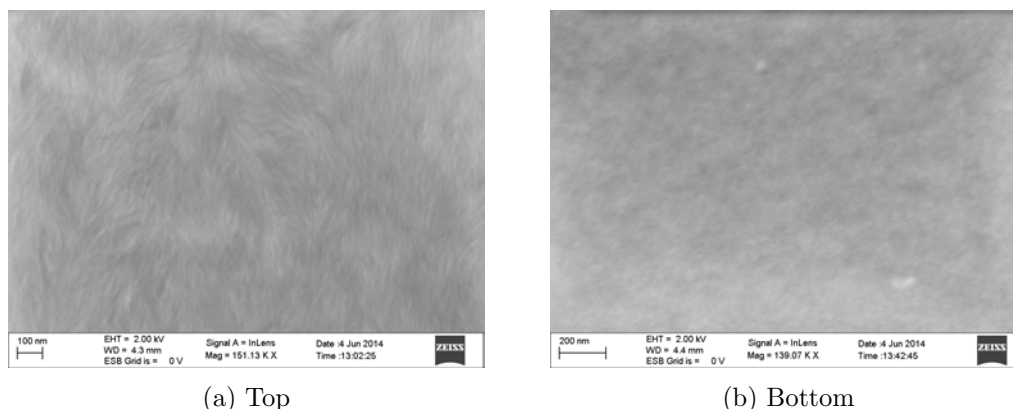


Figure 4.13: Film of TQ1:N2200, 1:1, spin coated with o-DCB and annealed at 170°C for 20 min imaged by secondary electrons collected by the InLens detector of the SEM. Both the top surface (side facing air during spin coating) and bottom surface (side facing PEDOT:PSS during spin coating) are shown. The fibrills are only seen on the top surface, much like the case of the pure films of N2200 spin coated from the same solvent.

does not say anything about if there are more randomly oriented fibrills also in the bulk of the film. Since it was seen that there are ordered crystal structures also in the bulk of pure films of N2200 it is not unlikely that there may be crystal structures also in the bulk of the mixed films spun with o-DCB.

In Figure 4.14 it can be seen that there are fibrillar structures also in films of TQ1:N2200 in a ratio of 4:1. These films were also imaged in the AFM.

In Figure 4.15, AMF images of films of TQ1:N2200 in a ratio of 4:1 spin coated with o-DCB are shown, showing fibrillar structures on the top surface for both the as-spun and the annealed films.

Since the 4:1 films were not imaged on both sides it is not possible to state for certain that the fibrillar structures can only be seen on the surface in these films, but it is likely that the ratio between the two polymers do not affect the arrangement of the fibrills.

4.1.3 p-Xylene

Mixed films of TQ1:N2200 spin coated with p-xylene were only investigated briefly.

Bright field images of films of TQ1:N2200 in a ratio of 4:1 spin coated from p-xylene and annealed at 170°C for 20 min are shown in Figure 4.16. Fibrillar structures are seen also in these films, similar to the films spin coated with o-DCB. The fibrills in the films spin coated with p-xylene appear to arrange themselves differently however. In these films the fibrills have additional ordering as they align along their neighbours over large distances.

The same film was imaged by AFM, which can be seen in Figure 4.17. Also in these images it is possible to see fibrillar structures with a similar arrangement as the one observed in the TEM images.

No further investigations were made on films spin coated from p-xylene. It is therefore not possible to say anything further about the fibrillar structures of these

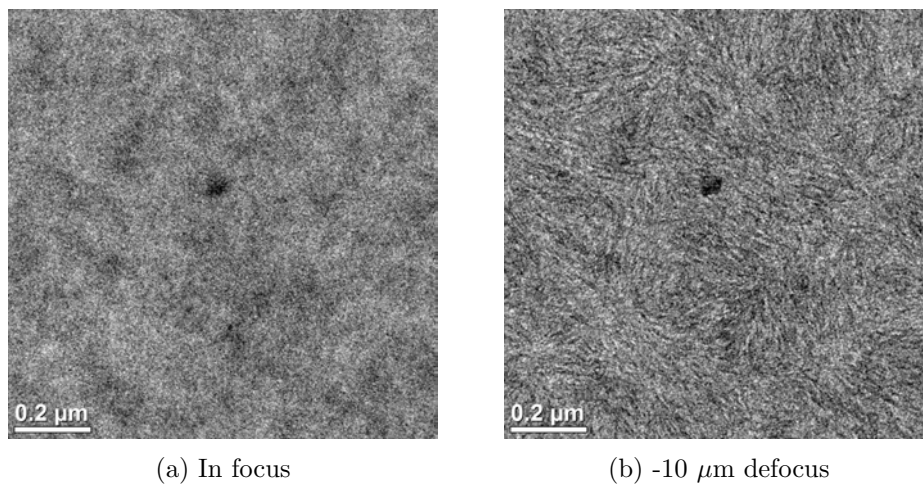


Figure 4.14: Film of TQ1:N2200, 4:1, spin coated with o-DCB and annealed at 170°C for 20 min, imaged by bright field imaging. There are fibrillar structures also in films of this polymer ratio.

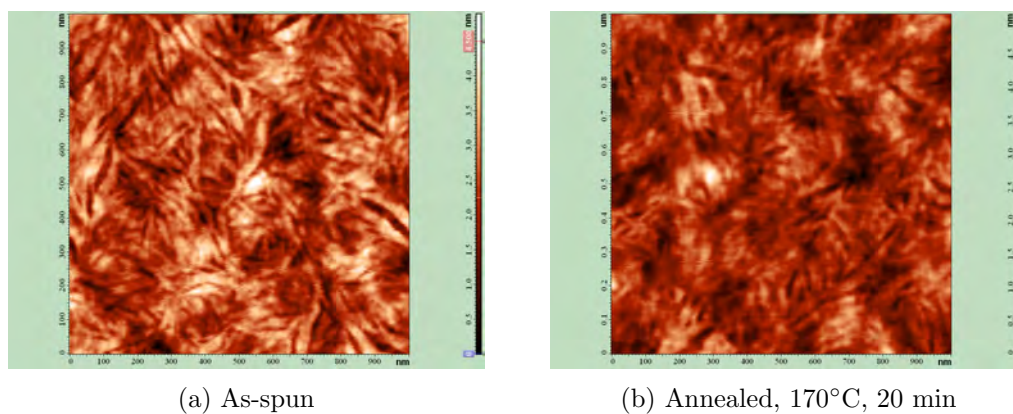


Figure 4.15: Film of TQ1:N2200, 4:1, spin coated with o-DCB imaged as height profiles by AFM in tapping mode. The images show fibrillar structures on the top surface film similar to those seen in the SEM images.

