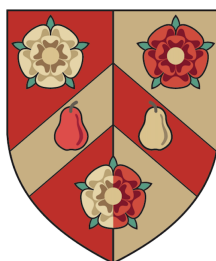




Neutron and X-ray scattering studies of organic thin films for photovoltaic applications

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To my mum and dad.

Germans! Frenchmen! Englishmen! Dutch people! Danes, Norwegians and Swedes! Prussians! Poles! Hungarians! Italians! Spaniards! Portuguese! Aren't you all Humans? All, as Humans, equal? - different Figures - different Colours - different Tones! - But tell me, you Geometer! Which Figure do you find the most necessary, the Square or the Circle? - Tell me, you Painter! Which of the Colours of the Rainbow is your most favoured? - Tell me, you Musician! Which of all the Tones of your Scale is the most indispensable to you? And yet you could calculate the Relationships and Influence of the Figures, Colours, and Tones in finite, limited Spheres - on the contrary, the various Peoples are lost in the Circle of Eternity. What Historian has measured, what Philosopher of History has dared to weigh out the Contributions of the different Nations to the Completion of the same great Purpose, against each other? What ridiculous Undertaking!

—Jens Baggesen, *The Labyrinth*

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Abstract

Organic Photovoltaics (OPVs) have the potential to play an important role in the green transition. The microstructure of OPVs plays a role in nearly all aspect of device operation such as exciton splitting and charge carrier transport. Scattering techniques, such as Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) or Small Angle Neutron Scattering (SANS), offer the possibility of both qualitative and quantitative analysis of OPV thin film microstructure. However, we remain challenged by our ability both to investigate all small molecule (SM) evaporated OPV thin films as well as by the subsequent physical modelling of the data. To this end, we develop a SANS sample holder and apply SANS to SM evaporated OPV thin films for the first time to understand the longer range microstructure of Bulk Heterojunctions (BHJs). We perform an initial study of model Donor (D) molecules (A6T, ZnPc, SubPc, Rubrene, DCV5T-me(3,3)) paired with the Acceptor (A) molecule C60. We find the ZnPc:C60, SubPc:C60 and Rubrene:C60 configurations to be highly intermixed whilst A6T:C60 and DCV5T-me(3,3):C60 show phase separation between D and A-rich domains. We apply the Debye-Anderson-Brumberger and *Mass Fractal* models to the scattering from A6T:C60 configurations with varied substrate temperature during growth (T_{sub}), molar mixing ratio and molecular deposition rate and determine how growth parameters affect the final blend mixing. DCV5T-me(3,3):C60 appears as phase separated with prominent Bragg feature indicating low domain polydispersity. A fine grained SANS study of DCV5T-me(3,3):C60 with varying T_{sub} shows phase separation to occur between $T_{sub} = RT$ and $T_{sub} = 60\text{ }^{\circ}\text{C}$ and using the *Broad peak* model we show the domain centre-to-centre distance to increase by $0.8\text{ }\text{\AA}/\text{K } T_{sub}$. Furthermore, we study DCV5T-me(3,3):C60 at $T_{sub} = 120\text{ }^{\circ}\text{C}$ via in situ GIWAXS and compare the blend to the neat D film. We attempt to identify the growth modes of each film and compare changes in preferred molecular orientations. We find the blend to appear as a two-phase system of

relative pure D domains and mixed D:A domains and that C60 appears to impact the $\pi - \pi$ packing of the blend. Finally, we use SANS to study carbon nanotube:polymer (CNT:P) organic electrode systems which are excellent candidates for transparent electrodes in a wide range of applications, including organic solar cells. Their scattering indicate them to be fractal-like and we analyse the viability of several models to describe the data. We find the accessible Q -range to be insufficient for models other than power law models. We quantify the packing density as polymer melt index is varied and find no systematic trend. We find film manufacturing by shear force mixing (SFM) to result in denser packing than tip sonication and demonstrate a positive correlation between a higher Porod exponent of the scattering data and a higher device Figure of Merit (FoM), σ_{dc}/σ_{op} .

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List of Abbreviations

A		Acceptor
AgBeh		Silver Behenate
BHJ		Bulk Heterojunction
CNT		Carbon Nanotube
D		Donor
DAB		Debye-Anderson-Brumberger
DI		Deionised
DREAM		DiffeRential Evolution Adaptive Metropolis
ECHO		Evaporation CHamber Oxford
EVA		Ethylene-Vinyl Acetate
FoM		Figure of Merit
GIWAXS		Grazing Incidence Wide Angle X-ray Scattering
GIXD		Grazing Incidence X-ray Diffraction
HOMO		Highest Occupied Molecular Orbital
IP		In-Plane
ITO		Indium-Tin-Oxide
LCOE		Levelised Cost of Energy
LUMO		Lowest Unoccupied Molecular Orbital
MC		Markov chain

ML		Monolayer
MLE		Maximum Likelihood Estimation
MWCNT		Multi-Walled Carbon Nanotube
NFA		Non-Fullerene Acceptor
OoP		Out-of-Plane
OPV		Organic Photovoltaic
OSC		Organic Semiconductor
P		Polymer
P3HT		Poly(3-Hexylthiophene)
PCE		Power Conversion Efficiency
QCM		Quartz Crystal Monitor
RSoXS		Resonant soft X-ray Scattering
SANS		Small Angle Neutron Scattering
SFM		Shear Force Microscopy
SIP		Substrate Induced Phase
SLD		Scattering Length Density
SM		Small Molecule
STEM-EDX	...	Scanning Transmission Electron Microscopy, Energy Dispersive X-ray spectroscopy
SWCNT		Single-Walled Carbon Nanotube
VTE		Vacuum Thermally Evaporated

1 | List of publications

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2. Anna Jungbluth, Pascal Kaienburg, Andreas E. Lauritzen, Thomas Derrien, and Moritz Riede. "Probing the energy levels of organic bulk heterojunctions by varying the donor content." *APL Materials* vol. 11, no. 6 (2023).
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4. Bernd K. Sturdza, Andreas E. Lauritzen, Suer Zhou, Andre J. Bennett, Joshua Form, M. Greyson Christoforo, Robert M. Dalgliesh, Henry J. Snaith, Moritz K. Riede, and Robin J. Nicholas. "Improving performance of fully scalable, flexible transparent conductive films made from carbon nanotubes and ethylene-vinyl acetate." *Energy Reports* 8 (2022): 48-60.
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2 | Introduction

2.1 Global warming and green energy

Since the coal powered Industrial Revolution the consumption of fossil fuels has been an integral part of modern society. This has led to many benefits. Coal and natural gas have powered the electricity networks, boilers and factories that have brought prosperity and warm homes to much of the world. The combustion engines of cars and planes, powered by petrol, diesel and kerosene, have given humanity an unprecedented ability to travel quickly and safely across nations and oceans. But there has also been a cost. When fossil fuels that were mined or extracted from the ground are burnt, new carbon enters the carbon cycle chiefly in the form of atmospheric CO_2 . As millions of tonnes of fossil fuels has been burnt throughout the last centuries the concentration of CO_2 in the atmosphere has steadily risen from pre-industrial levels of 280 ppm to 417 ppm in 2022 [1].

The Earth exists in a black body radiation equilibrium with the Sun. Energy from the sun's rays is absorbed chiefly near the surface of the Earth and energy leaves the Earth system from the upper atmosphere. CO_2 is a so-called greenhouse gas that strongly absorbs light with wavelengths within the infrared part of the solar spectrum. As atmospheric CO_2 levels increase, so does the absorption of infrared light being emitted from the Earth's surface. This results in heat now escaping from higher and colder altitudes. As this colder air emits less radiation, the system is thrown out of balance with more energy entering the system than leaving it. To reach equilibrium once more, the surface temperature rises to consequently heat up the upper atmosphere. Emitted energy once more matches energy absorbed and balance is restored.

Whilst the two sides of the equal sign now match again, this explanation belies the impact on the planet's flora, fauna and humans. The Intergovernmental Panel on Climate Change (IPCC) estimates an increase in global surface temperature of 1.09 °C in 2011 - 2020 above the 1850 - 1900 time period with projected temperatures in 2050 likely to increase by 1.5 or even 2.0 °C depending on how emission levels develop [1]. The consequences are legion. Future droughts are expected to be more intense and last longer [2]. Biodiversity will also be put under stress with the IPCC estimating 9% of species at risk of extinction if global warming reaches 1.5 °C with the likely maximum range of 14 % of species at risk. Rising sea levels, due to the loss of ice from glaciers and Arctic regions, with more than a billion people being at risk from coast-specific climate hazards with those in small island states and the Arctic being especially at risk [3].

There are thus clear and pressing reasons to reduce our CO₂ emission levels by phasing out fossil fuels. However, this is no easy task. Global energy consumption is forecast to increase by 20-30 % by 2040 without the implementation of ambitious climate policy [4]. Such ambitious policy would involve energy efficiency measures such as improved housing insulation, but also massive deployment of CO₂ neutral energy sources such as solar photovoltaics or wind power. Such a roll-out, however, is costly. This is a particular worry for developing nations where the populace are less able to shoulder higher energy prices and where electricity demand is expected to increase rapidly (by 3.3% p.a. in countries outside the Organisation for Economic Co-operation and Development between 2011 and 2035) [5]. The electricity grid of the future must thus not only be green to combat global warming, but also affordable to help eradicate energy poverty.

The price of renewable energy technologies has decreased greatly in recent years, with the weighted average Levelised Cost Of Energy (LCOE) for onshore wind having decreased from \$0.107/kWh in 2010 to \$0.033/kWh in 2022 and power purchase agreements for solar photovoltaics having reached prices below \$0.025/MWh at utility scale [6, 7]. The current photovoltaic market is dominated by silicon based solar cells which account for around 95% of total global PV production in 2021 with the bulk of modules (84% share) being mono-crystalline Silicon [8]. While the success of silicon based solar cells represent a multitude of scientific and technological advancements, Si-based solar cell modules are not suited for all applications. For example, the modules are relatively heavy which limits their installation capacity on walls or roofs that may not be sufficiently sturdy or where the weight will make the deployment process prohibitively costly. Such considerations are the basis for the continued research of thin film photovoltaics such as perovskites or organic photovoltaics, the latter of which is the focus of this thesis.

2.2 The potential of organic photovoltaics

Organic photovoltaics are semi-conductor devices based on organic materials i.e. molecules composed of carbon and hydrogen typically in conjunction with other light elements such as O, N and S. They can be made from either solution-processed polymers in conjunction with so-called small molecules (SMs) or be composed solely of SMs that are vacuum thermally evaporated (VTE) onto a substrate.

Unlike silicon-based solar cells, which have active layer i.e. photon-absorbing thicknesses in the hundreds of μm , Organic Photovoltaic (OPV) active layers are in the tens to hundreds of nm. OPVs can be mechanically flexible and be manufactured with active layers and electrodes simply encapsulated between flexible

plastic sheets. The thin layers and minimalist module design lead to OPVs only weighing on the order of 1 kg per m² covered area which is more than a magnitude less than typical silicon solar cells [9]. Such low weight solar cells that appear almost as simple sheets of plastic can thus readily be glued to the walls or surfaces of buildings where silicon solar cells would have been too heavy. The flexibility of OPV modules also enables the application to curved surfaces.

The field of organic synthesis is well developed and organic molecules can be modified to a near infinite degree by varying the constituent atoms as well as the configuration of those atoms. This in turn changes the physical properties of the thin films opening the door to new application areas. For example, the absorption of OPVs can be tuned to primarily absorb near-infrared radiation whilst retaining high visible light transmittance due to the thinness of the films. OPVs have been called "an ideal candidate as greenhouse shading material" as solar heat stress of the growing plants can be reduced whilst enabling simultaneous food and energy production, reducing land use [10]. OPVs, which can be made from non-toxic components, are also advantaged when combined with food production compared to other thin film solar cell technologies, such as perovskites, which often have heavy metal elements. However, the production of current high performing OPVs often involve highly toxic chlorinated and/or aromatic solvents, which greatly increases their environmental impact across the life cycle, necessitating further work on improving the production stage of OPVs [11].

Whilst OPVs have a strong potential to play a part in the green transition, key scientific challenges still need to be overcome to unlock their full potential.

2.3 The challenges of OPVs

In recent years, the record performance of OPVs has increased greatly from 8.1% Power Conversion Efficiency (PCE) in 2010 to 19.2% in 2023. Compared to other types of solar cells, OPVs generally suffer from a low light-to-electricity conversion and it has been a key scientific challenge to alleviate this issue. Unlike in inorganic solar cells, when a photon is absorbed by an OPV thin film a tightly bound hole-electron pair, a so-called exciton, is formed. If the electron and the hole are not separated into free charge carriers, the exciton will shortly recombine, dissipating the absorbed energy. To enable charge separation, OPVs are made from a mix of two or more components with off-set energy levels. At the interface between the materials, called (electron) donors and acceptors (D and A), the exciton splits into free electrons and holes which must then travel towards their respective electrodes for charge extraction.

To ensure efficient exciton splitting, smaller and more crystalline domains of D and A are preferred as it increases the chances an exciton will diffuse towards a D:A interface before recombining [12]. Once charge carriers are separated, bi-continuous D and A pathways are needed to help travelling holes and electrons reach their respective electrodes without meeting a counterpart at a D:A interface and recombining. This favours larger D and A domains to reduce interfaces. Balancing the need for charge carrier separation with efficient charge carrier extraction is one of the key challenges for OPVs. To optimise performance we must be able to both study and control the microstructure of OPVs, the topic of this thesis.

In 2022, L. Zhu, M. Zhang, J.Xu et al. of Shanghai Jiao Tong University produced OPVs with a record breaking certified 19.2% PCE, very close to the PCE of com-

mercial Si solar cells [13]. This was achieved using a solution processed blend of two polymers (PM6 and D18) and one so-called Non-Fullerene Acceptor (NFA) L8-BO. Through the addition of a smaller amount of the highly crystalline D18 polymer, the crystallinity of the more absorbing PM6 is increased. The increase in crystallite size and crystallinity results in excitons being able to move farther and enhances short range (charge carrier) mobility. This is studied via Grazing Incidence X-ray Diffraction (GIXD) which also reveals how the orientation of the molecules is favourable to light absorption. In this thesis, we will also use X-ray scattering to reveal the shorter-range (0-5 nm) microstructure and orientation of SM OPV thin films and we will exploit the grazing-incidence geometry to overcome the inherent difficulty of probing thin films only 100s of nanometres thick. The combination of polymers chosen by Zhu et al. also results in a bi-continuous fibrous network of D and A molecules thus creating longer-range pathways for the freed charge carriers to reach the electrodes. The statistical properties of the fibril radii are probed via Resonant soft X-ray scattering (RSoXS), a scattering technique that probes the longer-range structure of thin films [13]. In this thesis, we will employ Small Angle Neutron Scattering (SANS) in a similar manner. SANS has been extensively used to qualitatively and quantitatively characterise polymer based OPV thin films at length scales on the order of tens to hundreds of nm, but has, to our knowledge, hitherto not been applied to small molecule VTE OPV thin films. In this thesis, we will seek to expand the applicability of SANS to VTE thin films. This is done starting at the experimental level with the design of a sample holder, to the selection of the most appropriate physical models that describe the data to finally derive quantitative results describing the processing-structure relationships of the studied films. In addition to opening up SANS analysis to VTE thin films, this thesis will also highlight the challenges of the technique and what steps should be taken to improve future use of the techniques.

While the current OPV PCE record is held by a polymer-based solution processed cell, there are reasons to study VTE all-small molecule solar cells. The development path of the technologically similar organic light emitting diodes was at times dominated by solution processed devices. As the technology developed, VTE based devices took over. With VTE multiple thin layers in a device can be defined very precisely, whereas this becomes difficult in solution processed layer stacks due to the complicated interplay between different solvents and different molecules. Avoiding the use of solvents altogether, which are in many cases environmentally harmful, is another benefit [9]. To help VTE OPVs, which are less studied than polymer based OPVs, reach commercial viability we must learn how to take full advantage of the high degree of control over processing parameters offered. In this thesis, we will use *in situ* X-ray scattering to study how the microstructure of a VTE SM binary thin film evolves as the film grows.

The active layer of a solar cell is not the only component which can be made from organic constituents. Anodes and transport layers made based on carbon nanotubes (CNTs) are a promising sustainable and flexible alternative to current inorganic layers, which are brittle and rely on scarce materials like indium. Whilst carbon nanotube based electrodes offer the possibilities of very high charge carrier transport, they are currently limited by bundling of nanotubes, which increases resistance. This bundling can be reduced by mixing the CNTs with polymers that wrap around the tubes and improve dispersion. In this thesis, we will use SANS to study how the choice of polymer and deposition parameters affects the microstructure of CNT:polymer films and the effect on device relevant performance parameters.

The overarching theme of this thesis is to study the microstructure of VTE OPV thin films and enhance our understanding of how different experimental techniques SANS and *in situ* X-ray scattering can be applied to the field and to use them to investigate processing-structure relationships. This is done with the hope that further studies may help improve the efficiencies, stability and costs of OPVs so that the technology may play its part in the world's green transition.

2.4 Thesis outline

This thesis focuses on studying organic thin films for OPV applications via scattering techniques such as SANS or Grazing Incidence Wide Angle X-ray Scattering (GIWAXS). Chapter 2 outlines the fundamentals of scattering, starting from point scattering and then expanding the principles to scattering from single molecules and then solid films. The different scattering mechanics of X-ray and neutron scattering are discussed in context of their respective applications and we introduce small angle neutron scattering as well as the Guinier and Porod regimes. Chapter 3 introduces organic molecules and the opto-electronic properties of organic semi-conducting molecules. We discuss the bulk heterojunction and relate structural properties such as orientation and crystallinity to opto-electronic properties such as exciton generation, transport and splitting. The three basic thin film growth modes are discussed. Carbon Nanotube:Polymer thin films, their properties and their application for photovoltaics are detailed. Chapter 4 outlines the manufacturing process of both vacuum evaporated and carbon nanotube:polymer thin film. We discuss the sample holder used for neutron measurements and the underlying design considerations. We describe the experimental process of both *ex situ* and *in situ* GIWAXS X-ray measurements. Chapter 5 features SANS studies and analysis of various organic donor:C60 evaporated thin films and we inves-

tigate the microstructural effect of changing device relevant growth parameters. We expand on these studies in Chapter 6, with a focused SANS study of DCV5T-me(3,3):C60 as the substrate temperature during growth is varied. The goal of these chapters is to demonstrate the qualitative and quantitative capabilities of SANS when applied to evaporated organic small molecule thin films. Chapter 7 is a comprehensive *in situ* GIWAXS study of neat DCV5T-me(3,3) and DCV5T-me(3,3):C60 evaporations. The microstructural evolution of the films in terms of crystallinity and orientation are studied as the films grow. In Chapter 8 we apply SANS to various Carbon nanotube:Polymer thin films and study the effect of polymer choice and manufacturing method. The focus of this chapter is on the limits and possibilities of different scattering modelling approaches. Chapter 9 serves as conclusion on the main findings of the dissertation as well as offering an outlook on how the discussed techniques and studies should be expanded in the future. This is followed by an appendix with additional information for keen readers.

3 | Scattering theory

3.1 Elemental particle scattering from matter

In this section, the fundamentals of elastic scattering will be outlined with a focus on X-ray and neutron scattering. The experimental application of the theory is discussed in Chapter 5.

Scattering, as a shorthand for "crystallographic scattering", refers to the process by which the particle-wave duality of elemental particles such as photons and neutrons can be exploited to probe the structure of matter via constructive interference.

To understand the device relevant microstructure of OPV thin films, we seek to probe features with length scales on the order of 10^{-10} to 10^{-7} m. This matches well with the wavelength of X-rays as well as thermal neutrons. Furthermore, such particles and neutrons in particular are able to penetrate beyond the surface of organic films, probing their inner structure. As the bulk structure is often of greater practical relevance, this offers a great advantage compared to microscopy based techniques.

3.1.1 The fundamentals of scattering

The following description of scattering is based on those of D. S. Sivia, the work which the reader is referred to for a more thorough discussion [14].

Scattering refers to when a particle interacts (scatters) with a scattering source and undergoes a change in momentum and, in the case of inelastic scattering, energy.

The change in momentum $\mathbf{P}$ is given by

$$\mathbf{P} = \hbar(k_i - k_f) = \hbar\mathbf{Q}, \quad (3.1)$$

defining the wavevector transfer $\mathbf{Q}$

$$\mathbf{Q} = k_i - k_f, \quad (3.2)$$

illustrated in Fig. 3.1. From the incident and final wavefactors k_i and k_f , respec-

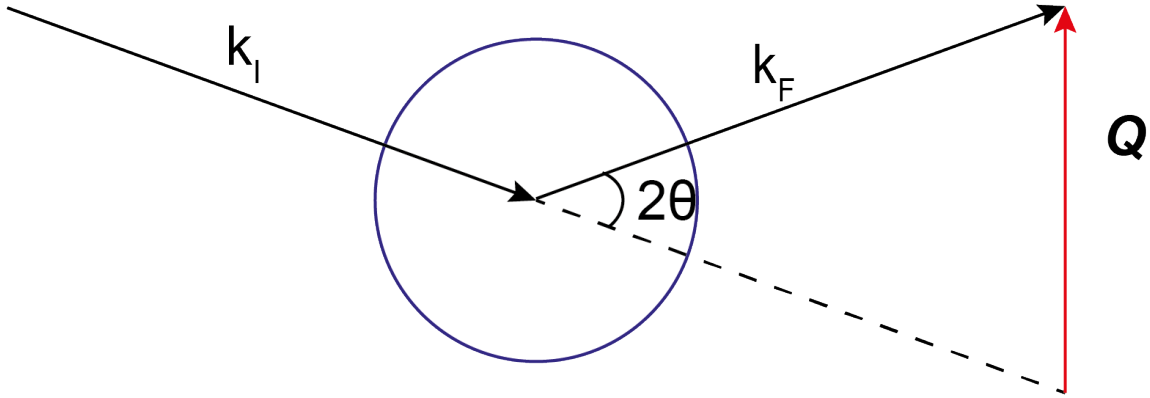


Figure 3.1: An illustration of a scattering event where Q is given by the difference between k_i and k_f .

tively. The changes in both energy and momentum of the particle are both equal and opposite to that of the scatterer. In this work, we will only be considering *elastic* scattering where there is no exchange of energy E where the incident and final angular frequencies remain the same

$$\omega_i = \omega_f \rightarrow E = 0, \quad (3.3)$$

Consequently, the magnitude of the momenta must remain constant

$$|k_i| = |k_f| = \frac{2\pi}{\lambda}, \quad (3.4)$$

where λ is the wavelength of the scatterer. From the geometric relation of the wave vectors we can define

$$Q = \frac{4\pi \sin \theta}{\lambda}. \quad (3.5)$$

3.2 X-rays and matter

3.2.1 Scattering from one electron

As a simply starting case for scattering we can imagine a single, fixed atom which is defined as being immobile and, since we have restricted ourselves to elastic scattering, unable to exchange energy with its surroundings. A beam of particles is defined as a complex plane wave with wavenumber k travelling along the z -direction

$$\psi_i = \psi_0 e^{ikz}, \quad (3.6)$$

with the pre-factor ψ_0 absorbing the phase-off set as well as the temporal variation of the wave.

When particles scatter off of the atom, placed at the origin, the wave will oscillate with distance r from the atom. As the waves are no longer travelling as a collimated bunch, but rather dispersing in space they will also be subject to the inverse-square intensity law, leading to radial part of the outgoing wave function being

$$\frac{e^{ikr}}{r}, \quad r > 0. \quad (3.7)$$

The dispersion of the outgoing photons is described by the retained ψ_0 which serves as a normalisation factor between the incident and outgoing flux as well

the dispersion function $f(\lambda, \theta)$. The outgoing wave function is thus described by

$$\psi_f = \psi_0 f(\lambda, \theta) \frac{e^{ikz}}{r}, \quad r > 0. \quad (3.8)$$

3.2.2 Dispersion of X-rays and neutrons

The dispersion function differs between X-rays and neutrons. For neutrons as used in this thesis, it can be approximated as an isotope specific constant

$$f(\lambda, \theta) = -b. \quad (3.9)$$

This constant is known as the *scattering length*. Neutrons scatter due to strong force interactions with nuclei which are small (10^{-14} m) compared to the wavelengths of the thermal neutrons used of small angle scattering (10^{-10} m). Regardless of element and reasonable variation in the neutron wavelength, the scattering nuclei will behave as point sources and scatter uniformly in all directions. We note here that the full expression of $f(\lambda, \theta)$ is actually also dependant on spin effects and can contain an imaginary term corresponding to absorption resonances. However, for the typical organic elements which comprise the molecules in this thesis such resonances are happily avoided. The negative sign of the expression is chosen by convention.

The magnitude and sign of b does not vary in a predictable way. Of key experimental relevance for the study organic matter is that fact that 'standard' hydrogen (Protium ^1H) has a negative scattering length. The scattering length is dependent on the spin state of the nucleus and its interaction with the spin state of the impinging neutron. Protium ^1H , which is essentially a proton, is a spin 1/2 particle as is the neutron. As a pair, their spin will combine to yield three spin 1 triplet

states and 1 spin 0 singlet state. Their scattering lengths are

$$b_{triplet} = 1.085 \times 10^{-14} \text{ m.} \quad (3.10)$$

$$b_{singlet} = -4.750 \times 10^{-14} \text{ m.} \quad (3.11)$$

The expectation value of b is then

$$\langle b \rangle = \frac{3}{4}b_{triplet} + \frac{1}{4}b_{singlet} = -0.374 \times 10^{-14} \text{ m,} \quad (3.12)$$

with expectation value of $\langle b \rangle = -0.374 \times 10^{-14} \text{ m}$. A negative b signifies a 180° phase shift of scattered particle wavefunctions compared to those scattering of particle with an equivalent positive b value and most elements, weighted by their isotopic average, have positive scattering lengths. The standard deviation of hydrogen is given by

$$\Delta b = \sqrt{\langle b^2 \rangle - \langle b \rangle^2} = \sqrt{\left[\frac{3}{4}(b_{triplet})^2 + \frac{1}{4}(b_{singlet})^2 \right] - \langle b \rangle^2}, \quad (3.13)$$

$$\Delta b = 2.527 \times 10^{-14} \text{ m.} \quad (3.14)$$

This is a relatively large standard deviation of scattering length, owing to the large difference in value and sign of $b_{triplet}$ and $b_{singlet}$.

For a heterojunction system, as discussed in Sec. 4.3, consisting of domains of hydrogen rich organic donors and domains of hydrogen deficient fullerenes a natural difference (known as a *contrast*) between the scattering length densities will arise. This makes neutron scattering a highly complementary technique to X-ray scattering for the study of dense organic systems as the X-ray contrast between different organic compounds is nigh zero.

The dispersion function of X-rays, known as the *atomic form factor* is given by

$$f(\lambda, \theta) = Zg(Q)r_e. \quad (3.15)$$

To elucidate how X-rays interact with matter, we will break up this equation.

The dispersion function is proportional to Z , the atomic number as X-rays scatter through electromagnetic interactions and (non-ionic) high Z elements will thus scatter more. This naturally poses a problem for X-ray diffraction studies of organic thin films as organic molecules are typically composed of lighter elements. A discussion of how this is overcome experimentally can be found in section 5.7. $g(Q)$ decreases non-monotonically from 1 at $Q = 0$ to 0 at infinity. Unlike for neutrons, atoms do not appear as points to X-rays. Instead the electronic cloud off which they scatter is now of a meaningful non-negligible size compared to the length scales of X-rays. X-rays thus have a propensity to scatter in 'forward' directions and taper off at higher angles. $g(Q)$ is element specific due to variation in atomic number with heavier elements having a more rapidly declining function.

The final term

$$r_e = \frac{e^2}{4\pi\epsilon_0 m_e c^2} = 2.818 \times 10^{-15} \text{ m}, \quad (3.16)$$

is the Thomson scattering length representing a classical radius of an electron.

3.2.3 Incoherent scattering

The total rate of scattering $R(2\theta, \phi)$ in a given direction is given by the norm square of the outgoing wave function (Eq. 3.8) integrated spherically to capture all outgoing scattering

$$R = \int_{2\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |\psi_f|^2 dA, \quad (3.17)$$

where $dA = r^2 \sin 2\theta d\phi d2\theta$, the area generated when a radius r is pointed towards ϕ , 2θ is moved infinitesimally in ϕ and 2θ .

By dividing the rate of scattering with the norm square of the normalisation factor ψ_0 we get the cross-section σ

$$\sigma = \frac{R}{|\psi_0|^2}. \quad (3.18)$$

The cross-section, as the name implies, is equivalent to a classical cross-section and has the dimensions of area squared. It signifies how 'large' a scatterer is. To obtain physical information about a sample, we are most often not looking at a total rate of scattering R , but rather scattering in a given direction $R(2\theta, \phi)$, which is also what we measure experimentally. This is the *Differential cross-section*

$$\frac{d\sigma}{d\Omega} = \frac{\# \text{ of particles scattered towards } (2\theta, \phi) \text{ per unit solid angle}}{\# \text{ of incident particles per unit area of beam}}, \quad (3.19)$$

which can be expressed as

$$\frac{d\sigma}{d\Omega} = \frac{R(2\theta, \phi)}{\Delta\Omega |\psi_0|^2}, \quad (3.20)$$

where $|\psi_0|^2$, the norm-square of the normalisation factor, is the incident flux and $\Delta\Omega$ is an subtended solid angle $\Delta\Omega = \Delta A/r^2$.

Treating only the case of neutron scattering, where the scattering length is a simple constant, Eq. 3.18 simplifies to

$$\sigma = 4\pi |b|^2. \quad (3.21)$$

The cross-section can be expressed as a sum of two contributions

$$\sigma = \sigma_{coh} + \sigma_{incoh}. \quad (3.22)$$

The coherent cross-section is what gives rise to structural scattering information whereas the incoherent cross-section, which arises from the standard deviation of b , gives rise to a background signal. Whilst background noise is in a sense featureless, the isotope dependence of b remains of experimental importance. ^1H , which will correspond to nearly all of hydrogen atoms in the organic films probed in this thesis, has a very large incoherent cross-section of 80.27×10^{-28} m. A high background signal can thus be used as sign of high hydrogen content in a measured sample.

3.2.4 Scattering from multiple atoms

To probe the structure of matter, we are seldom interested in scattering from a single atom, but rather from an assembly of atoms. We first generalise Eq. 3.8 to represent the scattering from an atom, indexed j , located at position $\mathbf{R}_j$

$$\psi_{f_j} = \psi_0 e^{i\mathbf{k}_i \cdot \mathbf{R}_j} f(\lambda, \theta)_j \frac{e^{i\mathbf{k}_f \cdot (\mathbf{r} - \mathbf{R}_j)}}{|\mathbf{r} - \mathbf{R}_j|}. \quad (3.23)$$

Here, the first exponential term displaces the incoming wave to the position of the scatterer. To get a total sum of scattering contributions from an assembly of atoms, we can sum over the total number of N scatterers

$$\psi_f = \psi_0 e^{i\mathbf{k}_f \cdot \mathbf{r}} \sum_{j=1}^N f(\lambda, \theta)_j \frac{e^{i\mathbf{Q} \cdot \mathbf{R}_j}}{|\mathbf{r} - \mathbf{R}_j|}, \quad (3.24)$$

where $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ (Eq. 3.2) is found again by moving terms around. Furthermore, by taking into account the experimental reality (the Fraunhofer approximation) that the sample-to-detector distance dwarfs that of the distance between the origin

and the summed scatterers ($\mathbf{R}_j \ll \mathbf{r} \Rightarrow |\mathbf{r} - \mathbf{R}_j| = |\mathbf{r}| = r$) the

$$\psi_f = \frac{\psi_0 e^{i\mathbf{k}_f \cdot \mathbf{r}}}{r} \sum_{j=1}^N f(\lambda, \theta)_j e^{i\mathbf{Q} \cdot \mathbf{R}_j}. \quad (3.25)$$

By treating the total outgoing wave function as a simple superposition of individual scattering events, we are making the assumption that the incident wave remains fundamentally unaltered (The *Born approximation*) and that scattered waves do not scatter more than once. These assumptions are generally valid for X-rays and neutrons interacting with organic thin films due to their low scattering volume. The differential cross-section i.e. strength of the scattering at a given angle will depend on the dispersion function

$$\frac{d\sigma}{d\Omega} \propto \left| \sum_{j=1}^N f(\lambda, \theta)_j e^{i\mathbf{Q} \cdot \mathbf{R}_j} \right|^2. \quad (3.26)$$

3.3 Small angle neutron scattering

Whilst the discussion of scattering so far has centered on scattering from *points*, scattering can also be used to illuminate the structure across larger length scales. The following derivation is taken from [15], to which we refer for a more thorough analysis. Instead of a dispersion function that guides the scattering from discrete points, we shift our frame of reference to that of scattering from a volume with scattering length density (SLD) ρ

$$\rho = \frac{b}{V}. \quad (3.27)$$

We can also define a number density of scatterers at a given point $n(\mathbf{r}) =$

$$n(\mathbf{r}) = \bar{n} + \Delta n(\mathbf{r}), \quad (3.28)$$

where $\bar{n}$ is the average number of scatterers and $\Delta n(\mathbf{r})$ is the deviation at point $\mathbf{r}$.

If we imagine a two-phase system with SLDs of ρ_1 and ρ_2 , the strength of scattering will be determined by the contrast between the SLDs

$$\Delta\rho = \rho_1 - \rho_2. \quad (3.29)$$

Similarly, it is the deviation from the average number density of scatterers $\Delta n(\mathbf{r})$ for a given volume which determines the strength of scattering.

We can now express the strength of scattering (Eq. 3.26) of a component with volume V_p , with contrast $\Delta\rho$ and number deviation $\Delta n(Q)$ as

$$\frac{d\sigma}{d\Omega} \propto \left| \sum_{j=1}^N V_p \Delta\rho \Delta n(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{R}_j} \right|^2. \quad (3.30)$$

Here, $\mathbf{R}_j$ again determines the position of the scatterer. This can be expanded to

$$\frac{d\sigma}{d\Omega} \propto V_p^2 (\Delta\rho)^2 \sum_j^N \sum_{i \neq j}^N \Delta n(\mathbf{Q})^2 e^{i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_i)}. \quad (3.31)$$

We expand with N , the total number of scattering volumes into

$$\frac{d\sigma}{d\Omega} \propto N V_p^2 (\Delta\rho)^2 \Delta n(\mathbf{Q})^2 \left(1 + \frac{1}{N} \sum_j^N \sum_{i \neq j}^N e^{i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \right). \quad (3.32)$$

We define the terms

$$P(\mathbf{Q}) = \Delta n(\mathbf{Q})^2, \quad (3.33)$$

as the single particle form factor, relating to the shape of individual particles, and

$$S(\mathbf{Q}) = \left(1 + \frac{1}{N} \sum_j^N \sum_{i \neq j}^N e^{i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \right), \quad (3.34)$$

as the structure factor, which describes inter-particle behaviour. The scattering from particles with volume can thus be described as

$$\frac{d\sigma}{d\Omega} \propto NV_p^2 (\Delta\rho)^2 P(\mathbf{Q}) S(\mathbf{Q}). \quad (3.35)$$

The five terms are thus, in order: The total number of scattering volumes (N); the square of the scattering volume (V_p^2); the square of the SLD contrast ($(\Delta\rho)^2$); the form factor ($P(\mathbf{Q})$); and the structure factor ($S(\mathbf{Q})$).

We see that scattering signal arises from *variations* in scattering length and scatter number density. A lack of signal (from a dense system) is thus evidence of a system with uniform SLD, whereas strong signal corresponds to large variations in SLD for the given length scale.

3.4 Guinier and Porod regimes

Small angle scattering can be delineated into different regimes. The first is the low- Q Guinier regime, which describes scattering as $|\mathbf{Q}| \rightarrow 0$. This differs from the scattering at $|\mathbf{Q}| = 0$ which is generally not experimentally relevant, as the scattered beam in this direction will be blocked by a beamstop to prevent detector damage. In the low- Q limit the scattering is approximately given by

$$\ln \left(\frac{d\sigma}{d\Omega} |\Delta\beta|^2 \right) \approx \ln \left(\frac{|\psi_0|^2 m}{\rho N_A} \right) - \left(\frac{R_g^2}{3} \right) Q^2, \quad (3.36)$$

where ρ is the density, m is the mass, N_A Avogadro's number and R_g is the radius of Gyration. In practise the second term, the slope, is of greater relevance as the first term, the intercept, is experimentally involved and hard to derive physical constants from. From the slope of low- Q scattering, however, we can derive the aforementioned Radius of gyration

$$R_g^2 = \frac{1}{V} \iiint r_{per}^2 d^3\mathbf{r}, \quad (3.37)$$

where r_{per} is the radius that a point mass would have to be from a centre of gyration to have the same moment of inertia as a spherical object with the same mass distributed uniformly. It is thus in some way a measure of the *size* of the scattering objects, but it does not yield information about their shape. Furthermore, the R_g does directly correspond to a radius of given scattering entities. For example, if the scatterers are taken to be spherical, the simplest shape we are often left to assume when lacking other information, with radius R then the relationship is

$$R_g = \sqrt{\frac{3}{5}} R. \quad (3.38)$$

Coupling R_g to a quantitative description of a system will thus require some knowledge of the scatterers, but can in any case still be used comparatively between systems assumed equivalent.

For the high- Q regime defined as $Q \gg R^{-1}$ where R represents the largest dimension of the scatterers, rather than strictly a radius, the scattering will give information about the shape of the scatterers. For a spherical object the scattering will generally decrease as $\frac{d\sigma}{d\Omega} \propto \frac{1}{Q^4}$, whereas for very thin rods it will decrease as $\propto \frac{1}{Q^1}$ and as $\propto \frac{1}{Q^2}$ for very thin disks. However, the $\propto \frac{1}{Q^4}$ is observed for most shapes without a very thin dimension due to rotational averaging. An illustration

of scattering trends in the Porod regime can be found in Fig. 3.2. A more rapid

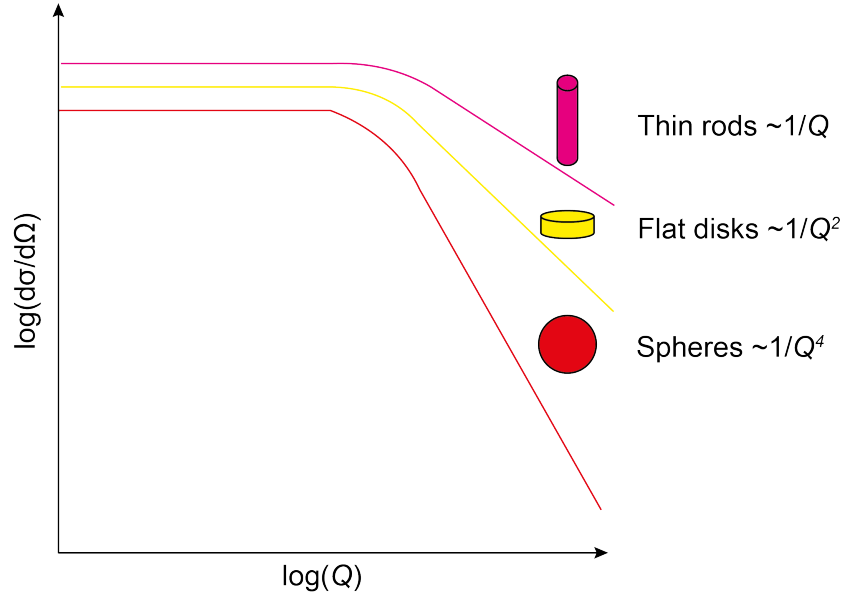


Figure 3.2: Representative scattering trends in the Porod regime for thin rods, thin disks and spheres.

decrease in intensity with increasing Q (for a given shape) will indicate a system where the boundary between regions of different SLD is rough.

3.5 Scattering from a crystalline solid

Returning again to the description of scattering from points, we move to smaller length scales and the idealised perfect crystalline lattice, a simplified schematic of which is shown in Fig. 3.3. A crystal lattice is defined by its periodic repetitions, which we will here state in terms of the SLD.

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}). \quad (3.39)$$

The scattering from a point $\mathbf{r}$ is defined as equivalent to that of point displaced by integer displacements (n_1, n_2, n_3) along the (a, b, c) directions. These vectors

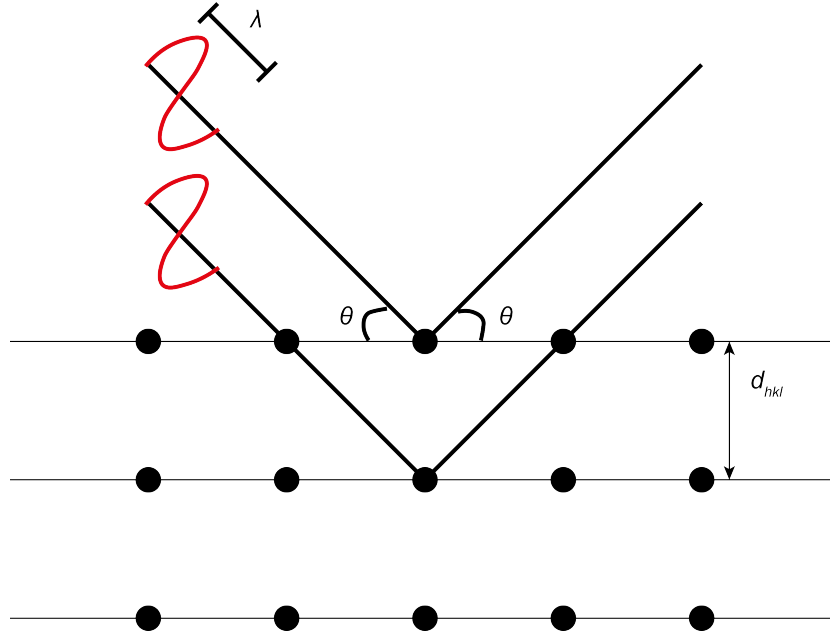


Figure 3.3: Representative a scattering under the Bragg condition from an idealised lattice.

directions are guided by the lattice angles (α, β, γ) . We can restate Eq.3.26 to instead describe a displaceable unit cell by writing it as

$$\iiint_V \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d^3 = L_R(\mathbf{Q}) \iiint_{V_{\text{cell}}} \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d^3. \quad (3.40)$$

Here, V_{cell} is the volume of the unit cell in question and

$$L_R(\mathbf{Q}) = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp(i\mathbf{Q} \cdot (\rho(n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}))), \quad (3.41)$$

sums over the lattice displacement. In a perfect crystalline lattice, these terms will cancel out unless Q satisfies

$$\mathbf{Q} \cdot (\rho(n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c})) = \phi_0 + 2\pi n, \quad (3.42)$$

where n is an integer. This is equivalent to

$$\mathbf{Q} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}, \quad (3.43)$$

where we define the reciprocal lattice vectors as

$$\mathbf{A} = \frac{2\pi\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{B} = \frac{2\pi\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{C} = \frac{2\pi\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}. \quad (3.44)$$

From Eq. 3.43 we can derive the fundamental Bragg's law. By defining a unit vector $\hat{\mathbf{n}}_{hkl}$ in the direction $h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ we can rewrite Eq. 3.43 as

$$\mathbf{Q} = \frac{2\pi n}{d_{hkl}} \hat{\mathbf{n}}_{hkl}. \quad (3.45)$$

d_{hkl} is the so called d -spacing denoting the distance between lattice planes with normal vectors along the $\hat{\mathbf{n}}_{hkl}$ direction. By using the prior definition of Q from Eq. 3.5 we can write

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi n}{d_{hkl}}, \quad (3.46)$$

and from this derive Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta, \quad (3.47)$$

which defines the conditions for a constructive signal from a perfect crystalline lattice. Combining Eqs. 3.46 and 3.47 we see one of the most beautifully simple results from which we can easily derive the d -spacing of crystalline matter from the scattered signal.

$$d_{hkl} = \frac{2\pi}{Q} \Leftrightarrow Q = \frac{2\pi}{d_{hkl}}. \quad (3.48)$$

4 | Organic photovoltaic thin films

Organic semiconductors (OSCs) are materials made from carbon and hydrogen-based molecules with conductivity between those of conductors, such as metals, and insulators, such as glass. Semi-conductors are characterised by having a band gap, an energy range between the valence and conduction bands with no allowed electronic states. This enables the basic principle of photovoltaics: The absorption of photons with sufficient quanta of energy to excite electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (equivalent to the valence and conduction band in in-organic semi-conductors). To harvest the energy absorbed, the charge (and energy) carrying electron and its corresponding holes must diffuse to their corresponding electrodes to create an electric current. In the following sections, we will explore the physics of OPVs related to photon absorption and charge carrier transport with a focus on how they relate to microstructure and associated challenges.

4.1 Organic semi-conducting molecules

Conductivity in OSCs arise from conjugation, which is the overlap of p -orbitals across a σ -bond leading to electron delocalisation. A typical basic building block of an OSC is an aromatic ring of C and H, with Benzene being a basic example of a monomer. The p_z -orbitals of the ring's carbon atoms hybridise, which results in the formation of so-called π -bonds. The π -bonds manifest as orbitals where shared electrons delocalise in the plane of the aromatic ring, laterally shifted to either side. A model of benzene and its delocalised orbitals can be seen in Fig. 4.1. Conjugation may also happen along an oligomer or polymer chain consisting of alternating single and double bonds, resulting in continuous charge delocali-

sation along the direction of the chain, enabling 1D charge transport. When a conjugated system is extended, the electron cloud is further delocalised. The syn-

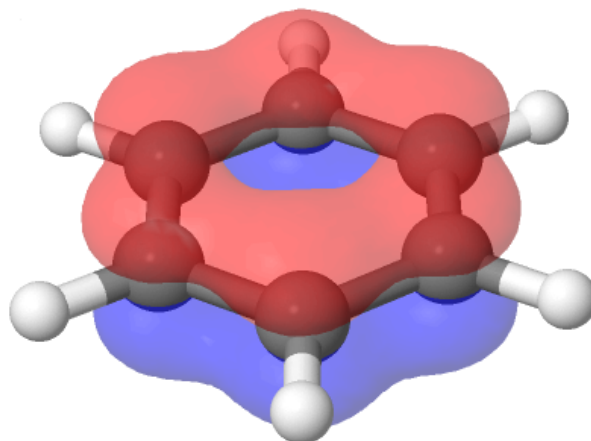


Figure 4.1: Atomic model of benzene showing π delocalised over the entire ring. From reference [16] with permission under [CC BY-NC-SA 4.0 DEED](#).

thesis of organic molecules allow for a great range in flexibility when it comes to the opto-electronic properties of OSCs which can be altered by the substitution of different elements, additional molecular groups or by altering the internal structure of the molecules.

One such property that can be altered is the HOMO-LUMO gap which determines what optical transitions are possible through the absorption of photons [17]. For example, the HOMO-LUMO gap can be decreased by increasing the number of thiophene rings of the molecules of an oligomer as shown in simulations by Bredas et al. [18]. However, it is not sufficient to consider only the chemical make up of molecules in isolation when trying to determine their device relevant properties. Increasing the distance between co-facial thiophene dimers similarly lowers the HOMO-LUMO gap, whilst simulating a lateral off-set between co-facial molecules results in periodic and independent variations of the HOMO and

the LUMO. These examples illustrate the complexity of describing the structure-property relationships of OSCs. As we see from these examples, understanding the structure-property relationships of OSCs even at the shortest length scales is complex.

4.2 Charge carrier generation

When a photon is absorbed by an OSC molecule, an electron is excited from the HOMO to the LUMO, leaving behind a hole. A feature of nearly all OSC materials is their low dielectric constant (3-5), resulting in a poor charge screening between the newly excited electron and its geminate hole. The reasons for this are complex. The dielectric constant corresponds to systems ability to respond to electromagnetic fields and has both electronic and nuclear contributions. The weak electronic contribution to the dielectric constant is influenced by the low atomic number Z and thus low mass density of OSCs as well as the van der Waals intermolecular binding, which does not involve the more mobile charge carriers of metallic or ionic compounds. The nuclear contribution to the dielectric constant can be increased by the addition of flexible and polar side chains, but such additions may decrease the effective mass density lowering the electronic contributions to the dielectric constant. For a more thorough discussion, we refer to Sami *et al.* [19].

The low dielectric constant keeps the charge carriers spatially close and highly localised, confining them to a single shared molecule [20]. Such tightly-bound electron-hole pair is known as a Frenkel exciton. Frenkel excitons will undergo recombination due to the charge carrier attraction, with a typical life time being on the order of 800 ps [21], causing the absorbed energy to be effectively lost. In order for charge splitting to occur, the exciton binding energy must be overcome

to allow the charge carriers to dissociate towards the electrodes. In Si-based solar cells, which have a higher dielectric constants, the electron and hole of a generated exciton will be more spatially distant and more delocalised (known as Wannier excitons) and thermal fluctuations are sufficient to let their charge carrier pair dissociate. However, for Frenkel excitons in organic materials, the binding energy can be several hundred meV, much higher than $k_bT \approx 25$ meV.

4.3 The bulk heterojunction

To induce the splitting of Frenkel excitons, the concept of the heterojunction was introduced by Tang [22]. The basis of the concept is that of an interface between two organic molecules with shifted energy levels. At the interface between a molecule with higher energy levels (labelled as the Donor (D)) and one with lower energy levels (labelled as the Acceptor (A)), a sufficient LUMO off-set will make it energetically favourable for the electron to move from the D to the A molecule, whilst it is favourable for the hole to remain on the D molecule. The free charge carriers are then free to travel towards their respective electrodes. The successful operation of OPVs thus require both 1) the successful generation of Frenkel excitons, 2) for excitons to reach a D:A interface, 3) for charge splitting to occur and 4) for the free charge carriers to reach the electrodes. To optimise performance the dominant OPV structure is that of the bulk heterojunction (BHJ), of which a simplified schematic is shown in Fig 4.2, where two or more D and A species are intermixed through simultaneous co-deposition. The BHJ allows for the overall optimisation of power generation by OPVs, balancing different physical processes that can have counter-acting needs.

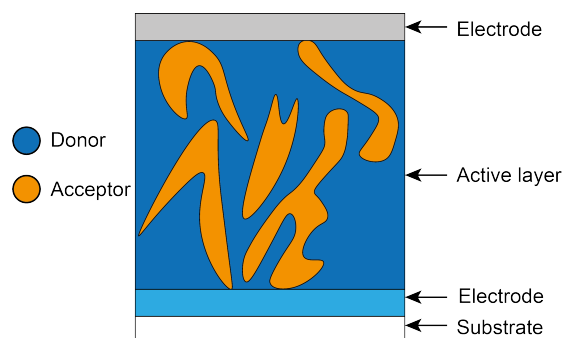


Figure 4.2: Simplified schematic of a bulk heterojunction.

4.4 Exciton generation and orientation

For an exciton to be generated, light must be absorbed and increased exciton generation is thus analogous to increased light absorption. Compared to inorganic photovoltaics, OPV materials have higher absorption coefficients and thus have thicknesses on the order of 100s of nm, compared to several μm . As previously discussed, the opto-electronic properties of a film can be tuned via molecular design. Another key parameter is that of molecular orientation. OSC molecules can be made in any matter of shape and size, but for small molecule OPV applications, typical shapes are those of a flat oligomer rod (such as α -sexithiophene, Sec. 5.12) or of a disk-like molecule (for example CuPc, Sec. 5.12). Edge-on orientation refers to when the molecular plane is parallel to the surface normal, whilst face-on orientation refers to the molecular plane. For molecules with oblong shape, the edge-on case can be further broken down into the case where the long axis is parallel to the surface normal ("standing") or parallel to the substrate plane ("lying"). A schematic of the different orientations is shown in Fig. 4.3. For OPV operation it is generally favourable for the molecules to be in the face-on configuration. This aligns the transition dipole moment along the substrate plane, which will increase the absorption of light incident to the substrate normal. In

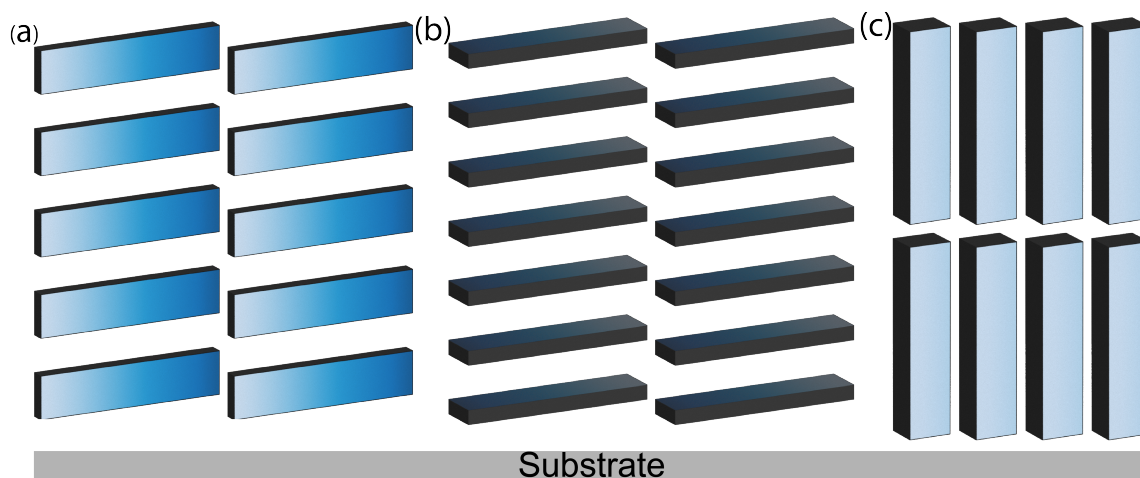


Figure 4.3: Schematic illustration of the various molecular orientations of a periodically stacked oblong molecule namely molecules a) lying edge-on, b) lying face-on and c) standing edge-on.

addition, once excitons are generated a face-on orientation will facilitate charge carrier transport along the substrate-normal direction due to π -orbital overlap. In a typical solar cell stack configuration, this will aid charge carrier transport towards the electrodes [23]. The orientation of molecules can be influenced by choices such as molecular design [23], underlying templating layers [24], substrate temperature during deposition [25] and molecular deposition rate [26].

4.5 Exciton transport and crystallinity

In order for charge splitting to occur, generated excitons must reach a D:A interface. The diffusion length, the average distance covered by a electron-hole pair before it recombines, is around 8 - 40 nm [27]. The recombination of a electron with its 'own' hole is known as geminate recombination. This limits the ideal size of single-phase D domains, which should be on the order of 10-20 nm for optimum OPV operation [12]. To facilitate high exciton mobility, a crystalline arrangement in these single phase domains is often preferable due to consistent

$\pi - \pi$ orbital overlap enabling charge carrier transport.

Controlling organic thin film structure, however, is a non-trivial task. Unlike most inorganic crystals, where the crystalline structure is dictated by strong ionic or covalent bonds, the organic molecules in a thin film are bound together by weak van der Waals forces. This results in a higher degree of disorder alongside microstructural diversity.

Structural disorder in OSCs appears across multiple length scales. The weak binding force means that crystallites are generally small (on the order of 10s of nm) and, as is the case for all non-idealised crystals, have point defects. They can also exhibit variations in terms of lattice parameters between crystallites in the same film. Whilst a BHJ is often described as an idealised two-phase system, reality is often more complex. A "donor crystallite" may not consist entirely of D molecules, but also contain impurities in the form of A molecules. It is for this reason that the term "donor/acceptor rich domains" is often used. Furthermore, in the case of some BHJ systems the two phase system may instead be formed by one crystalline phase and one amorphous phase or a tri-phase system may emerge, consisting of two D/A domains as well as a mixed domain [28]. Defects can result in trap states in the HOMO-LUMO gap or in energetic disorder at charge-splitting sites, creating trap states that hinder charge carrier transport. In scattering experiments, the small and varied crystallites in OSC thin film will often result in a dearth of scattering features (such as peaks or rods) and disorder will result in peak broadening, reflecting a variety in packing across crystallites in the film. Scattering features will often also appear with an azimuthal smear or even be isotropic. Rather than variation in lattice parameters, this reflects that individual crystallites of the same nominal crystalline phase in a film may have a range of different orientations [12].

4.6 Exciton splitting and acceptor molecules

At the D:A interface, excitons can split into unpaired charge carriers driven by a favourable energy difference between the D and A LUMOs. This process involves an intermediate stage where the hole and the electron are still bound, but situated on adjacent molecules. It is favourable to minimise the duration of this stage, as the energy levels of the ionised molecules reorganise, increasing the binding energy needing to be overcome. For this reason, C₆₀ has been the A molecule of choice for evaporated OPV systems due to the low reorganisation energy loss due to their relatively low reorganisation energies which is related to their rigidity and symmetry [29, 30].

4.7 Charge carrier diffusion and phase separation

Once split into free electrons and holes, the charge carriers must travel 100s of nm to reach their respective electrodes for energy production. Tang's first heterojunction iteration was a planar heterojunction (PHJ) whereby layers of D and A were stacked upon each other [22]. Due to the short exciton diffusion distance of OSCs, the performance of PHJ configuration OPVs will either be limited by thicker layers, which will increase geminate recombination, or by thinner layers, which will reduce photon absorption. To overcome this issue, the bulk heterojunction was developed [31, 32]. In BHJs, the D and A molecules are interdispersed through simultaneous deposition. This greatly increases the effective D:A interface area accessible to diffusing excitons. A complete statistical mixture is not desired, however, as a greater D:A interface area will also increase the rate of (non-geminate) recombination between electrons and holes travelling towards their electrodes. Rather, the formation of a bi-continuous network of interdigitated

D and A phases allow the charge carriers to reach the electrodes. This favours larger D and A phase length scales to reduce non-geminate recombination. As discussed in Sec. 4.5, disorder is inherent at all length scales and the BHJ should not be thought of as an idealised structure. In most practical applications, the bi-continuous pathways will have imperfect phase purities, increasing non-geminate recombination. Optimising longer range transport is complicated by concerns at other length scales. Changing film growth parameters to increase order may increase phase purity as well as uniform crystal packing, but can for example lead to domains increasing in size beyond that of the exciton diffusion length, reducing exciton splitting efficiency [33].

4.8 Organic thin film growth

The process of creating a VTE organic thin film is the process of heated vapour of organic molecules depositing on a substrate. As molecules sublime from the crucibles in which they are heated, they are sent on a ballistic trajectory before impinging on the substrate. Film formation is not purely driven by kinetic processes, however, as thermodynamic contributions also play a part. As the evaporation chamber fills with sublimated molecules, the vapour pressure above the substrate will increase until it reaches the equilibrium vapour pressure, which will initiate the process of film nucleation whereby the phase change from gas to solid lowers the Gibbs free energy per unit volume. In order for film growth to begin in earnest, however, the vapour pressure must exceed the equilibrium vapour pressure as early nucleation clusters have high surface-to-volume ratios increasing the effective rate of re-evaporation compared to that of the bulk material. The creation of a surface increases the free (surface) energy providing a counteracting drive to cluster growth. Clusters must thus reach a critical ratio between surface area and

volume in order to reach stable growth allowing for film formation. For a detailed treatment we refer to J. E. Greene [34].

The final film, however, depends on a number of dynamic processes that occur during growth and thin film growth is thus inherently a non-equilibrium process. The outcome of these processes are determined by both energetic and kinetic concerns and can, over length scales large compared to individual molecules, be described via their statistical properties.

Molecules arriving on a substrate can undergo several processes, illustrated in Fig. 4.4: The initial arrival and diffusion along the surface, the absorption and

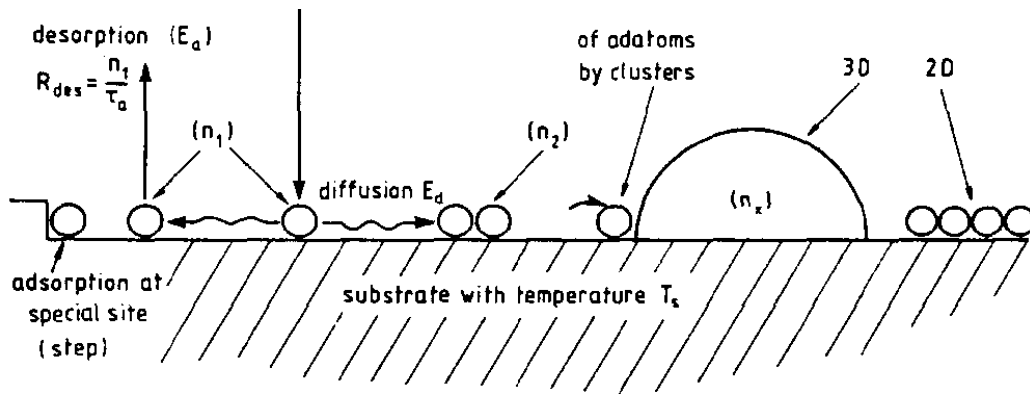


Figure 4.4: Schematic illustration of the various processes molecules can undergo when landing on a substrate surface. Adapted from reference [35] with permission. Copyright 1988 Elsevier Ltd.

desorption at nucleation sites, adsorption by existing clusters or inter-layer transport across a step-barrier. Molecules can also desorb from the surface entirely. For a mathematical description of these processes, we refer the reader to [35] for an in-depth treatment. Many of these processes are affected by contact with or proximity to the substrate surface, such as the mode of growth which will be further discussed in Sec. 4.9.

Whilst thin film growth mechanisms are generic, special consideration has to

be taken with regard to organic thin films. Organic thin films are composed of molecules rather than single atoms. These atoms are in most cases asymmetric and thus have rotational degrees of freedom. This gives rise to different possible molecular orientations (Sec. 4.4) between which molecules can transfer as the film grows and can greatly affect the opto-electronic properties of a film. Their larger size also generally result in larger and lower symmetry unit cells compared to inorganic thin films. This may contribute to a lattice mismatch between the substrate and the growing film, inducing strain [36]. In addition, molecules are not perfectly rigid and may contort, which can alter their packing as well as ability to overcome Ehrlich-Schwöebel step barriers [37].

The inter-atomic relations between molecules in an organic thin film are primarily governed by van der Waals forces. This generally results in a lower surface energies compared to inorganic thin films and on a per-atom basis, the interaction between the organic molecules and the underlying substrate is lower. However, when summing the total interaction contributions of a molecule, the energy is comparable to chemisorbing adsorbates. By using so-called strongly interacting underlayers that increases the molecule-substrate interaction, the ability to diffuse or preference for different molecular orientations may be affected [38, 36].

Thin films may experience strain and this strain may increase or decrease as the film grows. The van der Waals bonds between organic molecules make organic films able to withstand a higher degree of strain [36]. Similar to a change from 2D to 3D growth, changes in strain along the surface normal direction can induce a change in packing behaviour and for organic thin films, the threshold at which behaviour changes will generally occur at higher thicknesses. Along side change in growth mode or molecular orientation, the crystal phase of the molecules may also change. The bottom-most phase will then be referred to as a substrate (or

surface) induced phases (SIPs) in contrast with the bulk phase, which will continue as the film progresses [39, 40]. A schematic of the transition from an SIP to a bulk phase shown in Fig. 4.5a. It would, however, be a simplification to think

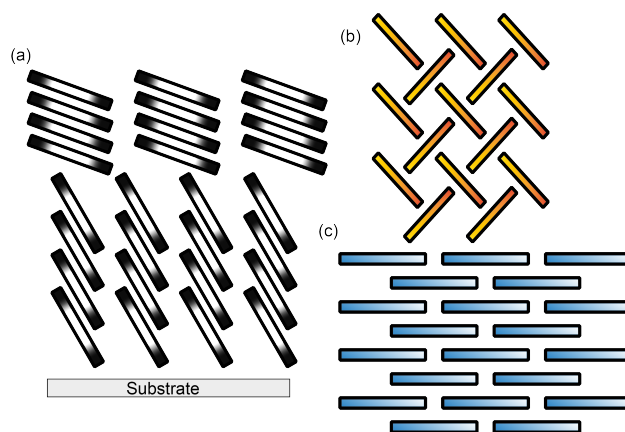


Figure 4.5: Schematics of a) film growth showing a substrate induced phase for the first 4 mono-layers of growth, followed by a bulk phase, b) Herringbone packing and c) brick-wall packing.

of organic thin films as only presenting a SIP and a bulk phase. The presence of multiple crystalline phases for a given material or in a given film is known as polymorphism. A6T, for example, has been reported to show four different crystal structures [41]. The high abundance of co-existing polymorphs of OSC thin films can be attributed to their so-called 'flat free energy landscape' [42]. Two common packing motifs, herringbone and brick-wall, are shown in Fig. 4.5b and c. Unlike co-valent or ionic bonds, van der Waals forces are non-specific and thus arise between any close organic molecules. In effect, organic films can have multiple free energy 'local minima' which manifest as different crystalline structures. By extension, the induction of different molecular orientations of crystalline grains can be seen as a result of this flat energy landscape where the energy difference between polymorphs can be less than 2 kJ/mol [40]. Polymorph control can be of vital importance to device performance as opto-electronic properties such as charge carrier mobility can vary greatly based how π - π orbitals overlap. For ex-

ample, TIPS-pentacene under strain exhibited hole mobilities more than a factor five higher compared to unstrained films. The power conversion efficiency of A6T based devices with molecules in the so-called 'Low Temperature' phase were similarly three times higher than devices based on the 'High Temperature' phase due to a better molecular orientation [43, 44]. Which polymorphs are expressed is dependant on both the choice of OPV system and on growth parameters during growth. The choice of molecules will inherently constrain which polymorphs are possible. Different substrates or (templating) underlayers can also be used to induce different polymorphs. The choice of constituents in a OPV solar cell stack is in turn also subject to other constraints such as e.g. well-matching energy levels. As such, varying the film deposition parameters during growth represents a valuable tool to enable tailored performance to be viable via polymorphic control. Parameters that can be varied include deposition rates (flux), D:A ratio and substrate temperature during growth. Of particular interest is the substrate temperature during growth, as the Gibb's free energy G as function of temperature T is given by $G = H - TS$, where the enthalpic H represents the lattice energy and the entropic S represents lattice vibrations and disorder. In monotropic systems, one polymorph will remain preferred for all energies below the melting point, whereas for enantiotropic systems, such as many organic thin films, the most stable system will depend on temperature and the entropic term. As fully formed films can sometimes 'kinetically trap' the molecules and lock in the microstructure determined during growth, it is thus possible to favour certain polymorphs with desired properties during growth by varying the substrate temperature during growth [40]. Similarly, by post-annealing a film at an elevated temperature after deposition, it is also possible to alter the polymorph (and thus orientation) of films [45].

4.9 Growth modes

The growth mode of a given material on a substrate will be determined by the contact angle ϕ at the triple point of a supposed 'droplet' of the material. The angle is given by

$$\cos \phi = \frac{\gamma_{sv} - \gamma_{sm}}{\gamma_{mv}}, \quad (4.1)$$

where γ_{sv} is the substrate-vapour surface energy, γ_{sm} is the substrate-material surface energy and γ_{mv} is the material-vapour surface energy. The three major growth modes are shown schematically in Fig. 4.6.

4.9.1 Volmer - Weber growth

$$\phi > 0, \gamma_{sv} < \gamma_{sm} + \gamma_{mv}. \quad (4.2)$$

Also known as island growth, this regime is the result of inter-molecular (cohesive) forces being dominant over surface (adhesive) forces. As the molecules have a propensity to avoid the surface, the initial molecular nucleation sites will grow primarily in the surface normal direction, forming at-first isolated islands that then grow together. Growth is considered 3D.

4.9.2 Franck - van der Merve growth

$$\phi = 0, \gamma_{sv} \geq \gamma_{sm} + \gamma_{mv}. \quad (4.3)$$

Also known as layer growth, in this regime, the adhesive surface forces instead dominate the cohesive inter-molecular forces. The initial arriving molecules will seek to maximise their contact with the substrate and thus completely cover the substrate before a second layer begins filling in. Successive layers grow as the film thickens in a 2D fashion.

4.9.3 Stranski-Krastanov growth

This growth regime is also known as layer-then-island growth. One or more complete mono-layers of molecules will first form on the substrate (2D), after which islands will begin to grow (3D). As the film grows layer-by-layer, the topmost molecules will experience less and less interaction with the substrate, which will result in layer-by-layer growth no longer being energetically favoured [35]. The bottom most layer(s) of the film may also experience strain due to a lattice mismatch with the underlying substrate and as this strain relaxes, transition to island growth [39]. Such a change from 2D to 3D growth may also be concomitant with change in crystal structure or orientation [39, 46].

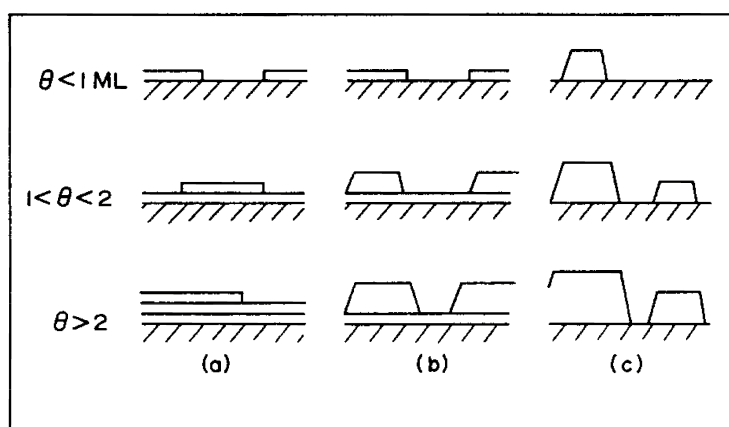


Figure 4.6: Early stage film growth following a) Volmer-Weber growth, b) Stranski-Krastanov growth and c) Franck - van der Merve growth. Copied from reference [35] with permission. Copyright 1988 Elsevier Ltd.

4.10 Carbon nanotube:Polymer films

Electrodes that are both transparent and conducting are a key component of photovoltaic devices. A standard choice for the anode of solar cells has been Indium-

Tin-Oxide (ITO) as its deposition can be readily controlled in terms of thickness and doping. However, indium is a scarce resource which mandates the need to change to alternative anode materials. In addition, ITO is brittle which makes it incompatible with future flexible solar cells. A leading candidate to replace ITO films are carbon nanotube (CNT) based films, where an overlapping network of CNTs provide charge carrier transport [47].

In terms of mechanical properties they are flexible in addition to having a Young's modulus of 1-2 TPa [48]. CNTs, being composed solely of carbon, can be manufactured from a variety of carbon sources, amongst them waste plastic [49].

A single-walled carbon nanotube (SWCNT) consists of a sheet of rolled up graphene. Graphene is a 2D material consisting of C atoms in a honeycomb lattice. Graphene is a semi-metal with zero bandgap due to sp^2 hybridisation. When rolled into a tubular shape, the bending results in the material becoming either metallic or semi-conducting. CNTs are described in terms of their chiral vector $\vec{C}$, see Fig. 4.7 for a visualisation of the concept.

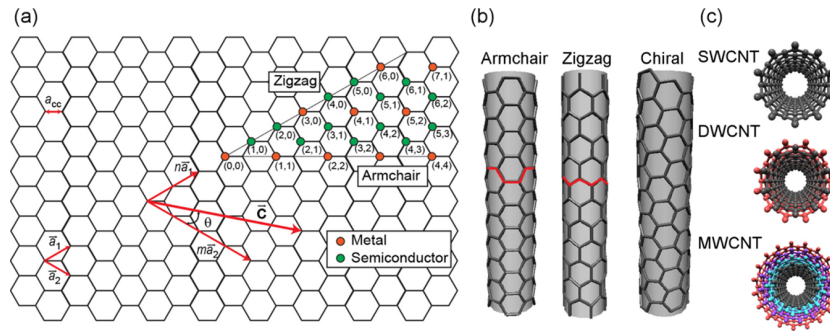


Figure 4.7: a) Graphene sheet with marking shows various values of n, m along the a_1, a_2 vector directions. b) Various CNTs made from rolled up graphene. c) Cross-sections of single, double and multiwalled carbon nanotubes. Copied from reference [48] with permission. Copyright 2016 American Chemical Society

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2. \quad (4.4)$$

n, m are integers representing increments along the graphene unit cell vectors a_1, a_2 . One C atom in a planar sheet of (infinite) graphene is chosen as the origin, which is then 'rolled' to another C atom at position displaced by $\mathbf{C}$. The electronic properties of a given CNT is by its chiral numbers

$$|n - m| = 3q. \quad (4.5)$$

For integer values of q the nanotube is metallic, whereas it is semi-conducting for other values. If the synthesis process of the CNTs is not controlled or the product is not sorted afterwards, this will correspond to a 1:2 ratio of metallic:semi-conducting CNTs [48, 50]. A way to increase the fraction of metallic films is to use multi-walled carbon nanotubes (MWCNTs). MWCNTs are composed of multiple layered concentric SWCNTs. If at least one SWCNT in a MWCNT group is metallic, the entire MWCNT will be metallic due to charge transfer between shells.

Individual CNTs have extremely high mobilities with values of $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or more reported [51]. However, this drops to around $10\text{-}20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in dispersive CNT networks due to junction resistance at the CNT-CNT charge transfer interface, especially at metal/semi-conductor junctions of CNTs that are only poorly connected with the rest of the branching network [52]. It is thus favourable to ensure that the CNT 'web' in a conductive film is highly overlapping.

To distribute CNTs over larger areas, solution processing is used. This process is made difficult by CNTs tendency to agglomerate into larger bundles in the solvent. This happens due to attractive van der Waals forces between the tubes. The effective conductivity of CNT deposited networks is then reduced as the average bundle diameter increases and thus it is desirable to minimise the bundling

of CNTs [53]. Conjugated polymers have successfully been used as a dispersing agent to keep the CNTs dispersed and well solubilised. Dispersing agents act to hinder the aggregation of particles in a solvent and thus increase the uniformity and stability of a solution. Before the deposition step, a mixture of CNTs in solvent is heavily mixed to separate the CNTs from each other and mixed with a polymer. For certain polymers, the side chains will wrap around the CNTs and creating a 'coating' that prevents the close CNT-CNT contact where van der Waals forces might cause them to bundle. Once the CNT:polymer (CNT:P) mixture has been deposited, additional processes can be used to remove the polymer to enable CNT-CNT overlapping junctions in the dry film.

The initial choice of polymer was the conjugated polymer poly(3-hexylthiophene) (P3HT). The wrapping mechanism was assumed to be driven by non-covalent i.e. π - π stacking [54]. Subsequent work revealed ethylene-vinyl acetate (EVA), a less costly polymer, to also functionalise CNTs via non-covalent wrapping, despite its non-conjugated nature [55, 56]. To optimise the application of EVA-based transparent conductive films, the ratio between the optical and the dc conductivities σ_{dc}/σ_{op} is used as a Figure of Merit (FoM) [57]. The resistances can be derived from the transmittance T

$$T = \left(1 + \frac{Z_0}{2R_s} \frac{\sigma_{op}}{\sigma_{dc}} \right), \quad (4.6)$$

where Z_0 is the impedance of free space, R_s the sheet resistance as measured via a 4-point probe, σ_{dc} is the bulk DC conductivity and σ_{op} is the optical conductivity at a given wavelength, typically at 550 nm [58]. To optimise this FoM, we must also understand the microstructure of CNT:P thin films and their structure-property relationships.

CNT:P composite systems are generally reported to behave as hierarchical systems with different structures at different length scales. At the smallest scale is the (diameter of) SWCNTs ($\sim 1\text{-}2$ nm) or MWCNTs (~ 10 nm), a longer length scales bundles of CNTs (< 100 nm) that may then comprise part of flocs that reach micrometre lengths. Such branched multi-level bulk systems are often studied via scattering methods, which enables a statistical description of how intertwined the branching CNT:P system is across length scales. SANS is a well-suited technique for the study of bulk films, as it offers greater penetration compared to X-ray based methods and because of the natural neutron SLD contrast between the fullerene CNTs and hydrogen-rich polymers (and voids) [59, 60]. A range of potential models exist to describe the small angle scattering from CNT:P system, which will be further expanded upon in Sec. 9.1.

5 | Methods

5.1 Vacuum thermal evaporation

In this thesis, SM OPV thin films are fabricated either in the Oxford-based evaporation chamber ECHO ("Evaporation CHamber Oxford") (Fig. 5.2) or made during *in situ* measurements at Minerva situated at the I07-beamline at the Diamond Light Source. A schematic of an evaporation chamber is shown in Fig. 5.1. The ECHO system has an integrated N₂ atmosphere glovebox through which samples can inserted or extracted via a fork. For both systems, materials in the form of loose powders are weighed out inside the glovebox. These powders are purchased purified by the manufacturer and used as is. The materials are then loaded into ceramic crucibles. In Minerva, the chamber is first pumped down until a minimum pressure of $<5 \times 10^{-5}$ mbar is reached and the chamber is vented with N₂. The substrate holder is then loaded at this stage and the vacuum chamber pumped down to vacuum again.

Prior to deposition, substrates are placed in cleaning racks and submerged in deionised (DI) water with Hellmanex soap (2.5% by vol.) and are then placed in a sonicator for 10 min at a temperature of 55 C. The substrates are then rinsed with DI water, before being placed in DI water and the sonication process is repeated for DI water, acetone and IPA. After the final IPA step, excess liquid is blown off with pressurised air and the samples are inspected visually for blemishes. Samples are then placed on clean room wipes in a closed container and moved to a UV-ozone cleaning machine where they are subjected to ozone for 10 minutes followed by a 10 min wait to allow for the safe exhaust of ozone.

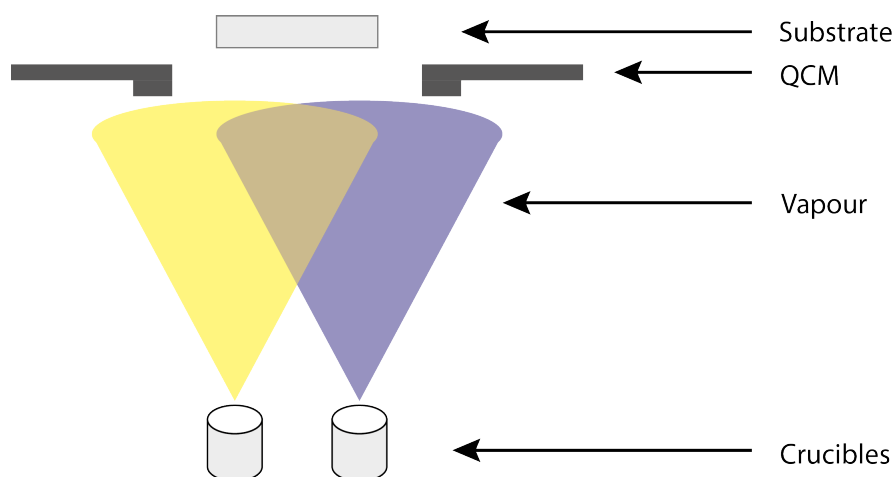


Figure 5.1: Stylised schematic of an organic film deposition chamber. At the bottom, crucibles are heated and organic vapours are expelled towards the substrate mounted at the top. Mounted quartz crystal microbalances measure the deposition rate of each organic compound.

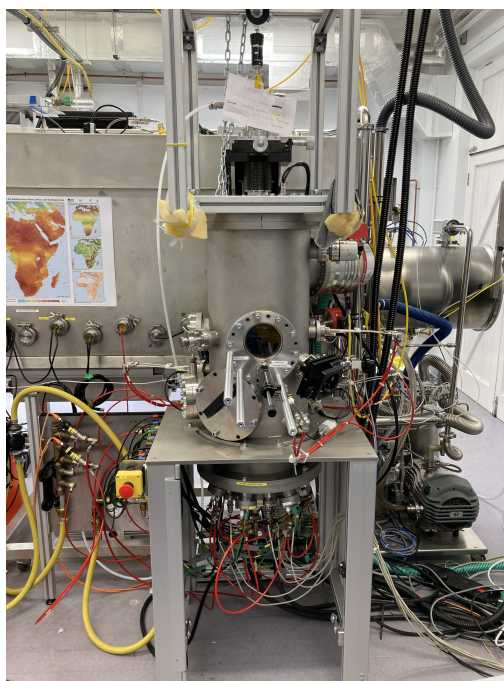


Figure 5.2: The ECHO evaporation system located at Oxford. The box behind the chamber is N₂ filled glovebox.

Substrates are placed into a holder and transferred via a load lock into a glove-box after which it is transferred through a separate load lock into ECHO and the chamber is pumped down. In the case of neutron samples, the quartz substrates are loaded into the aluminium insert first. In both chambers, heating of the crucibles or the sample holder is not begun until a pressure of a maximum of 5×10^{-6} mbar has been reached. Both crucibles and holders are heated at a maximum rate of 12.5 K per minute. Whilst crucibles are heating up, a wedging piece of metal shield the substrate to ensure no premature deposition of material. When the material powders in the heated crucibles reach a sufficient temperature they will begin sublimating or, in certain cases, melt and then evaporate. The rate of evaporation is monitored via Quartz Crystal Monitors (QCMs) that have been calibrated via X-ray reflectivity. Prior to evaporation, the target rates to achieve the desired molar ratio (mol/mol%) between D and A materials has been calculated via the formula found in appendix [A](#). The temperature of the sources are raised until target rates are hit.

Sample heating is done via a resistive heating element that is part of the evaporation set-up. In ECHO, to improve the thermal contact between the heating element and the substrates, a copper block is pressed between the heating element and the samples. When samples for neutron measurements were manufactured, a customised copper block and aluminium spacing insert was designed and manufactured to accommodate their different thickness. In Minerva, samples are attached directly to the heated rotator stage.

Once target rates and substrate temperature are reached the substrate shutter is extracted and material is allowed to accumulate on the substrates. The rates of the evaporating materials are continuously monitored and the crucible temperatures are adjusted to maintain steady rates until the target film thickness is reached. Then, the wedging piece is inserted to stop film accumulation and the heating of

the crucibles is ceased.

5.2 Substrates

Samples in this thesis are fabricated on two kinds of substrates: glass (Thin Film Devices Inc., Eagle XG) and quartz (Knight Optical Ltd, Type WHQ). Glass is used for any X-ray measurement and quartz substrates are used for all neutron measurements. The quartz substrates will be further discussed in section 5.4. In the following *sample* will denote a single quartz (or glass) substrate with deposited organic film and *configuration* will denote a stack of 16 samples of VTE deposited SM films each with nominally identical deposited films or of 10 P:CNT samples with 6 blank spacer substrates.

5.3 Post-annealing

Two configurations were annealed post-deposition. This was done on a hotplate inside an N₂ filled glovebox which was held at 80 °C and 140 °C. In the case of the configuration annealed at 140 °C a partial and patching change in colour from purple to grey was observed, see Fig. 5.3.

5.4 Neutron measurement sample holder

The type of quartz (*WHQ* from Knight Optical) was selected based on recommendations by neutron beamline staff due to its low neutron absorption (on the order of 99% transmission per substrate based on tests at Larmor) and low incoherent scattering. Preliminary neutron scattering trials revealed very low scattering from 100 nm thickness films. To increase scattering volume the decision was made to stack nominally identical films on substrates made during the same evaporation



Figure 5.3: Photograph of film substrates in the process of being post-annealed at 140 °C. Samples appear to be partially changing colour from purple to grey.

session. This technique is also used for polymer based samples, for example in [61].

Whilst it is possible to overcome the low scattering when dealing with solution based processing by e.g. drop casting films with thicknesses on the order of ~ 1 mm, this is not desirable for VTE films for several reasons. Firstly, rates are kept low ($0.15 \text{ \AA/s}$) for most samples which, even for films on the micrometre scale, would make sample preparation very time consuming and increase the likelihood of inconsistent evaporation conditions during manufacture. At a rate of $0.15 \text{ \AA/s}$, the deposition of a $1 \text{ }\mu\text{m}$ thick film would take more than 18.5 hours and the deposition of a 1 mm thick film would take more than 771 days. Secondly, substrate-induced phases (SIPs) that may be present in films would make up an appreciable part of the total film thickness, but not so in very thick films. This would make samples less representative of the thin films that would be used in OPV devices. Thirdly, due to the high material costs of research grade OPV materials manufacturing very thick films would be costly whereas manufacturing several substrates

simultaneously is cost-effective. In order to demonstrate the viability of SANS on SM thin films experiments must be able to be carried out in a way that is viable for replication and further development.

The ability to manufacture multiple substrates during one evaporation is limited by the area of the ECHO sample holder. An area of 12 mm x 12 mm per individual quartz substrate was chosen as this allowed samples to be made in a 4 x 4 grid. Whilst a 5 x 5 grid would have resulted in more than 50% additional substrates such small substrates were deemed too difficult to handle. Note that due to shadowing effects during evaporation, the coated area on each substrate is roughly 10 mm x 10 mm. A substrate thickness of 0.5 mm was similarly chosen to limit neutron absorption during measurement whilst ensuring the substrates could be handled without breaking.

A neutron sample holder was manufactured to contain the samples during SANS experiments. The holder had the following design goals:

- It must keep samples in an upright position to ensure a normal incidence of incoming photons as to not create angular distortions of the scattering pattern.
- Samples must be kept closely together. If neutrons were to scatter from films spaced sufficiently far apart compared to the sample-to-detector distance the signal would be smeared in reciprocal space and lowering the resolution of the data. This is not considered a major as long as the sample-to-detector distance dominates the sample stack length.
- It must not be made of materials that do constitute a safety risk due to neutron activation. Similarly, the entry and exit points of the neutrons should

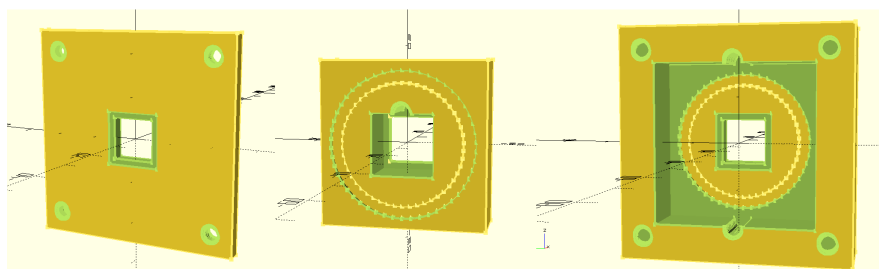


Figure 5.4: CAD designs of the three components of the neutron sample holder.

be fashioned to minimise neutron absorption and secondary diffraction.