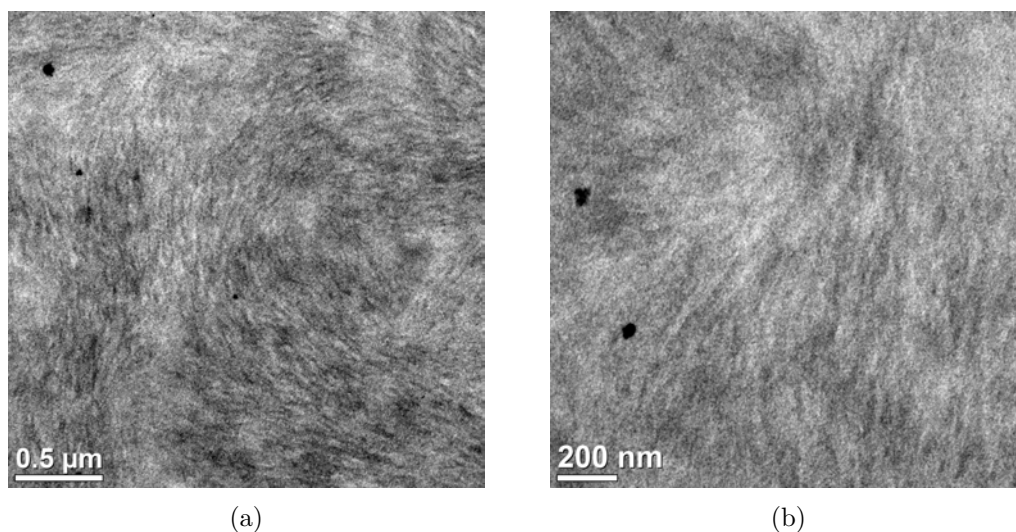


Figure 4.16: Film of TQ1:N2200, 4:1, spin coated with p-xylene and annealed at 170°C for 20 min imaged by bright field imaging at approximately $-10\text{ }\mu\text{m}$ defocus. The film has fibrills similar to those seen in films spin coated with o-DCB, but the fibrills in these films arrange in larger domains with parallel fibrills.

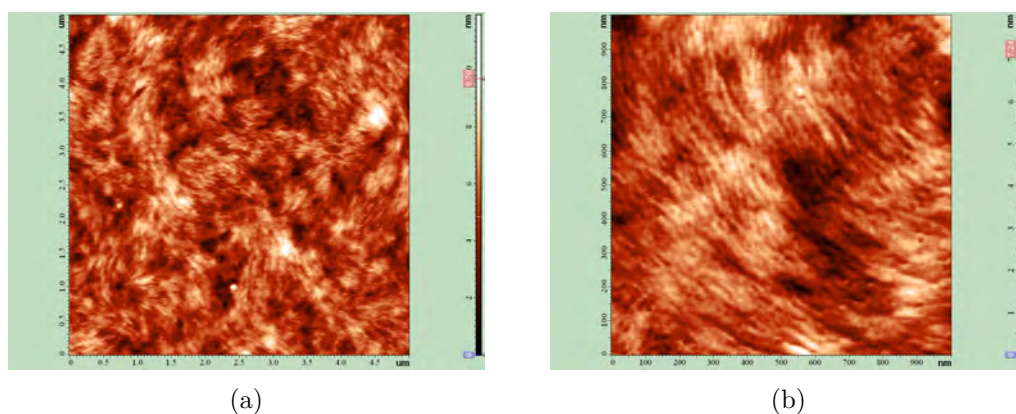


Figure 4.17: Film of TQ1:N2200, 4:1, spin coated with p-xylene and annealed at 170°C for 20 min imaged as height profiles by AFM. The film has fibrills similar to those seen in films spin coated with o-DCB, see Figures 4.8 and 4.15, but the fibrills in these films arrange in larger domains with parallel fibrills.

films.

4.2 Crystalline order

Diffraction patterns were acquired for as-spun and annealed films spin coated with chloroform and o-DCB. Selected area apertures with diameters of 200 and 750 nm were used.

4.2.1 Chloroform

In Figure 4.18 diffraction patterns from as-spun and annealed films of TQ1:N2200 in a ratio of 1:1 spin coated from chloroform are presented. The diffraction patterns acquired from the as-spun film show no clear diffracted rings indicating that there is no particular crystalline order in the as-spun film. Since the films of pure N2200 spin coated with chloroform show clear rings with angular dependence, see Figure 3.10, it is probable that the presence of TQ1 in solution and during spin coating partially hinders the crystallisation of N2200.

After annealing, a relatively clear ring appears in the diffraction pattern of Figure 4.18b, indicating that crystallisation occurs during annealing. The angular dependence seen for the pure films of N2200 is not seen in Figure 4.18b, indicating that the crystallites formed do not orient along a preferred direction over large enough distances for there to be a preferred orientation over the area used to collect the diffraction pattern. This indicates that although crystallisation occurs during annealing the formed crystallites are not able to orient in the same way as in the pure film. This could be because of the different conditions between crystallisation during solvent evaporation as in spin coating or crystallisation in a melt as during annealing. It is also possible that the presence of TQ1 hinders larger domains of ordered N2200 to form.

4.2.2 o-DCB

For the films of TQ1:N2200 in a ratio of 1:1 spin coated with o-DCB diffracted rings can be seen in both as-spun and annealed films, see Figure 4.19. When a selected area aperture of 200 nm is used a similar angular dependence of the intensity around the ring is seen as was seen in the diffraction patterns of the pure films of N2200 spin coated with the same solvent.

The angular dependence seen in both as-spun and annealed films indicates that the crystallites formed in the mixed films orient along a preferred direction over distances on the order of 200 nm. Similar to the case of the pure films the angular dependence is lost when the size of the selected area aperture is increased from 200 nm to 750 nm, see Figure 4.19c and 4.19d.

Also in agreement with the films of pure N2200 spin coated with o-DCB there is still a diffraction pattern to be seen after plasma cleaning, and thus after removing the fibrillar surface structure. This indicates that there is crystallinity also in the bulk of the sample, and that these crystalline regions have crystallites with a preferred orientation over a range on the order of 200 nm.