- Samples should ideally be kept in an inert atmosphere to minimise degradation prior to the experiment.
- Facilitation of easy and safe handling of samples, both when putting samples into the holder, in a glovebox or when handling the holder at the beam-line.

The holder was designed being composed of an inner and an outer part with a screw-on lid. CAD drawings of the holder's component's design can be seen in Fig. 5.4. This design was chosen for the following reasons:

- A tray-like design, where each substrate was slotted into a separate ridge, was considered. This idea was deemed impractical as slotting the substrates in and out individual grooves using tweezers could easily result in substrate breakage. Taking tolerances and machining practicalities into account such a tray system would also result in films being spaced further apart. Instead, a simple chamber, slightly wider and taller than the substrates, was chosen. This is the cavity in the inner part. Samples are dropped into the chamber and stay near-upright due to the length of the chamber being compared to the total 8 mm thickness of 16 stacked substrates. This also ensures minimised distances between scattering films reducing reciprocal space smear-



Figure 5.5: Five neutron holders mounted on the changing rack.

ing.

- The holder itself was made out of aluminium, a durable material that is also well suited to custom fabrication via machining. Compared to other metals, it has a short activation time if excited by neutrons and does not scatter strongly. The beam path entry and exit windows are of the same dimensions and materials as the quartz substrates as they indeed have minimum absorption and incoherent scattering. The windows were fastened via glue.
- Samples can then be sealed inside the holder inside the nitrogen atmosphere of the glovebox. To keep films in inert conditions, grooves for O-rings were made to create a seal between the inner and the outer chamber as well and between the outer chamber and the lid. This helps keep the samples in an N_2 atmosphere, which reduces degradation. Samples are also kept covered with aluminium foil before experiments to reduced exposure to light.
- The modular design of the individual holders mounted on a larger rack was chosen as this means the often lengthy procedure of mounting and coarse-calibration has to be done only once per beamtime. After this, individual configurations inside holders can easily be swapped around simply by lifting them up and out of their guide rails.

Each configuration destined for SANS measurements were sealed inside a neutron

sample holder whilst inside a nitrogen filled glovebox and transported between Oxford and the neutron beamlines inside the holder. This was done to keep the organic films in an inert atmosphere, however it cannot be guaranteed that exposure to atmospheric air (and thus e.g. oxygen and water molecules that may lead to sample degradation), was zero due to the gas-proofness of the holders not being tested. In addition, the neutron holders were covered with aluminium foil during transport to minimise optical degradation.

5.5 Neutron beamlines

In this thesis, the majority of SANS measurements are taken at the Larmor beamline at the ISIS Neutron and Muon Source (UK). The measurements of series DCV5T:C60 configurations discussed in chapter 7 was taken at the SANS-I beamline at the Paul Scherrer Institute (PSI). Both ISIS and PSI are *spallation sources*, where pulses of protons are accelerated to near-relativistic speeds through the use of accelerators such as synchrotrons or linear accelerators (LINACs). The high-energy protons are then guided to strike a target composed of a heavy element such as lead, bismuth, tungsten or tantalum. When impinging upon a high Z nucleus, the proton is absorbed resulting in a highly excited, but unstable state. The excited nucleus quickly decays into lighter elements and elementary particles, amongst them neutrons [62]. The neutrons then pass through *moderators* made from various materials where the neutrons collide with the nuclei of the material and via energy exchange eventually thermalising at the same temperature as the moderator. Various types of moderators exists e.g. water at room temperature or liquid hydrogen at 20 K so that the energy range of the emergent neutrons can be controlled.

Once a pulse of neutrons leave the moderator they are guided by an optics systems

towards the configuration. After passing through the sample the transmitted and diffracted neutrons travel towards the detector where their position is recorded. At Larmor, these pulses are polychromatic and well separated in time, with neutrons arriving at different times due to the relationship between neutron energy and speed with the flight time t being determined by

$$t = \frac{m_n}{h} L \lambda, \quad (5.1)$$

where L is the source-to-detector distance, λ is the wavelength and m_n is the non-relativistic neutron mass. The time of exit of the pulses which are leaving the neutron source are known. Similarly, the time of arrival at the detector can be determined for each each neutron. Thus, for each detected neutron its energy can be determined and its momentum displacement can be found using eq. 5.1.

Due to the potentially large variation in speed of the emitted neutrons, *choppers* that periodically block the beam can be employed at intervals along the beam path to limit the range of wavelengths.

At SANS-1 at PSI, however, the pulses are spaced closely together as to create a continuous beam and subsequently monochromated using chopper systems. This replicates the instrumentation routinely utilised at reactor SANS instruments and provides a greater time-averaged flux than at ISIS.

During a measurement session, up to five configurations are mounted side and measured in a looping manner. For each sample, the diffraction of the configuration is measured for roughly 4 hours to ensure sufficient counts.

The transmission of the empty beam i.e. a beam travelling unimpeded from the source to the detector is measured to get a measure of the total incident flux to which the transmitted and diffracted neutrons can be normalised. In addition, the

transmission of the configurations are also measured to normalise for transmission through the sample.

As detector arrays also do not subtend an equal solid angle, the scattering is also geometrically normalised. This is done both 'automatically' based on the fixed positions of the detector setup, and at PSI, using the transmission and diffraction from water (H_2O) due to its isotropic properties and high incoherent scattering due to the abundance of hydrogen. For a thorough treatment of the various corrections applied to the raw neutron data, please see section 10.1.4 of [62].

In addition, both the diffraction and the transmission of a 'can', that is a sample holder with 16 uncoated substrates, is measured. This is done to separate out the scattering (and transmission) from the substrates and windows, which are magnitudes thicker than the films. An overview of the different types of samples measured is shown Tab. 5.1.

Purpose	Outer container	Content	(T)ransmission/(D)iffraction	Source
Normalisation	Al	Empty	T/D	ISIS/PSI
Normalisation	Al	Uncoated substrates	T/D	ISIS/PSI
Sample	Al	Coated substrates	T/D	ISIS/PSI
Normalisation	Water container	Water	T/D	PSI

Table 5.1: An overview of the different samples measured at the SANS experiments in this thesis.

5.5.1 Measurements at Larmor

Measurements at Larmor (set-up shown in Fig. 5.6) are taken using a wave length of 0.9 - 13.5 Å with a $dQ/Q = 8\%$. The Q -resolution is calculated as in [63, 64] and determines the error bars shown in SANS plots in this thesis. The beam size is restricted to a rectangular 6 mm x 6 mm to avoid edge effects from both the thin film and potentially from the holder. The data collected at this beamline has a momentum transfer range of 0.0052 to 0.67 Å⁻¹. However, due to edge effects

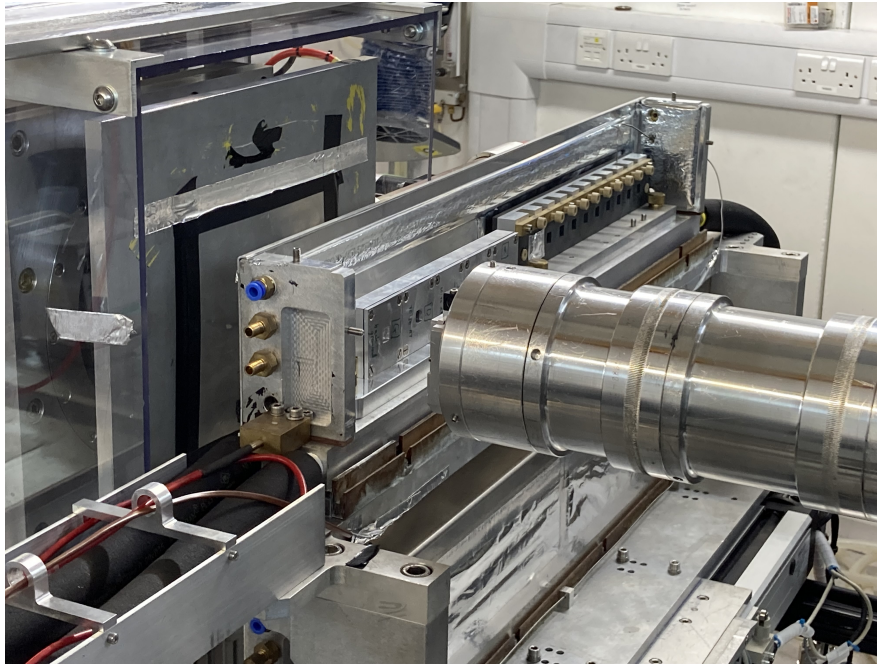


Figure 5.6: Measurement setup for SANS at Larmor at the ISIS Neutron and Muon Source.

of the detector at the lower- Q range limit and highly variable noise at the high Q limit, functions are generally fitted only in the range from 0.0055 to 0.3 $\text{\AA}^{-1}$. Measurement times per configuration were generally on the order of four hours per configuration to ensure sufficient counts.

Data from Larmor was collected at beamtime sessions RB2010523, RB 2000203 and RB2210342.

5.5.2 Measurements at SANS-I

Measurements at SANS-I (set-up shown in Fig. 5.7) are taken using a wave length of 6 $\text{\AA}$. The beam size is restricted to a rectangular 6 mm x 6 mm to avoid edge effects from both the thin film and potentially from the holder. The data collected at this beamline has a momentum transfer range of 0.007 to 0.33 $\text{\AA}^{-1}$. Measurement

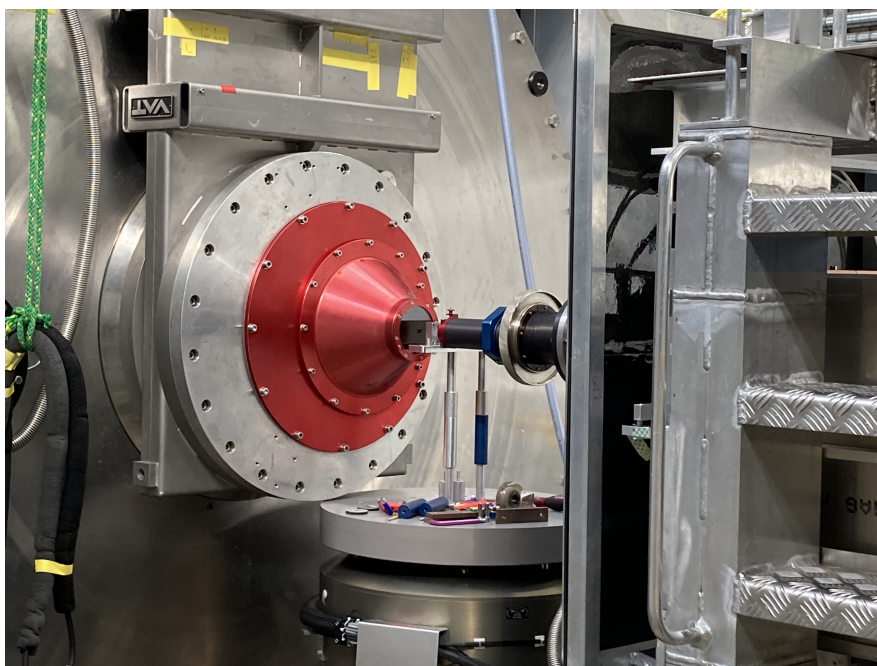


Figure 5.7: Measurement set-up for SANS at SANS-I at the Paul Scherrer Institute.

times per configuration were generally on the order of four hours per configuration to ensure sufficient counts.

Data from SANS-I was collected at beamtime 20202338.

5.6 Manufacture of Carbon Nanotube:Polymer films

CNT:P films investigated in this thesis were all manufactured by Dr Bernd Sturza. The manufacturing method of tip sonicated samples is as described by Mazota et al. [55].

Polymer pellets of a given type and concentration were dissolved in chlorobenzene solvent (Acros Organics, ACS reagent grade). The solution was then stirred

at RT for at least 24 hrs. A quantity CNTs were then added to the solution and subjected to an ultrasonic probe for 10 min, followed by 8 min of centrifuging at 10,000*g* to remove non-functionalised nanotubes and impurities. The supernatant liquid was collected and then added to 20 mL of toluene (Sigma-Aldrich, puriss. p.a. grade), and then heated for 1 hr to dissolve excess polymer and induce aggregation of functionalised tubes. The mixture was then centrifuged at 16,000*g* for 4 min and the precipitate was collected and dispersed in 10 mL of chloroform (Acros Organic, for HPCL grade, stabilised with 25 ppm amylene). The solution was then treated with an ultrasonic probe for 2 min at ~40 W of output power.

The manufacturing method of shear force mixed samples is as described by Sturza et al. [65]. Polymer pellets of a given type and concentration were dissolved in 100 mL chlorobenzene (Acros Organics, ACS reagent grade) and stirred at 50 °C overnight. A quantity of CNTs were then added to the solution and it was shear force mixed at 10,000 rpm (Silverson L5M-A) for 48 hrs at a constant temperature of 28 °C. The mixture was then centrifuged at 10,000*g* for 8 min and the supernatant liquid was collected. The supernatant liquid was added to 200 mL of toluene and placed on a hotplate at 50 °C for 24 hrs to induce aggregation of CNTs while keeping excess polymer dissolved. After letting the solution cool back to room temperature, the mixture was centrifuged at 16,000*g* for 4 min or until the supernatant liquid was fully transparent. The precipitate then contains pellets of functionalised CNTs, while excess EVA is removed with the supernatant. This excess polymer removal step is carried out 0,1 or 2 times depending on the sample. The remaining CNT:EVA pellets are then dissolved in 500 mL of chloroform (Acros Organics, for HPCL grade, stabilised with 25 ppm amylene).

CNT:P films were deposited using a custom-made open science hardware spray coater [66]. The exact deposition parameters of given samples can be found in

Tab. 5.3.

5.7 Grazing Incidence Wide Angle X-ray Scattering

Grazing Incidence Wide Angle X-ray Scattering, as the name implies, refers to X-ray scattering experiments where the sample is illuminated by X-ray at a shallow angle incidence angle $\alpha_i \ll 1$. The basis for GIWAXS will be outlined here following the treatment by Müller-Buschbaum [20]. The mean refractive index of a film is given by

$$n = 1 - \delta(\lambda) - i\beta(\lambda), \quad (5.2)$$

where $\beta(\lambda)$ is the absorption as function of wavelength λ and the dispersion $\delta(\lambda)$ is given by

$$\delta(\lambda) = \frac{e^2 \lambda^2}{2\pi^2 m_e c^2 \epsilon_0} \rho \frac{\sum_k [f_k^0(\lambda) + f'_k(\lambda)]}{\sum_k M_k}, \quad (5.3)$$

where e is the elementary charge, m_e is the electron rest mass, c is the speed of light, ϵ_0 is the vacuum permittivity. ρ is the mass density, M_k is the atomic weight and $f_k^0(\lambda)$ and $f'_k(\lambda)$ are dispersion corrections. The index k over which we sum refer to each atom in a molecule. The wavelength specific refractive index n of our materials is below 1 for light in the X-ray spectrum which means that below a sufficiently shallow angle, the so called critical angle, impinging X-rays will experience total external reflection. The critical angle is determined by

$$\alpha_c = \sqrt{\delta}. \quad (5.4)$$

α_c will generally be higher for (electronically) denser materials. This can be exploited when investigating organic thin films, which are almost always less dense than their underlying substrates. We can thus distinguish between the critical angle of the organic thin film α_o and of the substrate α_s where generally $\alpha_o < \alpha_s$.

This results in three measurement regimes:

$$\alpha_i < \alpha_o. \quad (5.5)$$

In this regime, known as the *evanescent regime*, total external reflection of the organic layer occurs and the X-ray beam only penetrates the top-most nanometres of the surface. Scattering will thus be spatially limited to the top of the film which can be probed separately.

$$\alpha_o < \alpha_i < \alpha_s. \quad (5.6)$$

In this regime, known as the *dynamic regime*, the X-rays will be able to penetrate the organic layer, but be reflected off the substrate. Once above the critical angle, the X-rays will typically be able to penetrate organic films fully. The resultant scattering will thus reflect an average structure of the film with only little signal due to the substrate. Due to the very low incidence angles, the interference between the incident beam, reflected and scattered photons can result in an enhancement of the scattering by more than a magnitude. However, as noted by others, a change of as little as one hundredth of a degree in incidence angle be the difference between "turning" this effect, known as waveguiding enhancement, on or off at 8 keV X-ray energies. The higher the X-ray energy, the lower the critical angle. As α_c cannot be negative, this results in the interval between α_o and α_s shrinking the higher X-ray energy is used. In this report, X-ray energies of up to 20 keV are used and the difference between critical angles is comparable to the resolution of the motor resolution of the sample alignment mechanics. This increases the difficulty of fully utilising the the dynamic regime and can lead to experimental uncertainty: *If the intensity of the scattering from two different samples greatly differ, does this reflect innate differences or simply a difference in*

alignment?

$$\alpha_s < \alpha_i \quad (5.7)$$

In this regime, known as the *kinematic regime*, the X-rays will penetrate both the organic film and the substrate surface. Due to the high penetration depth, the scattering will be dominated by the substrate signal and the waveguiding enhancement of the film scattering will be lost. This regime is generally to be avoided.

5.8 Alignment procedure - ex situ

This section will detail how samples are aligned for *ex situ* measurements. *Ex situ* measurements were taken either at XMaS at the ESRF or at I07 using the MINERVA chamber. At the ESRF the sample is positioned on a flat surface with the film facing upwards inside a small plastic box with a lid. The sample is placed upon a small gas inlet, which keeps the sample in place at a slight under-pressure. The lid is placed on the box and the box is flooded with N_2 to reduce degradation. As the box is not sealed for safety reasons, the atmosphere is kept N_2 simply via a continuous flow of gas. When using the MINERVA chamber, the sample is placed on a small metal piece (a so-called flag) via carbon tape, a vacuum-safe adhesive. The sample is then inserted with the film facing downwards and fastened to the sample stage mechanisms via an inbuilt gripping mechanism. The chamber is then sealed and pumped down to vacuum.

After the sample is mounted, the experimental hut is searched and sealed for beam operation. The alignment procedure is an iterative process primarily consisting of two steps known as the *half-cut* and the *rocking curve*. The purpose of the alignment procedure is to get the sample surface to be parallel to the X-ray beam and for the surface to be positioned halfway into the beam.

When doing a half-cut, the sample is moved in finely spaced steps in the vertical (z) direction, starting from a downwards off-set. The beam is kept at a highly attenuated level to prevent detector damage and for each step an image is taken. The integrated intensity of the direct beam is recorded. As the sample moves upwards (or downwards in the MINERVA set-up) the integrated intensity. The sample is then moved to the height position corresponding to the integrated direct beam intensity being half of the maximum. Half-cutting thus helps position the sample midway into the beam and generally involves.

This is followed by a rocking curve, where the sample is rotated around the x -axis. The sample is moved in finely spaced increments around the previously found neutral position. The beam is kept at a highly attenuated level to prevent detector damage and for each step an image is taken. The integrated intensity of the direct beam is area is recorded. The higher the angular off-set, the more either end of the flat sample will be tilted into the traversing X-ray, reducing the amount of photons reaching the detector. The intensity will be at the maximum when the sample is parallel to the beam direction. When the sample has an angular off-set in either direction the recorded intensity will decrease giving rise to an intensity curve similar to that of a Gaussian. The sample is then moved to the motor position corresponding to the highest intensity.

In practice, the half-cut and rocking curve do not align the sample in the first go. Each step is repeated following the other with progressively smaller step sizes to reach a finer alignment until the motor position converges upon itself. The intensity attenuation filters are then removed and instead a beamstop is placed at the position of the beam. A preliminary image is taken to ensure the sample is in

focus. Sometimes the sample can appear to have a roll compared to the direction of the beam and will need to be rotated around the y -axis potentially resulting in the need to redo the half-cutting and rocking process.

Measurements can then begin in earnest. Whilst critical angles of the film and substrate support could be calculated, the calculated angles would be similar to the motor step size. For time efficiency reasons measurements are taken by varying the incidence angle from 0° to 0.15° in increments of 0.01° and taking an image at each step, typically with an exposure time of 5-10 seconds.

5.9 *in situ* GIWAXS measurements

The *in situ* data in this thesis was collected at beamtime SI28849-1 at beamline I0-7. Prior to *In situ* measurements samples are cleaned as described in Section 5.1. Samples are cleaned on-site at the Diamond Light Source prep-lab and transported in a sealed plastic container to MINERVA, where they are inserted in the upper part of the minerva chamber. Powdered organic materials are added to ceramic crucibles in the prep-lab fumehood and are sealed with stretchy-tape before being being transported to MINERVA and inserted in the lower part of the chamber. The chamber is then sealed and pumped down to vacuum.

In situ X-ray measurements require compromises when it comes to the measurement parameters. Longer illumination times will increase the scattered signal, but lower the time resolution as the image will be an average over a growing film. Taking images at more closely spaced intervals will improve the time resolution, but, like longer illumination times, increase the potential for beam damage. *In situ* GISAXS measurements were recorded every 10 s using an exposure time of 5 s.

The sample alignment is similar to that described in section. However, as in the initial state there is no film from which to scatter the decision of incidence angle must be made prior to deposition of organic material and cannot be changed during the *In situ* measurements as a change in incidence angle could result in a misleading change in intensity. *In situ* measurements could be done in both the evanescent and dynamic regimes. Whilst the evanescent regime allows for a more precise recording of change in composition as the signal is not averaged over the entirety of the film, the waveguide scattering enhancement counterweighs this by offering much stronger signal. For the *in situ* experiments in this thesis a nominal incidence angle of 0.1° was used based on prior successful attempts [67]. We must stress, however, that due to the alignment procedure being an imperfect process that reported motor angle is likely not the true angle. It is expected that measurements were taken in the dynamic regime.

Beam damage was seen post measurement by a greyish line across the film corresponding to the beam footpath. As this was expected based on prior experiments involving prolonged X-ray exposure, GIWAXS images were recorded post-deposition after moving the sample laterally to access areas of the film unexposed to the beam. The scattering signal at both the site of *in situ* measurements and the yet unexposed site were found to be similar, indicating that the beam damage did not materially affect the crystalline properties of the film.

5.10 Calibration

X-ray samples, both *ex situ* and *in situ* are calibrated using silver behenate (AgBeh - $\text{AgC}_{22}\text{H}_{43}\text{O}_2$). AgBeh is used as a calibration standard due to its well-defined *d*-spacing and high crystallinity resulting in a large amount of visible Bragg rings.

For each measurement session, including movement of the detector or set-up, a small amount of AgBeh is placed on a substrate and measurements are taken as standard *ex situ* measurements. An image showing clear diffraction rings are then used for calibration in the *Dawn* programme using the calibration tool using the material and X-ray energy as input parameters.

5.11 Data treatment

5.11.1 X-ray data treatment

Raw X-ray images are converted from their native .tiff or .edf file format in the processing software DAWN [68]. Using the known X-ray energy, a AgBeh image is first used to determine the sample-to-detector distance as well as the centre of the X-ray beam. This calibration information is then used for all associated X-ray images.

Images are converted to reciprocal space using the DAWN software with solid angle and polarisation corrections applied. Images are further treated visually in MATLAB.

5.11.2 Neutron processing

Detector images from Larmor are first treated in MANTID and converted into 1D q vs intensity data series with 2-dimensional uncertainties. A similar process is carried out for data from PSI using the MATLAB software toolkit GRASP. These data series are then analysed in SASview using a variety of fitting functions which are further outlined in Chaps. 6 and 7.

5.12 Molecules

Acronym	Name	Purity	Supplier
A6T	α -sexithiophene (b)	>99%	Lumtec
C60	C ₆₀ (f)	>99.5%	Lumtec
DCV5T-me(3,3)	Methylated 2,2'-dicyanovinyl-5-thiophene (a)	Unknown	Synthon Chemicals
Rubrene	5,6,11,12-Tetraphenylnaphthacene (c)	>99%	Lumtec
SubPc	Boron subphthalocyanine chloride (e)	>99%	Lumtec
ZnPc	Zinc phthalocyanine (d)	>99%	Lumtec
EVA	Ethylene-vinyl acetate (g)	ACS reagent grade	Acros Organics

Table 5.2: Acronyms, chemical names and suppliers of the molecules used in this thesis. The letter for each molecule in the 2nd column is matched to a molecule schematic in Fig. 5.8. The purity of DCV5T-me(3,3) is not determined as this was a custom ordered material.

Figure 5.8 shows a schematic representation of the molecules and polymers used in films in this thesis. The acronyms, chemical names and suppliers of the molecules used in this thesis can be found in Table 5.2.

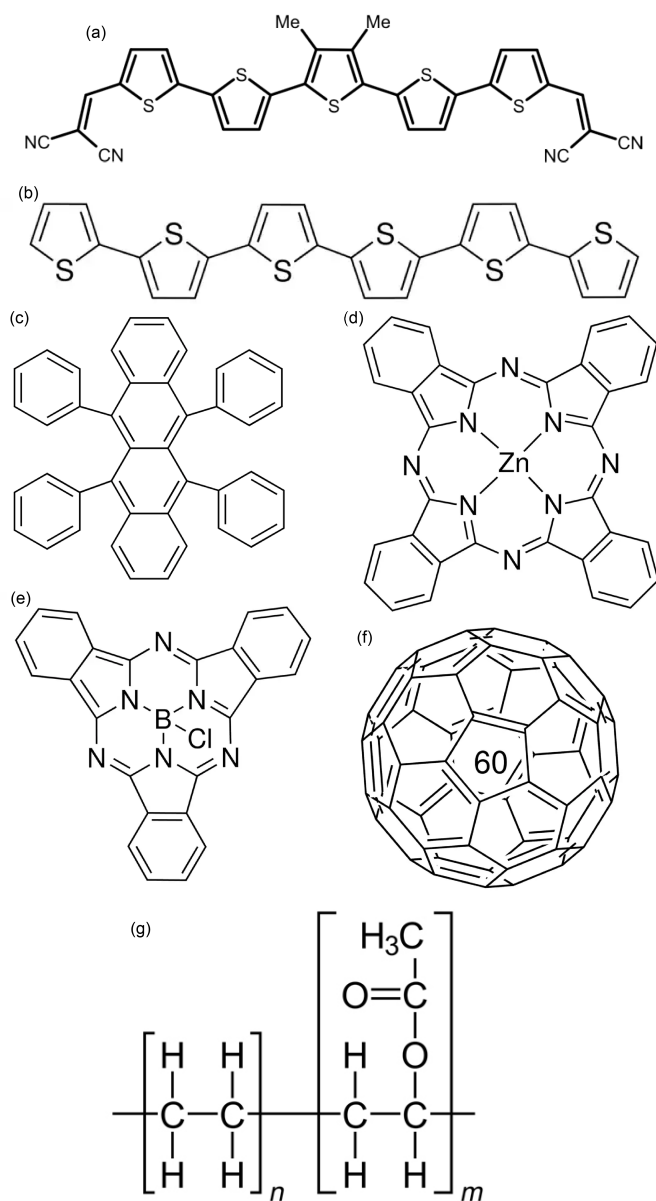


Figure 5.8: Molecular structures of the molecules used in this thesis. The acronyms, chemical names and suppliers of the molecules can be found in Tab. 5.2.

Name	CNT type	CNT conc. [g/L]	Mixing	Polymer	Poly. conc. [g/L]	Poly. remo. #	Tube diameter [nm]	Tube length [μ m]	VA content [wt%]	Poly. melt index
SFMx1S	Tuball	0.5	6h SFM	Elvax 150	4	1x	1.6 $\pm$ 0.4	>5	32	43
SFMx2	Tuball	0.5	6h SFM	Elvax 150	4	2x	1.6 $\pm$ 0.4	>5	32	43
TipSonx0	Tuball	0.5	10min tip son.	Elvax 150	5	0x	1.6 $\pm$ 0.4	>5	32	43
TipSonx1	Tuball	0.5	10min tip son.	Elvax 150	5	1x	1.6 $\pm$ 0.4	>5	32	43
TipSonx2	Tuball	0.5	10min tip son.	Elvax 150	5	2x	1.6 $\pm$ 0.4	>5	32	43
Elvax 4355	Tuball	0.25	10min tip son.	Elvax 4355	2.5	1x	1.6 $\pm$ 0.4	>5	25	5.7
40L-03	Tuball	0.25	10min tip son.	Elvax 40L-03	2.5	1x	1.6 $\pm$ 0.4	>5	40	3
40W	Tuball	0.25	10min tip son.	Elvax 40W	2.5	1x	1.6 $\pm$ 0.4	>5	40	52
4320	Tuball	0.25	10min tip son.	Elvax 4320	2.5	1x	1.6 $\pm$ 0.4	>5	25	150

Table 5.3: Composition and manufacturing specifications of the studied CNT:P thin film systems. "Name" refers to handle by which they are referred to in this thesis. "CNT type" refers to their manufacturer label of the CNTs. "Polymer" is likewise the manufacturer label of the ELVAX (DuPont) branded EVA type polymers. "VA content" is the vinyl acetate content.

6 | Small angle scattering of all small molecule Donor:Acceptor bulk heterojunctions

SANS is able to probe the longer-range ordering and phase separation behaviour of OPV systems, which is key to improving free charge carrier transport and limit recombination. The technique has been used to investigate solution processed polymer-based OPV films, giving quantitative and qualitative information about how the choice of molecular system and deposition parameters influence the resultant microstructure [69, 70]. In this chapter, we present the first SANS studies of evaporated SM OPV BHJ films. As an initial study, we combine the fullerene acceptor molecule C60 with organic donor molecules such as the high efficiency DCV5T-me(3,3) [71], the prototypical A6T [72] as well as the phthalocyanine ZnPc, the sub-phthalocyanine SubPc and the planar molecule Rubrene, which are used as representative molecules for relevant donor classes of molecules. We demonstrate SANS as a viable tool for identifying phase separation between D and A rich domains and how scattering models can be used to quantify this behaviour. We follow with additional SANS studies of DCV5T-me(3,3) and A6T, varying deposition parameters such as mixing ratio, molecular deposition rate and substrate temperature during film growth, demonstrating how model fits of SANS data can be used to quantify the effects of varying deposition parameters.

6.1 Fitting methodology

Experimental data was fitted to quantitative models in SASView version 4 and 5. To estimate the correlation between fitted parameters, the population based Differential Evolution Adaptive Metropolis (DREAM) fitting optimiser is employed

in Sasview. Whilst this optimiser is not the fastest, it is chosen because it generates plots of the cross-correlation between parameters as well as histograms of the found values from different members of the population. This visualisation enables a better understanding of which model parameters the model is sensitive to and whether two parameters are correlated. This is unlike other optimisers, which provide simpler Hessian uncertainty estimates of the best fitted values. The parameter visualisation allows us to understand whether select parameters of a given model might not provide physically meaningful output and thus provide a better understanding of the limitations of applied models.

The DREAM algorithm is a Markov Chain Monte Carlo method developed by J.A. Vrugt *et al.*. For a given model with defined parameters and a set of experimental data, Maximum Likelihood Estimation (MLE) is used to update fitting parameters through a 'guessing' sampler [73]. A decision whether to move to the position in the parameter space is then made based on the *a posteriori* likelihood. As each new position in the parameter space is dependant on the prior position, this constitutes a form of a *Markov chain* (MC) where the 'guesses' move gradually (but randomly) towards parameters that cause a high degree of concordance between model and posterior parameters and the given data. It is important to note that Markov Chain will continue traversing the parameter space even when (close to) optimal parameters have been found and instead of stopping will 'orbit' around the optimal parameters until the chosen amount of iterations have been run. After the initial traversal of the parameter space (the 'burn in'), the orbiting points are used to calculate the joint posterior ('covariance') of different model parameters. When employing the DREAM algorithm, a multitude of chains are run in parallel to obtain a better statistical description of the relation between the model and the data.

The DREAM algorithm with the following parameters are used:

Samples - 100,000

The number of sampling points from the Markov Chain which are used to calculate the best estimate of the parameters. 100,000 samples is the required amount to ensure two digit precision of the one standard deviation interval.

Burn-in steps - 7,000

The number of initial steps taken by the chains before reaching an area of the parameter space with high likelihood. These points are discarded and not used in the uncertainty estimation. A value of 7,000 was chosen based on an evaluation of the *convergence* plots described below.

Population scale factor - 10

The scale factor between the number of parameters and the total number of chains.

Initialiser

"cov (covariance matrix), in which the uncertainty is estimated using the covariance matrix at the initial point, and points are selected at random from the corresponding Gaussian ellipsoid"

Thinning -5

A parameter for removing outlier chains. The purpose of thinning the chain population is to ensure a better statistical description.

The lowest Q data point is generally not included in the fitting as it is often associated with a large error due to being on the edge of the detector acquisition range.

6.1.1 Fit evaluation of the DREAM model

The DREAM fitting optimiser in SASview provides several outputs to both judge the validity and completeness of the fit. The descriptions below are based on the information found at the software documentation repository [\[74\]](#).

6.1.2 Convergence

The convergence plot shows the χ^2 values of the MCs as a function of fit iteration. An example can be seen in Figure 6.1 The solid green line at the bottom of Fig.

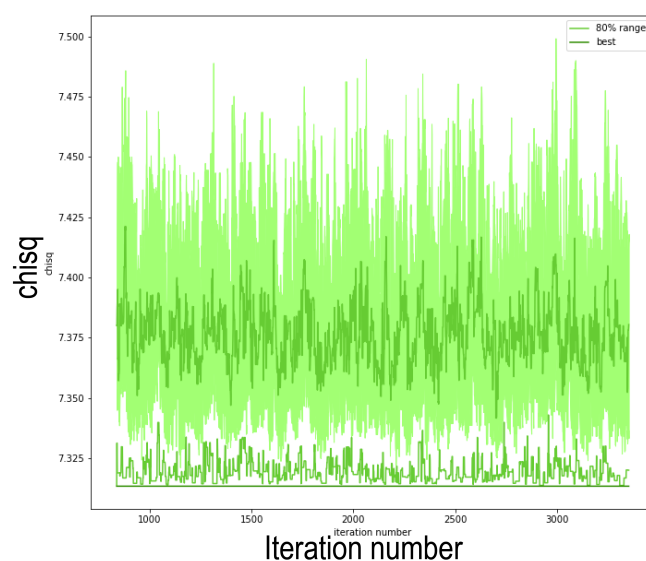


Figure 6.1: Convergence plot of A6T:C60 (2:1 mol, $T_{sub} = 80^\circ\text{C}$) using the Debye-Anderson-Brumberger model.

6.1 show the lowest χ^2 amongst the MCs. The wide light green band shows the 60% interval around the median, the solid green line in the middle. A complete fit, shown in the example, is characterised by having a relatively flat convergence graph both in terms of the median and the lowest value of χ^2 .

6.1.3 Correlations

The correlations plot shows the cross correlations between pairs of individual parameters. An example can be seen in Figure 6.2 The example in Fig. 6.2 shows the pairwise cross correlations (hereafter denoted as $A \times B$) between the 8 pa-

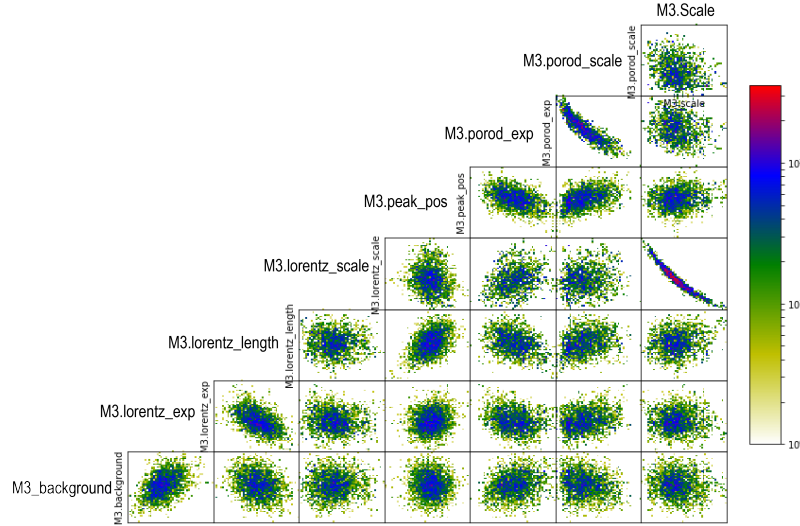


Figure 6.2: Correlations plot of DCV5T-me(3,3):C60 (2:1 mol, $T_{sub} = 140$ °C) using the *Broad peak* model.

rameters forming a so called *triangle plot*. For each box, the relevant parameters can be read from the text by the left-most box of the row and the text at the top of the corresponding column. The range of the parameter values are determined by the uncertainty plot which will be described next. The scale bar on the right indicates how many computations reached a given parameter value.

If two parameters are uncorrelated, their box will contain a circular blob. As example of this is the *background* $\times$ *C* correlation. If the fit is not sensitive to one or more of the parameters, the box will contain a square smear of data points. For models with several parameters such behaviour will indicate the model is overparameterised. For correlated parameters, their blob will be slanted down-wards for anti-correlation ($Q_0 \times m$) or upwards ($Q_0 \times C$). Thin, line-like correlations (*scale* $\times$ *C*) often indicate that the two parameters are products of each other.

6.1.4 Uncertainty

The uncertainty plot shows, for each parameter, histograms of the values from all the MCs. An example is shown in Figure 6.3. For each parameter, the MC values

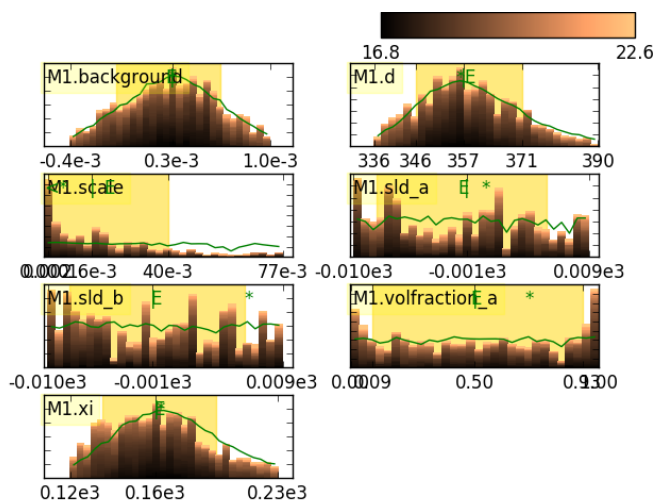


Figure 6.3: Uncertainty plot of Rubrene:C60 (2:1 mol, $T_{sub} = 80^\circ\text{C}$) using the *Broad peak* model.

are binned into a histogram. Within each bar, values are displayed from lowest χ^2 (black) to highest χ^2 (copper). The plots each cover the 95% confidence interval, marked as the lowest and highest value on the x-axis, for each parameter with a yellow block showing the 60% confidence interval. The median value is marked by a green vertical bar. The green line tracks the maximum likelihood for each bar, with the green asterisk marking the best value (as defined by the lowest χ^2) and the green *E* marking the mean value.

For a converged model fit, we should see a black or dark brown hump with light brown edges. This is seen for the *background* parameter in Fig. 6.3. If the fit is incomplete, the histogram will have black bars due to outlier chains skewing the χ^2 or range or it might appear jagged. If the fit is not sensitive to a given parameter, the histogram and green line will appear flat such as is the case for the

SLD_B parameter.

6.1.5 Trace

The trace plot shows the evolution of a parameter value as the model iterates. An example is shown in Figure 6.4. The trace plot should, as it does in Fig. 6.4, show

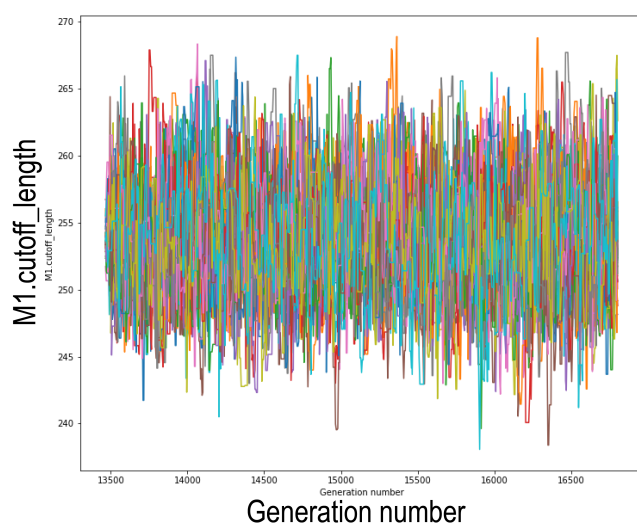


Figure 6.4: Trace plot of A6T:C60 (1:2 mol, $T_{sub} = 80\text{ }^{\circ}\text{C}$) using the *Mass Fractal* model.

a chaotic intermixing of the values surveyed by different MCs.

In the following sections, only the correlations and the uncertainty plots are shown and discussed.

6.2 SANS studies of D:A systems

An initial selection of interesting model donor molecules for BHJ system with C60 was made in order to probe their longer range ordering and phase separation and assess the suitability for further SANS studies. As a strong SANS signal is

predisposed on a phase separation between different molecular constituents with different SLDs, a BHJ resembling the active layer with documented phase separation was chosen. The system in question was the DCV5T-me(3,3):C60 system evaporated at $T_{sub} = 80^\circ\text{C}$ reported by Mönch *et al.* [71]. This equivalent configuration shows a two-phase system with carbon-rich islands, corresponding to C60, (diameters of 10 nm) enmeshed in a sulfur-rich network, corresponding to DCV5T-me(3,3). In addition to being suitable for SANS measurements, the order of magnitude of domain sizes are close to what is considered optimal for some OPV device systems, making this system of particular interest for initial study [12].

The experimental details of the compositions are shown in Table 6.1. The choice

T _{sub} [°C]	80
D:A ratio [mol]	2:1
Nominal film thickness [nm]	100
D rate [Å/s]	0.1
A rate [Å/s]	0.05
Underlayer	15 nm C60

Table 6.1: Experimental details of ZnPc/SubPc/Rubrene/DCV5T-me(3,3)/A6T:C60 compositions.

of a C60 underlayer in the original study was preserved. This was done to ensure equivalency and mimic any templating effects that might arise from organic-on-organic growth. The underlayer thickness of 15 nm was also preserved, however, in retrospect, this thickness is excessive to ensure a full coverage of the substrate that would achieve certainty about any templating effects and 5-10 nm would likely have been enough. As there is no SLD contrast between regions in the C60 layer no contribution to the coherent scattering in the probed Q -range is expected. In addition to DCV5T-me(3,3), BHJs with donor molecules ZnPc, SubPc, Rubrene and A6T were made in similar fashion with $T_{sub} = 80^\circ\text{C}$. Scattering

curves are shown in Figure 6.5. From the scattering curves in Fig. 6.5, a number

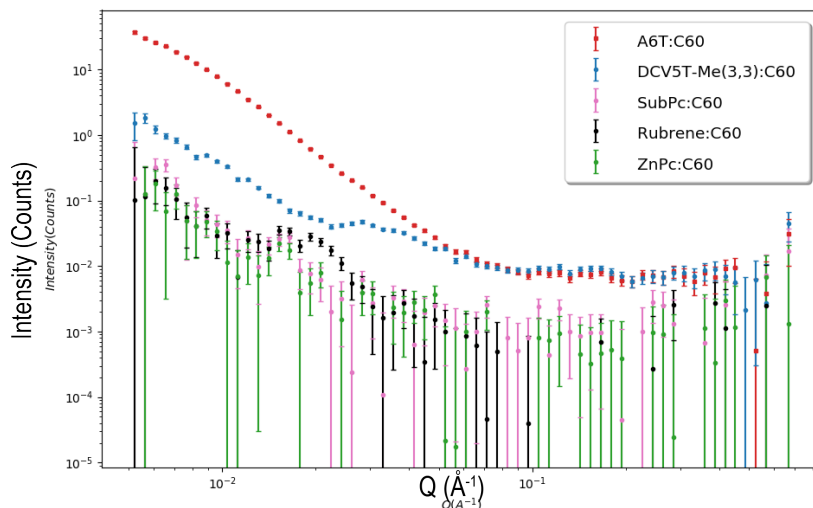


Figure 6.5: Log-log plot of small angle neutron scattering curves of DCV5T-me(3,3):C60, ZnPc:C60, SubPc:C60, Rubrene:C60 and A6T:C60 all deposited at $T_{sub} = 80^\circ\text{C}$ with 2:1 mol ratios.

of things become apparent. The ZnPc:C60, SubPc:C60 and Rubrene:C60 all have roughly similar intensity profiles across the chosen Q -range, featuring a general upwards slope towards the low- Q limit. This trend appears roughly linear in in log-log space, corresponding to a power-law decay, with each having a small and broad peak around $2 \times 10^{-2} \text{ \AA}^{-1}$. This bump is broader and more pronounced for Rubrene:C60. The intensities of the curves are generally low as evident from the large error bars (note that the logarithmic nature exaggerates this visually). The transition to background noise is not readily apparent, but comparing to the higher intensity curves, this is assumed to occur at around $0.1 \text{ \AA}^{-1}$.

The intensity profile of the scattering of DCV5T-me(3,3):C60 is roughly one magnitude higher than those of the three aforementioned films. It also has an upwards slope towards the low- Q limit with roughly the same Porod gradient. Towards the high- Q limit, the intensity reaches a stable level around $0.1 \text{ \AA}^{-1}$. A broad peak on

top of the power-law decay can be seen between $2 \times 10^{-2} \text{ \AA}^{-1}$ and $6 \times 10^{-2} \text{ \AA}^{-1}$. The intensity profile of the scattering of A6T:C60 is again roughly one magnitude higher than those of the three weakly scattering films. It has an upwards slope towards the low- Q limit with the Porod exponent being higher than those of the other curves. A possible flattening of the curve is observed right at the low- Q limit, although as can be observed across the scattering curves the data points closest to the detector limits are associated with greater uncertainties. There is also an apparent drop in intensity below the trend-line. The intensity curve otherwise appears without any features and reaches a constant level at around $0.1 \text{ \AA}^{-1}$. In the region between roughly $0.1 \text{ \AA}^{-1}$ and $0.4 \text{ \AA}^{-1}$, the intensity profiles of DCV5T-me(3,3):C60 and A6T:C60 appear similar and at a stable level with higher scattering than from the other three configurations. Above $0.4 \text{ \AA}^{-1}$, all data points appear highly noisy.

6.3 Scattering length densities of chosen molecules

The neutron SLDs of the chosen molecules are found in Table 6.2. The neutron SLDs are calculated through SASview's inbuilt SLD calculation tool based on the molecular composition of the molecule as well as the thin film densities which are taken from the cited sources. See notes below table. The SLD of a given material can also be determined from (amongst other methods) neutron reflectivity via the critical angle. For a detailed explanation, we refer to H. Börner et al. [75].

6.4 ZnPc and SubPc

The scattering of the ZnPc:C60 and SubPc:C60 systems are treated together due to their similar scattering curves. Both display weak scattering, with their inten-

Name	Chemical formula	Density [gcm ⁻³]	Neutron SLD [10 ⁻⁶ Å ⁻²]	Imaginary SLD component [i Å ⁻²]
C60	C60	1.65 [76]	5.5	8.05×10^{-13}
A6T	C ₂₄ H ₁₄ S ₆	1.54 [77] !	2.33	4.13×10^{-11}
ZnPc	C ₃₂ H ₁₆ N ₈ Zn	1.55 [78]	3.77	9.77×10^{-11}
SubPc	C ₂₄ H ₁₂ BN ₆ Cl	1.53 [79]	3.97	4.85×10^{-9}
Rubrene	C ₄₂ H ₂₈	1.3 [80]	2.56	3.87×10^{-11}
DCV5T-me(3,3)	C ₃₀ H ₁₆ N ₄ S ₅	1.33 [81]	2.58	5.89×10^{-11}

Table 6.2: Complex neutron scattering length densities of the chosen molecules. For A6T, the reported polycrystalline density is used. Note it is different from the density used for evaporation of 1.40 g/cm³. The imaginary scattering length density component is not used in this thesis.

sities being roughly one magnitude lower than that of DCV5T-me(3,3) and two magnitudes lower than those of A6T. As can be seen from Tab. 6.2, the contrast between the neutron SLD of C60 (5.5×10^{-6} Å⁻²) and those of the donors range between 1.53×10^{-6} Å⁻² for SubPc and 3.17×10^{-6} Å⁻² for A6T. Whilst SubPc and ZnPc have the lowest scattering contrast with C60, the difference between contrasts is only of a factor of ~2 which could only explain a small fraction of the observed differences in intensity. Additionally, Rubrene and DCV5T-me(3,3) have roughly equal SLDs of 2.56×10^{-6} and 2.58×10^{-6} Å⁻² respectively, yet the intensity of the latter is roughly one magnitude higher across the measured range.

This suggests that the weak signal of SubPc and ZnPc cannot be primarily attributed to the lower scattering contrast between moieties, but instead due to volumes with differing SLDs not being present in the film in the probed Q -range. This, in other words indicate no phase separation at the mesoscale (~10s of nm). The upwards slope towards the low- Q limit is attributed to the general scattering behaviour that cannot be attributed to any particular structure due to a lack of statistics that is left after the background subtraction. These scattering curves

are thus seen as being representative of BHJ films where phase separation is not achieved.

The intensity curves of SubPc and ZnPc both display a potential small peak positioned at around $1.6 \cdot 10^{-2} \text{ \AA}^{-1}$ as seen by the increase in intensity with regard to the trendline as well as the decreased experimental uncertainty. As this peak is present for both films at the same position, it is assumed that it arises due to a background subtraction artifact. This view is further supported by fitting the peak of the ZnPc:C60 intensity curve using the *Broad Peak* model, see Eq. 6.1 for further introduction. Figure 6.6 shows the fitted curve. Fitted values are shown in Table 6.3.

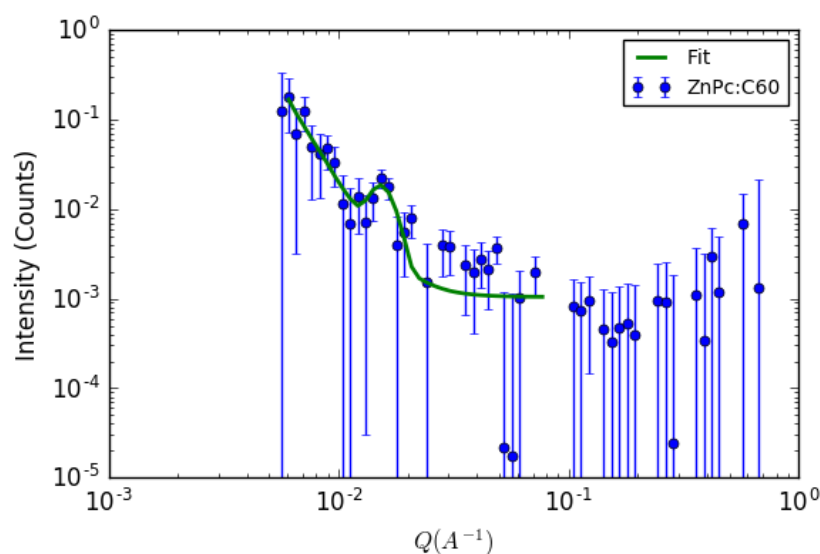


Figure 6.6: Small angle neutron scattering curve of ZnPc:C60 2:1 mol deposited at $T_{sub} = 80^\circ \text{C}$ fitted with the *Broad peak* model.

The fitted model can be seen to capture the shape of the small peak, whilst falling below the data points at higher Q -values. Whilst a feasible peak position and shape is described by the mode, the fitted value of ξ , corresponding to the coherence length, of $\sim 180 \text{ nm}$ would imply an incredibly well ordered organic system.

<i>Parameter</i>	<i>Fitted value</i>
<i>Scale</i> [a.u]	0.001 ± 0.007
<i>Background</i> [cm^{-1}]	0.001 ± 0.003
<i>A</i> [a.u]	$(6 \pm 200) \times 10^{-8}$
<i>n</i> [a.u]	4.1 ± 0.5
<i>C</i> [a.u]	$(1.4 \pm 1.7) \times 10^2$
ξ [$\text{\AA}$]	$(1.8 \pm 1.5) \times 10^3$
Q_0 [$\text{\AA}^{-1}$]	0.016 ± 0.001
d_0 [$\text{\AA}$]	396
<i>m</i> [a.u]	28 ± 344
χ^2	0.63763

Table 6.3: Table of *Broad peak* fitted values of ZnPc:C60 2:1 mol deposited at $T_{\text{sub}} = 80^\circ \text{C}$. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

However, this would not be congruent with the low intensity, despite the ~four hour measurement time, indicating a highly mixed system. In addition, the fitted peak only covers a total of four data points, increasing the likelihood that a 'peak' may arise from just one or two spurious data points. This fit thus supports the view that this feature is either an artifact or arises due to scattering from total 9 mm of quartz the beam passes through.

This peak is potentially also present for Rubrene, where a broader peak is observed at around the same position in Q -space. This peak features a single data point in the middle which appears as having a lower intensity. It is thus unclear whether the broader feature is composed of two overlapping peaks, with the lower- q feature being an artifact, or is one single broader feature. This will be treated further in the following section.

We note here and for future models applied in this chapter that the *Scale* (and similarly the Porod law Scale factor of Eq. 6.1) parameter of applied models only represents a simple mathematical scaling factor which serve to scale the 'shape'

of the model to the intensity of the data. These scale factors can thus serve as part of a comparative analysis, but do not directly yield physical information about the investigated systems. Keeping that in mind, we also stress that the scattering observed for configurations studied in this thesis is generally very low compared to 'standard' SANS, where e.g. polymer samples would usually have thicknesses on the order of millimeters compared to the micrometre-scale total thickness of the studied SM evaporated thin films. We mention this both to highlight limitations of SANS scattering when applied to such systems, but also the achievement of extracting meaningful physical information via the technique.

6.5 Rubrene:C60

The SANS scattering data of the Rubrene:C60 system is shown in Figure 6.7. The scattering intensity, similar to those of ZnPc and SubPc, is low with large error bars and appears to follow a power law decay with a broad peak centred roughly at $0.02 \text{ \AA}^{-1}$. This motivated using the *Broad Peak* SASview function

$$I(Q) = \text{scale} \left(\frac{A}{Q^n} + \frac{C}{1 + (|Q - Q_0|\xi)^m} \right) + B, \quad (6.1)$$

where *scale* is a general scaling factor, *A* is the Porod law scale factor, *n* the Porod exponent, *C* is the Lorentzian scale factor, *m* the exponent of the Lorenz function, ξ is the Lorentzian screening length and *B* a flat background. Q_0 is the peak position which corresponds to a real-space characteristic distance between volumes of different SLDs. Here, the peak is fitted as a single feature rather than as a composition of two features. The *Broad Peak* model is an empirical model and as such does not make any physical assumptions about the system it describes.

The SANS and *Broad Peak* fit of Rubrene:C60 can be found in Figure 6.7. A plot of fitting correlations and the ensemble uncertainties can be found in Figure 6.8

and Figure 6.9 respectively. Fitted values can be found in Table 6.4. The *Broad*

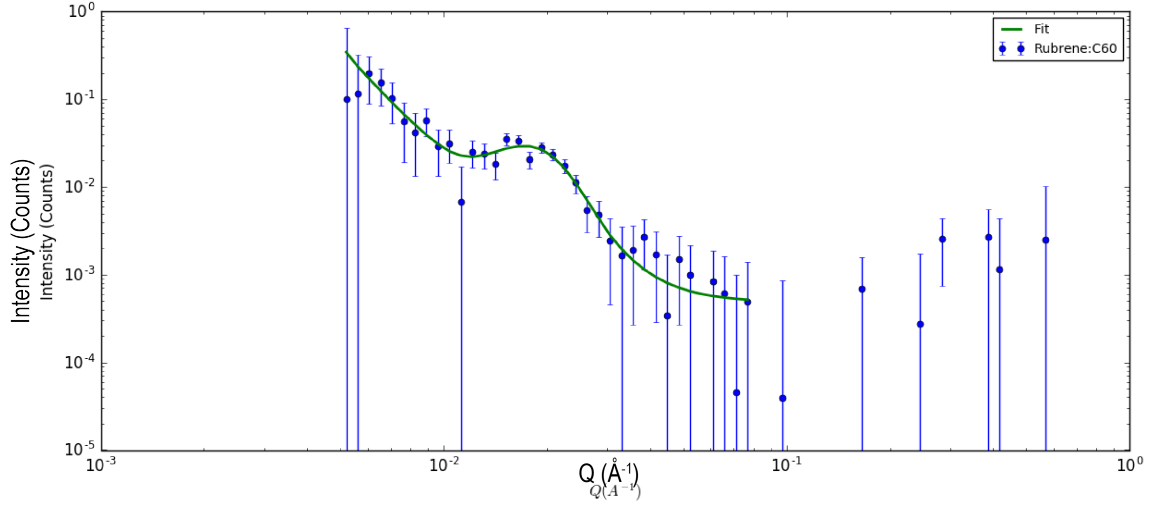


Figure 6.7: Small angle neutron scattering curve of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80$ °C fitted with the *Broad peak* model.

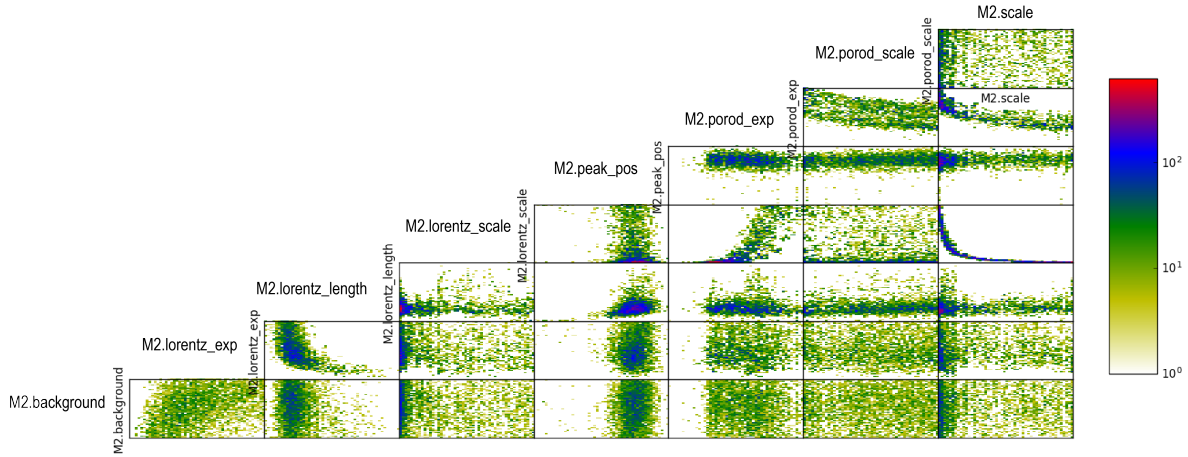


Figure 6.8: Fitting parameters correlations of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80$ °C fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M2.background \hat{=} B$, $M2.lorentz_exp \hat{=} m$, $M2.lorentz_length \hat{=} \xi$, $M2.lorentz_scale \hat{=} C$, $M2.peak_pos \hat{=} Q_0$, $M2.porod_exp \hat{=} n$, $M2.porod_scale \hat{=} A$ and $M2.scale \hat{=} scale$.

peak model (Table 6.4) shows the system as having a characteristic distance of

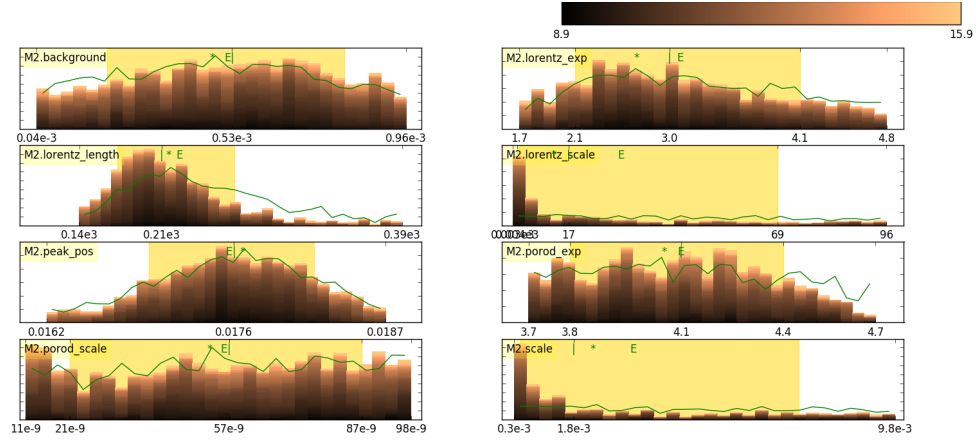


Figure 6.9: Ensemble uncertainties of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ when fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $\text{M2.background} \hat{=} B$, $\text{M2.lorentz_exp} \hat{=} m$, $\text{M2.lorentz_length} \hat{=} \xi$, $\text{M2.lorentz_scale} \hat{=} C$, $\text{M2.peak_pos} \hat{=} Q_0$, $\text{M2.porod_exp} \hat{=} n$, $\text{M2.porod_scale} \hat{=} A$ and $\text{M2.scale} \hat{=} \text{scale}$.

Parameter	Fitted value
Scale [a.u]	0.002 ± 3
Background [cm^{-1}]	0.005 ± 0.003
A [a.u]	$(5 \pm 3) \times 10^{-8}$
n [a.u]	4.1 ± 0.3
C [a.u]	12 ± 32
$\xi [\text{\AA}]$	$(2.0 \pm 0.4) \times 10^2$
$Q_0 [\text{\AA}^{-1}]$	0.0177 ± 0.0006
$d_0 [\text{\AA}]$	36 ± 1
m [a.u]	2.7 ± 1
χ^2	0.63763

Table 6.4: Table of *Broad peak* fitted values of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

36 ± 1 nm and a screening length of $(2.0 \pm 0.4) \times 10^2$.

From shapes of the histogram uncertainty plot (Fig. 6.9), only ξ and Q_0 appear as meaningful parameters showing clear hump, although for ξ the best value trace (green line) appears skewed compared to the histogram. The triangle plot (Fig.

6.8) show mostly disperse or stretched rectangular plots, with only $\xi \times Q_0$ appearing relatively blob-like. The fitted Q_0 value corresponds to a coherence length of close to 40 nm. Additional fitting was carried out using the Teubner-Strey model which is intended to describe two-phase microemulsions [82]. We stress that the explored system is of course not a microemulsion, but the model remains of interest as it is intended to describe two phase systems with a loss of long range order resulting in a broad peak. The Teubner-Strey model describes a system assumed to be isotropic and consisting of aggregates of variable size and shape that may be bicontinuous. The theory is derived from an order parameter expansion of the free energy density with a term favouring the creation of interfaces balanced by a term favouring stability [82].

$$I(Q) = scale \frac{8\pi\phi_a(1-\phi_a)(\Delta\rho)^2 c_2/\xi}{Q_a + c_1 Q^2 + c_2 Q^4} + background. \quad (6.2)$$

With constants defined as

$$a_2 = \left(1 + \left(\frac{2\pi\xi}{d}\right)^2\right)^2, a_2 > 0. \quad (6.3)$$

$$c_1 = -2\xi^2 \left(\frac{2\pi\xi}{d}\right)^2 + e\xi^2, c_1 < 0. \quad (6.4)$$

$$c_2 = \xi^4, c_2 > 0. \quad (6.5)$$

Where *scale* is a scaling factor, d is the periodicity, ξ is the correlation length, ϕ_a is the explicit volume fraction of one phase and $\Delta\rho = \rho_a - \rho_b$ is the SLD contrast between phases. The model thus has two characteristic length scales. The periodicity d represents the distance between the two different phases (polar and nonpolar molecules in a typical microemulsion). The correlation length ξ represents the loss of longer range order and thus the dispersity of d [83].

The SANS and *Teubner Strey* fit of Rubrene:C60 can be found in Figure 6.10. A plot of fitting correlations and the ensemble uncertainties can be found in Figure 6.11 and Figure 6.12 respectively. Fitted values can be found in Table 6.4.

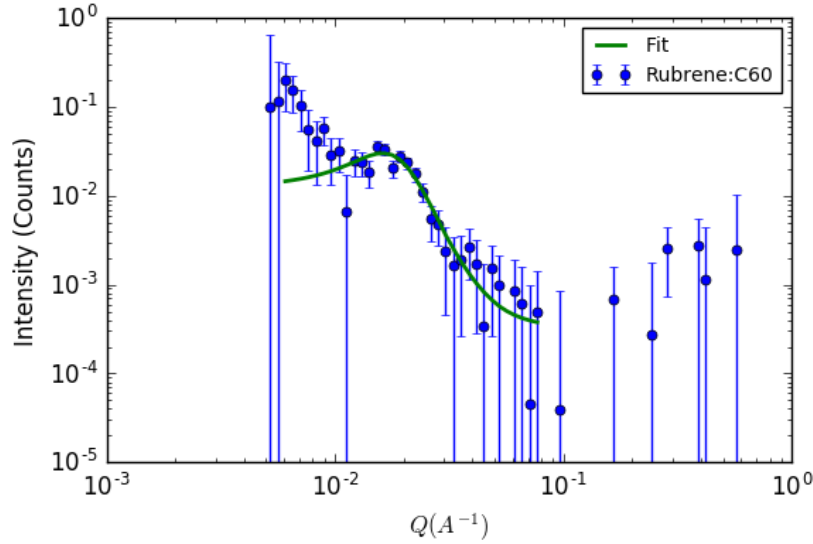


Figure 6.10: Small angle neutron scattering curve of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the *Teubner Strey* model.

Parameter	Fitted value
Scale [a.u]	0.00 ± 0.02
Background [cm^{-1}]	$3 \pm 4 \times 10^{-4}$
ϕ_a [a.u]	(0 ± 0.4)
ρ_a [$10^{-6} \text{ \AA}^{-1}$]	1 ± 7
ρ_b [$10^{-6} \text{ \AA}^{-1}$]	6 ± 7
d_0 [$10^{-6} \text{ \AA}^1$]	$(36 \pm 1) \times 10^2$
ξ [$\text{\AA}^1$]	$1.7 \pm 0.3 \times 10^2$
χ^2	1.2446

Table 6.5: Table of *Teubner Strey* fitted values of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

The Teubner-Strey model shows the system as having a periodicity of 36 ± 1 nm and a correlation length of 17 ± 3 nm. Whilst the model does indeed produce

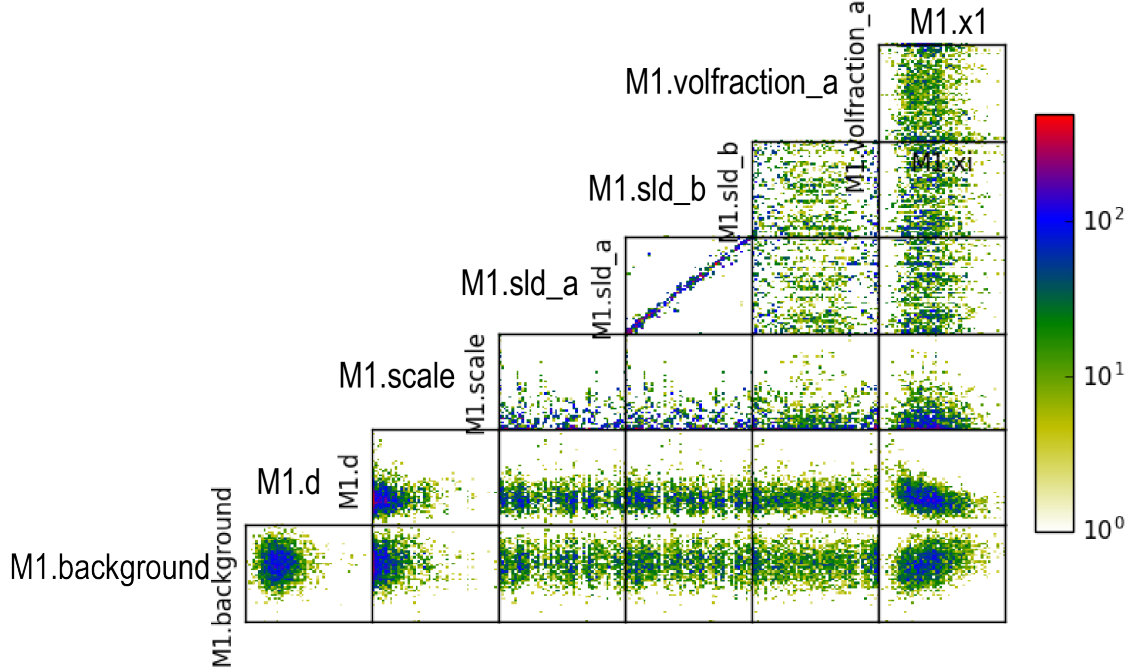


Figure 6.11: Fitting parameters correlations of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the *Teubner Strey* model. The shown parameters map as follows to the coefficients in Eq. 6.2: $M1.background \hat{=} background$, $M1.d \hat{=} d$, $M1.scale \hat{=} scale$, $M1.SLD_a \hat{=} \rho_a$, $M1.sld_b \hat{=} \rho_b$, $M1.volfraction_a \hat{=} \phi_a$ and $M1.x1 \hat{=} \xi$.

a broad peak at the right position in reciprocal space, it is immediately apparent from the discrepancy between the fitted curve and the experimental data points that the model does not describe the low- Q behaviour. From Fig. 6.12 it can be seen that fitted values relating to the SLDs or the volume fraction are not meaningfully fitted. The histograms of d_0 and ξ show well-shaped distributions and their correlation square (Fig. 6.11) is blob-like with with a negative correlation. It is possible that this negative correlation relates to the skew of histogram bars with regard to the best value trace.

Both models give a characteristic in-plane feature size of around 35 nm and at

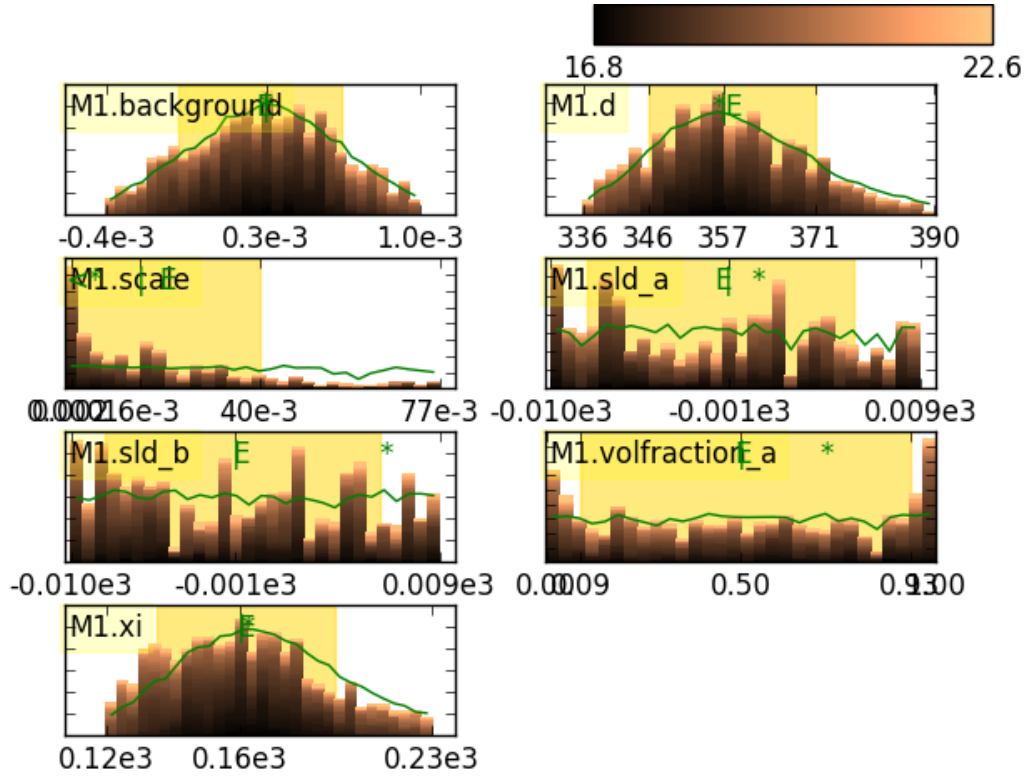


Figure 6.12: Ensemble uncertainties of Rubrene:C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ when fitted with the *Teubner Strey* model. The shown parameters map as follows to the coefficients in Eq. 6.2: $M1.background \hat{=} background$, $M1.d \hat{=} d$, $M1.scale \hat{=} scale$, $m1.SLD_a \hat{=} \rho_a$, $m1.sld_b \hat{=} \rho_b$, $M1.volfraction_a \hat{=} \phi_a$ and $M1.xi \hat{=} \xi$.

a correlation length of 17 nm (*Teubner Strey*) to $(2.0 \pm 0.4) \times 10^2$ nm (*Broad Peak*). Together with the low scattering intensity levels, this suggests that the Rubrene:C60 system manifests as a two-phase system composed of fullerene-rich and organic-rich domains that are relatively impure. It should be noted that a more detailed model to describe the system could be found or developed, but this would require better statistics and contrast variation to determine, for example, the purity of phases. Whilst single crystal Rubrene thin films have displayed some of the highest charge carrier mobilities of organic films on the order of $13\text{ cm}^2/\text{Vs}$,

this observed weak phase separation with relatively large domains could offer a possible explanation for their lacking application in studied devices [84].

6.6 DCV5T-me(3,3):C60 evaporated at 80 °C

The neutron intensity scattering curve of the DCV5T-me(3,3):C60 system is shown in Figure 6.5. The scattering increases towards the low- Q limit following a power law. A broad flat bump begins around $0.02 \text{ \AA}^{-1}$ ranging to $0.05 \text{ \AA}^{-1}$. A stable background level is reached at around $0.1 \text{ \AA}^{-1}$ although the background appears more variable than in previous cases.

The study of this system was motivated by prior works by Mönch *et al.* [71]. In this work, see Figure 4., scanning transmission electron microscopy, energy dispersive X-ray spectroscopy (STEM-EDX) was used to image films made in an equivalent way showing fullerene-rich islands in a sulfur-rich DCV5T-me(3,3) matrix. The work also included films made at $T_{sub} = \text{RT}$ and $T_{sub} = 140^\circ\text{C}$. Going further, these islands can be viewed as connected C60-rich roughly spherical shapes of various sizes.

This motivated the use of the *sphere* form factor model described in Eq. 6.6

$$I(Q) = \frac{scale}{V} \cdot \left[3V(\Delta\rho) \cdot \frac{\sin(Qr) - Qr \cos(Qr)}{(Qr)^3} \right]^2 + background, \quad (6.6)$$

where *scale* is a scaling factor, V is the volume of the scatterer, r is the radius of the sphere (here modelling the C60 rich islands) and *background* is a flat background. $\Delta\rho$ is the contrast between (SLDs) of the scatterer (the assumed C60-rich islands) and the matrix (the assumed DCV5T-me(3,3) rich mesh). These values are taken from table 6.2. Note that it implies perfectly pure domains as impure domains would reduce the contrast. However, the *scale*-prefactor will absorb this

difference in the case where the SLD contrast is left to float.

The *sphere* model by itself models disperse spheres in a matrix, most often a liquid solution. In the heuristic view of the system we have chosen, the C60-rich spheres are no longer disperse, but instead connect to form islands due to the high molar fraction of C60. This motivates the use of an applied structure factor. A potential candidate is the *StickyHardSphere* structure factor in SASview [85]. The *StickyHardSphere* structure factor functions as an excluded volume potential where

$$U(r) = \begin{cases} \infty & r < \sigma, \\ -U_0 & \sigma \leq r \leq \sigma + \Delta, \\ 0 & r > \sigma + \Delta. \end{cases} \quad (6.7)$$

The repulsive short range terms makes the spheres 'hard' and thus unable to overlap within the range $\sigma = 2r$, whilst the second term serves as a short range attractive potential with well-depth U_0 in units of kT . Δ and σ is determined by the stickiness parameter ϵ and the perturbation parameter τ as

$$\epsilon = \frac{1}{12\tau} \exp U_0/kT, \quad (6.8)$$

$$\tau = \Delta/(\sigma + \Delta). \quad (6.9)$$

A smaller ϵ corresponds to a stronger attraction. A radii polydispersity is also added to the model to accommodate the varying sizes of C60 globules. This implementation of the *StickyHardSphere* structure factor is based on a perturbative solution of the Percus-Yevick closure relation of the Ornstein-Zernike equation [85].

The SANS and *StickyHardSphere* fit of DCV5T-me(3,3):C60 can be found in Fig. 6.13. A plot of fitting correlations and the ensemble uncertainties can be found in

Figure 6.14 and Figure 6.15 respectively. Fitted values can be found in Table 6.6.

Whilst the blob-like subplots of Fig. 6.14 show that many of the fitted param-

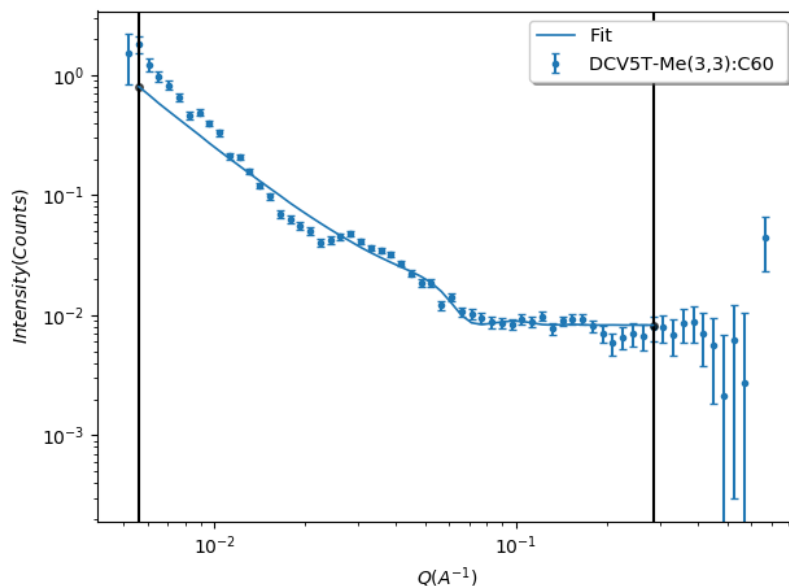


Figure 6.13: Small angle neutron curve of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ fitted with the *Sphere x StickyHardSphere* model. Black vertical bars show the range of the fit.

<i>Parameter</i>	<i>Fitted value</i>
<i>Scale</i> [a.u]	0.0011 ± 0.0001
<i>Background</i> [a.u]	0.0083 ± 0.0002
SLD_A	5.5
SLD_D	2.58
V	0.1 ± 0.2
τ	0.010 ± 0.005
ϵ	0.097 ± 0.001
Polydispersity	0.00038
χ^2	10.223

Table 6.6: Table of *Sphere x StickyHardSphere* fitted values of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$. SLD_A and SLD_B are kept fixed. *Scale* parameter is a scaling parameter that scales the model to the empirical data.

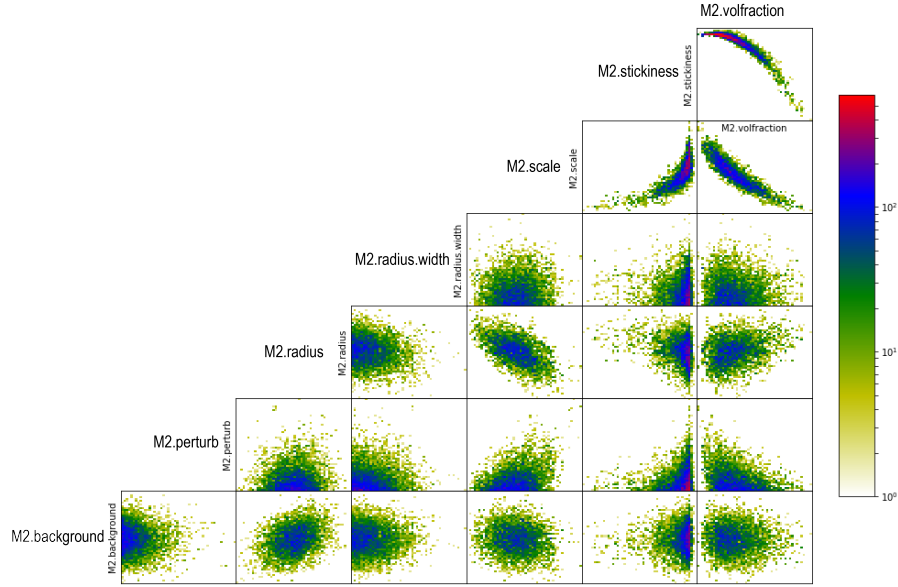


Figure 6.14: Fitting parameters correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the *Sphere x StickyHardSphere* model. The shown parameters map as follows to the coefficients in Eq. 6.6: M2.background $\hat{=}$ *background*, M2.radius $\hat{=}$ *r*, M2.scale $\hat{=}$ *scale*, M2.volume $\hat{=}$ *V*. M2.perturb $\hat{=}$ τ and M2.stickness $\hat{=}$ ϵ in Eq. 6.8. Additionally, M2.radius.width $\hat{=}$ polydispersity.

eters are generally uncorrelated and thus behave as independent parameters, the ensemble uncertainties of Fig. 6.15 show that the τ (perturbation) and ϵ (stickiness) parameters show ensemble values that slope towards the lower and higher end, respectively of the fitting range showing. The polydispersity (*radius.width*) is also sloped towards zero polydispersity. This suggests that the applied structure factor and polydispersity is not well suited for the data. The poor alignment between the data and fitted curve (Fig. 6.13) and the high χ^2 (Tab. 6.6) suggest the applied model is generally unfit.

A *BroadPeak* model (Eq. 6.1) is instead applied as a parametrically simpler model with a clearer link between observed scattering features and physical feature size. The SANS and *Broad Peak* fit of DCV5T-me(3,3):C60 2:1 mol can be found in

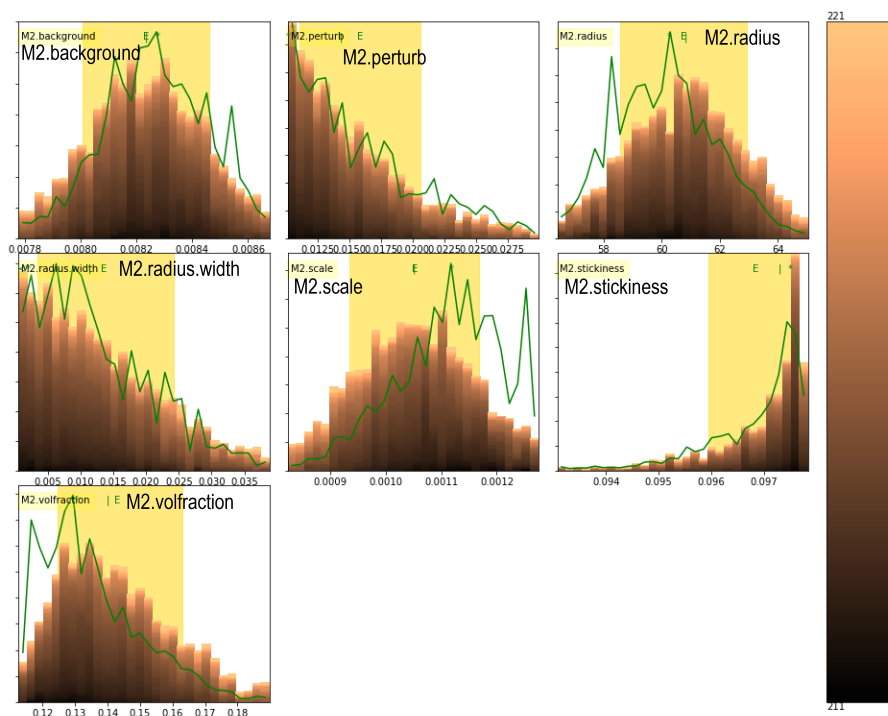


Figure 6.15: Ensemble uncertainties of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80^\circ \text{C}$ when fitted with the *Sphere x StickyHardSphere* model. The shown parameters map as follows to the coefficients in Eq. 6.6: $M2.background \hat{=} background$, $M2.radius \hat{=} r$, $M2.scale \hat{=} scale$, $M2.volume \hat{=} V$. $M2.perturb \hat{=} \tau$ and $M2.stickiness \hat{=} \epsilon$ in Eq. 6.8. Additionally, $M2.radius.width \hat{=}$ polydispersity.