The interplanar distances corresponding to the two innermost rings in the diffraction patterns of the mixed films are stated in Table 4.1. The values correspond well

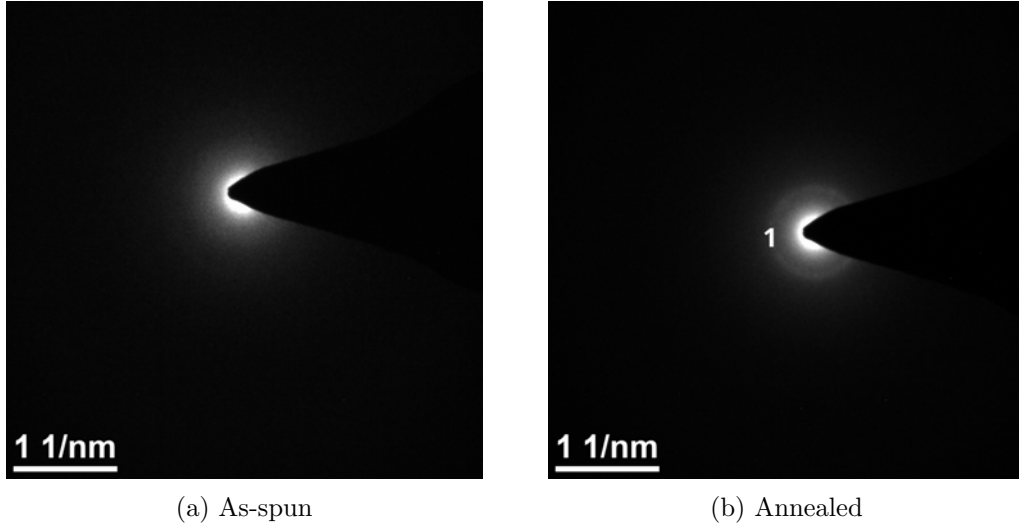


Figure 4.18: Diffraction patterns of as-spun and annealed films of TQ1:N2200, 1:1, spin coated with chloroform, acquired with a selected area aperture with a diameter of 200 nm. There are no clear rings for the as-spun films but after annealing a ring appears. This indicates that crystallisation occurs during the annealing step.

Table 4.1: The distance in the diffraction pattern (DP) and corresponding lattice parameter in the sample for the inner ring in the diffraction patterns for mixed films of TQ1 and N2200 with different solvents. The values are the mean value of the measured wavevectors from 8 diffraction patterns.

TQ1:N2200	Solvent	Annealing	Dist. in DP [nm^{-1}]	Lattice param. [nm]
1:1	Chloroform	170°C, 20 min	0.414 ± 0.010	2.419 ± 0.055
1:1	o-DCB	-	0.425 ± 0.012	2.353 ± 0.067
1:1	o-DCB	170°C, 20 min	0.419 ± 0.008	2.385 ± 0.045

to the values obtained for the films of pure N2200. This gives an indication that the crystalline regions are of pure N2200.

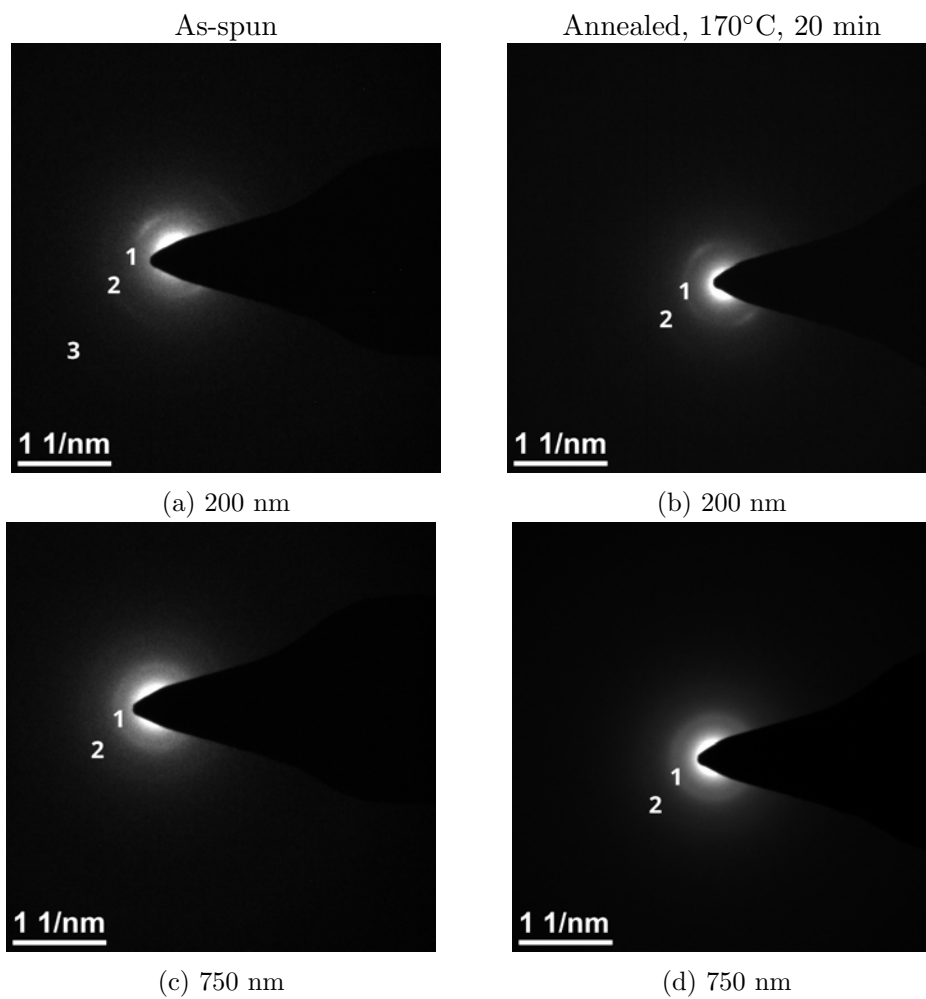


Figure 4.19: Diffraction patterns of as-spun and annealed films of TQ1:N2200, 1:1, spin coated with o-DCB. The diffraction patterns were acquired with two different sizes on the selected area aperture, indicated in the caption. The diffraction patterns show crystalline structure already in the as-spun films and also similar angular dependence on the intensity as for the pure films of N2200 spin coated with the same solvent.