Figure 6.16. A plot of fitting correlations and the ensemble uncertainties can be found in Figure 6.17 and Figure 6.18 respectively. Fitted values can be found in Table 6.7. The model (Table 6.7) shows a characteristic length of 19.2 ± 0.4 nm and a screening length of 9 ± 1 nm. The fitted curve in Fig. 6.16 shows good visual agreement with the experimental data and the χ^2 (Tab. 6.7) is much lower than that of *sphere* model. The histogram uncertainty plot (Fig. 6.17) show good overlap between the best value trace (green line) and the smoothly peaked histogram bars, with this concordance being less clear for the scaling parameters *scale*, *A* and *C*. This is further evident in the correlations plot (Fig. 6.18) where

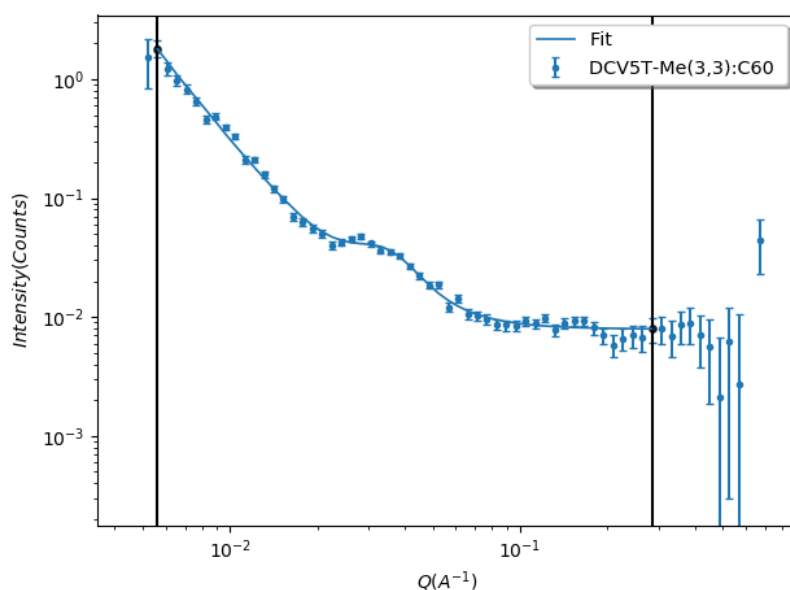


Figure 6.16: Small angle neutron scattering curve of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ fitted with the *Broad peak* model. Black vertical bars show the range of the fit.

<i>Parameter</i>	<i>Fitted value</i>
<i>Scale</i> [a.u]	0.012 ± 0.03
<i>Background</i> [cm^{-1}]	0.0079 ± 0.0003
<i>A</i> [a.u]	$(2.7 \pm 0.9) \times 10^{-5}$
<i>n</i> [a.u]	2.97 ± 0.06
<i>C</i> [a.u]	2.1 ± 0.6
ξ [$\text{\AA}$]	91 ± 11
Q_0 [$\text{\AA}^{-1}$]	0.0328 ± 0.0007
d_0 [$\text{\AA}$]	192 ± 4
<i>m</i> [a.u]	2.0 ± 0.3
χ^2	1.9609

Table 6.7: Table of *Broad peak* fitted values of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

scale and *C* appear highly correlated. Other correlation subplots generally appear blob-like indicating that all parameters are meaningful.

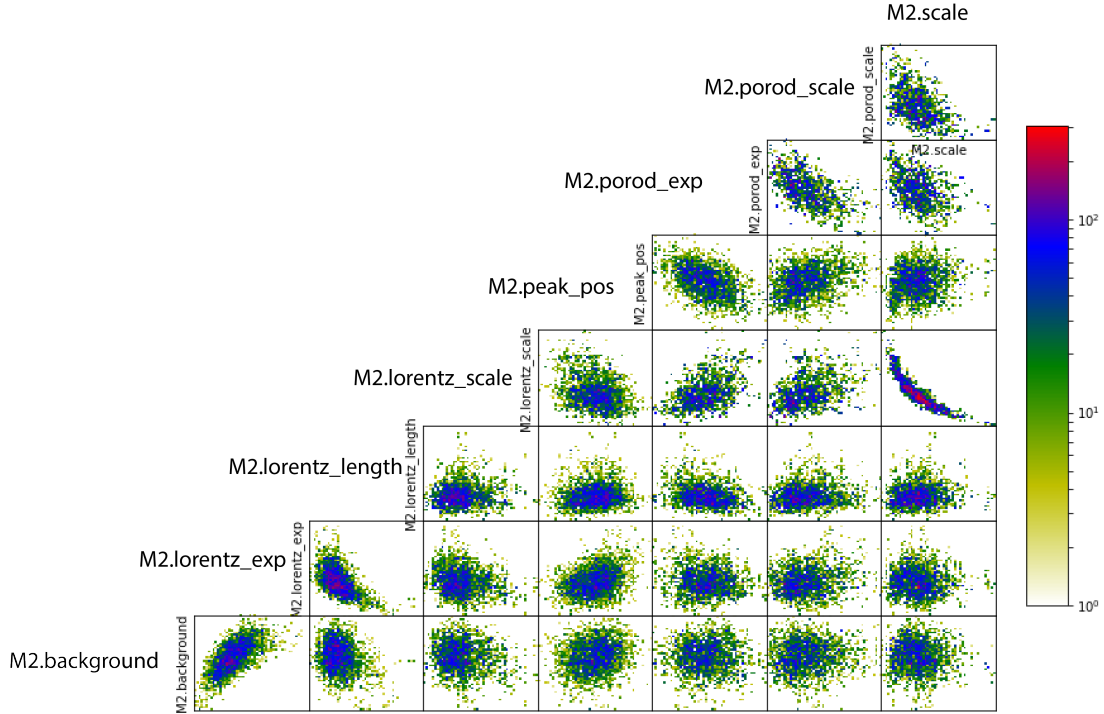


Figure 6.17: Fitting parameters correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M2.background \hat{=} B$, $M2.lorentz_exp \hat{=} m$, $M2.lorentz_length \hat{=} \xi$, $M2.lorentz_scale \hat{=} C$, $M2.peak_pos \hat{=} Q_0$, $M2.porod_exp \hat{=} n$, $M2.porod_scale \hat{=} A$ and $M2.scale \hat{=} scale$.

The fitted model suggests that DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ appears as a two-phase system with organic- and fullerene-rich domains of around 19.2 ± 0.4 nm in diameter with correlation length of approximately half that. The higher intensities of the scattering compared to Rubrene:C60 suggests a higher scattering contrast and thus that DCV5T-me(3,3) manifests with smaller, but purer domains, although, as will be discussed in Chap. 8, the C60-rich phase likely has a significant DCV5T-me(3,3) presence. These results are in concordance with the results from Mönch *et al.* where the radius of equivalent spheres of DCV5T-me(3,3) and C_{60} were found to be 10.6 and 9.8 nm respectively, which

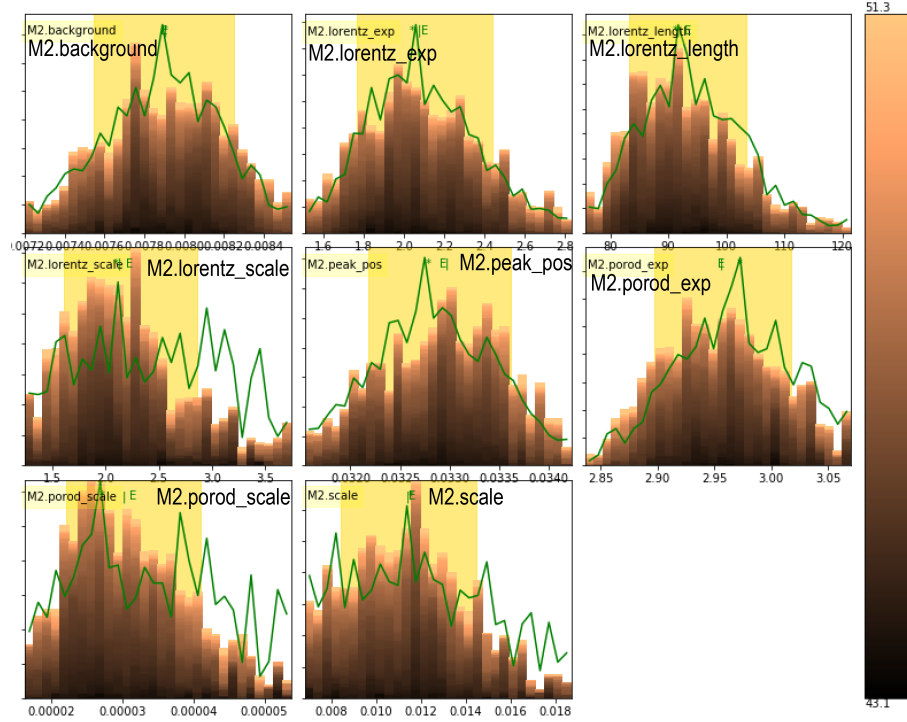


Figure 6.18: Ensemble uncertainties of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ when fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M2.background \hat{=} B$, $M2.lorentz_exp \hat{=} m$, $M2.lorentz_length \hat{=} \xi$, $M2.lorentz_scale \hat{=} C$, $M2.peak_pos \hat{=} Q_0$, $M2.porod_exp \hat{=} n$, $M2.porod_scale \hat{=} A$ and $M2.scale \hat{=} scale$.

correspond to roughly half the fitted feature size [71].

6.6.1 DCV5T-me(3,3):C60 evaporated at RT and 140°C

Mönch *et al.* studied films of DCV5T-me(3,3):C60 at mixing ratios of 2:1 made at $T_{sub} = RT, 80, 140^\circ\text{C}$ [71]. STEM-EDX of the films showed that films evaporated onto substrates held at $T_{sub} = RT^\circ\text{C}$ show a highly intermixed film with no proper domains whereas the films evaporated onto substrates held at $T_{sub} = RT$ show stronger phase separation than at $T_{sub} = 80^\circ\text{C}$. In both cases, the performance of corresponding OPV devices were lower as the phase separation was found to be either too weak or too strong. This motivated the SANS study of films

made on substrates held at $T_{sub} = RT$ and $140^\circ C$ during evaporation. The experimental details of the compositions can be found in Table 6.8. Figure 6.19 shows

Name	RT	$T_{sub} = 80^\circ C$	$T_{sub} = 140^\circ C$
D:A ratio [mol]	2:1	1:1	1:2
Nominal film thickness [nm]	100	100	100
$T_{sub} [C^\circ]$	RT	80	140
$R [\text{\AA}/s]$	0.15	0.15	0.15

Table 6.8: Experimental details of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = RT, 80, 140^\circ C$.

the SANS scattering curves of 2:1 DCV5T-me(3,3):C60 evaporated on substrates held at $T_{sub} = RT, 80, 140^\circ C$. The scattering of the RT film can be seen to be

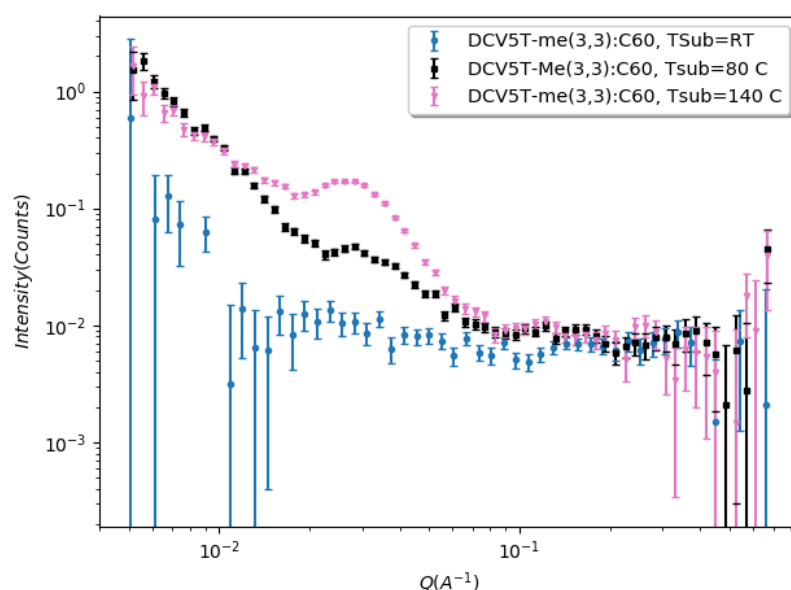


Figure 6.19: Small angle neutron scattering curves of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = RT, 80, 140^\circ C$.

at a background level from $0.01 \text{ \AA}$ and towards the high- Q limit. At lower Q , the scattering appears as increasing linearly in the log-log view, however these data points are associated with increasingly large uncertainties and some data points

having a 'negative' intensity. The negative intensities, which appear after the subtraction of scattering from the 'can' (i.e. uncoated substrates and windows), are assumed to arise due to the absolute scattering being very low in both cases. Statistical variations in what is essentially noise can thus result in scattering from the background measurements being larger than the scattering from the measured sample configurations at certain points in reciprocal space.

The scattering of the 140 °C film is similar to that of 80 °C film with scattering intensity that decays from low- Q towards higher Q following a power law with a superimposed broad peak centred around $0.02 \text{ \AA}^{-1}$ before reaching a flat background level at around $0.08 \text{ \AA}^{-1}$. Compared to the 80 °C film, the peak is broader, more intense and well-defined compared to the base trend and appears to be centred at lower Q -value.

The sample manufactured at $T_{sub} = RT$ is interpreted as showing no signal due to a lack of longer-range contrasting domains. This is in agreement with the reported results from the simulated 3D morphologies of equivalent sphere radii of 3.1 nm and 2.8 nm corresponding to reciprocal length of $\sim 0.1 \text{ \AA}^{-1}$ which is in the noise regime of the measured scattering. As the scattering is interpreted as describing an intermixed system with only background features present, no model is applied to the data.

The 140 °C sample is now treated and the *BroadPeak* model (Eq. 6.1) is again applied based on the similarity of the scattering features. The SANS and *BroadPeak* fit of DCV5T-me(3,3):C60 can be found in Figure 6.20. A plot of fitting correlations and the ensemble uncertainties can be found in Figure 6.21 and Figure 6.22 respectively. Fitted values can be found in Table 6.9.

The *BroadPeak* model is seen to describe the scattering well. The ensemble uncertainties (Fig. 6.22) show smoothly peaked histograms for each parameter with best value traces that match the histogram shape well, although the trace for m

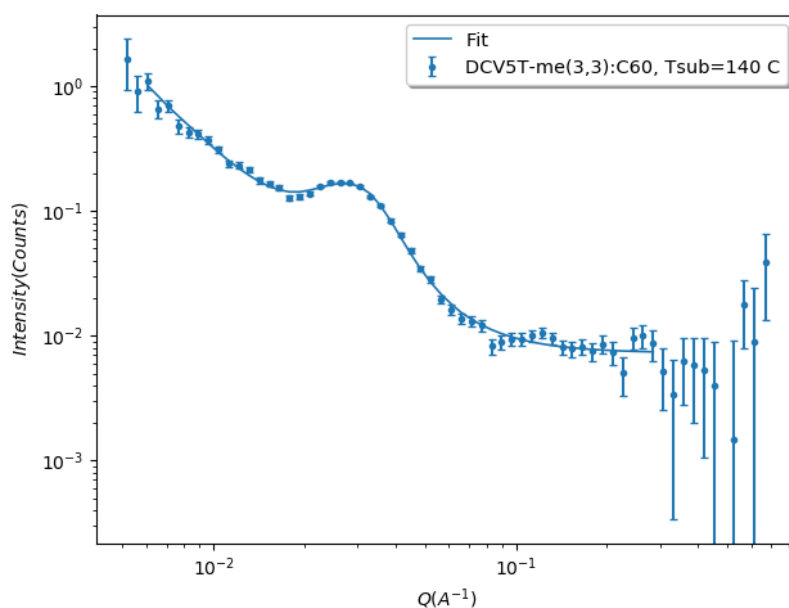


Figure 6.20: Small angle neutron scattering curve of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 140$ °C fitted with the *Broad peak* model.

Parameter	Fitted value
Scale [a.u]	0.011 ± 0.02
Background [cm^{-1}]	0.0073 ± 0.0004
A [a.u]	$(5 \pm 2) \times 10^{-4}$
n [a.u]	2.34 ± 0.07
C [a.u]	13 ± 2
ξ [Å]	109 ± 4
Q_0 [$\text{\AA}^{-1}$]	0.0282 ± 0.0002
d_0 [Å]	223 ± 2
m [a.u]	2.4 ± 0.1
χ^2	1.6012

Table 6.9: Table of *Broad peak* fitted values of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 140$ °C. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

appears skewed towards a slightly higher values. The parameter correlations (Fig. 6.21) appear blob-like with the exception of $C \times scale$ and $n \times A$, presumably due these pairs acting as scalars for their respective terms of Eq. 6.1.

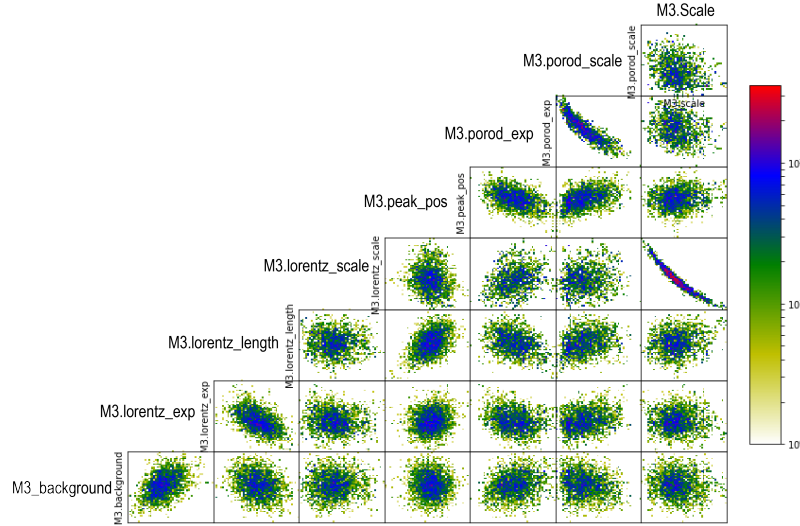


Figure 6.21: Fitting parameters correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 140^\circ\text{C}$ fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M3.background \hat{=} B$, $M3.lorentz_exp \hat{=} m$, $M3.lorentz_length \hat{=} \xi$, $M3.lorentz_scale \hat{=} C$, $M3.peak_pos \hat{=} Q_0$, $M3.porod_exp \hat{=} n$, $M3.porod_scale \hat{=} A$ and $M3.scale \hat{=} scale$.

The model describes a two-phase system with a characteristic size of 22.3 ± 0.2 nm and a coherence length of 10.9 ± 0.4 nm.

Comparing the scattering of the films made at three different substrate temperatures, a general trend of increased phase separation with increased substrate temperature can be observed (from 19.2 ± 4 nm at $T_{sub} = 80^\circ\text{C}$ to 22.3 ± 0.2 nm at $T_{sub} = 140^\circ\text{C}$). The lack of scattering in the RT samples when compared to those made at elevated temperatures show that substrate heating is required to achieve phase separation.

Films made at 80 and 140°C both appear as phase separated systems. Compared to the 80°C film, the 140°C film shows an increase of fitted characteristic size of 3.1 nm and of coherence length by 1.8 nm. This suggests that keeping the substrate at an elevated temperature during growth results in a greater degree of phase

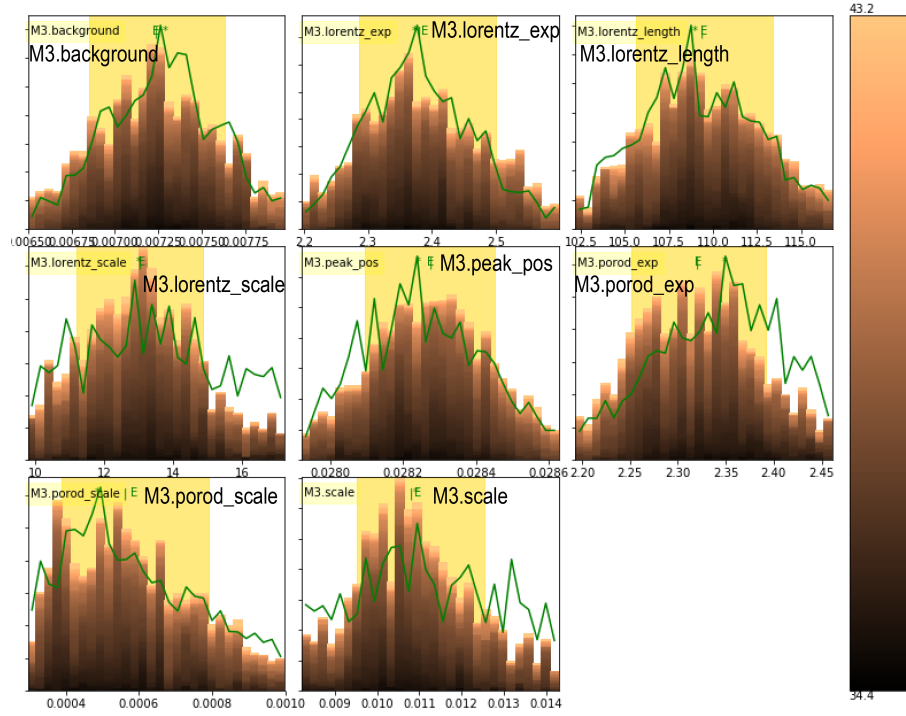


Figure 6.22: Ensemble uncertainties of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 140$ °C when fitted with the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M3.background \hat{=} B$, $M3.lorentz_exp \hat{=} m$, $M3.lorentz_length \hat{=} \xi$, $M3.lorentz_scale \hat{=} C$, $M3.peak_pos \hat{=} Q_0$, $M3.porod_exp \hat{=} n$, $M3.porod_scale \hat{=} A$ and $M3.scale \hat{=} scale$.

separation with larger domains. The greater coherence length and the higher intensity broad peak also potentially suggests a greater phase purity resulting in an increased scattering contrast. This hypothesis could be potentially be investigated via techniques such as STEM-EDX. These results are in good agreement with the results reported by by Mönch *et al.* [71]. A further exploration of the interplay between substrate temperature during growth and emergent microstructure is found in Chapter 7.

6.7 Alpha-Sexithiophene:C60

The SANS scattering of A6T:C60 2:1 evaporated on substrates kept at 80 °C is shown in Figure 6.23. Of the hitherto discussed systems, the A6T SANS scattering is of the highest intensity and features an upwards sloping intensity curve towards the low- Q limit that possibly shows signs of plateauing. Similar scattering curves in prior studies of polymer:fullerene systems motivates the choice of the Debye-Anderson-Brumberger model (DAB) (Equation 6.10) to describe the system [70, 69]

$$I(Q) = scale \cdot \frac{L^3}{(1 + (QL)^2)^2} + background, \quad (6.10)$$

where *scale* is a scaling factor, *background* is a flat background and L is a characteristic correlation length, that corresponds to the average spacing between regions of phase A and regions of phase B in a two-phase system. As such, L does not correspond directly to the size of either phase A or phase B domains.

The model is derived by imagining that a 'measuring rod' of length AB is placed at a random position and with a random orientation in the system. For a system with a given size and distribution of domains of phase A and phase B , this will result in a series of linked probabilities that the rod has ends that span between AA , AB , BA and BB . The scattering expression is then derived from the probability the rods has ends in regions of contrasting SLDs.

The model assumes a two-phase system consisting of a homogeneous medium (in terms of SLD) with holes of perfectly random size and spatial distribution. The DAB model assumes smooth interfaces (and thus that the SLD changes only as a step function) between the medium and the holes which results in a $I \propto Q^{-4}$ behaviour when $QL \gg 1$ [86].

For the studied experimental data series, a high- Q limit at which the signal is dominated by noise is reached at around $Q = 0.1 \text{ \AA}^{-1}$.

The DAB fit of A6T:C60 can be found in Figure 6.23. A plot of fitting correlations and the ensemble uncertainties can be found in Figure 6.24 and Figure 6.25 respectively. Fitted values can be found in Table 6.10. The DAB model (Table

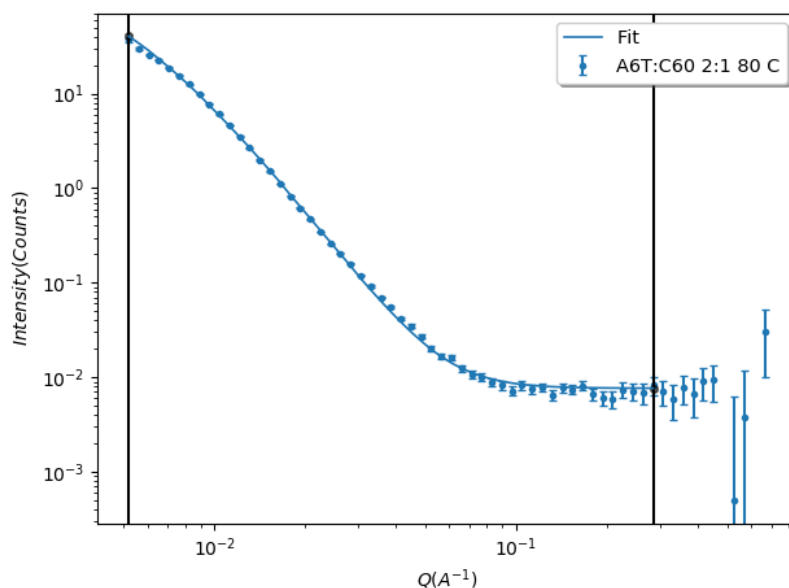


Figure 6.23: Small angle neutron scattering curve of A6T:C60 2:1 mol deposited at $T_{sub} = 80 \text{ }^{\circ}\text{C}$ fitted with the DAB model. Black vertical bars show the range of the fit.

<i>Parameter</i>	<i>Fitted value</i>
<i>Scale</i> [a.u]	$(1.93 \pm 0.06) \times 10^{-5}$
<i>Background</i> [cm^{-1}]	0.0077 ± 0.0002
<i>L</i> [$\text{\AA}$]	215 ± 1
χ^2	5.4585

Table 6.10: Table of A6T:C60 2:1 mol deposited at $T_{sub} = 80 \text{ }^{\circ}\text{C}$ fitted with the DAB model. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

6.10) shows the system to have a correlation length of $21.5 \pm 0.1 \text{ nm}$. The model

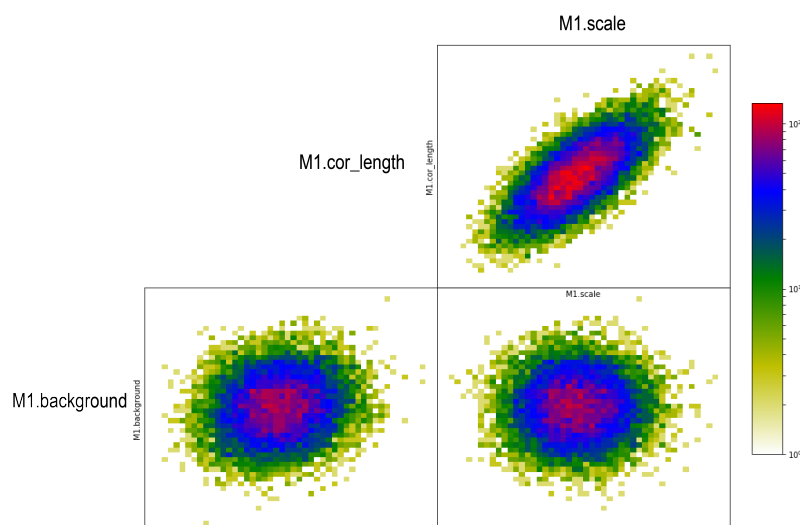


Figure 6.24: Fitting parameters correlations of A6T:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the DAB model. The shown parameters map as follows to the coefficients in Eq. 6.10: $M1.background \hat{=} background$, $M1.cor_length \hat{=} L$ and $M1.scale \hat{=} scale$.

is seen to generally describe the data well, however for the data points closest to the low- Q limit (Fig. 6.23) the fitted curve can be seen to overshoot the data points to a small degree. Each parameter is seen to be meaningfully fitted with a peaked histogram uncertainty distribution (Fig. 6.25), however for the correlation plot (Fig. 6.24) the $L \times scale$ subplot shows a strong positive correlation between L and $scale$. As the scaling parameter determines the overall magnitude of the fit, it is possible that this leads to the fit overshooting the data at the lower end of the Q -range.

Following a similar approach by Zhang *et al.* [69], the *Mass Fractal* model is employed as an alternative model. The *Mass Fractal* model is described in Equation

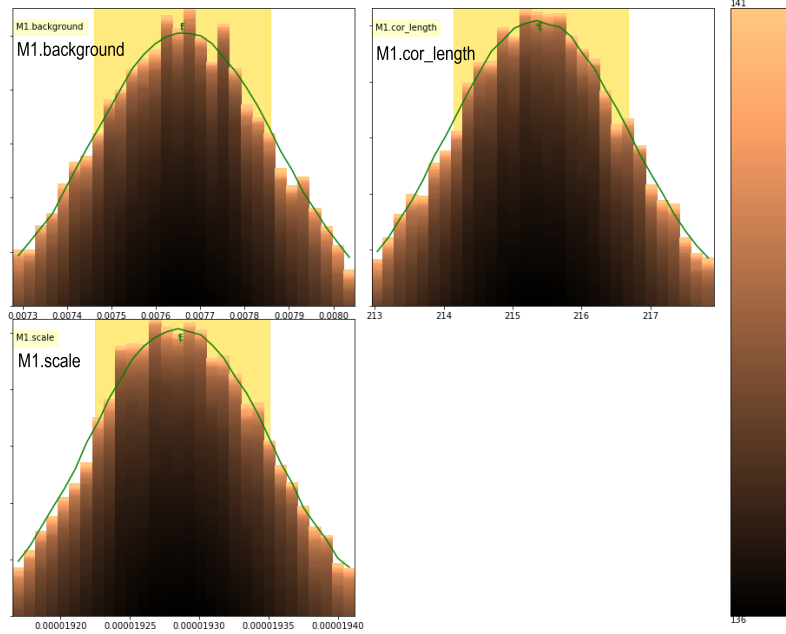


Figure 6.25: Ensemble uncertainties of 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ fitted with the DAB model. The shown parameters map as follows to the coefficients in Eq. 6.10: $M1.background \hat{=} background$, $M1.cor_length \hat{=} L$ and $M1.scale \hat{=} scale$.

6.11.

$$\left\{ \begin{array}{l} I(Q) = scale \cdot P(Q)S(Q) + background, \\ P(Q) = F(Qr)^2, \\ F(x) = \frac{3[\sin x - x \cos x]}{x^3}, \\ S(Q) = \frac{\Gamma(D_m - 1)\xi^{D_m - 1}}{[1 + (Q\xi)^2]^{(D_m - 1)/2}}, \\ scale = kNV^2(\rho_A - \rho_B)^2, \\ V = \frac{4}{3}\pi r^3. \end{array} \right. \quad (6.11)$$

The model describes scattering from fractal-like aggregates constructed from a basic spherical building block. Here, r is the radius of the basic unit, D_m is the mass fractal dimension, ξ is the cut-off length and $\rho_{A,B}$ is the SLD of the building block and the medium in which the fractal resides. The radius of C60 of $3.5 \text{ \AA}$

is used as the radius of the basic unit. The fitted values are shown in Table 6.11.

<i>Parameter</i>	<i>Fitted value</i>
<i>Scale</i> [a.u]	$(10.0 \pm 0.1) \times 10^{-6}$
<i>Background</i> [cm^{-1}]	0.0074 ± 0.0002
r [$\text{\AA}$]	3.5
D_m [a.u]	2.99 ± 0.01
ξ [$\text{\AA}$]	220 ± 3
χ^2	5.4864

Table 6.11: Table of A6T:C60 2:1 mol deposited at $T_{\text{sub}} = 80^\circ \text{C}$ fitted with the *Mass Fractal* model. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.)

The *Mass Fractal* model shows the system to have a correlation length of 22.0 ± 0.3 nm. ξ , the cut-off length, is implemented to describe an exponential loss of order with distance and corresponds to a maximum distance at which fractal behaviour is observed i.e. a correlation length. Here, the results of both 22.0 ± 0.3 nm of the *Mass Fractal* model and 21.5 ± 0.1 nm of the *Mass Fractal* model are seen to matching despite the different underlying model bases. The results of the agreeing models indicate that A6T:C60 2:1 $T_{\text{sub}} = 80^\circ \text{C}$ manifests as a two-phase system with a inter-domain distance of around 22 nm. Compared to the DCV5T-me(3,3):C60 system at equivalent T_{sub} , we find the A6T:C60 system to have a larger feature size, but we hypothesise that the A6T:C60 system has a greater domain size polydispersity based on the lack of Bragg-like broad peak. The high scattering of the A6T:C60 system motivated further exploration of the system as it allows for the study of alterations of the deposition process even if they reduce the scattering by the order of a magnitude. The often varied parameters of mixing ratio, substrate temperature and deposition rate are thus investigated.

6.7.1 Mixing ratio of A6T:C60

A6T:C60 films in molar mixing ratios of 2:1, 1:1 and 1:2 were studied. The experimental details of the compositions can be found in Table 6.12. The 2:1 sample configuration, whilst nominally identical to the one described in Section 6.7, was remade to account for any variation in the manufacturing environment that might have occurred between beamtime sessions (see Ch. 5).

The scattering curves of the three configurations are shown in Figure 6.26. The shape of all three scattering curves appear similar to each other and to the scattering curve of the original 2:1 A6T:C60 composition. A main difference is the higher background scattering levels of the 1:2 composition seen at higher Q . This is unexpected, as the 1:2 composition has the highest fullerene content of all three films and thus the least (natural) hydrogen, which is a strong source of incoherent scattering. All three film compositions are fitted using both the DAB model and

Name	2:1	1:1	1:2
D:A ratio [mol]	2:1	1:1	1:2
Nominal film thickness [nm]	100	100	100
T_{sub} [°C]	80	80	80
R [Å/s]	0.15	0.15	0.15

Table 6.12: Experimental details of 2:1,1:1 and 1:2 mol A6T:C60 deposited at $T_{sub} = 80$ °C sample compositions

the *Mass Fractal* model. DAB fits are shown in Figures 6.27, 6.28 and 6.29. Fitted values can be found in Table 6.13. Figure 6.30 shows the fitted feature sizes as a function of molar ratio. The 2:1, 1:1 and 1:2 A6T:C60 systems (Table 6.13) are shown as having correlation lengths of 19.2 ± 0.1 nm, 22.9 ± 0.2 nm and 25.1 ± 0.2 nm using the DAB model, respectively, and 21.7 ± 0.3 nm, 26.6 ± 0.5 nm and 25.4 ± 0.4 nm, using the *Mass Fractal* model respectively. We note that the fitted feature size of the 'newer 2:1 configuration is smaller on the order of

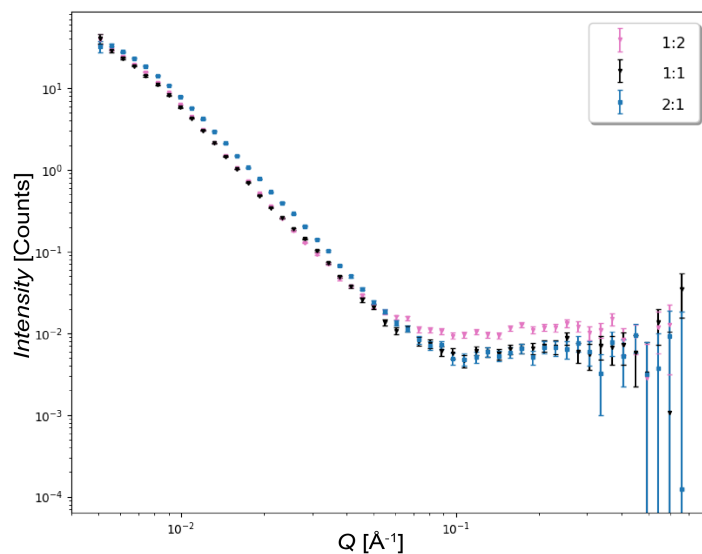


Figure 6.26: Small angle neutron scattering intensity curves of A6T:C60 deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ in molar ratios of 2:1, 1:1 and 1:2.

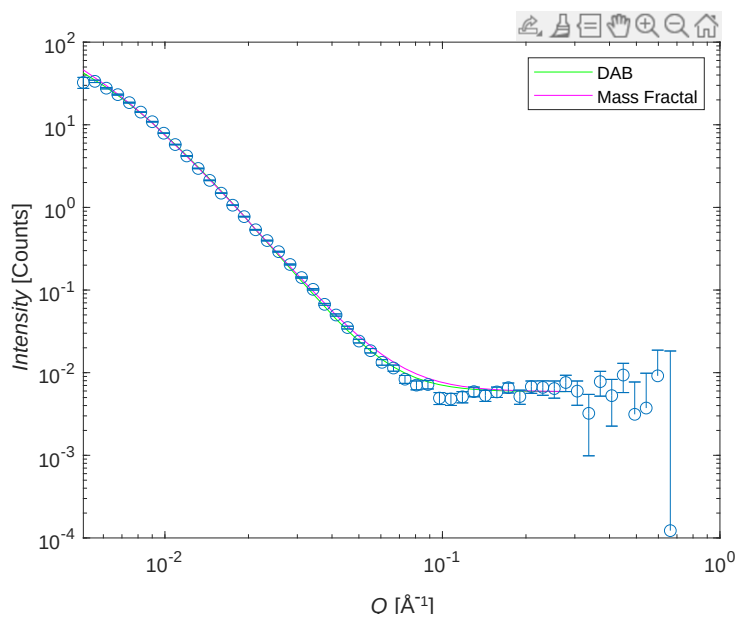


Figure 6.27: Small angle neutron scattering curve of A6T:C60 2:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ fitted with the DAB and *Mass Fractal* models.

~10% than the configuration described in Sec. 6.7. We ascribe this to potential human variation in sample manufacture as well as the use of VTE tools such as

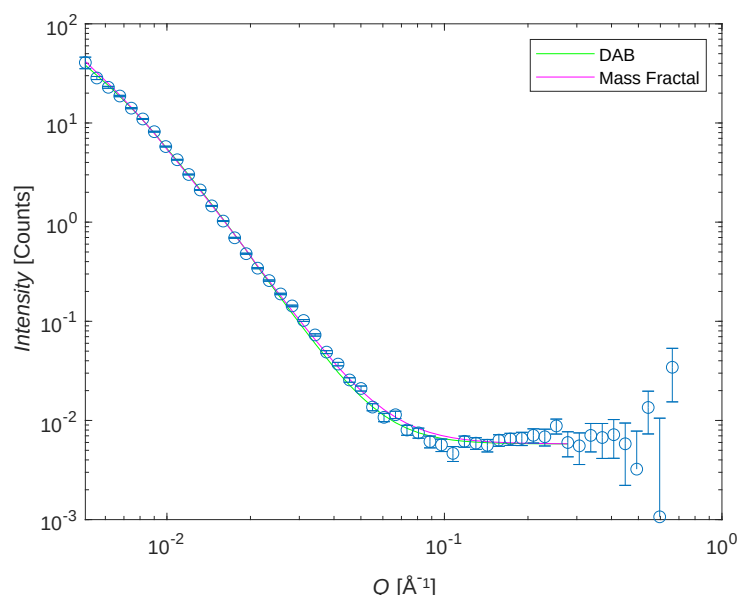


Figure 6.28: Small angle neutron scattering curve of A6T:C60 1:1 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ fitted with the DAB and *Mass Fractal* models.

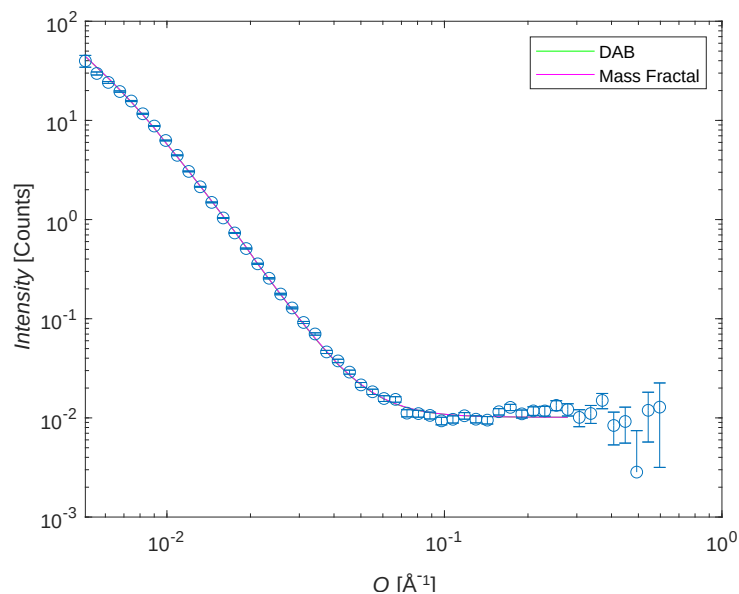


Figure 6.29: Small angle neutron scattering curve of A6T:C60 1:2 mol deposited at $T_{sub} = 80\text{ }^{\circ}\text{C}$ fitted with the DAB and *Mass Fractal* models.

ECHO that are not in a pristine condition due to a multitude of users and chemicals used.

	DAB d_0 [Å]	χ^2_{DAB}	Mass Fractal ξ [Å]	Mass Fractal Dimension	$\chi^2_{MassFractal}$
2:1	192 ± 1	11.111	217 ± 3	2.962 ± 0.003	7.3135
1:1	229 ± 2	10.843	266 ± 5	2.963 ± 0.003	8.1685
1:2	251 ± 2	5.3003	254 ± 4	2.997 ± 0.003	5.4277

Table 6.13: Fitted values of A6T:C60 in 2:1, 1:1 and 1:2 mol ratios deposited at $T_{sub} = 80^\circ\text{C}$ using the DAB and *Mass Fractal* models. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

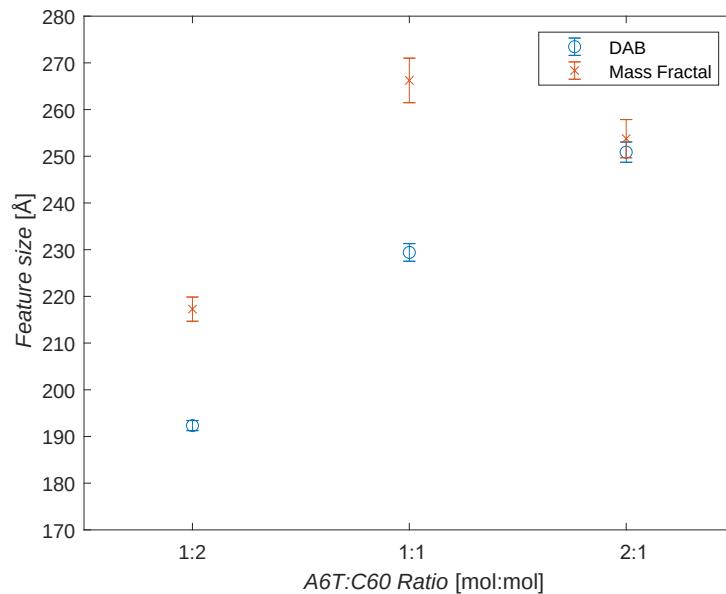


Figure 6.30: Fitted feature sizes of A6T:C60 deposited at $T_{sub} = 80^\circ\text{C}$ in molar ratios of 2:1, 1:1 and 1:2 using the DAB and *Mass Fractal* models.