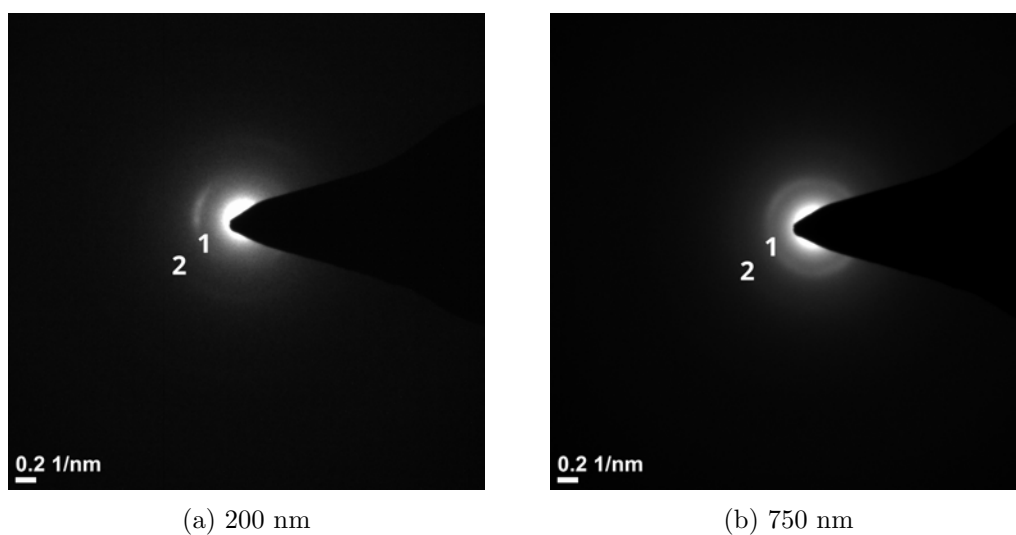


Figure 4.20: Diffraction patterns of an annealed film of TQ1:N2200, 1:1, spin coated with o-DCB after plasma cleaning. The diffraction patterns were acquired with two different sizes on the selected area aperture, indicated in the caption. The diffraction patterns show crystalline structure also after plasma cleaning.

Chapter 5

Beam induced effects

The electron beam was found to affect the films, and in particular films containing N2200. This chapter is dedicated to presenting these effects. An example of a dark contrast from where the electron beam was previously placed can be seen in Figure 5.1.

5.1 The effect of the electron beam on N2200

The films of pure N2200 are affected by the electrons in the electron beam in the TEM. The area where the electron beam was previously placed get darker when imaged in the TEM and the surrounding areas gets spotwise lighter. This effect can be seen in Figure 5.2 for both films spin coated o-DCB and films spin coated with chloroform. In the image showing the films spun from o-DCB the fibrillar structure is still visible.

The darker area where film has been exposed to the beam and the lighter surroundings may be an indication that the beam induces diffusion from the bulk. The fact that the thinning of the surrounding film appears to occur in patches could be interpreted as material being drawn only from areas of certain structure in the film. It is also possible that contamination contributes to the darkening of the area where the beam hit.

5.2 Bulk heterojunctions

Similarly to the films of pure N2200, the mixed films of TQ1:N2200 are affected by the electron beam. Similarly to the case of the pure N2200 films the areas where the electron beam previously hit appear darker when imaged in the TEM. One can, however, detect differences when comparing images of the pure N2200 films with images of the mixed films spin coated with the same solvent.

In Figure 5.3 the effect of the beam on the pure film of N2200 spin coated with chloroform is compared with the effect of the beam on a film of TQ1:N2200, 1:1, spin coated with the same solvent. The beam profile itself looks similar but the area outside where the electron beam previously hit is different in structure. The piecewise lighter areas seen in the pure film are not encountered in the mixed film which has a much more diffuse and barely detectable lighter area around it.

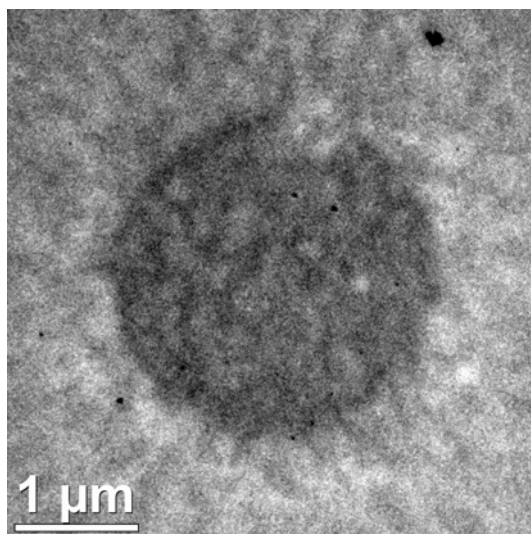
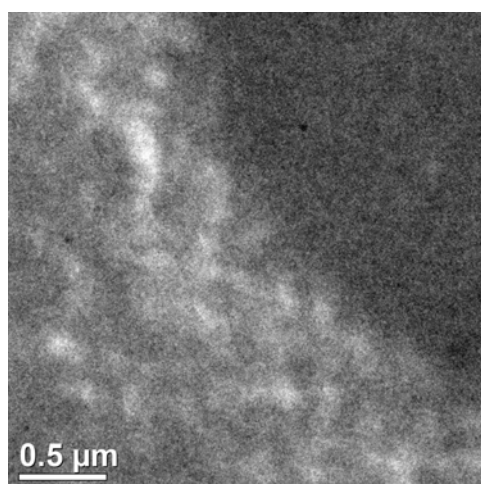
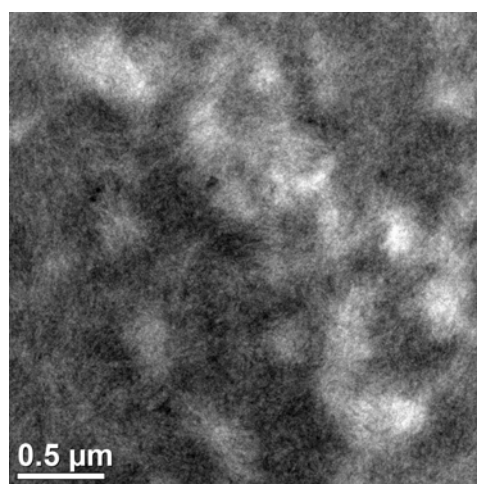


Figure 5.1: Film of TQ1:N2200, 1:1, spin coated with o-DCB and annealed at 170°C for 20 min. The dark circle is the area where the electron beam was previously focused. This beam profile was for illustrative purposes created with a less spread beam than what was commonly used in this work for imaging.