As seen in Figs. 6.27, 6.28 and 6.29, the DAB and *Mass Fractal* models both match the experimental data well in all three cases. For the 2:1 and 1:1 compositions, the *Mass Fractal* model describes a slightly higher intensity than the DAB model, most visible near the high- Q background limit. For the 1:2 composition, the models produce near identical fitting curves. The results of the DAB model (Table 6.13) shows that the feature length of the A6T:C60 system increases as the molar fraction of C60 is increased, potentially suggesting more C60 result in better overall phase separation. The *Mass Fractal* trend is less clear as the fitted feature length of the 1:1 composition is greater than that of the 1:2 composition.

Complementing the SANS results with STEM-EDX measurements would be a potential way to investigate the size and purity of domains.

6.7.2 Substrate temperature during growth of A6T:C60

To investigate the effect of substrate temperature during growth of an A6T:C60 system, a composition was made with the substrate held at $T_{sub} = \text{RT}$ during film deposition. The experimental details of the composition as well as the chosen base case with $T_{sub} = \text{RT}$ can be found in Table 6.14. The SANS scattering curve of the RT composition is shown in Figure 6.31. The SANS scattering curves shown

Name	RT	80 °C
D:A ratio [mol]	2:1	2:1
Nominal film thickness [nm]	100	100
T_{sub} [C°]	RT	80
R [Å/s]	0.15	0.15

Table 6.14: Experimental details of A6T:C60 2:1 mol deposited at RT and 80 °C compositions.

in Fig. 6.31 are qualitatively similar. The intensity curve of the RT configuration shows a lower background at the high- Q background limit, although we note both configurations should have equal amounts of hydrogen and background subtractions were carried out in the same manner i.e. subtracting the diffraction from a 'can' containing only uncoated substrates and normalising to transmission. The two configurations were manufactured at different points in time and likewise measured at different beamtimes. We speculate that the difference in high- Q background intensities may arise due to trace contamination by other organic species during film deposition due to the vacuum deposition chamber being used for multiple molecular species. At the low- Q limit, the scattering of the RT configuration is higher than that of the 80 °C and a higher slope is observed. This is indicative of a greater degree of long range ordering.

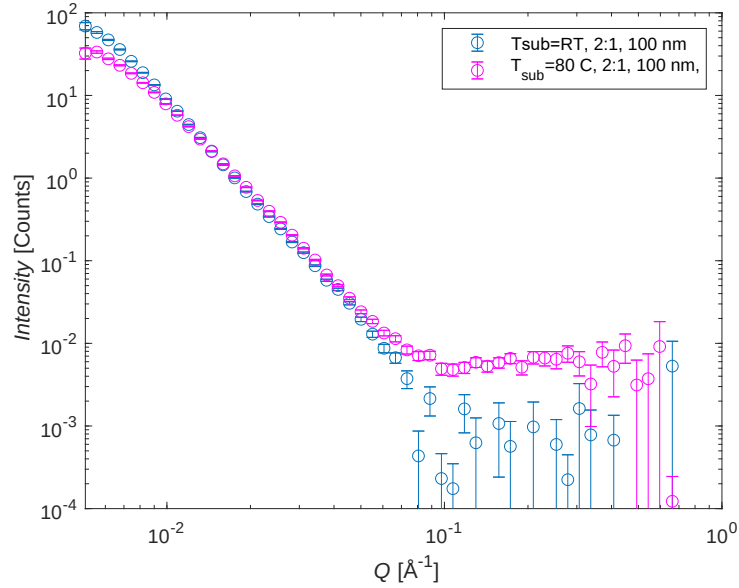


Figure 6.31: Small angle neutron scattering curve of A6T:C60 2:1 mol evaporated on substrates held at $T_{sub} = RT$ and $T_{sub} = 80\text{ }^{\circ}\text{C}$ during growth.

The RT scattering is again fitted using the DAB and *Mass Fractal* models. The fitted curves are shown in Figure 6.32 and the fitted values are shown in Table 6.15. The RT configuration is shown (Table 6.15) to have a correlation length

	DAB d_0 [Å]	χ^2_{DAB}	Mass Fractal ξ [Å]	Mass Fractal Dimension	$\chi^2_{MassFractal}$
80 $^{\circ}\text{C}$	192 ± 1	11.111	217 ± 3	2.962 ± 0.003	7.3135
RT	324 ± 3	11.893	401 ± 9	2.976 ± 0.001	7.3696

Table 6.15: Fitted values of A6T:C60 2:1 mol deposited at $T_{sub} = RT$ with the DAB and *Mass Fractal* models. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

of 32.4 ± 0.3 nm using the DAB model. Both models shown in Fig. 6.32 fit the experimental data well with the DAB model having a modelled lower intensity curve across the Q -range. The fitted values (Tab. 6.15) show that an increase in T_{sub} from RT to $80\text{ }^{\circ}\text{C}$ leads to a decrease in the fitted feature size corresponding to a decrease of 13.2 nm using the DAB model and 18.4 nm using the *Mass Fractal* model. This suggests that a more energetic environment during growth seemingly

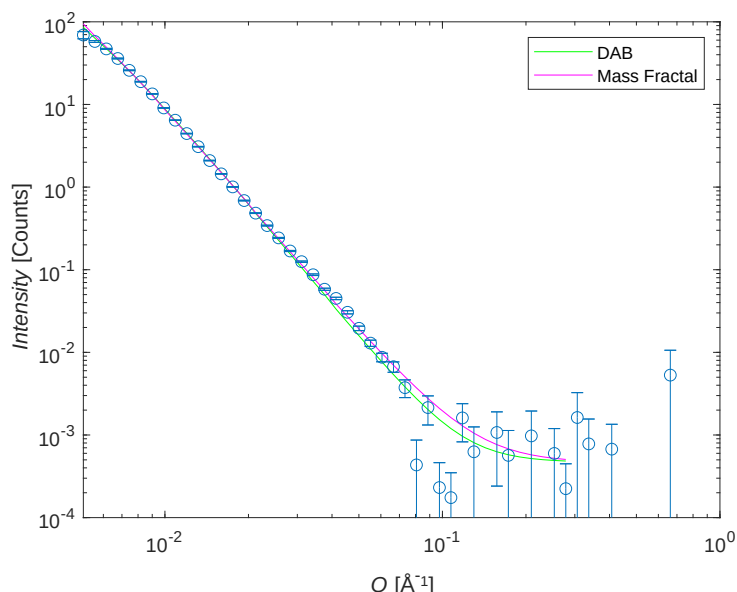


Figure 6.32: Small angle neutron scattering curve of A6T:C60 2:1 mol deposited at $T_{sub} = RT$ fitted with the DAB and *Mass Fractal* models.

reduces phase separation. In line with previous fitted results, the *Mass Fractal* model also shows a higher feature size than the DAB model.

6.7.3 Deposition rate during growth of A6T:C60

To investigate the effect of molecular deposition rate during growth of an A6T:C60 system, a composition was made with the total deposition rate doubled to $R = 0.30 \text{ Å/s}$ during film deposition. A higher deposition rate will increase the amount of molecules per area per time, resulting in increased molecular interaction and increased nucleation [87]. The experimental details of the composition as well as the chosen base case with $R = 0.15 \text{ Å/s}$ can be found in Table 6.14. The SANS scattering curve of the Base Rate composition and the High Rate composition is shown in Figure 6.33. The SANS scattering curves shown in Fig. 6.33 are qualitatively similar. The intensity curve of Base Rate composition is generally higher below around $7 \times 10^{-2} \text{ Å}^{-1}$, however towards the low- Q limit the slope of the

Name	High Rate	Base Rate
D:A ratio [mol]	2:1	2:1
Nominal film thickness [nm]	100	100
T_{sub} [°C]	80	80
R [Å/s]	0.30	0.15

Table 6.16: Experimental details of the High Rate and Base Rate compositions of A6T:C60 2:1 mol deposited at $T_{sub} = 80$ °C

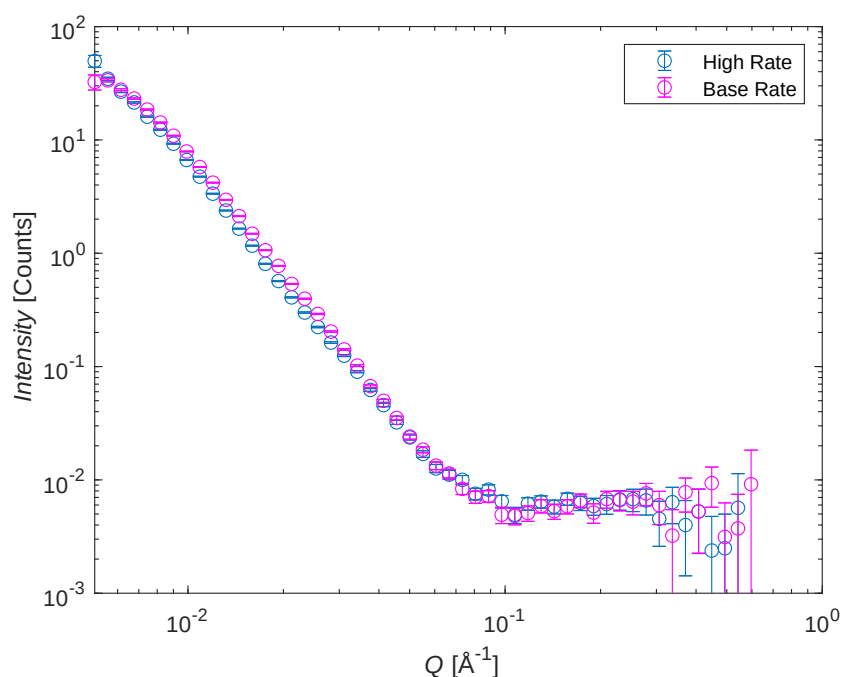


Figure 6.33: Small angle neutron scattering curve of A6T:C60 2:1 mol deposited at $T_{sub} = 80$ °C evaporated using total rates of $R = 0.30$ Å/s and $R = 0.15$ Å/s.

Base Rate intensity curve flattens compared to that of the High Rate. This is indicative of a greater degree of long range ordering.

The High Rate scattering is again fitted using the DAB and *Mass Fractal* models. The fitted curves are shown in Figure 6.34 and the fitted values are shown in Table 6.17. The High Rate configuration is shown (Table 6.17) to have a correlation length of 22.2 ± 0.2 nm using the DAB model and 29.6 ± 0.6 nm using the *Mass Fractal* Model. Both models shown in Fig. 6.34 fit the experimental data well

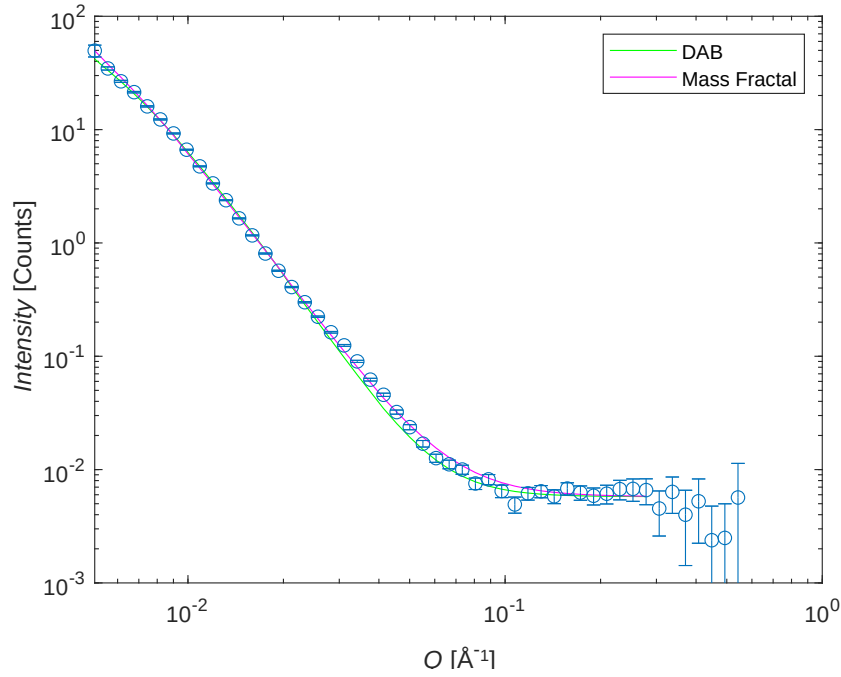


Figure 6.34: Small angle neutron scattering curve of A6T:C60 Base Rate and High Rate compositions fitted with the DAB and *Mass Fractal* models.

	DAB d_0 [Å]	χ^2_{DAB}	Mass Fractal χ [Å]	Mass Fractal Dimension	$\xi^2_{MassFractal}$
Base Rate	192 ± 1	11.111	217 ± 3	2.962 ± 0.003	7.3135
High Rate	222 ± 2	18.895	296 ± 6	2.937 ± 0.003	7.9254

Table 6.17: Fitted values of A6T:C60 2:1 mol deposited at $T_{sub} = 80^\circ\text{C}$ Base Rate and High Rate compositions fitted with the DAB and *Mass Fractal* models. The *Scale* parameter is a scaling parameter that scales the model to the empirical data.

with the DAB model having a modelled lower intensity curve across the Q -range. The fitted values (Tab. 6.17) show that an increase in deposition rate from 0.15 to $R = 0.30 \text{ Å/s}$ leads to an increase in the fitted feature size corresponding to 3.0 nm using the DAB model and 7.9 nm using the *Mass Fractal* model. A potential explanation is that a more rapid arrival of new molecules results in faster nucleation, leading to molecules forming clusters where they land rather than diffusing and travelling on the surface, thus resulting in more spaced out domains. In line

with previous fitted results, the *Mass Fractal* model also shows a higher feature size than the DAB model.

6.8 Discussion

In this chapter, the microstructure of various D:A systems has been interpreted through model fits of SANS data. The focus of the chapter has been to explore the viability of SANS when applied to SM evaporated OPV systems and what models might be suitable. As such, the discussion of models that did not prove suitable for the given data has been deliberately included to explicate the SANS analysis of SM OPV films. The discussion of 'feature poor' systems such as ZnPc:C60 and SubPc:C60 is included for similar reasons.

A6T:C60 based systems, which displayed the strongest scattering, were chosen to investigate the effect of varying common deposition parameters such as the D:A mixing ratio or the molecular deposition rate. The scattering data revealed that microstructural changes due to different deposition conditions are detectable by SANS. The feature paucity of A6T:C60 scattering, however, made it difficult to discern whether the DAB or *Mass Fractal* models, both describing two phase systems, were most suitable. Likewise, whether increasing the T_{sub} of DCV5T-me(3,3):C60 result in an increase in phase purity cannot be decisively determined from the SANS data.

Such questions could potentially be answered via extended variation of a given parameter (an approach explored in the following chapter) to explore if one model yield more persistent and predictive results. Additionally, the SANS data could be complemented by microscopy techniques such as STEM-EDX or atomic force microscopy with infrared spectroscopy which yield information about the chemical composition of areas of the film. This can be exploited to understand the relative

phase purity of domains and thus inform the interpretation of SANS results.

Negative intensity values appear in the background noise regimes for several data sets. This issue is assumed to be related to the low scattering intensities of the measured configurations. This could potentially be rectified by improved scattering statistics, the means to which are discussed in Ch. 10, or by repetition of the experiments with a more elaborate background subtraction procedure including the use of standard scattering samples for better normalisation.

6.9 Chapter conclusions

In this chapter, we use SANS to study organic thin film BHJ systems with the goal of expanding the viability of SANS to evaporated SM systems. We conduct an initial study of D:C60 in 2:1 mol ratios evaporated at $T_{sub} = 80^\circ\text{C}$ on a C60 underlayer, with D=[DCV5T-me(3,3), A6T, ZnPc, SubPc, Rubrene].

From the lack of scattering, we identify the ZnPc:C60 and SubPc:C60 systems as being highly intermixed and thus lacking phase separation between D and A rich domains for the investigated processing parameters.

The scattering from the Rubrene:C60 system appears with weaker scattering and a broad bump. Applying the *Broad peak* model we identify a characteristic feature size of 36 ± 1 nm, suggesting a two-phase system which we hypothesise as consisting of domains that are either Rubrene-rich or C60-rich, but of low purity, resulting in the still-weak scattering.

The scattering of the DCV5T-me(3,3):C60 system appears with a clear bump and a stronger power law increase in scattering intensity towards the low- Q limit com-

pared to the ZnPc, SubPc and Rubrene based systems. We apply several model fits to the scattering data and find the *Broad peak* model to best describe the data, with a fitted feature size of 19.2 ± 0.4 nm which is well in line with literature reports of equivalent systems using microscopy. Following the model fit and the stronger scattering, we describe the system as a two-phase system with at least one relatively pure domain as evident by the higher scattering contrast. We interpret the broad feature as potentially representing the relatively heterogeneously sized C60-rich globular domains previously reported in literature for DCV5T-me(3,3):C60 evaporated at $T_{sub} = 80$ °C. Motivated by the high congruence, equivalent DCV5T-me(3,3):C60 films evaporated at RT and $T_{sub} = 80$ °C were manufactured and probed with SANS. The $T_{sub} = 80$ °C configuration shows no appreciable scattering in the probed range, indicative of a highly intermixed system, again in line with prior reported microscopy for DCV5T-me(3,3):C60 evaporated at $T_{sub} = RT$. The $T_{sub} = 140$ °C configuration shows a higher intensity and more well defined feature, that when fitted with the *Broad peak* model shows an increase in feature size to 22.3 ± 0.2 nm compared to the $T_{sub} = 80$ °C configuration, showing increased T_{sub} results in increased phase separation in line with reported literature.

The scattering from A6T:C60 evaporated at $T_{sub} = 80$ °C is stronger than the other configurations evaporated at $T_{sub} = 80$ °C and features an upturn in scattering intensity towards the low- Q limit. The scattering data is found to be described well using both the DAB model, describing of a two-phase system with a characteristic spacing between different regions, and the *Mass fractal* model, describing a fractal-like aggregating system yielding a characteristic length scale of $L = 21.5 \pm 0.1$ nm and coherence length $\xi = 22.0 \pm 0.3$ nm, respectively. Despite having a higher overall intensity than the DCV5T:C60-me(3,3) system, we interpret its

lack of peak-like feature as implying a higher polydispersity in terms of domain size.

Motivated by the strong scattering, further SANS studies of A6T:C60 configurations were carried out with varied D:A mixing ratios, T_{sub} and molecular deposition rate. In each case, both the DAB and the *Mass fractal* model fits were applied to the scattering data.

- We find that a higher C60 fraction results in a higher fitted length scale using the DAB model, with the *Mass fractal* model results being less clear. This potentially suggests C60 more readily phase separates than A6T.
- Conversely to DCV5T-me(3,3):C60, increasing the T_{sub} seems to decrease the feature length size when fitted with both DAB and *Mass fractal* models.
- Increasing the molecular deposition rate appears to increase the characteristic feature size using both the DAB and *Mass fractal* models. This could potentially be due to a higher deposition rate inducing more spatially distant nucleation sites rather than allowing for molecules to diffuse to more closely spaced sites.
- We find that both models are able to provide quantitative descriptions of the A6T:C60 system, with the *Mass fractal* model fits consistently yielding a higher (0-30%) fitted feature size. Given the nature of the data, it is difficult to ascertain which model is most accurate although identified trends when varying deposition parameters remain the same in almost all cases.

7 | Substrate temperature variation during growth of DCV5T:C60 studied via SANS

Using SANS data, Sec. 6.6.1 shows that the long range ordering of DCV5T-me(3,3):C60 blends changes as T_{sub} is varied during growth. The blend appears as intermixed when evaporated on RT substrates and when the temperature during growth, T_{sub} , is increased to 80 °C (for constant molar ratio and deposition rate), phase separation between DCV5T-me(3,3) and C60 is seen as evident through the appearance of a broad peak in the scattered intensity as function Q with a fitted inter-domain distance of 19.2 ± 0.4 nm. When T_{sub} is further increased to 140 °C, the broad peak shifts towards a lower position in Q and increases in intensity, corresponding to a fitted inter-domain distance increase to 22.3 ± 0.2 nm and a presumed higher phase purity. The success in probing the qualitative and quantitative behaviour of the DCV5T-me(3,3):C60 system as the T_{sub} is varied using neutron scattering motivated a study of the same system where T_{sub} is varied in smaller 20 K increments ranging from $T_{sub} = RT$ to 140 °C to highlight how SANS can be used for systematic and quantitative studies of evaporated SM OPV films. In addition, two sample compositions were evaporated at RT and then thermally post-annealed at 80 and 140 °C for 30 min on a hotplate in an N_2 atmosphere. This was done to investigate the different effects of applying increased thermal energy during and after growth.

The experimental details of the compositions can be found in Table 7.1. Sample configurations are named after their place of measurement, the Paul Scherrer Institute. The SANS scattering curves of the six films evaporated onto substrates held at $T_{sub} = RT, 60, 80, 100, 120, 140$ °C during growth are shown

Name	P-RT	P-60	P-80	P-100	P-120	P-140	P-Ann80	P-Ann140
T_{sub} [°C]	RT	60	80	100	120	140	RT	
D:A ratio	2:1							
Nominal film thickness [nm]	100							
Total rate [Å/s]	0.15							
Underlayer	10 nm C60							
T_{anneal} [°C]	N/A						80	140
Annealing duration [min]	N/A						30	30

Table 7.1: Experimental details of sample compositions of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80$ °C evaporated onto substrates held at $T_{sub} =$ RT, 60, 80, 100, 120, 140 °C during growth.

together in Figure 7.1 to emphasise the apparent change in scattering as T_{sub} is varied. The same scattering curves are shown vertically shifted intensities and with associated fits in Figure 7.2 to allow the reader to better discern each curve. The *Broad Peak* model (Eq. 6.1) is applied each intensity curve featuring a broad peak. The *Power Law* (Eq. 9.3) model is applied to the RT configuration as it does not display any clear features aside from a rise in intensity towards the low- Q limit. Table 7.4 shows the *Power Law* fitted values of the P-RT configuration.

Figure 7.3 and Figure 7.4 show the correlation and uncertainty plots of the 100 °C configuration, P-100, fitted using the *Broad peak* model and is shown as representative of the *Broad peak* model fits. The other correlation plots can be found in the appendix (Fig. A.2 to A.5). For the P-RT configuration (A.1) the parameters appear as highly cross-correlated due to lack of degrees of freedom of the model.

The *Broad Peak* cross-correlations generally appear blob-like, indicating that each fitting parameter is independent and meaningful. The exception is the $C \times \zeta$ (*Lorentzian scale* $\times$ *Lorentzian screening length*) cross-correlation which is strongly correlated due to both controlling the shape of the top of the peak. The ensemble uncertainties generally show the uncertainty histograms to be smoothly peaked with best estimate lines that generally fit the shape of the histograms.

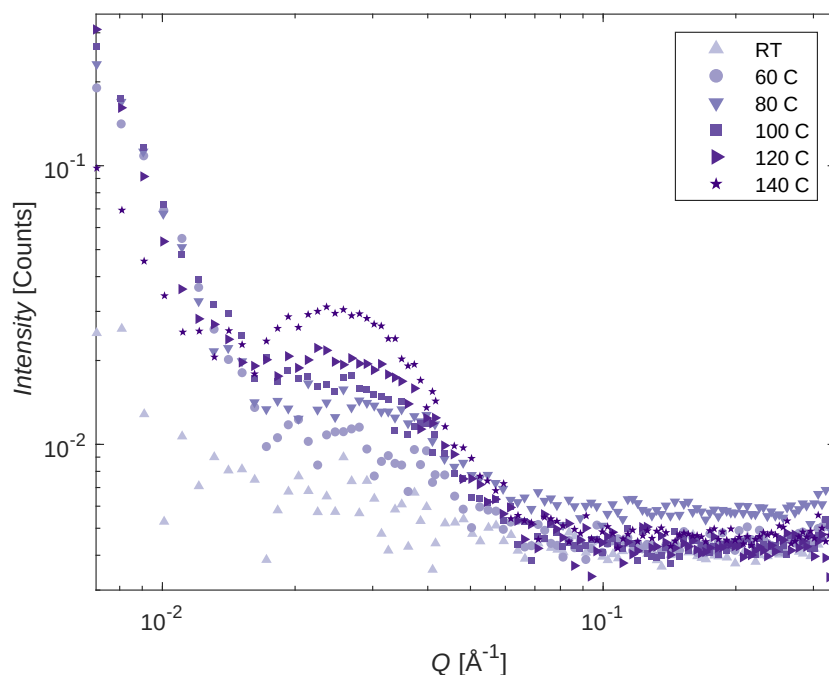


Figure 7.1: Log-log plot of small angle neutron scattering intensities of DCV5T-me(3,3):C60 2:1 mol evaporated onto substrates held at $T_{sub} =$ RT, 60, 80, 100, 120, 140 °C during growth. Error bars are not shown to reduce visual clutter.

For P-60, the 60 °C configuration, the cross-correlations of the ζ parameter are generally smeared out indicating the peak is too poorly defined to estimate this parameter (Fig. 7.5). For the P-RT configuration (Appendix) the parameters appear as highly cross-correlated due to lack of degrees of freedom of the model. Table 7.2 shows the fitted values of DCV5T-me(3,3):C60 evaporated at $T_{sub} =$ 60, 80, 100, 120, 140 °C using the *Broad Peak* model.

The intensity curves in Fig. 7.1 and Fig. 7.2 show the scattering intensity of DCV5T-me(3,3):C60 to generally increase as T_{sub} is increased. The scattering of the P-RT composition is seen to not increase beyond the background level until below $0.02 \text{ \AA}^{-1}$ and the increase in scattering at low- Q is associated with larger experimental error bars compared to the other compositions (Fig. 7.2). The lower Porod exponent (Tab. 7.4) reflecting the lower slope towards the low- Q limit, to-

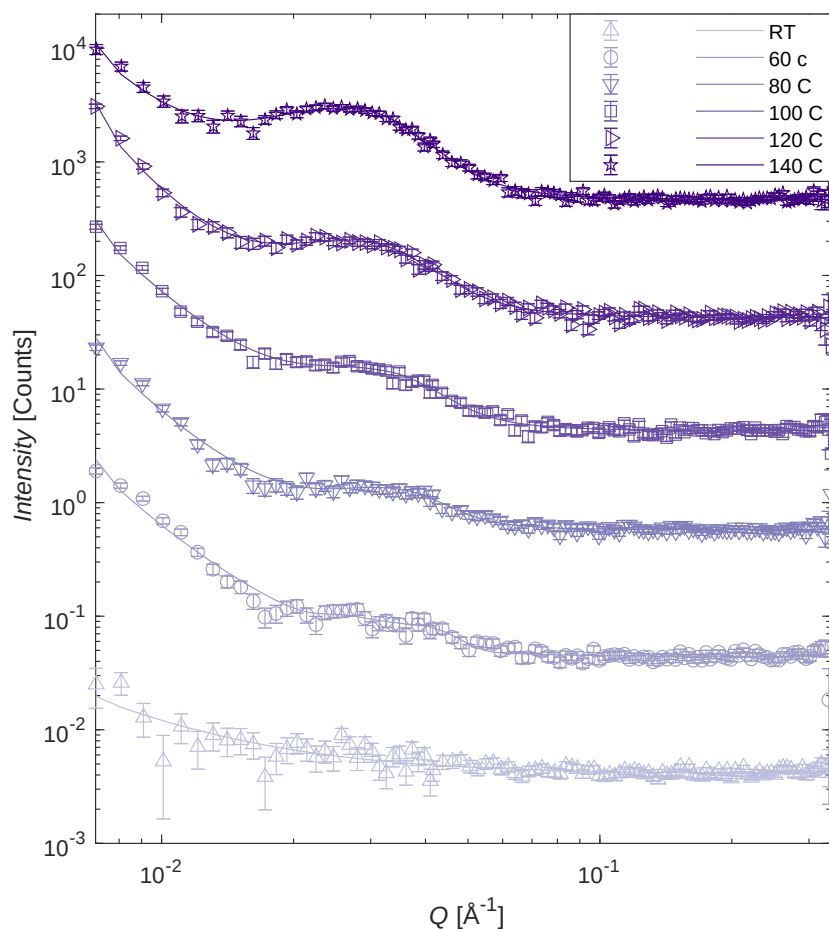


Figure 7.2: Log-log plot of small angle neutron scattering intensities of DCV5T-me(3,3):C60 2:1 thin films evaporated at $T_{sub} = \text{RT}, 60, 80, 100, 120, 140\text{ }^{\circ}\text{C}$. Solid lines represent *Broad Peak* fits with the exception of the line of the RT curve which a *Power law fit*. Intensities are vertically shifted for easier distinction.

gether with the lack scattering features is taken as a sign of lack of long range ordering or phase separation between the DCV5T-me(3,3) and the C60.

As T_{sub} is increased to $60\text{ }^{\circ}\text{C}$, a broad peak centred around $0.03\text{ }\text{\AA}^{-1}$ emerges for P-60, although the peak is very broad and not well defined, as reflected in the poor fitting of the peak shape (Fig. 7.5). At the low- Q edge of the peak, approximately at $0.02\text{ }\text{\AA}^{-1}$, the scattering increases towards the low- Q limit ap-

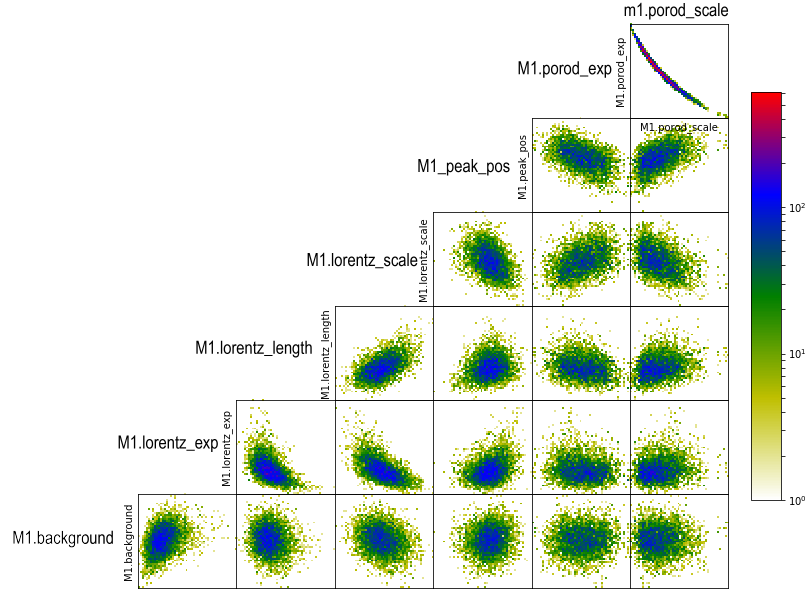


Figure 7.3: Fitting parameter cross-correlations of P-100, DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 100^\circ\text{C}$ during growth. The $T_{sub} = 100^\circ\text{C}$ sample was fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

pearing linear in the log-log plot with the intensity at the low- Q limit being about an order of magnitude higher than that of the RT configuration. The strong increase in low- Q scattering suggests a regime change occurs between $T_{sub} = \text{RT}$ and $T_{sub} = 60^\circ\text{C}$ and the emergence of longer range phase separation between C60 and DCV5T-me(3,3).

As the substrate temperature is increased further to 80°C , the broad peak of P-80 becomes more well defined, reflected in all fitting cross-correlations of the Lorentzian peak becoming independent (see Appendix A) and an increase of the Lorentzian scale C from $(2.8 \pm 0.4) \times 10^{-3}$ to $(6.5 \pm 0.6) \times 10^{-3}$. Whilst other models, such as the DAB model, also model an average centre-centre distance

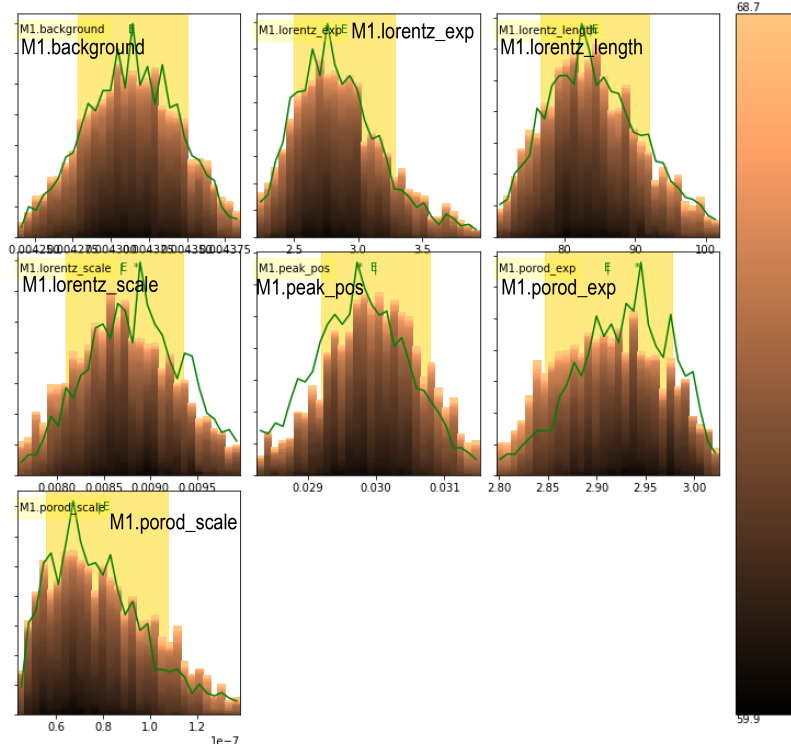


Figure 7.4: Sample uncertainties of P-100, DCV5T-me(3,3):C60 2:1 mol deposited $T_{sub} = 100$ °C at fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

between contrasting domains, the emergence of a Bragg-like feature suggests a greater degree of ordering.

As the temperature is increased further to 100 and 120 °C the peaks of P-100 and P-120 gradually increases in intensity, with C reaching $(8.8 \pm 0.6) \times 10^{-3}$ and then $(15.0 \pm 0.6) \times 10^{-3}$, respectively. As the temperature is increased to 140 °C, the broad peak of P-140 increases greatly in intensity, with the Lorentzian scale factor C reaching $C = (24.44 \pm 0.01) \times 10^{-3}$, and appears well defined.

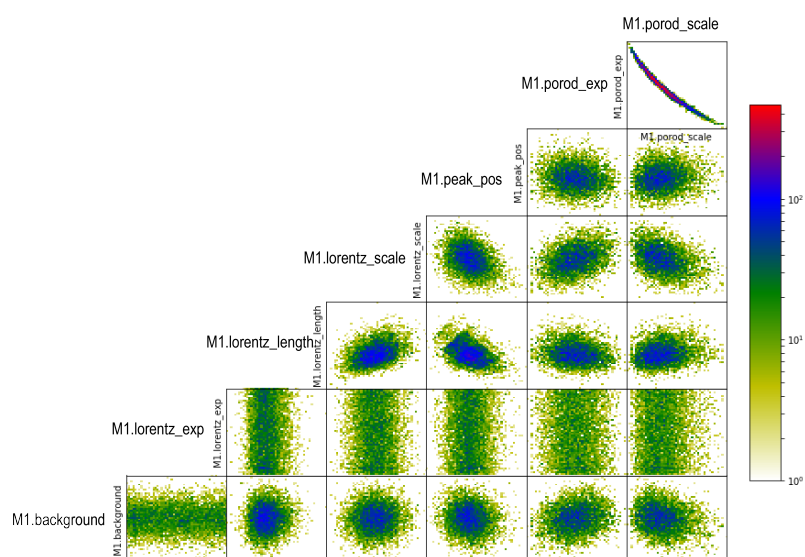


Figure 7.5: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 60^\circ\text{C}$ during growth. The $T_{sub} = 100^\circ\text{C}$ sample fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $\text{M1.background} \hat{=} B$, $\text{M1.lorentz_exp} \hat{=} m$, $\text{M1.lorentz_length} \hat{=} \xi$, $\text{M1.lorentz_scale} \hat{=} C$, $\text{M1.peak_pos} \hat{=} Q_0$, $\text{M1.porod_exp} \hat{=} n$, $\text{M1.porod_scale} \hat{=} A$ and $\text{M1.scale} \hat{=} scale$.

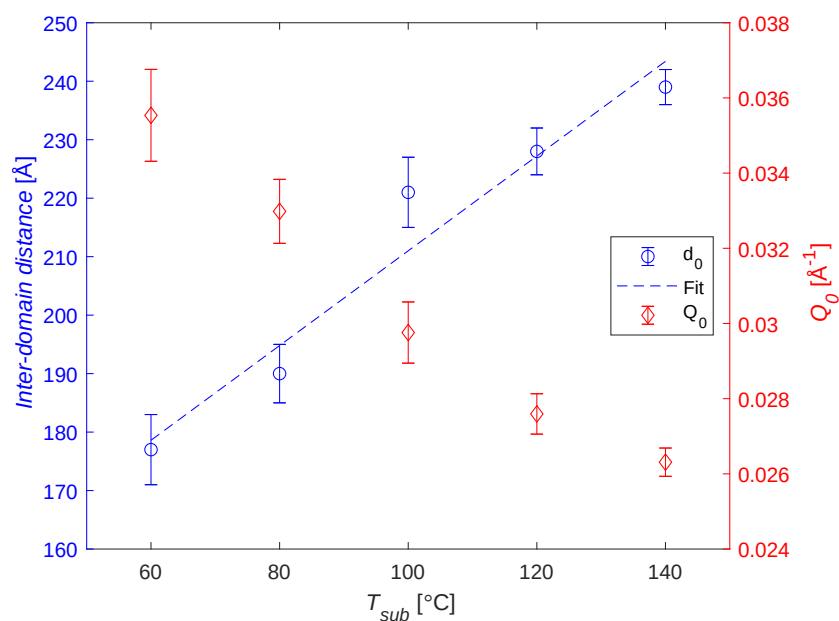


Figure 7.6: Plot of fitted Q_0 (right axis) fitted using the *Broad Peak* model and the corresponding real-space inter-domain distance (left axis) for DCV5T-me(3,3):C60 2:1 mol configurations evaporated at $T_{sub} =$ RT, 60, 80, 100, 120, 140 °C. The dotted line represents a first degree polynomial fit of the real-space positions.

<i>Name</i>	P-60	P-80	P-100	P-120	P-140	P-Ann80
<i>Scale</i> [a.u]	1					
<i>Background</i> [10^{-4}cm^{-1}]	4.5 ± 0.3	5.8 ± 0.4	4.3 ± 0.4	4.3 ± 0.4	4.7 ± 0.4	0.0048 ± 0.0001
<i>A</i> [a.u]	$(1.2 \pm 0.4) \times 10^{-7}$	$(4 \pm 1) \times 10^{-8}$	$(7 \pm 3) \times 10^{-8}$	$(5 \pm 2) \times 10^{-9}$	$(2 \pm 4) \times 10^{-8}$	0
<i>n</i> [a.u]	2.79 ± 0.06	3.03 ± 0.06	2.94 ± 0.06	3.44 ± 0.07	3.0 ± 0.2	N/A
<i>C</i> [10^{-3}a.u]	2.8 ± 0.3	6.5 ± 0.6	8.8 ± 0.6	15.0 ± 0.6	24.44 ± 0.01	0.004 ± 0.002
ξ [Å]	81 ± 10	92 ± 11	83 ± 8	81 ± 5	87 ± 4	$(2 \pm 2) \times 10^2$
Q_0 [Å $^{-1}$]	0.036 ± 0.001	0.033 ± 0.001	0.030 ± 0.001	0.028 ± 0.001	0.026 ± 0.001	0.026 ± 0.001
d_0 [Å]	177 ± 6	190 ± 5	221 ± 6	228 ± 4	239 ± 3	238 ± 14
<i>m</i> [a.u]	85 ± 290	2.7 ± 1.1	2.8 ± 0.4	2.5 ± 0.2	2.6 ± 0.1	1.15 ± 1.45
χ^2	1.6891	1.4709	1.1416	1.2229	0.8981	0.8373

Table 7.2: Table of *Broad Peak* fitted values of DCV5T-me(3,3):C60 2:1 mol evaporated at $T_{sub} =$ RT, 60, 80, 100, 120, 140 °C (P-60, P-80, P-100, P-120, P-140) as well as the configuration post-annealed at 80 °C for 30 min (P-Ann80). *Scale* parameter locked at 1 for all configurations to ensure consistency between fitted values.

The trends in fitted Q_0 , the peak centre, and the equivalent $d_0 = 2\pi/Q_0$ of the films with $T_{sub} = \text{RT}, 60, 80, 100, 120, 140^\circ\text{C}$ are shown in Fig. 7.6. The trend in d_0 , which we interpret as the domain centre-to-centre distance, appears linear with increasing T_{sub} and is thus fitted with a first degree polynomial ($d_0(T_{sub}) = aT_{sub} + b$). The fitted parameters are shown in Tab. 7.3. As evident by the high

Parameter	Fitted value
a [$\text{\AA}/\text{K}$]	0.8 ± 0.3
b [$\text{\AA}$]	130 ± 40
R^2	0.95

Table 7.3: First order polynomial fit ($d_0(T_{sub}) = aT_{sub} + b$) parameters of the trend in d_0 as T_{sub} of the DCV5T-me(3,3):C60 is increased.

R^2 , we find a 1st order polynomial model to describe the fitted parameters well and thus observe that in the range $T_{sub} = 60^\circ\text{C}$ to $T_{sub} = 140^\circ\text{C}$ the centre-to-centre distance between domains in DCV5T-me(3,3):C60 appear to increase linearly with temperature at a rate of $0.8 \pm 0.3 \text{ \AA}/\text{K}$. We highlight this as an example of SANS being capable of providing both qualitative and quantitative information of evaporated SM thin films. The fitted $d_0 = 19.0 \pm 0.5 \text{ nm}$ of P-80 is near-identical with the fitted $d_0 = 19.2 \pm 0.4 \text{ nm}$ of the equivalent configuration discussed in Sec. 6.6, whereas the fitted $d_0 = 23.9 \pm 0.3 \text{ nm}$ of P-140 is 1.6 nm larger than its equivalent. We attribute these slight differences to human variations in the sample manufacturing process. Another potential factor could be the state of vacuum deposition system at their respective times of manufacture.