(a) Chloroform



(b) o-DCB

Figure 5.2: Films of pure N2200 imaged in bright field. The images show the darker area where the electron beam was previously placed.

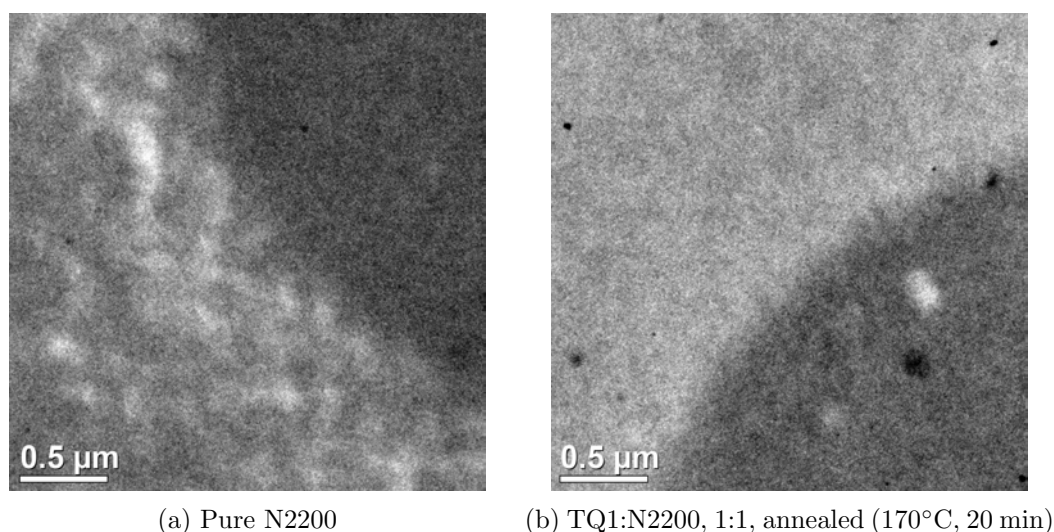


Figure 5.3: Films spin coated with chloroform. The images show the darker area where the electron beam was previously placed. Both images are acquired in bright field.

If the beam can be assumed to thin out only surrounding regions of N2200 this could be an indication that the domains of N2200 are too small in the heterojunctions for any visible lighter areas around the beam profile. Small volumes of crystalline material would be consistent with what was seen in Section 4.2 for the lack of correlation between crystal orientation in mixed films spun from chloroform.

If one instead studies the films spin coated with o-DCB with respect to the beam induced structure, see Figure 5.4, the image of the mixed film more closely resembles the image of the pure N2200. Similar lighter areas can be found outside the beam profile. The lighter areas do, however, seem somewhat reduced in size in the mixed film and there are areas of different contrast detectable also in the beam profile. This could indicate that the domains of N2200 are of similar size to the lighter areas, the size would be consistent with the diffraction pattern seen for a small selected area aperture in Section 4.2, which require larger areas of ordered crystallites.

The difference in how the beam affects the sample in mixed films spin coated with chloroform and o-DCB compared to the pure N2200 films spin coated with the same solvents in addition to the diffraction patterns could thus give an indication of how the two polymers arrange in the films.

The fact that the beam modifies the film during TEM can also be seen when the films are subsequently looked at in the SEM. Circular shapes from the electron beam in the TEM can be seen in the SEM images of Figure 5.5. From the SEM images it appears as if the film indeed gets thicker under the electron beam.

The diffraction patterns from the films, and thereby also the crystal structure, is sensitive to and change under the electron beam. If the beam is held over an area the ring pattern will gradually fade as shown in Figure 5.7. Already after 10 s there is a substantial loss of intensity for the diffracted rings and after 1 min most of the diffraction pattern indicating crystallinity is gone.

In Figure 5.7 the intensity in the diffraction patterns of Figure 5.6 along a line

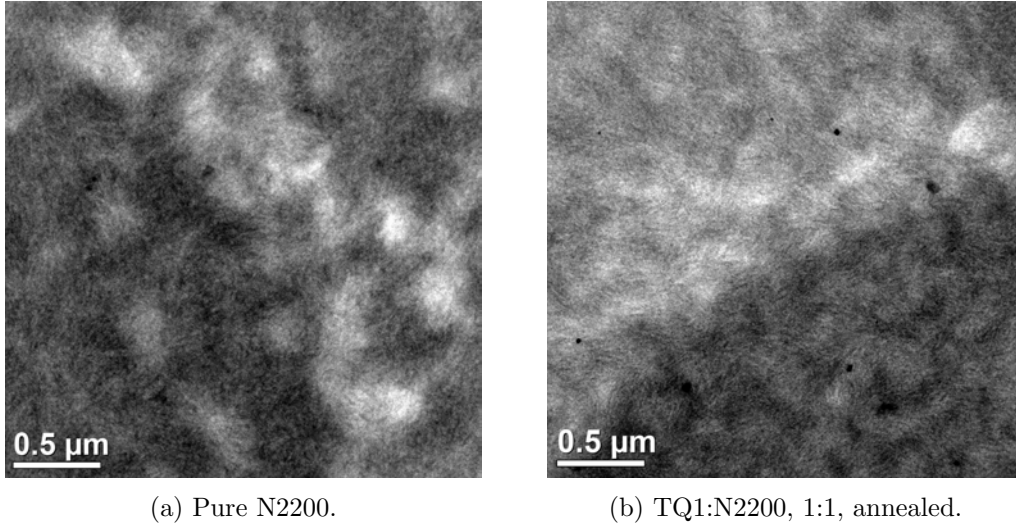


Figure 5.4: Films spin coated with o-DCB. The images show the darker area where the electron beam was previously placed. Both images are acquired in bright field.

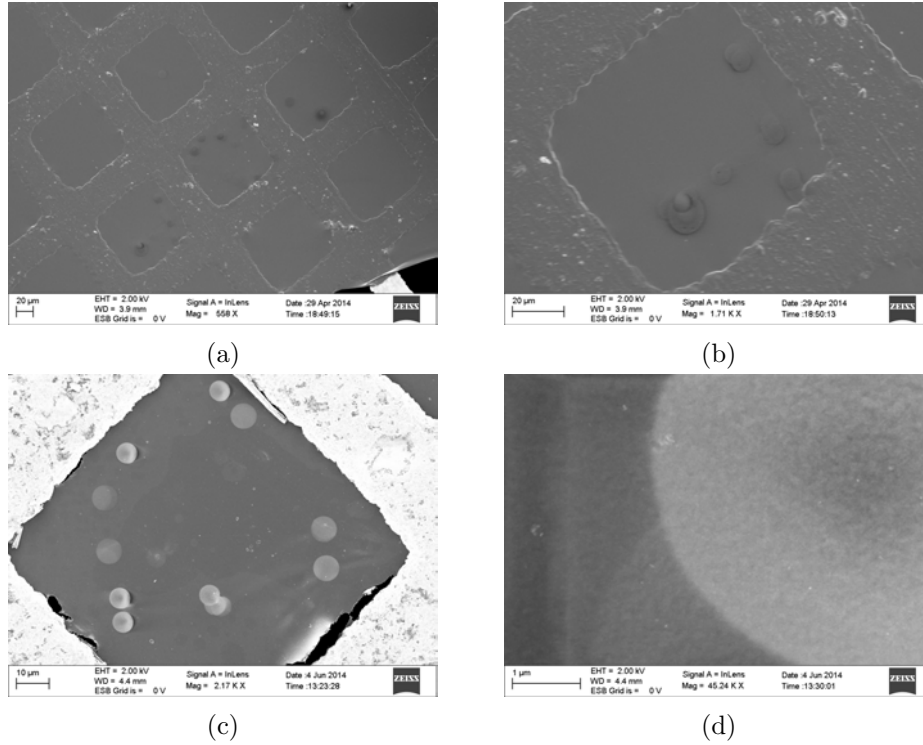


Figure 5.5: SEM imaging of an annealed TQ1:N2200 1:1 film spin coated with o-DCB. The film has earlier been imaged by TEM and the circles are the result of the electron beam of the TEM affecting the film. The images (a) and (b) are taken on the side facing air during spin-coating and the images (c) and (d) are taken at the side facing PEDOT:PSS during spin coating. Image (d) shows a circle at higher magnification.

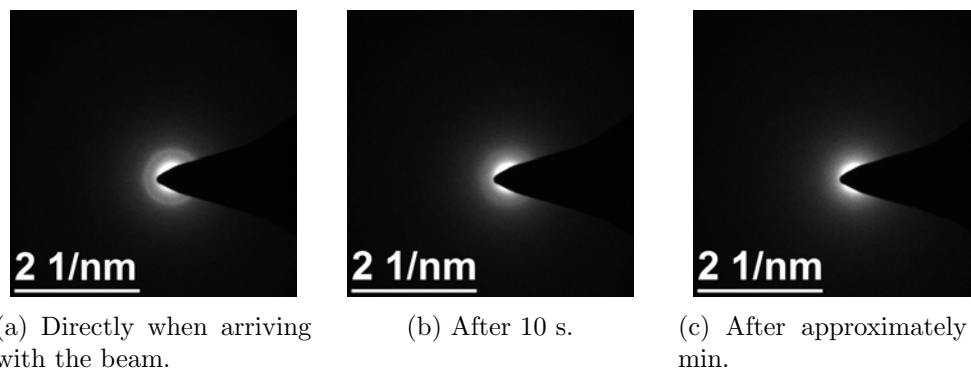


Figure 5.6: Diffraction patterns from films of pure TQ1:N2200, 1:1 spin coated with chloroform and annealed at 170°C for 20 min, showing the decay of the diffraction pattern under the electron beam.

from the center is plotted as a function of the distance from the center of the direct beam. The peak from the diffracted ring disappears already after 10 s. What is also worth noting is that the intensity of the direct beam also decreases. This indicates that the film gets thicker under the electron beam and thus scatters more electrons.

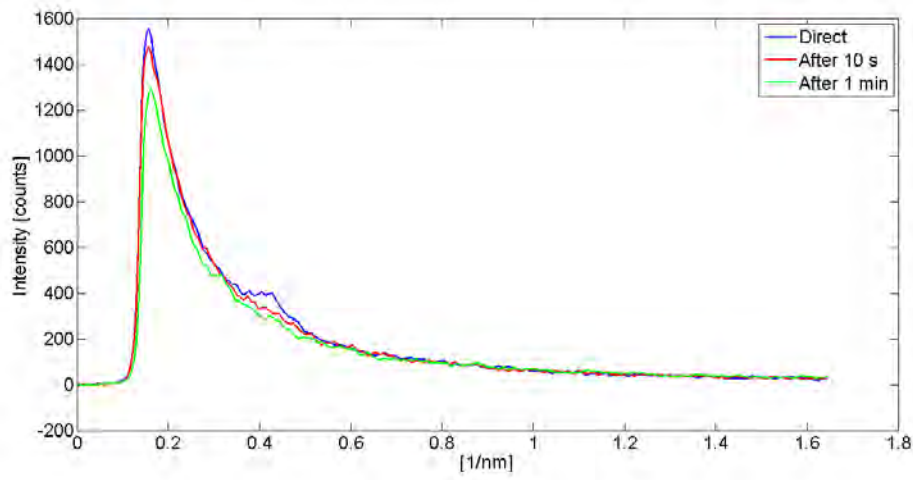


Figure 5.7: Intensity in the diffraction patterns of Figure 5.6 from a certain spot in the sample as a function of distance in the diffraction pattern plotted at three different times. The peak of the diffracted ring around $0.4/\text{nm}$ disappears almost instantaneously and the intensity of the direct beam gets lower with time, indicating a thickening of the film.

Chapter 6

Discussion

The diffraction patterns suggest that the bulk heterojunctions spin coated with o-DCB have domains rich in N2200 that are large enough to show correlated crystal orientation on the 200 nm scale. This could be inconvenient for efficient diffusion of excitons to the donor/acceptor interface since the domains would be too large in comparison to the exciton diffusion length of 5-20 nm. The chance of having continuous percolation paths to the electrodes for charge carriers is however increased with the larger morphology. The N2200 domains are also semi-crystalline which should increase the electron mobility through the active layer.

The diffraction patterns of films spin coated with chloroform indicate that N2200 is locked in an amorphous state during spin coating. The increased crystalline signal found in the annealed film shows that N2200 may crystallize during annealing, but that it may not arrange its crystal orientation in a preferred direction over larger domains. This could be an indication that the domains of different polymers are much finer in films spin coated with chloroform when compared to films spin coated with o-DCB. This would make chloroform a better solvent for producing solar cells with efficient charge dissociation.