The trend for other fitted parameters is less clear (Tab. 7.2). The Lorentzian exponent m appears to remain approximately the same in the range 2.5 – 2.8 for $T_{sub} = 80^\circ\text{C}$ (as the peak is not fully defined at $T_{sub} = 60^\circ\text{C}$) to $T_{sub} = 140^\circ\text{C}$. Likewise, the fitted Lorentzian screening ξ length does not show a clear trend, varying between 81 and 92 $\text{\AA}$ in the fitted range. Following analysis of mesh gels and polymers in solution, we interpret ξ as a correlation length [88, 89]. On

the other hand, the Lorentzian scale C increases at first moderately (by $\Delta C = 3.7 \times 10^{-3}$ between configurations with $T_{sub} = 60^\circ\text{C}$ and $T_{sub} = 80^\circ\text{C}$, $\Delta C = 2.3 \times 10^{-3}$ between $T_{sub} = 80^\circ\text{C}$ and $T_{sub} = 100^\circ\text{C}$). The increase accelerates to $\Delta C = 6.2 \times 10^{-3}$ between $T_{sub} = 100^\circ\text{C}$ and $T_{sub} = 120^\circ\text{C}$ and even further to $\Delta C = 9.4 \times 10^{-3}$ between $T_{sub} = 120^\circ\text{C}$ and $T_{sub} = 140^\circ\text{C}$. The almost 9-fold increase in C as T_{sub} is increased from 60°C to 140°C is much larger than the 35% increase in d_0 , which, together with the roughly invariant ξ , suggests that the increase in scattering intensity does not derive solely from larger domains in a two-phase system. A potential explanation could be that an increase in T_{sub} promotes a higher degree of phase purity which in turn increases the scattering contrast. Another potential explanation could be the emergent demixing of the system, as reported for higher T_{sub} for an equivalent system by Mönch et al., potentially resulting in strong organic-void contrast [71].

7.1 Post-annealing of DCV5T-me(3,3):C60

The SANS scattering curves of the two films thermally post-annealed from RT to 80 and 140°C as well as the films evaporated at $T_{sub} = 80$ and 140°C are shown together in Figure 7.7. This is shown to emphasise the apparent change in scattering between post-annealing and depositing at equivalent temperatures. The same scattering curves are shown with vertically shifted intensities in Figure 7.8 to allow the reader to better discern each curve. The *Power Law* model

$$I(Q) = A \cdot Q^{-P_1} + \text{background}, \quad (7.1)$$

further discussed in Ch. 9 is applied to the RT and Ann140 configurations as these do not display any clear features aside from a rise in intensity towards the low- Q limit. In addition, the DAB (Eq. 6.10) model is applied to the Ann140 configu-

ration. Table 7.2 shows fitted values for the *Broad Peak* fit of Ann80 where the

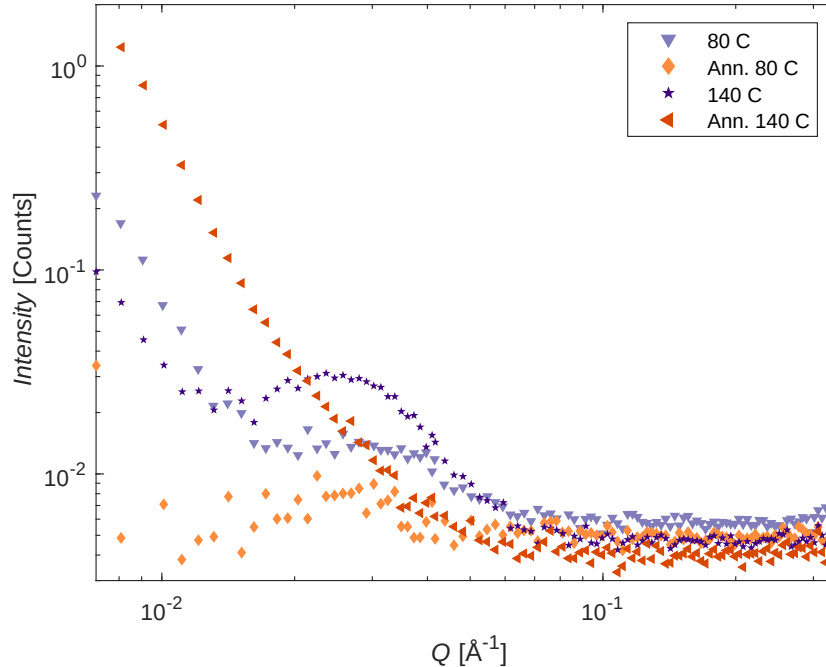


Figure 7.7: Log-log plot of small angle neutron scattering intensities of DCV5T-me(3,3):C60 2:1 mol thin films evaporated at $T_{sub} = RT$ and thermally post-annealed to 80 and 140 °C for 30 min as well as the films evaporated at $T_{sub} = 80$ and 140 °C. Error bars are not shown to reduce visual clutter, but shown in Fig. 7.8.

Porod term is not fully resolved.

Fig. 7.8 show the fits to generally fit the data well. Agreement between the fitted models and the experimental data is generally better the more well defined the broad peak is, with some discrepancies being visible at low- Q limit of the peak. Correlation plots are found in their appendix (Fig. A.6 to A.8). For the RT configuration (Fig. A.1), the parameters appear as highly cross-correlated due to lack of degrees of freedom.

For the Ann80 configuration, most cross-correlations appear as smeared out or as highly correlated, indicating that the peak is too ill defined to be properly fitted.

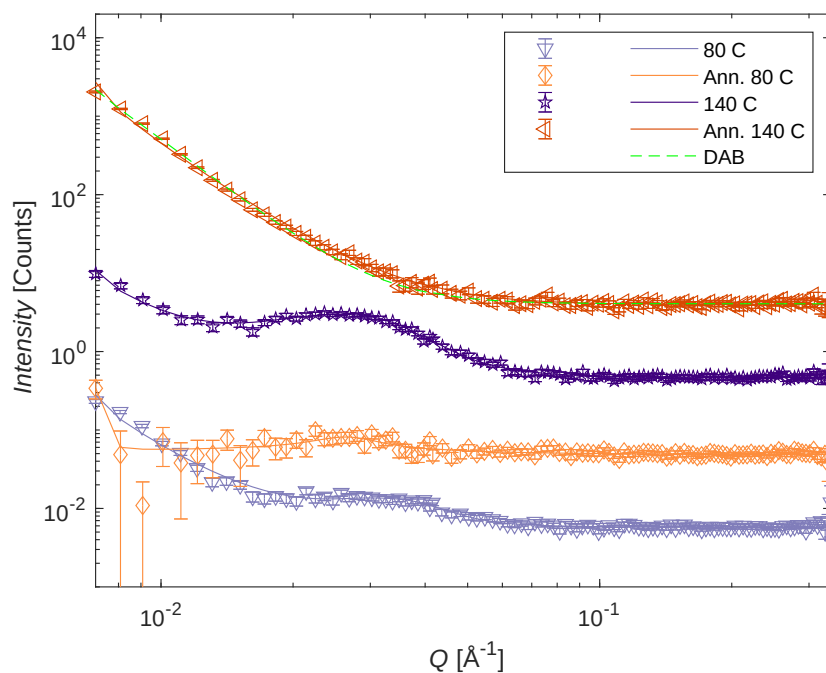


Figure 7.8: Log-log plot of small angle neutron scattering intensities of DCV5T-me(3,3):C60 2:1 mol thin films evaporated at $T_{sub} = \text{RT}$ and thermally post-annealed to 80 and 140 °C as well as the films evaporated at $T_{sub} = 80$ and 140 °C. Solid lines represent fits, using *Power law* models for the annealed samples and *Broad Peak* for the configurations deposited at elevated T_{sub} . The dotted line represents an alternate DAB fit of Ann140 sample. Intensities are vertically shifted for easier distinction.

For the *Power Law* and DAB model fits of the Ann140 system (See [A](#)) the parameter cross-correlations generally appear blob-like with the exceptions of the $P \times scale$ and $\zeta \times scale$ parameters respectively.

Table 7.2 shows equivalent values for the *Broad Peak* fit of Ann80 where the Porod term is not fully resolved. Table 7.4 shows the *Power Law* fitted values of the RT and Ann140 configurations and Table 7.5 shows the DAB fitted values of the Ann140 configuration. The intensity curves in Fig. 7.7 and Fig. 7.8 show that thermal post-annealing does not have the same effect as raised T_{sub} during growth.

	RT	Ann140
<i>Scale</i> [a.u]	$(6 \pm 8) \times 10^{-6}$	$(5.8 \pm 0.4) \times 10^{-8}$
<i>Background</i> [cm ⁻¹]	0.0041 ± 0.0001	0.0040 ± 0.0001
<i>P</i>	1.6 ± 0.2	3.37 ± 0.01
χ^2	1.0058	4.7849

Table 7.4: Table of *Power Law* fitted values of the RT and Ann140 DCV5T-me(3,3):C60 2:1 mol sample configurations.

	Ann140
<i>Scale</i> [a.u]	1.37 ± 0.02
<i>Background</i> [cm ⁻¹]	0.0041 ± 0.0001
<i>L</i> [Å]	322 ± 6
χ^2	2.0144

Table 7.5: Table of DAB fitted values of the Ann140 DCV5T-me(3,3):C60 DCV5T:C60 2:1 mol sample configurations.

The scattering of the configuration post-annealed at 80 °C is similar to that of the RT configuration (Fig. 7.1), however no clear upturn in intensity towards the low- Q limit is observed. A small and ill-defined increase in intensity is observed as a broad peak at around 0.02 Å^{-1} where a peak is also observed for other heated configurations. The absence of change in scattering intensity across the probed Q -range suggests that post-annealing at 80 °C (for 30 min) is insufficient to induce larger range phase segregation between the two molecular species to an appreciable degree. The lack of upturn in scattering towards the low- Q limit compared to the RT configuration is curious, as it would seemingly imply that annealing at 80 °C might even reduce phase separation. However, as the scattering intensity near the low- Q limit is very low, it is difficult to make a clear interpretation.

The scattering of the configuration post-annealed at 140 °C does not appear similar to that of the $T_{sub} = 140 \text{ °C}$ sample (Fig. 7.8). No broad peak is observed, instead the intensity is seen to increase linearly in the log-log plot towards the low- Q limit where the scattering intensity is about a magnitude higher than those

of the P-140 configuration. The strong increase in scattering towards the low- Q limit suggests that annealing at 140 °C for 30 min results in longer-range phase separation between DCV5T-me(3,3)-rich and C60-rich domains. Comparing the quantitative descriptions between Ann140, as fitted with the DAB model (Tab. 7.5), and P-140, as fitted with the *Broad peak* model, the P-140 has a centre-to-centre distance of $d_0 = 23.9 \pm 0.3$ nm and Ann140 has a correlation length of $L = 32.2 \pm 0.6$ nm. Whilst the larger fitted feature size of the Ann140 configuration compared to the PSI140 configuration implies a greater degree of phase separation between DCV5T-me(3,3)-rich and C60-rich domains, the absence of a Bragg-like bump in the Ann140 configuration suggests that the phase separation is less regular. Even when equivalent T_{sub} and annealing temperatures both induce phase separation in DCV5T-me(3,3):C60 thin films, there thus appears to be a qualitative difference in how this separation manifests. We note the apparent colour change in the Ann140 films (Fig. 5.3), which we attribute to potential change in the molecular or crystal structure of the film. However, this should not result in the movement of atoms (and thus change in SLD contrast) over length scales relevant to SANS.

7.2 Discussion

The *Broad peak* model has been the tool of choice for analysing scattering data in this chapter as it is able to describe the intensity curves well. It is, however, difficult to determine the link between scattering features and their physical origin. The *Broad peak* model is mathematically involved and has not previously been used to describe SM systems. The link between model parameters and physical attributes is thus not well established, but rather extrapolated from types of systems (e.g. polymer blends) that are similar, but not fully equivalent. Fur-

ther experimental investigations of the system, such as additional SANS measurements involving contrast variation or microscopy measurements potentially help determine the physical significance of the fit parameters. An alternative approach would be the simulated scattering from DCV5T-me(3,3):C60 systems with varied phase purities and domain sizes or to develop more specific models to describe SM thin film systems.

A full structural analysis is also limited by the Q -range of the data. For example, the decrease in Porod exponent between P-120 and P-140 is of note, as is the low- Q behaviour of the Ann140 configuration. Extending the Q -range further towards lower Q (and thus longer real space distances) could further elucidate how changing T_{sub} affects the microstructure of DCV5T-me(3,3):C60.

7.3 Chapter conclusions

In this chapter, we use SANS to investigate DCV5T-me(3,3):C60 2:1 mol systems deposited at $T_{sub} = \text{RT}, 60, 80, 100, 120, 140^\circ\text{C}$. The material system transitions from being highly intermixed at $T_{sub} = \text{RT}$ to showing phase separation between DCV5T-me(3,3)-rich and C60-rich domains. We observe an increased phase separation as T_{sub} is increased and we quantify this phase separation using *Broad peak* model fits. The fitted feature size increases from 17.7 ± 0.6 nm at $T_{sub} = 60^\circ\text{C}$ to 23.9 ± 0.3 nm at $T_{sub} = 140^\circ\text{C}$. We find the fitted centre-to-centre distance between domains in the two-phase system to increase linearly with T_{sub} at a rate of 0.8 ± 0.3 Å/K in the investigated temperature range. It cannot be determined from the investigated data whether the increase in T_{sub} is also concomitant with an increase phase purity or increased roughness.

The effect of post-annealing DCV5T-me(3,3):C60 deposited at $T_{sub} = \text{RT}$ at 80°C

and at 140 °C is investigated. Post-annealing at 80 °C does not induce phase separation, as evident from the lack of scattering signal, unlike the P-80 configuration. Post-annealing at 140 °C does result in a strong increase in scattering indicative of phase separation between that when fitted with the DAB model yields a correlation length of 32.2 ± 0.6 nm. Whilst this is larger than the phase separation between DCV5T-me(3,3)-rich and C60-rich domain fitted feature size of the equivalent P-140 configuration, we interpret the qualitative difference in scattering signal as indicative of P-Ann140 having a greater degree of polydispersity.

In this chapter we thus demonstrate that SANS is a viable technique to reveal the qualitative and quantitative effects of varying common film deposition parameters such as T_{sub} or thermal post-annealing.

8 | In situ X-ray diffraction study of DCV5T-me(3,3):C60

In situ X-ray growth studies of active layer materials of OPV BHJs offer the possibility of microstructural insight into spatially transient growth phenomena that are not accessible post-deposition. A few studies of mixed film systems with two molecular constituents have been reported, but the topic is generally underexplored in part due to the high experimental difficulty [72, 90]. Our group has previously reported in situ GIWAXS studies of single molecular organic thin films using the Minerva system [91, 67, 39]. We here present the first bi-molecular in situ evaporation X-ray diffraction study from the Minerva system. We investigate DCV5T-me(3,3):C60 at 2:1 mol ratio evaporated onto glass held at 120 °C under X-ray illumination, a system involving a high efficiency donor previously explored ex situ [81, 92]. We report on the growth of neat DCV5T-me(3,3) as well as the blend to explore the effect of C60 on growth in situ. We report on the crystalline behaviour of both films and find both their $\pi - \pi$ and long axis stacking to be similar, albeit with a possible loss of unit cell symmetry for the blend. The potential growth mode of both films is explored via different techniques and found to possibly be Volmer-Weber growth for the blend and growth reminiscent of Stranski-Krastanov growth for the neat film.

8.1 Experimental outline

Three separate evaporations under X-ray illumination were carried out in the Minerva chamber. Blank and cleaned substrates were mounted and then heated to a substrate temperature of 120 C° prior to alignment to prevent thermal drift. They were then aligned as described in sections 5.8 and 5.9. The incidence angle was

kept at the aligned 0° angle, resulting in scattering patterns similar to those of the so-called GTSAXS regime [93]. The choice of a nominally zero degree incidence angle was motivated by earlier test evaporations under illumination during the same beamtime, where shallow incidence angles on the order of $\sim 0.1^\circ$ yielded a poor scattering whereas scattering at the aligned zero angle yielded strong scattering. We consider the actual incidence angle to be low, but non zero (due to an observed reflected beam) and stress that whilst operating with a controlled incidence angle would be preferable, the experimental difficulties of achieving an in situ X-ray study of a bimolecular system under the time pressure of a beamtime necessitates choices that achieve the best practical results.

A high X-ray energy of 20 keV was chosen to ensure the visibility of the $\pi - \pi$ peaks, as the Minerva chamber has a narrow exit beam window and energy increases the Q-range with the field of view of the detector (Pilatus 2M).

For each evaporation, the temperature of the crucibles were heated until the desired rate was achieved. The rates were kept steady (Fig. 8.1) during the evaporation rates by manual adjustment of the crucible temperature. The evaporation of pure DCV5T-me(3,3) was ended earlier than anticipated as rates started dropping due to the material in the crucible running low. The pure C60 evaporation will not be detailed in this chapter due the lack of crystalline C60 scattering in the blend (see Sec. 8.2.2). Images of the blend and DCV5T-me(3,3) depositions were recorded via a macro that took an image with an exposure time of 5 s per image followed by a 10 s pause before beginning the recording of the next image. The length of scans were chosen as a compromise between ensuring scans are long enough to capture weak scattering versus reducing the temporal and thus thickness resolution of the image. The relatively long wait is to reduce the beam

damage (further discussed in Sec. 8.2.1) of the growing film. Images were calibrated via silver behenate (AgBeh) and the sample to detector distance was found to be 448.7 mm. Data reduction was performed in DAWN with output data in reciprocal space having a data point resolution of $0.004 \text{ \AA}^{-1}$.

The experimental details of each evaporation is outlined in Table 8.1.

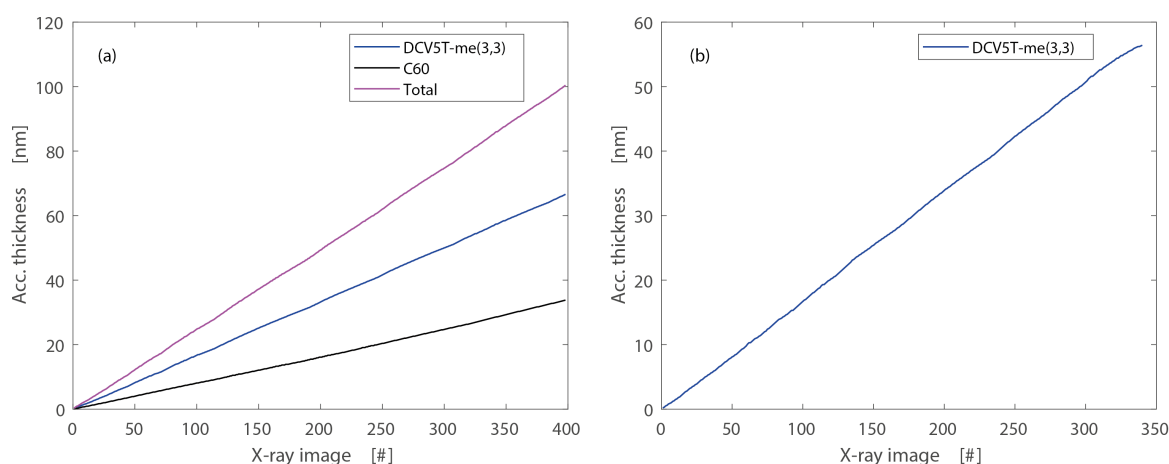


Figure 8.1: Accumulated film thicknesses of the a) DCV5T-me(3,3):C60 and b) pure C60 films. Thicknesses are with respect to measured X-ray images.

	DCV5T-me(3,3):C60	Pure DCV5T-me(3,3)	Pure C60
DCV5T-me(3,3) Rate [$\text{\AA}/\text{s}$]	0.1	0.1	0
C60 rate [$\text{\AA}/\text{s}$]	0.05	0	0.05
Final thickness [nm]	100.4	56.4	
Capture time [s]	5		
T_{sub} [$^{\circ}\text{C}$]	120		
Substrate	Glass (Eagle XG)		
Image resolution [$\text{\AA}$]	0.83	0.56	0.28
Acc. thickness/image [$\text{\AA}$]	2.5	1.7	0.8

Table 8.1: Experimental details of the in situ evaporations under X-ray illumination. "Image resolution" refers to the film thickness accumulated during the recording of one image. "Acc. thickness/image" is the change in accumulated thickness between each X-ray image and, for data analysis purposes, is assumed to be constant throughout the evaporation.

8.2 Evaporation summary

The following sections will provide a brief qualitative overview of the two in situ evaporations before quantitative analysis.

8.2.1 Pure DCV5T-me(3,3)

Reciprocal space maps at various stages of growth are shown in Fig. 8.2. Thickness indicated in each subfigure corresponds to the thickness of the film when the corresponding detector image finished averaging. In each case, the first recorded image of the glass substrate has been used as a subtracting background.

Weak Out-of-Plane (OoP) scattering features appear at $Q_z = 0.85 \text{ \AA}^{-1}$ after only $\sim 2 \text{ nm}$ of growth (Fig. 8.2b) which suggests stacking of upright standing DCV5T-me(3,3) molecules from the very onset of growth. This preferred orientation remains throughout the growth process. The OoP feature is smeared azimuthally, as is common for organics and suggests a variation in crystallite orientations along the OoP substrate normal (mosaicity). At around 3.3 nm of film growth (Fig. 8.2c), two faint In-Plane (IP) features near $Q_z = 0 \text{ \AA}^{-1}$ appear around $Q_{xy} = 1.8 \text{ \AA}^{-1}$. We identify these as corresponding to the π - π stacking between molecules based on prior studies of the material [81]. Their lower intensity and later onset suggest a lower degree of ordering IP in the early stages of growth. A diffuse background spanning the azimuthal at around $Q = 1.5 \text{ \AA}^{-1}$ seem to correspond to the diffuse glass background signal, which should be removed by the background subtraction process. It is possible this background appear to increase during early growth due to motor drift of the equipment, slightly changing the incidence of the x-rays. We also observe two qualities of the OoP feature: Firstly, the feature seems to have a double, shifted along the OoP direction. We attribute this double to scattering from the reflected beam, a phenomenon

observed for scattering at low incidence angles [94]. To verify the doubling was due to this effect, scans at varied angles (at range of 0.3°) were taken post deposition. As expected for this type of doubling, the upper feature moved with the varying angle, whilst the lower angle stayed immobile [95].

Secondly, it becomes apparent that the now more well-defined OoP peak appears as split into three, with the two additional features appearing as peak maxima symmetrically along the azimuth. We do not find reports of this in literature for DCV5T-me(3,3) thin films [81] and we are unsure of what potential optical or symmetry effects this could be attributed to.

At around 11.6 nm film thickness (Fig. 8.2d), faint higher order features start to emerge. As the film grows thicker (Figs. 8.2e and 8.2e) these features grow stronger. From the azimuthal spread of both the OoP and IP features, it is apparent that the film crystallites have a notable degree of mosaicity around the preferred direction of upright standing molecules.

To gauge the extent to which beam damage might have affected the structure of the growing film, images at different positions on the film were captured post-deposition (Fig. 8.4a). The film at an undamaged position appear with similar features, including a lack of higher order Bragg features.

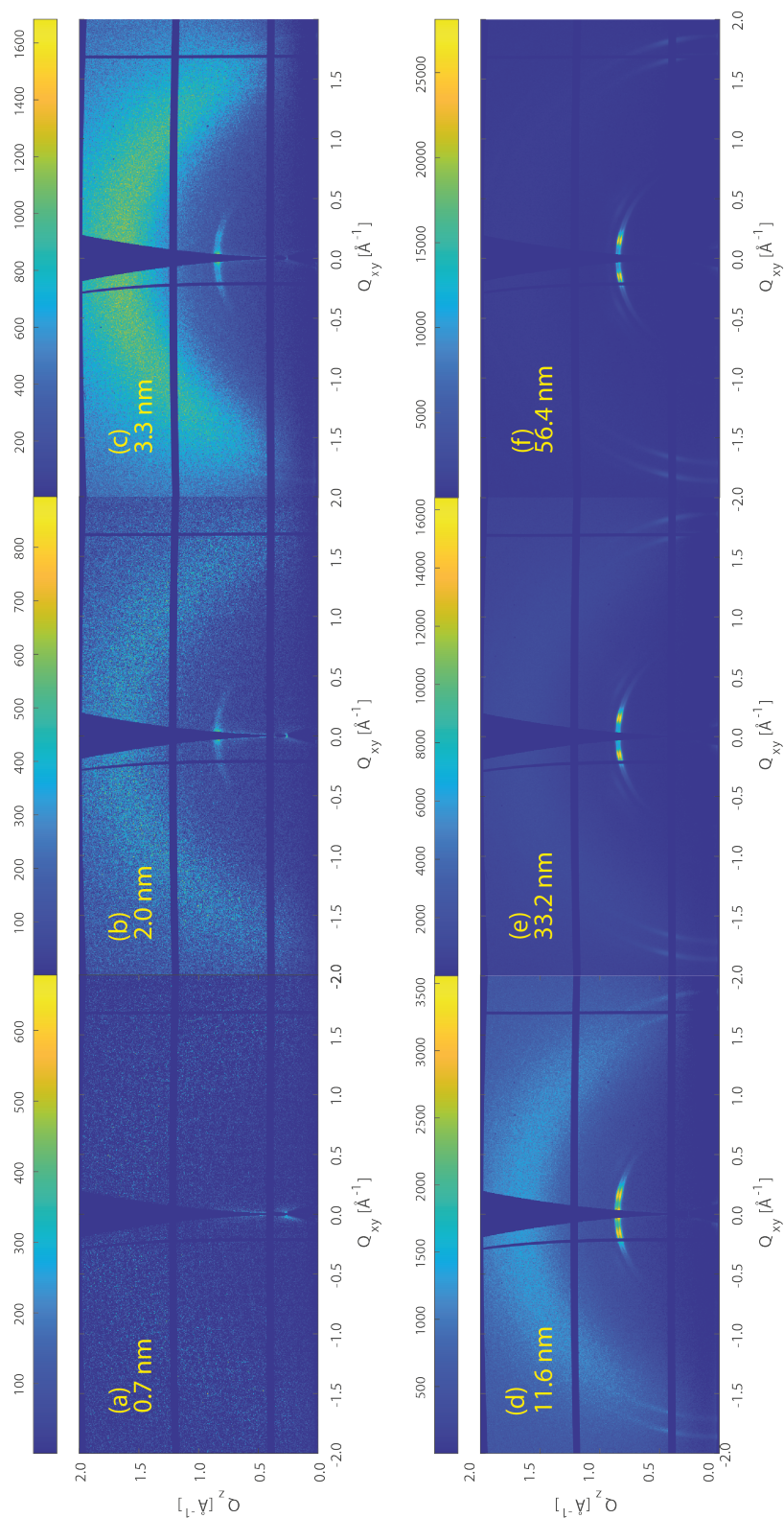


Figure 8.2: GIWAXS 2D reciprocal space maps of neat DCV5T-me(3,3) at a film thickness of a) 0.7 nm, b) 2 nm, c) 3.3 nm, d) 11.6 nm, e) 33.2 nm and f) 56.4 nm. Background scattering has been subtracted from each image. Note the different colour maps shown above the corresponding subfigure.

8.2.2 DCV5T-me(3,3):C60 blend

Reciprocal space maps at various stages of growth are shown in Fig. 8.3. Thickness indicated in each subfigure corresponds to the thickness of the film when the corresponding detector image finished averaging. In each case, the first recorded image of the glass substrate has been used as a subtracting background.

Faint OoP features appear at ~2-4 nm of growth (Fig. 8.3a) at around $Q_z = 0.85 \text{ \AA}^{-1}$, similar to the pure film again suggesting rapid onset of ordered OoP packing. A diffuse background is seen at low Q_z potentially indicating IP disordered packing. The seemingly abrupt cessation of this signal at around $Q_z = 0.6 \text{ \AA}^{-1}$ is due to the gap between subdetectors. At ~8.75 nm of growth (Fig. 8.3b), the OoP feature also appears as duplicated in the radial direction and split into three azimuthally. Faint signs of the two IP features at around $Q_{xy} = 1.8 \text{ \AA}^{-1}$ start to appear and become fully visible at around 17.5 nm (Fig. 8.3c). A greater mosaicity of the main OoP feature compared to the neat film also seems to manifest as scattering at $Q_{xy} = 0.85 \text{ \AA}^{-1}$, although as there is increase in intensity at an azimuth of $Q_z = 0.6 \text{ \AA}^{-1}$, this could also correspond to a different hkl -indexation. The feature intensities increase along with thickness (Fig. 8.3d) until higher order features start to appear at around ~50 nm (Fig. 8.3e). These strengthen in intensity, but remain relatively faint until the end of film growth (Fig. 8.3f) at 100.4 nm. Images taken at different positions post-growth (Fig. 8.4b) highlight the high degree of mosaicity of the blend film. The peak around $Q_z = 1.8 \text{ \AA}^{-1}$, corresponding to π - π stacking, indicate the film crystallites are clustered around two preferred direction - primarily standing molecules with long axis perpendicular to the substrate plane and secondarily with long axis lying in the plane. These features are also present in the in situ images (Fig. 8.3f), but appear weaker, possibly due to worse alignment or accumulated beam damage.

Only a weak signal from crystalline C60 is observed, corresponding to a weak Bragg feature around around $Q_{xy} = 0.75 \text{ \AA}^{-1}$ (Fig. 8.6b), corresponding to the [111] reflection [96]. This suggest that any significant ordered clustering of C60 is interrupted by DCV5T-me(3,3) molecules. We thus interpret the scattering results as arising from a two-phase system, where one phase consists of relatively pure and crystalline DCV5T-me(3,3) domains on one hand and the other phase consists of a disordered mix of C60 and DCV5T-me(3,3).

Whilst single crystal characterisations of DCV5T-me(3,3) has been carried out, the single crystal structure (with the longest axis reported as $b = 15.9 \text{ \AA}$) does not match the thin film structure as reported by others and is indeed similar to observed in our study [81, 92].

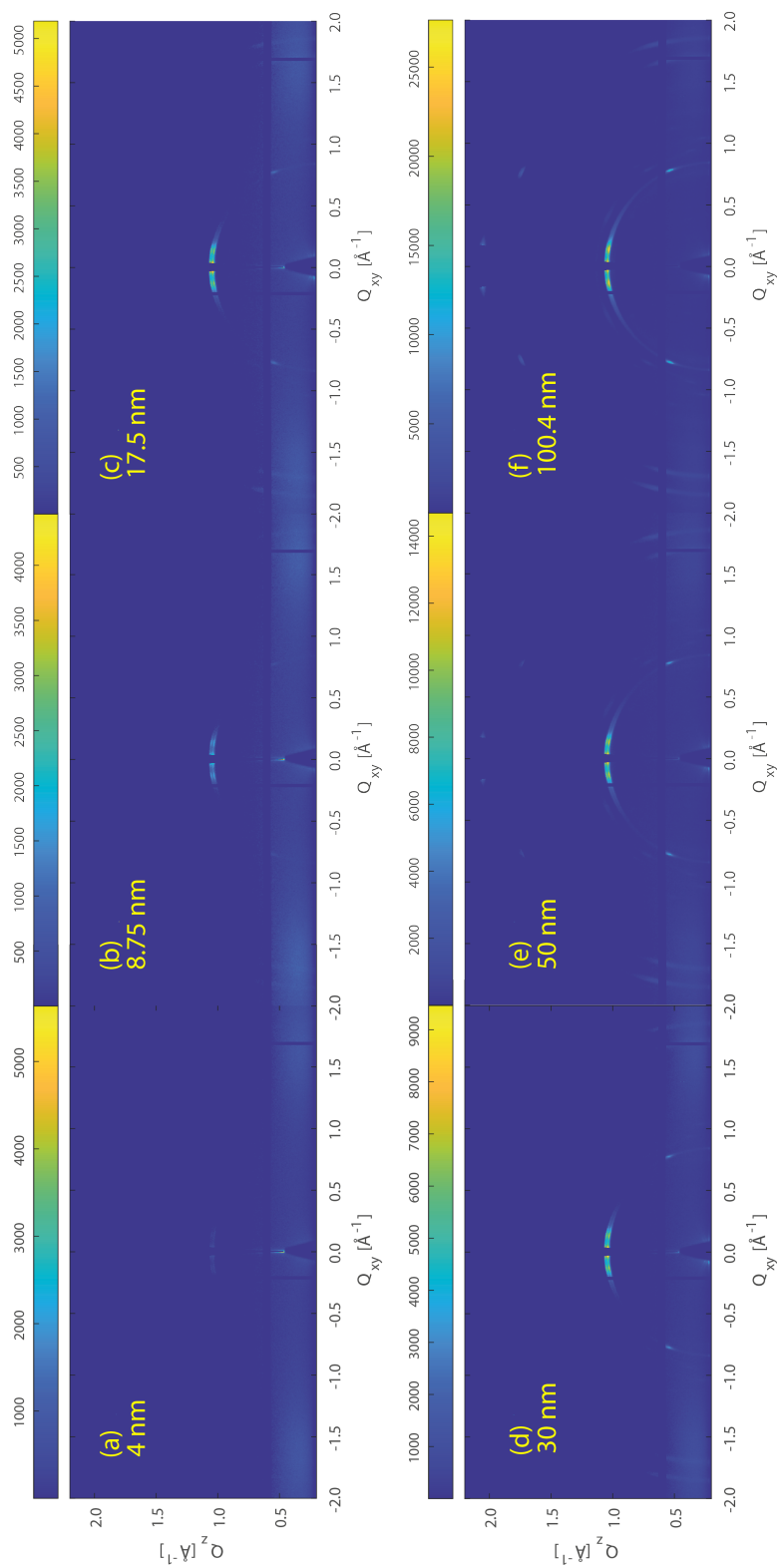


Figure 8.3: GIWAXS 2D reciprocal space maps of DCV5T-me(3,3):C60 at a film thickness of a) 4 nm, b) 8.75 nm, c) 17.5 nm, d) 30 nm, e) 50 nm and f) 100.4 nm. Background scattering has been subtracted from each image. Note the different colour maps shown above the corresponding subfigure.

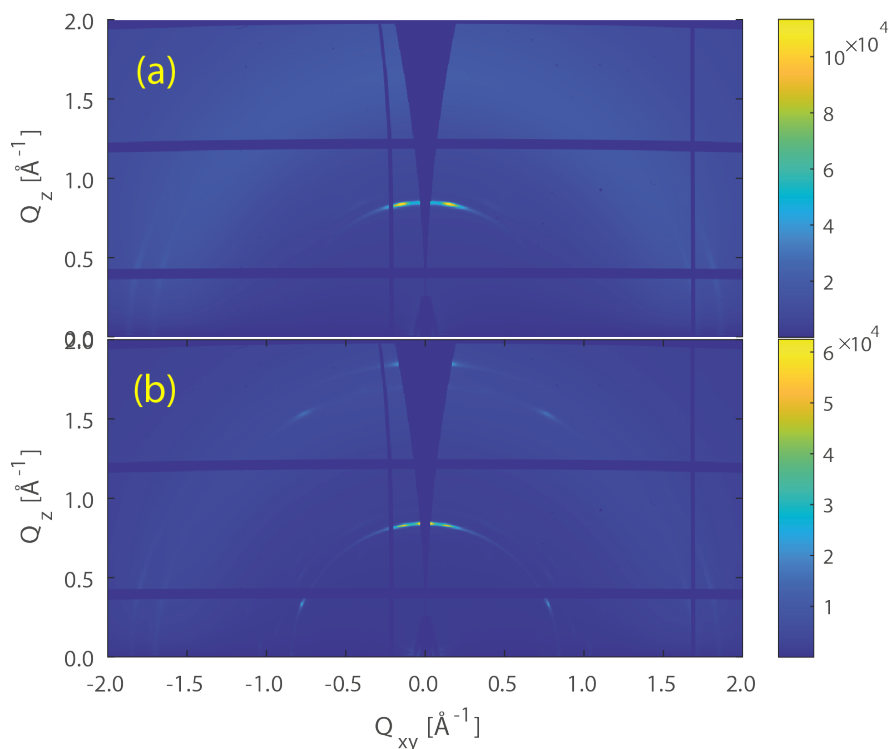


Figure 8.4: WAXS 2D reciprocal space maps of a) neat DCV5T-me(3,3) at 56.4 nm and b) DCV5T-me(3,3):C60 2:1 mol at 100.4 nm taken post deposition at a film location away from the scanned area during growth.

8.3 π - π stacking features

To track the π - π stacking as growth develops, cut-outs centered on the Yoneda-band ($\approx Q_z = 0.02 \text{ \AA}^{-1}$) were taken from each image and summed across a $0.02 \text{ \AA}^{-1}$ range. A Yoneda band is a line spanning a given Q_z , equivalent to the critical angle of the scattering film, where scattering is enhanced. At the critical angle α_c the reflected and incident beams will interfere constructively due to being in phase. This leads to a waveguide resonance of the scattered wave and thus a maximum in scattering, which is often exploited to discern scattering features [97]. The evolution is shown for the neat DCV5T-me(3,3) film in Fig. 8.5a and for the blend in Fig. 8.6a with background subtracted equivalents in, respectively,

Figs. 8.5b and 8.6b. Quantitative analysis of the Bragg features in the following sections are based on background subtracted data. The two π - π features do not

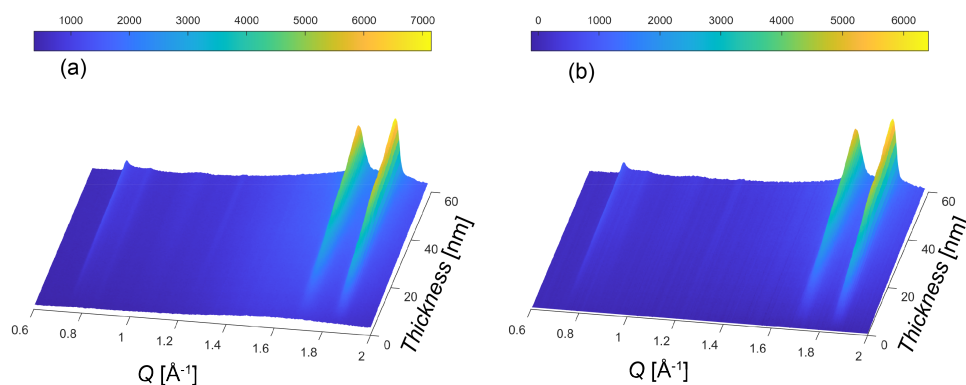


Figure 8.5: a) Surface plot from WAXS 2D reciprocal space maps of neat DCV5T-me(3,3) as function of film thickness taken from the Yoneda band of neat DCV5T-me(3,3). b) Same plot with the background subtracted.

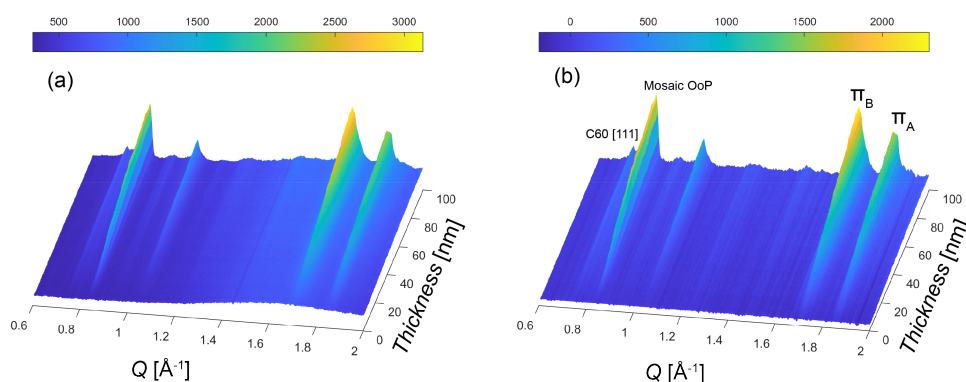


Figure 8.6: a) Surface plot from WAXS 2D reciprocal space maps of DCV5T-me(3,3):C60 as function of film thickness taken from the Yoneda band of neat DCV5T-me(3,3). b) Same plot with the background subtracted. Four peaks are labelled as [111] reflection of C60, the 'Mosaic OoP' reflection as well as the π_A and π_B peaks.

appear to change strongly in position as the film grows in Figs. 8.5, 8.6. We label the feature at $\sim Q_{xy} = 1.85 \text{ \AA}^{-1}$ as π_A and the feature at $\sim Q_{xy} = 1.7 \text{ \AA}^{-1}$ as π_B . The position of both features were fitted as Gaussians with a flat background (Eq.

8.1)

$$I = h e^{-(x-x_0)^2/\sigma^2} + c, \quad (8.1)$$

where h is the peak height, x_0 is the fitted peak position, σ is the standard deviation and d is a flat background.

The fitted positions of the neat film are shown in Figs. 8.7a and 8.8a for π_A and π_B , respectively. The fitted positions of the blend film are shown in Figs. 8.7b and 8.8b for π_A and π_B , respectively. In each case, there seems to be an initial increase in peak position followed by decrease in position as the films grow towards bulk. However, in each case the difference is minimal and within a 0.5% of the final position. While an absolute strain cannot be determined due to a lack of appropriate reference thin film crystalline structure, IP strain does thus not appear to change as the film grows for neither the neat film nor the blend. Table 8.2 shows the fitted position in reciprocal and real space of the fitted features. The stacking distances of the blend appear slightly longer than those of the neat film, possibly due to disorder induced by the C60, but remain similar. The $\pi-\pi$ d -spacing thus does not indicate any major change in crystal packing by the introduction of C60.

	π_A [$\text{\AA}^{-1}$]	π_A [$\text{\AA}$]	π_B [$\text{\AA}^{-1}$]	π_B [$\text{\AA}$]
DCV5T-me(3,3)	1.86 ± 0.01	3.38 ± 0.01	1.71 ± 0.01	3.67 ± 0.01
DCV5T-me(3,3):C60 2:1	1.85 ± 0.01	3.39 ± 0.01	1.70 ± 0.01	3.69 ± 0.01

Table 8.2: Fitted positions in reciprocal and real space of the π_A and π_B features of neat DCV5T-me(3,3) and the DCV5T-me(3,3):C60 blend. Values in the Table represent the value at the final thickness of the film. The uncertainties represent the 95% confidence range of the fits.

The peak areas ($A = \sqrt{\pi} h \sigma$) (A of Eq. 8.1) of the π_A and π_B features of the neat film are shown in Fig. 8.10a and in Fig. 8.11a for the blend. The ratio between their areas are shown in Fig. 8.10b for the neat film and in Fig. 8.11b for the blend.

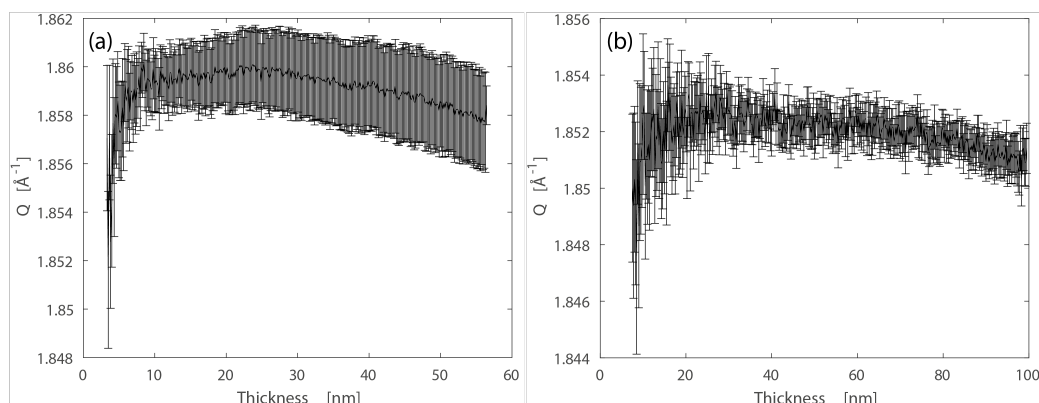


Figure 8.7: Peak position of π_A fitted as the centre of a Gaussian with a flat background for a) neat DCV5T-me(3,3) and b) blend DCV5T-me(3,3):C60. Fitted points are shown from the approximate onset of the Bragg feature. Error bars represent the 95% confidence range of the fit.