A sketch of the proposed morphology during solidification before the crystallisation of N2200 may be seen in Figure 6.1.

6.1 Conclusions

- Differences were found between films spin coated with the two different solvents. Bulk heterojunctions of TQ1 and N2200 spin coated with chloroform showed no crystalline structure in as-spun films. Considering that pure N2200 films spin coated with chloroform showed crystalline order similar to that in pure films spin coated with o-DCB, it is likely that the presence of TQ1 hindered larger domains of N2200 to be formed. Bulk heterojunctions of TQ1 and N2200 spin coated with o-DCB showed crystalline domains with preferred orientation of the crystallites of approximately the same size as in pure N2200 films. These films also had the characteristic fibrillar surface structure and the thickness variations of films of pure N2200 spin coated with o-DCB.
- Annealing lead to the formation of detectable crystalline domains in bulk heterojunctions spin coated with chloroform, but no preferred orientation was

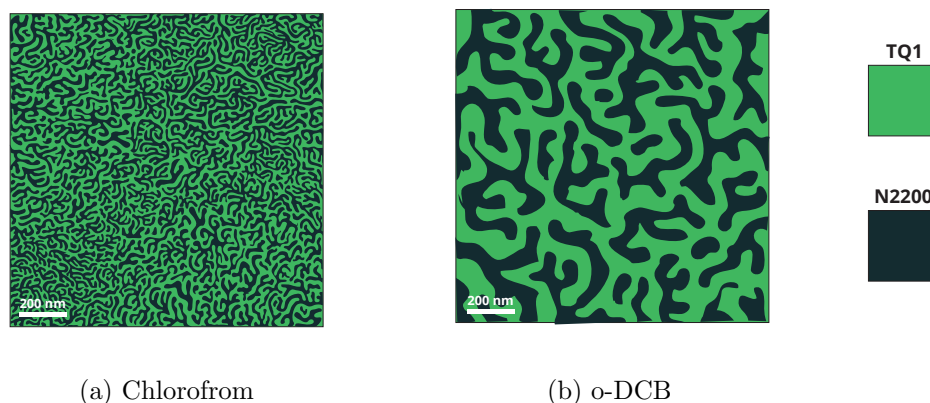


Figure 6.1: Proposed structure developed during solvent evaporation of different solvents.

seen over large enough distances to detect with the selected area aperture. In bulk heterojunctions spin coated with o-DCB no difference was found between as-spun and annealed films.

- The same type of electron diffraction patterns consisting of rings corresponding to the same interplanar distances were found in films of N2200 as have previously been found in grazing incidence x-ray diffraction.
- Plasma cleaning has been used to remove surface layers. In films of N2200 and in bulk heterojunctions spin coated with o-DCB the diffraction pattern was still present after plasma cleaning indicating that it is not only the surface that is crystalline.
- The data on the bulk heterojunctions suggests that the size of domains rich in one polymer is on different length scales depending on the solvent used for spin coating, indicating a smaller length scale for films spin coated with chloroform when compared to films spin coated with o-DCB.

6.2 Outlook

One challenge with these films is to find a contrast mechanism that makes it possible to differentiate between the two polymers. Further studies directed at finding a contrast mechanism could possibly provide very useful information about the microstructure of the film. The band gap is one thing that could be investigated as a means for differentiating between the two polymers. Spectroscopic techniques could be of interest.

Different ratios between the two polymers could be investigated more thoroughly and compared with each other. This could give a more clear idea of what is really seen during bright field imaging and how the polymers arrange in the film.

It should also be interesting to look at films spin coated with chloroform, both pure polymer films and bulk heterojunctions, in the SEM. Since differences have been found between the morphologies of the side facing air during spin coating and

the side facing PEDOT:PSS during spin coating for films spin coated with o-DCB, it would be of interest to continue investigating these effects also for different types of films and by using different techniques.

Different acceleration voltages were only investigated very briefly. It would be of interest to continue investigating the effects of changing the acceleration voltage, especially considering if different acceleration voltages change the rate at which the diffraction pattern fades under the electron beam.

There is more information to be obtained from the data already acquired that was not extracted and presented in this thesis. For example one could try to acquire the degree to which the polymer crystallites correlate their orientation.

Further studies of these films in devices would also deepen our understanding of these polymer blends and could give information about which processing parameters that are favourable for increasing the power conversion efficiency of devices.

Chapter 7

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Appendix A

List of samples

Here follows lists of all the manufactured samples.

For the mixed films the parameters for spin coating were the same for all samples spin coated from the same solvent. Films spin coated with chloroform were spun at 3000 rpm for 60 seconds. Films spin coated with o-DCB were spun at 500 rpm for 60 second followed by 3000 rpm for 30 seconds to remove excess solution. Films spin coated with p-xylene were spun at 500 rpm for 60 seconds and thereafter heated at 200°C for 60 seconds to evaporate any remaining solvent.

The thickness is measured including the thickness of the PEDOT:PSS layer, which is approximately 40 nm thick. Thickness measurements were carried out by Amaia Diaz de Zerio Mendaza at Polymer Technology, Department of Chemical and Biological Engineering, Chalmers University of Technology.

Table A.1: Samples of polymer mixtures.

TQ1:N2200	Solvent	Conc.[mg/mL]	Annealing temp./time [°C]/[min]	Thickness [nm]	Fabrication date
1:1	Chloroform	12	-	-	2014-01-22
3:2	Chloroform	12	-	-	2014-01-22
7:3	Chloroform	12	-	-	2014-01-22
4:1	Chloroform	12	-	-	2014-01-22
4:1	Chloroform	12	-	-	2014-02-14
4:1	Chloroform	12	150/20	-	2014-02-14
1:4	Chloroform	12	-	-	2014-02-14
1:4	Chloroform	12	150/20	-	2014-02-14
9:1	Chloroform	12	-	-	2014-02-21
9:1	Chloroform	12	200/40	-	2014-02-21
9:1	Chloroform	12	-	-	2014-02-28
9:1	Chloroform	12	170/20	-	2014-02-28
9:1	Chloroform	12	-	-	2014-03-06
9:1	Chloroform	12	170/20	-	2014-03-06
4:1	p-Xylene	12	-	-	2014-03-10
4:1	p-Xylene	12	170/20	-	2014-03-10
4:1	p-Xylene	12	-	-	2014-03-10
4:1	o-DCB	12	-	-	2014-03-10
4:1	o-DCB	12	170/20	-	2014-03-10
4:1	o-DCB	12	-	-	2014-03-10
1:1	o-DCB	12	-	141 ± 2	2014-03-28
1:1	o-DCB	12	170/20	251 ± 6	2014-03-28
1:1	Chloroform	12	-	209 ± 6	2014-03-28
1:1	Chloroform	12	170/20	227 ± 1	2014-03-28
1:1	o-DCB	5	-	114 ± 6	2014-03-28
1:1	o-DCB	5	170/20	114 ± 1	2014-03-28
1:1	o-DCB	12	170/20	-	2014-05-28
4:1	o-DCB	12	-	-	2014-05-28
4:1	o-DCB	12	170/20	-	2014-05-28
9:1	o-DCB	12	-	-	2014-05-28
9:1	o-DCB	12	170/20	-	2014-05-28
4:1	Chloroform	12	-	-	2014-05-28
4:1	Chloroform	12	170/20	-	2014-05-28
9:1	Chloroform	12	-	-	2014-05-28
9:1	Chloroform	12	170/20	-	2014-05-28

Table A.2: Samples of pure polymers.

Polymer	Solvent	Conc. [mg/mL]	Spin speed/time [rpm]/[s]	Thickness [nm]	Fabrication date
N2200	Chloroform	12	3000/60	-	2014-01-22
N2200	Chloroform	10	3000/60	246 ± 4	2014-03-19
N2200	Chloroform	10	2000/60	218 ± 4	2014-03-19
TQ1	Chloroform	10	2000/60 + 3000/60	215 ± 1	2014-03-28
N2200	Chloroform	5	3000/60	128 ± 2	2014-04-24
TQ1	Chloroform	5	3000/60	146 ± 7	2014-04-24
TQ1	o-DCB	12	500/60 + 3000/30	125 ± 4	2014-04-29
N2200	o-DCB	12	500/60 + 3000/30	249 ± 2	2014-04-29

Appendix B

Polymers

Polymers are molecules consisting of one small unit, known as a monomer, that is repeated in a long covalently bonded chain [14]. Most polymers contain carbon, and polymer chemistry is therefore commonly labeled as a branch of organic chemistry [14].

The molecular shape of polymers give them many interesting properties, but because the structure of the polymer may vary there are also specific properties that can vary widely between different polymers [14].

When polymers are synthesised in the laboratory or in industry it is generally not possible to achieve a batch with polymers of all the same lengths. Polymers are therefore often characterised by an average molar mass and an average chain length [5]. A common way to measure the average molar mass of a polymer blend is by the number average, which is given as

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (\text{B.1})$$

where N_i is the number of moles of polymers with a specific molecular weight M_i .

The mechanical strength of a polymeric material will increase with chain length and increasing intermolecular forces between chains. This is caused by an overall larger interaction between the chains [5]. Single chains may form closely packed crystalline regions that improve the strength of the material [5].

Polymers may also have branches. These branches introduce an intrinsic disorder that hinders crystal formation [14].

Polymeric materials are generally in one of four different physical states [14]:

- Liquid
- Crystalline
- Glass (amorphous)
- Liquid crystalline

Melts and solutions of polymers are liquids with a chain length-dependent viscosity. Longer chains may cause more entanglements between chains and therefore melts and solutions of polymers with a higher molecular weight are generally more viscous [5].

Some polymers may form liquid crystalline phases. This is only possible if the polymer chains are more or less rigid [14].

B.1 Crystalline polymers

Not all polymers may form crystal regions, and among the polymeric materials that may form crystalline structure the majority will only reach a semi-crystalline state with small crystals in an amorphous bulk [14].

Most polymers crystallise by folding the chains in lamellae, separated by regions of amorphous polymers. One polymer chain may be involved in several lamellae and the amorphous regions in between [14]. The thickness of the lamellae depend on the crystallisation temperature, and the thickness also determines the melting temperature. Therefore the melting temperature is ultimately determined by the temperature at which the crystallisation occurs [22]. By increasing the temperature of a semi-crystalline polymeric material it is possible to increase the lamellar thickness to the thickness that would have been obtained if the original crystallisation had occurred at the higher temperature, provided that the higher temperature is still below the melting temperature [22].

Lamellae are rarely found alone in the bulk of the sample, but rather organise to form larger ordered structures [22]. On a larger length scale the lamellae organise themselves in spherulites of several micrometers in size [14]. These spherulites start as a group of stacked lamellae, as additional lamellae are added to the group they start to spread around the edges and eventually the cluster of lamellae take the shape of a spherulite [22].

Spherulites are the main type of lamellar organisation in polymeric materials, but not the only one [22]. Applied stress during crystallisation can also lead to the formation of fibrillar nuclei on which lamellae crystallise giving rise to row-nucleated structures, also known as "shish-kebabs" [22].

Data on diffraction from polymeric crystals may give information on many different topics. From the diffraction peaks the dimensions of the unit cell may be calculated, and by comparing the intensity of the crystalline peaks with the amorphous scattering the degree of crystallinity may be calculated [22]. Typical polymers reach a degree of crystallinity in the range between 20 and 60% [14].

Not all polymer crystallise in lamellae, if the polymer backbone is too stiff it might not be possible for the chain to fold in ways necessary to form lamellae.

B.2 The glass transition

Whilst not all polymers may easily crystallise, almost all polymers form glasses, which are materials with a state of order like a liquid but mechanical properties like a solid [14]. When the temperature of the polymer in liquid state is lowered the viscosity is increased and thereby also the relaxation time. When the temperature is lowered to the point where the relaxation time becomes comparable to the experimental time scale, the system will fall out of equilibrium and no longer be able to adopt all possible microstates during the time of the experiment, this is known as the glass transition and occurs at the glass transition temperature T_g [14]. The value

of T_g depend on the time scale of the experiment, if the rate of cooling is increased, T_g will also increase [14].

The glass transition may only occur if it is possible to cool the material below the crystallization temperature without it crystallising. This may be made possible by either cooling the material fast enough so that it will not have time to form crystals or if the molecules possess some permanent disorder that does not allow for crystals to be formed [14]. Because of the disorder present in a glass it would still have a finite entropy if cooled to absolute zero [14].

The glass transition possesses properties similar to those of a second-order phase transition, such as discontinuous changes of heat capacity and thermal expansivity at the glass transition temperature [14]. The glass transition is, however, not a thermodynamic phase transition because the transition temperature varies with the rate of the experiment and the glass is not the state of lowest free energy and therefore not at equilibrium [14]. The glass transition is instead a kinetic transition [14].