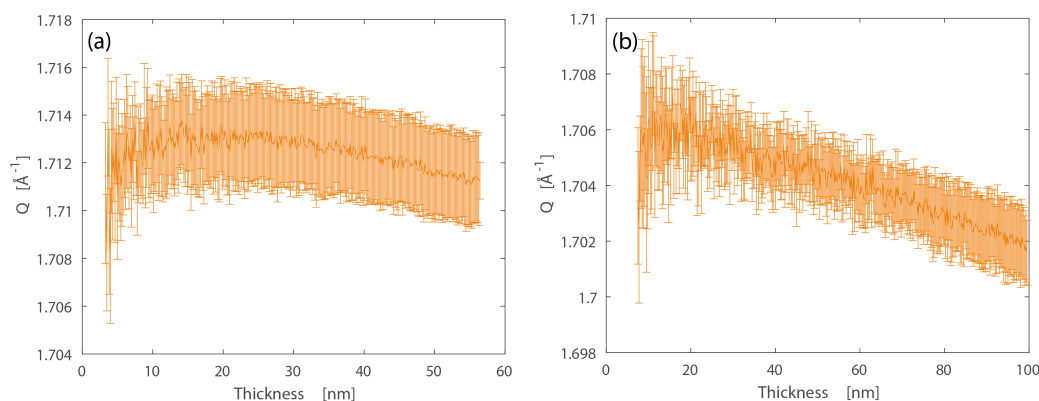


Figure 8.8: Peak position of π_B fitted as the centre of a Gaussian with a flat background for a) neat DCV5T-me(3,3) and b) blend DCV5T-me(3,3):C60. Fitted points are shown from the approximate onset of the Bragg feature. Error bars represent the 95% confidence range of the fit.

There are clear differences between the neat film and the blend. In the case of neat DCV5T-me(3,3), the areas of the two π - π peaks increase uniformly as the film grows. The ratio between the two areas π_A/π_B decrease rapidly from $\sim 180\%$ to an equal ratio of around 1:1 which is maintained as the film grows. The initial difference in ratio is likely due to poorer fitting of the emerging Bragg features.

In the case of the blend, the peak areas of the π_A and π_B feature start at roughly equal levels after which the intensity of the π_B increase more strongly as the film grows. As the film approaches the 100.4 nm full thickness, the π_A/π_B ratio rate appears to slow down, with the ratio stabilising below around 60%.

The explanation for the difference in behaviour between the neat film and the blend is not obvious. One possible explanation could be competing polymorphs with different stacking lengths due to e.g. different unit cell angles. π_A and π_B would in this scenario be ascribed to individual polymorphs. However, in such a case, the volume of the unit cell would be expected to stay approximately constant and a longer $d_{\pi-\pi}$ -spacing would thus be counter acted by a shorter OoP stacking distance. In such a scenario, we would expect to see two OoP features in contrast to the one OoP feature observed (as we ascribe the duplicate to scattering from the reflected beam). The 1:1 $\pi_A:\pi_B$ ratio of scattering intensity of the neat film (Fig. 8.10) could suggest that each $\pi-\pi$ feature arises from different symmetries of the same unit cell i.e. from different inter-atomic distances between aromatic ring pairs of the unit cell. An illustrative example of how two adjacent DCV5T-me(3,3) molecules could exhibit different π - π distances are illustrated in Fig. 8.9. As the change in relative peak intensities is not associated with a considerable change in the packing distances (Tab. 8.2), a change in unit cell dimensions does not appear to be likely explanation. A potential explanation is thus a change in the internal symmetry of some proportion of the crystallites of the film due to the introduction of C60, resulting in a change in the ordering of π_A stacking.

Another notable difference observed between the neat film and the blend is the difference in the peak areas of the $\pi-\pi$ features. Despite less total DCV5T-me(3,3) having been deposited at the end of the evaporation, the peak areas of the

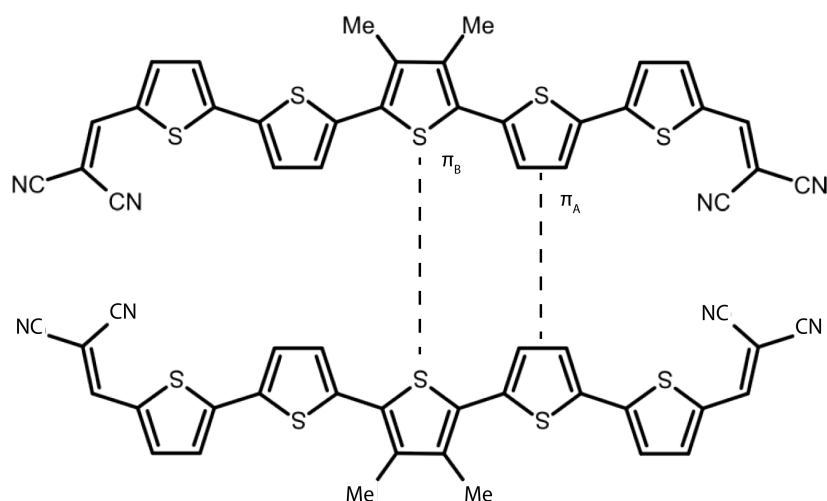


Figure 8.9: Schematic of two DCV5T-me(3,3) with dotted lines representing hypothetical π - π stacking distances. We note that the shown π - π distances are illustrative and do not accurately represent how π - π bonds are formed between co-planer aromatic rings.

neat film are more than three times higher than those of the blend. This could possibly be attributed to C60 molecules interrupting the IP crystalline packing of DCV5T-me(3,3), resulting in fewer and smaller crystalline grains and thus reduced scattering. However, the introduction of a second molecular species will always lead to impure domains even in a strongly phase separated blend and it must be cautioned that comparisons between absolute scattering intensities between GI-WAXS measurements is difficult due to the high sensitivity to the alignment of the beam.

8.4 Out of Plane features

To track the stacking of the main OoP feature as growth develops, cut-outs centered on the feature were taken at an angle of 4° from the normal (to escape the missing centre wedge) from each image and summed across a $0.11 \text{ \AA}^{-1}$ range for

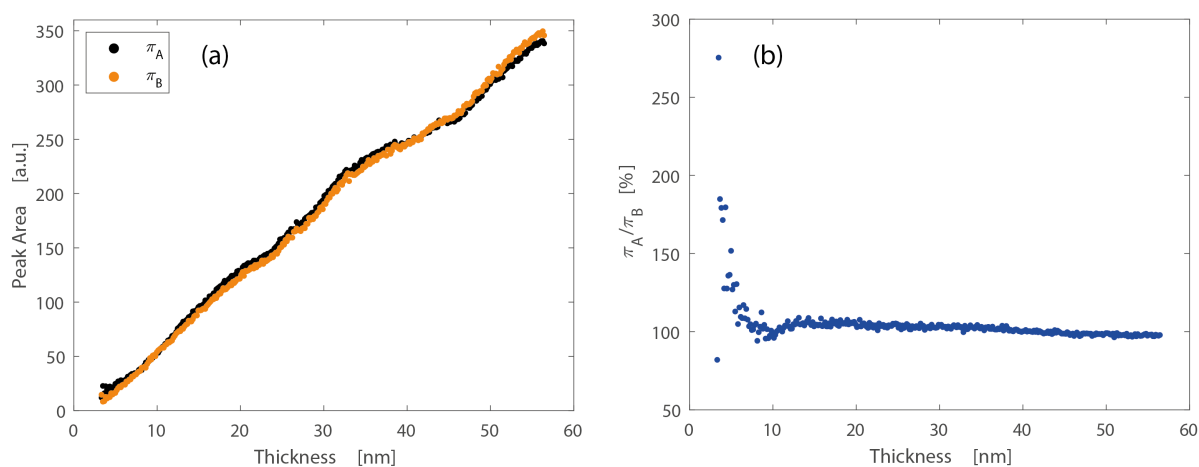


Figure 8.10: a) Fitted peak areas of the π_A and π_B features from the on-set of the peak features of the neat DCV5T-me(3,3). b) Ratio between peak areas of π_A and π_B as the film grows.

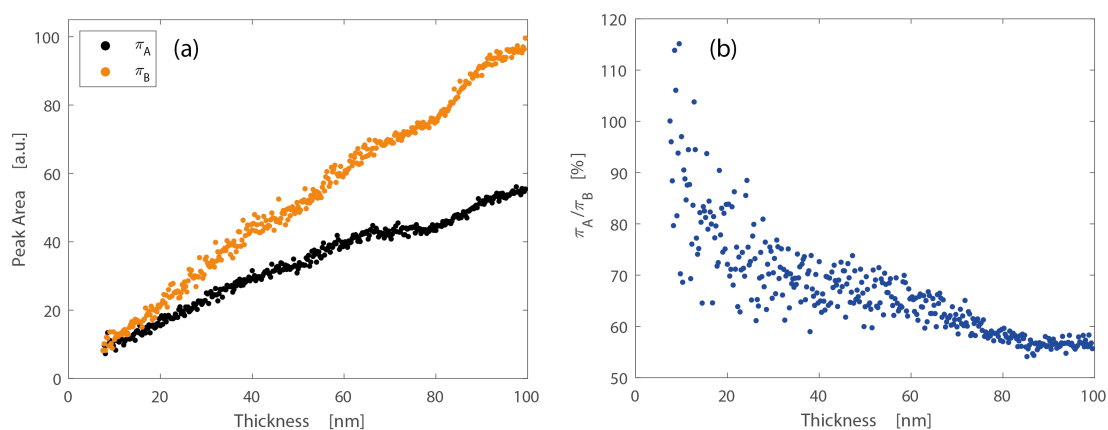


Figure 8.11: a) Fitted peak areas of the π_A and π_B features from the on-set of the peak features of the blend DCV5T-me(3,3):C60 film. b) Ratio between peak areas of π_A and π_B as the film grows.

the neat film and $0.08 \text{ \AA}^{-1}$ range for the blend film. A longer cut-out was taken for the neat film due to its stronger intensity and broader peak. The peaks are fitted as Gaussians (Eq. 8.1) and the evolution is shown for the neat DCV5T-me(3,3) film in Fig. 8.12a and for the blend in Fig. 8.13a.

Within the cut-out, two peaks are identified for both the neat film and the blend

with one at higher Q_z identified as the "Upper" peak and the one at lower Q_z identified as the "Lower" peak. Such peak splitting is sometimes observed in thin films measured at low incidence angles [94, 95]. The Lower peak arises from direct beam scattering whilst the Upper peak arises from scattering from the outgoing beam experiencing full external reflection. We follow the analysis methods presented by Mrkyvkova et al. and refer to their paper for detailed mathematical analysis. The fitted positions of the both the Upper and the Lower peaks are shown in Fig. 8.12b and for the blend in Fig. 8.13b. The stacking periodicity of the neat

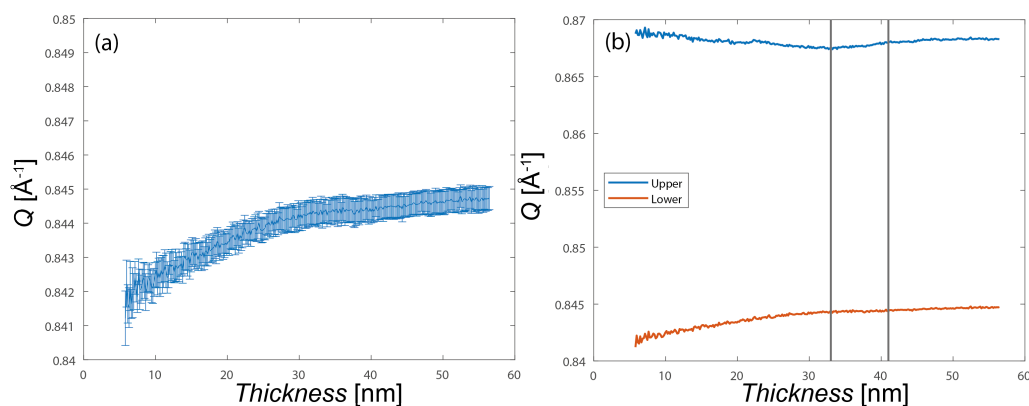


Figure 8.12: a) Fitted peak position of the lower reflection of the main OoP feature of the neat DCV5T-me(3,3) film. Error bars represent the 95% confidence range of the fit. b) Fitted peak position of the both the Upper and Lower reflections of the main OoP feature of the neat film. Vertical lines at 33 nm and 41 nm represent points of change in the relative position of the two peaks.

and the blend film (Figs. 8.12a, 8.13a) appear near-identical with fitted positions around $Q_z = 0.845 \text{ \AA}^{-1}$ at the final film thicknesses. In each case, the fitted position seem to move to a higher position as the film grows, however the difference is within 1% of the final position. We thus do not observe any appreciable difference in the OoP stacking distance due to the introduction of C60. The fitted position of the lower peaks are shown in Table 8.3. We note that the real space position is calculated as $d = 2 \cdot 2\pi/Q$ as the fitted reflections are assumed to correspond to d_{200} based on the length of a near-upright standing pentacene molecule [98]. The fitted

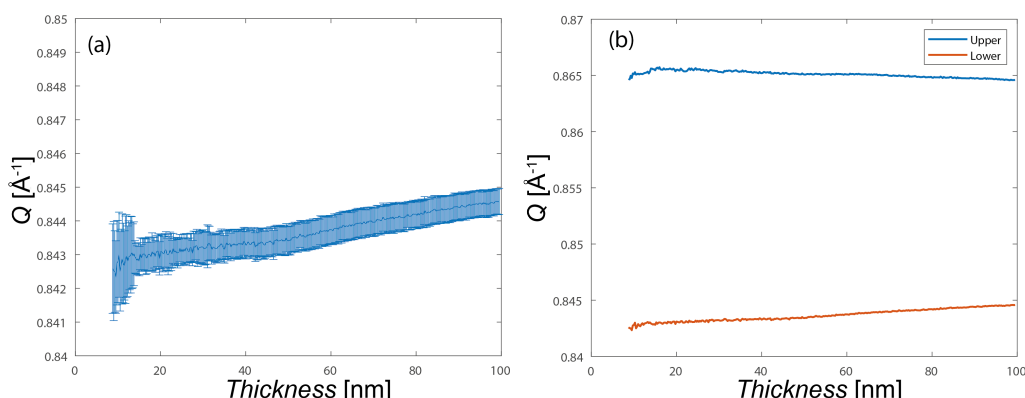


Figure 8.13: a) Fitted peak position of the lower reflection of the main OoP feature of the blend DCV5T-me(3,3):C60 film. Error bars represent the 95% confidence range of the fit. b) Fitted peak position of the both the upper and lower reflections of the main OoP feature of the neat film.

	OoP [$\text{\AA}^{-1}$]	OoP [$\text{\AA}$]	Mosaic OoP [$\text{\AA}^{-1}$]	Mosaic OoP [$\text{\AA}$]
DCV5T-me(3,3)	0.845 ± 0.01	14.87 ± 0.01	N/A	N/A
DCV5T-me(3,3):C60	0.845 ± 0.01	14.87 ± 0.01	0.840 ± 0.01	14.96 ± 0.01

Table 8.3: Fitted positions in reciprocal and real space of the OoP feature as well as its azimuthally shifted equivalent of neat DCV5T-me(3,3) and the DCV5T-me(3,3):C60 blend. Values in the Table represent the value at the final thickness of the film. The uncertainties represents the 95% confidence range of the fits.

positions of the Upper and the Lower split OoP peaks are shown in Fig. 8.12b and for the blend in Fig. 8.13b. For the blend, we see the two peak positions gradually approach each other as the film grows. Following the analysis by Mrkyvkova et al. we take this to possibly represent film refractive index that varies along the OoP direction and thus representative of 3D island Volmer-Weber growth. The peak positions converge towards the middle in a uniform fashion which is seen as indicative of a lack of strain.

The case of the neat film is less clear. The two peak positions approach each other until around 33 nm of growth, grow further apart until ~41 nm of growth, then finally remain at approximately the same distance for the final 15 nm of

growth. Mrkyvkova et al. identify a constant Upper-Lower peak distance as being indicative of 2D-then-3D Stranski-Krastanov growth. However, it is difficult reconcile such a behaviour with converging peak behaviour during the early stages of growth, indicative of 3D growth. Whilst so-called "inverse Stranski-Krastanov" growth is observed, it appears to be associated with highly ordered films, which DCV5T-me(3,3) grown in such a manner cannot be said to be. It is thus difficult to make a clear analysis of the growth mode of neat DCV5T-me(3,3) based on peak splitting. Microscopy studies of a series of film in the initial stages of growth could potentially help answer this question.

As can be seen in Figs. 8.5 and 8.6 the OoP features can also be seen for the blend along the Yoneda band due to a greater mosaicity of the film. The smaller peak observed at $\sim 1.04 \text{ \AA}^{-1}$ (Fig. 8.6b) is a higher order peak which maintains its same relative position as the OoP peak (Fig. 8.4). The "Mosaic OoP" feature is fitted in a similar fashion to the other peaks for the blend film and the fitted values at the final peak position are presented in Table 8.3. The d -spacing of $14.96 \text{ \AA}$ is larger than those of the OoP. The associated $\pi - \pi$ peaks for crystallites with long-axis along the IP, the 2nd preferred axis, appear along the OoP for the blend (Fig. 8.3f). Their fitted positions are shown in Tab. 8.4. Comparing the fitted positions with the equivalent $\pi - \pi$ peaks along the Yoneda band (Tab. 8.2), π_{OoP-A} and π_{OoP-B} appear with slightly larger d -spacings than π_A and π_B , respectively. The shorter "mosaic OoP" stacking distance and the longer $\pi - \pi$ -spacings suggest that crystallites oriented with the long axis along the IP are elongated compared to those oriented with their long axis along the OoP. As a final point of the section, we highlight again the two reflections that appear as azimuthally shifted versions of the main OoP feature. Each peak position is rotated by around 10° from the surface normal. Such splitting of peaks has not been observed prior for

	$\pi_{OoP-A} [\text{\AA}^{-1}]$	$\pi_{OoP-A} [\text{\AA}]$	$\pi_{OoP-B} [\text{\AA}^{-1}]$	$\pi_{OoP-B} [\text{\AA}]$
DCV5T-me(3,3):C60	1.87 ± 0.01	3.36 ± 0.01	1.72 ± 0.01	3.65 ± 0.01

Table 8.4: Fitted positions in reciprocal and real space of the π_{OoP-A} and π_{OoP-B} features of neat DCV5T-me(3,3) and the DCV5T-me(3,3):C60 blend. Values in the Table represent the value at the final thickness of the film. The uncertainties represents the 95% confidence range of the fits.

DCV5T-me(3,3) nor are we aware of similar 'azimuthal mirroring' being observed for similar organic molecule systems [81, 92]. One possibility could be a crystallite preferred orientation at an angle $\sim 10^\circ$ from the surface normal, however we do not identify any obvious features of DCV5T-me(3,3) that would lead to such behaviour. Another possibility would be the two shifted peaks belonging to different hkl -indexing, although this would not explain their absence from prior observations or their seeming azimuthal alignment.

8.5 Near-specular reflection

Following prior work, we attempt to use the anti-Bragg reflection found at $Q_{1/2} = Q_{OoP}/2$ to determine the growth mode [39]. At this point, the specular reflection acts like a 'forbidden' reflection, where waves scattering from 'monolayer' (ML) N of a layered film experience destructive interference with waves scattering from ML $N \pm 1$ whilst scattering constructively with scattered waves from layer $N \pm 2$. An oscillating intensity pattern is thus a sign of layer-by-layer growth whilst a non-oscillating and decreasing intensity is a sign of rough or island like growth [99].

Regrettably, the exact $Q_{1/2}$ position is found in the dead space between the sub-detectors. Instead, we use the summed intensity of the near-specular reflection found above the beamstop. The region of interest, taken directly from the detector

data, is shown in Fig. 8.14. The intensity as function of thickness for the first 25

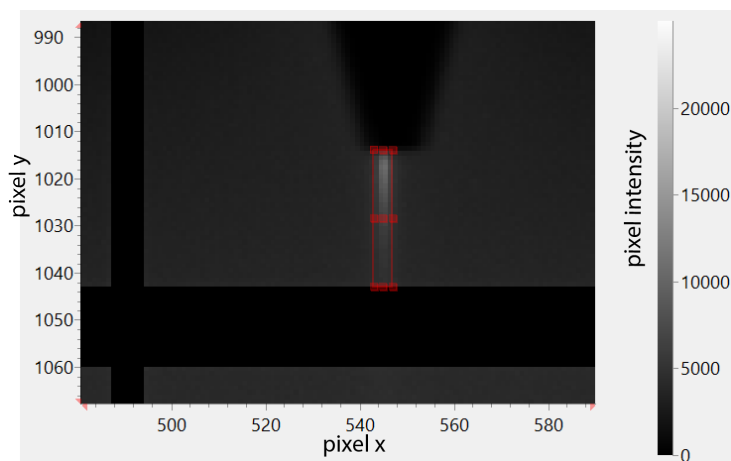


Figure 8.14: Raw detector image from the blend evaporation. The pixel x and pixel y indices refer to the detector pixel indexation and the colour scale corresponds to the raw pixel photon detection count. The near-specular reflection is described by the summed intensity within the region of interest (red box).

nm is plotted in Fig. 8.15a and Fig. 8.15b for the neat and blend film, respectively. The near-specular reflection intensity of the neat film (Fig. 8.15a) appear to show

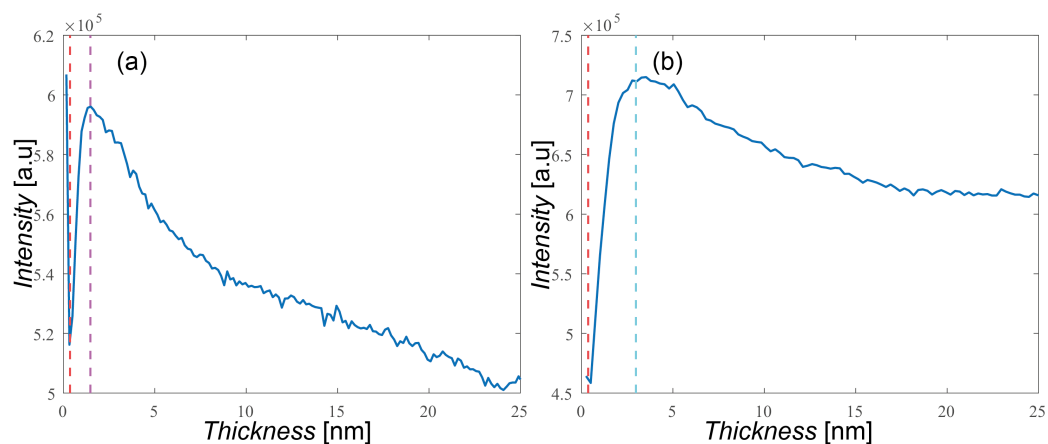


Figure 8.15: Summed intensity of the near-specular reflection of the a) neat DCV5T-me(3,3) film and b) blend DCV5T-me(3,3):C60 film for the first 25 nm of film growth. The red dotted lines marks 0.25 times the ML stacking distance of 14.87 Å. The magenta and cyan dotted lines mark thicknesses equivalent to 1 ML and 2 ML, respectively.

one 'oscillation' with a dip in intensity followed by an increase. The 'peak' intensity after the dip occurs at exactly one times the OoP stacking distance (Tab. 8.3), which is marked with a magenta line. After this thickness, the near-specular intensity decreases gradually with film thickness. The almost perfect alignment between a 1 ML distance of 14.87 Å suggests that the intensity variation is indeed due to one ML having formed. We note, however, that the decrease in intensity between the point at ~0 nm and at the point of lowest intensity is only 15% and that the point of lowest intensity does not coincide with 1 ML thickness. Furthermore, no further oscillations are observed past the first one. This could possibly suggest that initial growth could be described by layer-by-layer growth, where the first mono-layer forms an imperfect complete layer. After the first layer, growth would continue in the form of 3D islands. The approximate $Q_{1/2}$ intensity thus possibly suggests that neat DCV5T-me(3,3) follows a 'weak' Stranski-Krastanov growth mode of one disordered ML followed by island growth.

The approximate specular intensity of the blend film (Fig. 8.15b) shows an increase in intensity from a lower initial intensity followed by a gradual decline. A slight upturn in intensity at the lowest thickness point is observed, but it does not match the oscillation behaviour of the neat film as the intensity maximum does not occur near 1 ML.

The decrease in intensity from ~3 nm onwards suggest a roughening growth consistent with island (Volmer-Weber) growth. The explanation for the initial increase in scattering intensity is harder to explain as initial reflection from the uncoated and smooth glass should be high. This could possibly be an optical effect due to variation in the final alignment of the substrate. Repeating the same experiment could potentially help determine if the phenomenon is an artefact or arises from physical conditions.

8.6 Discussion

This chapter is based on the thorough *in situ* GIWAXS analysis of neat DCV5T-me(3,3) and the blend DCV5T-me(3,3):C60. This analysis could potentially have been expanded through Scherrer analysis. Whilst Scherrer analysis can provide a lower bound for the crystallite size, 'proper' application of the Scherrer equation necessitates accounting for instrumental contributions to peak broadening. For this reason, Scherrer analysis is often used only for comparative analysis between equivalently measured samples. As the proper attribution of instrumental contributions is mathematically involved and, as discussed in Sec. 8.3, there are differences in absolute scattering intensity which could possibly be attributed to differences in alignment. For these reasons, we have chosen to eschew Scherrer analysis of the various scattering peaks.

The growth modes of the two studied films are discussed in Sec. 8.5 where the analysis is based on wide angle scattering. A more direct way to determine the growth mode would be to deposit series of films with finely spaced staggered thicknesses (e.g. 3 Å, 6 Å, 9 Å etc.) and then carry out microscopy measurements using techniques such as atomic force microscopy or scanning electron microscopy. Qualitative assessment of the measurements, which would cover a select area of the film rather than a statistical average, could then be used to complement the analysis.

As noted in Sec. 8.1, *in situ* studies of evaporated thin films often require compromises to be made. Further work on *in situ* OPV studies could help optimise parameter choices such as exposure and pause duration during the evaporation in terms of image resolution or to minimise beam damage.

8.7 Chapter conclusions

In this chapter, we use in situ GIWAXS to study the evaporation of neat DCV5T-me(3,3) and a DCV5T-me(3,3):C60 2:1 mol blend evaporated onto glass substrates held at 120 °C.

From the position of Bragg features, we find DCV5T-me(3,3)'s preferred orientation to be that of molecules standing on glass with their long axis primarily aligned along the surface normal with a d -spacing 14.87 Å in both cases, similar to reported literature. The blend film shows a greater mosaicity, which we attribute to disruption caused by the C60. This results in a secondary preferred orientation with the molecular long axis parallel to the substrate surface. These crystallites appear slightly elongated. We only observe a very faint crystalline C60 signal, and we thus classify the blend as a two-phase system consisting of crystalline DCV5T-me(3,3) and a disordered mixed DCV5T-me(3,3):C60 phase.

From line cuts along the Yoneda band, we identify two $\pi - \pi$ stacking features, which designate as π_A and π_B with respective d -spacings of $\pi_A = 3.38 \pm 0.01$ Å and $\pi_B = 3.67 \pm 0.01$ Å for the neat film and $\pi_A = 3.39 \pm 0.01$ Å and $\pi_B = 3.69 \pm 0.01$ Å for the blend film. We similarly attribute the slightly longer d -spacing to interruption from C60.

Tracking the relative scattering intensity of π_A and π_B as the film grows, we observe a change from a 1:1 ratio of the neat film to a dominance of π_B in the blend that increase as the film grows before possibly reaching a plateau towards the end of recorded film growth. We hypothesise that the increased disorder in the blend may result in a reduction in unit cell symmetry leading to the reduction in scattering attributable to $\pi_A - \pi_A$ stacking.

We do not observe any SIPs and change in relative strain as the film grows is minimal at less than 1%. We attempt to classify the growth modes of both the neat film and the blend film using both the relative positions of split OoP Bragg features as well as anti-Bragg scattering. From the approaching split peaks and the lack of anti-Bragg oscillations, we tentatively hypothesise the blend film as growing by 3D Volmer-Weber growth. This is further supported by the emergence of OoP Bragg features prior to the emergence of $\pi - \pi$ features. We consider the case of the pure film to be more complex, with the anti-Bragg scattering possibly indicating the initial imperfect layer-by-layer growth for the first ML, followed by island growth. The split peak analysis as well as observations of the relative emergence of OoP and IP features as the neat film grows could possibly support this hypothesis, although we express uncertainty about the explanation.

Lastly, we highlight the splitting into three of the primary OoP feature with two analogues appearing rotated $\sim 10^\circ$ rotated around the azimuth. We hypothesise this could be due to crystalline symmetry, but we cannot fully explain the phenomenon at the present time.

9 | Small angle neutron scattering of Carbon Nanotube:Polymer thin film systems

SANS has been used to study CNT-composite systems using a variety of physical models to describe their often fractal-like structure across multiple length scales. In this chapter, we seek to use SANS to study the microstructure of CNT:Polymer based anode films and to establish the relationship between processing conditions, microstructural properties and the electronic FoM. We first study CNT:Polymer systems manufactured using EVA polymers with varying melt indices. This is used as an opportunity to compare the viability of a range of different models often applied to CNT-based systems and compare their structure to the FoM. After a thorough discussion of the models, we establish the simpler power-law models as the most appropriate. We then use these models to describe CNT:Polymer systems manufactured using different mixing methods. Using the model results, we link their packing structure as quantified by their Porod exponent to the FoM. We thus demonstrate how SANS can be used to establish processing-property relationships of CNT:Polymer films for OPV anode applications whilst highlighting the complexities of the data analysis.

9.1 Applied models

In the following section, we will introduce the physical models that apply to the studied CNT:P systems. As will be demonstrated in subsequent sections, our CNT:P systems display scattering that generally appears as being linear in a Porod plot ($\log(Q)$ vs $\log(I)$), that is $I \propto q^{-power}$, a clear indicator of fractal systems (Fig. 9.1). CNT:Polymer systems often manifest as fractal systems as reported in literature [59, 60, 100]. When viewed as fractal systems, the Porod exponent guid-

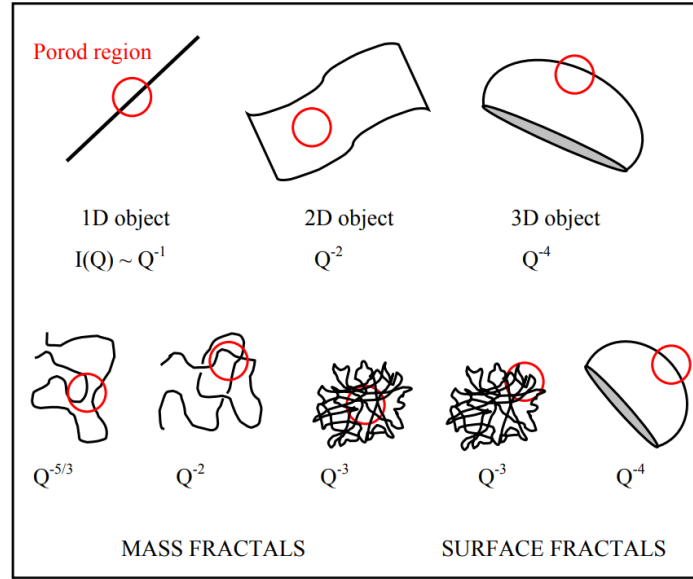


Figure 9.1: Overview of the Porod exponent behaviour of various types of objects. The red ring signifies the region which is being probed by small angle scattering. Copied from reference [101] by B. Hammouda.

ing this relation ranges between 1 and 3 for mass fractal systems, with a higher exponent representing a more densely packed mesh where scattering arises from contrast between the strands that compose the mesh and the voids between them or matter with different SLD. In surface fractal system, the bulk is sufficiently dense and thus homogenous SLD-wise that scattering primarily arises from the jagged surface of the scattering objects. There, the exponents range between 3 (rough surfaces) and 4 (smooth surfaces). The following models are explored:

9.1.1 The Beaucage model

The Beaucage model is defined as [102]

$$I(Q) = background + \sum_{i=1}^N \left[G_i \exp -\frac{q^2 R_{gi}^2}{3} + B_i e^{-\frac{q^2 R_{gi}^2}{3}} \left(q \operatorname{erf} \left(\frac{q R_{gi}}{\sqrt{6}} \right)^{3P_i} \right) \right], \quad (9.1)$$

where G_i and B_i are scaling factors for the Guinier and Porod terms respectively, R_{gi} is the Radius of Gyration and P_i is the Porod exponent. i indexes the N different structural levels from which scattering arises.

A similar model to the Guinier-Porod model described below, the Beaucage model allows for multiple levels of fractal systems with different R_g and Porod exponents to be described simultaneously [100]. The model is often used to describe CNT:P composites. Tehrani *et al.* uses the model to describe a CNT:(PEDOT:PSS) composite system studied via SANS and Ultra-SANS (USANS) [59]. Here, a total of five structural levels are investigated to describe a hierarchical structure ranging from fibrils to bundles to flocs. A general weakness of the model of the is the requirement of $4N + 1$ fitting parameters. A large number of fitting parameters increase the risk of overfitting and makes computation more difficult.

9.1.2 The Guinier-Porod model

The Guinier-Porod model is described as

$$I(Q) = \begin{cases} \frac{G}{Q^s} e^{-\frac{Q^2 R_g^2}{3-s}}, & Q \leq Q_1 \\ \frac{D}{Q^m}, & Q \geq Q_1, \end{cases} \quad (9.2)$$

where G and D are scaling factors of Guinier and Porod terms where $D = G \exp \frac{-Q_1^2 R_g^2}{3-s} Q_1^{m-s}$ to ensure continuity, $Q_1 = \frac{1}{R_g} \sqrt{(m-s)(3-s)/2}$ is defined as the cross-over between the Guinier and Porod regimes, R_g is the Radius of Gyration, s is a dimensionality factor of the scattering objects relation to the degree of symmetry ($s = 0$ for (3D symmetric) spheres, $s = 1$ for 2D symmetry objects such as e.g. cylinders and $s = 2$ for 1D symmetry objects such as platelets) and m is the Porod exponent.

The Guinier-Porod model is an empirical model developed by B. Hammouda describing power law (fractal) systems that accounts for symmetry dimensionality

of the scattering objects [103]. Whilst it can be expanded to describe multiple dimensions of asymmetric objects (e.g. the length and width of a cylinder), it does not allow for the description of multiple 'levels' of fractal systems. It seeks to improve on the Beaucage model which B. Hammouda declares as having an artefact at the transition between the modelled Guinier and Porod regimes. The artefact arises due to B_i , the scaling factor for the Porod term, being allowed to vary indecently of G_i , the scaling factor for the Guinier term, in the Beaucage model (see Eq. 9.1). This can result in an erroneous kink in the slope of the Porod region when using the Beaucage model. The Guinier-Porod model does not share this shortcoming, as the scaling factors of the Guinier and Porod terms are linked.

9.1.3 Scale factor models

Power law models are simple models described as

$$I(Q) = A \cdot Q^{-P_1} + background, \quad (9.3)$$

for one level and for two levels as

$$I(Q) = \begin{cases} Scale(AQ^{-P_1}) + background, & Q \leq Q_c \\ CQ^{-P_2}, & Q > Q_c, \end{cases} \quad (9.4)$$

where $Scale$, A , C are scale factors and P_1 , P_2 are Porod exponents. C is defined $C \frac{AQ_c^{P_2}}{Q_c^{P_1}}$. The scale power models are a simple way to describe fractal systems with one or two apparent hierarchical levels where no low- Q Guinier region is apparent in the scattering.

9.1.4 The Mass Fractal model

The Mass Fractal model is described as

$$\left\{ \begin{array}{l} I(Q) = scale \times P(Q)S(Q) + background, \\ P(Q) = F(QR)^2, \\ F(x) = \frac{3[\sin(x) - x \cos(x)]}{x^3}, \\ S(Q) = \frac{\Gamma(D_m - 1)\zeta^{D_m - 1}}{[1 + (Q\zeta)^2]^{(D_m - 1)/2}} \frac{\sin[(D_m - 1) \tan^{-1}(Q\zeta)]}{q}, \\ scale = kNV^2 (\rho_A - \rho_B)^2, \\ V = \frac{4}{3}\pi R^3, \end{array} \right. \quad (9.5)$$

where R is the radius of the basic unit of the fractal, D is the mass fractal dimension, ζ is the cut-off length corresponding to a coherence length at which the fractal principle of scale invariance is limited by finite aggregation size and $\rho_{A,B}$ correspond to the SLDs of the assumed two-component system.

This corresponds to a different way of approaching a physically fractal system, where, instead of being described by a mesh density, the model is developed from the concept of an aggregating smallest unit which is clustered in a way that exhibits self-similarity at successive length scales [100].

9.2 Guinier analysis

In addition to analysis with specific models, Guinier analysis of the scattering is also carried out through the use of a so-called Guinier plot. In a Guinier plot $\ln(I(Q))$ is plotted against Q^2 to highlight the Guinier regime of scattering. At the lower Q^2 range, a linear trend should be observed from which the Radius of Gyration R_g can be fitted from the slope. A Guinier plot is valid for the region

where $QR_g \leq \sqrt{3}$ [101].

9.3 Melt index variation of EVA polymer

Ethylene-vinyl acetate (EVA) is a co-polymer of ethylene and vinyl acetate (the n and m unit shown in Fig. 5.8, respectively). By varying the ratio of ethylene and vinyl acetate monomers the mechanical and chemical properties of CNT:P films can be tuned. A way to quantify the polymer chain length is via the melt index which is inversely related to the molecular weight and thus polymer chain length. A lower melt index i.e. longer polymer chains will result films with higher viscosity, higher chemical resistance and improved mechanical properties, but worse solubility and processability [65]. A SANS study of CNTs mixed with four different variations of EVA and thus melt index was conducted to relate the microstructure as probed by SANS with the effect on performance as detailed in [65]. The four different compositions are shown under the names 4355, 40L-03, 40W and 4320 in Tab. 9.1, which is repeated here for the ease of the reader. We note that the polymer melt index is not determined solely by vinyl acetate content, but also by additives included in the polymer synthesis process. The films, as are all CNT:P films in this chapter, each have thicknesses of around 200 nm, yielding a total configuration thickness of 2 μm organic material for 10 stacked films.

Name	CNT type	CNT conc. [g/L]	Mixing	Polymer	Poly. conc. [g/L]	Poly. remo. #	Tube diameter [nm]	Tube length [μ m]	VA content [wt%]	Poly. melt index
SFMx1S	Tuball	0.5	6h SFM	Elvax 150	4	1x	1.6 $\pm$ 0.4	>5	32	43
SFMx2	Tuball	0.5	6h SFM	Elvax 150	4	2x	1.6 $\pm$ 0.4	>5	32	43
TipSonx0	Tuball	0.5	10min tip son.	Elvax 150	5	0x	1.6 $\pm$ 0.4	>5	32	43
TipSonx1	Tuball	0.5	10min tip son.	Elvax 150	5	1x	1.6 $\pm$ 0.4	>5	32	43
TipSonx2	Tuball	0.5	10min tip son.	Elvax 150	5	2x	1.6 $\pm$ 0.4	>5	32	43
4355	Tuball	0.25	10min tip son.	Elvax 4355	2.5	1x	1.6 $\pm$ 0.4	>5	25	5.7
40L-03	Tuball	0.25	10min tip son.	Elvax 40L-03	2.5	1x	1.6 $\pm$ 0.4	>5	40	3
40W	Tuball	0.25	10min tip son.	Elvax 40W	2.5	1x	1.6 $\pm$ 0.4	>5	40	52
4320	Tuball	0.25	10min tip son.	Elvax 4320	2.5	1x	1.6 $\pm$ 0.4	>5	25	150

Table 9.1: Composition and manufacturing specifications of the studied carbon nanotube:polymer thin film systems. "Name" refers to handle by which they are referred to in this thesis. "CNT type" refers to their manufacturer label of the carbon nanotubes. "Polymer" is likewise the manufacturer label of the ELVAX (DuPont) branded EVA type polymers. "VA content" is the vinyl acetate content.

The studied films span from low over medium to high melt indices relative to the range of EVA. Scattering data in this chapter is not normalised to film thickness. The scattering curves of the four compositions are shown together in Figure 9.2 to emphasise the apparent change in scattering. The same scattering curves are shown with vertically shifted intensities and with associated fits in Figure 9.3 to allow the reader to better discern each curve. We note the data intensity data range in these plots have been limited to not fully include outlier points and their associated uncertainties near the high and low- Q limits for better visual representation. These data points are shown in completeness when each data series is discussed in isolation. All four scattering curves appear (Fig. 9.2, Fig. 9.3) as linear in a

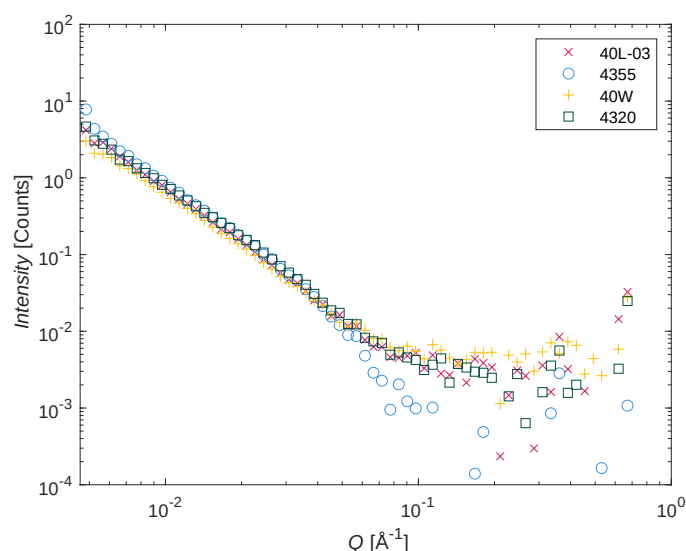


Figure 9.2: Log-log plot of small angle neutron scattering intensities of the 40L, 4355, 40W and 4320 carbon nanotube:polymer systems. Errorbars are omitted for easier comparison, but shown in Fig. 9.3.

log-log plot. This is typical of CNT systems showing multi-scale self-similarity i.e. fractal growth. All four intensity curves look similar with the 4355 SANS pattern showing a lower background level at the high- Q limit and potentially a higher slope at the low- Q limit, although this could be within statistical variation.

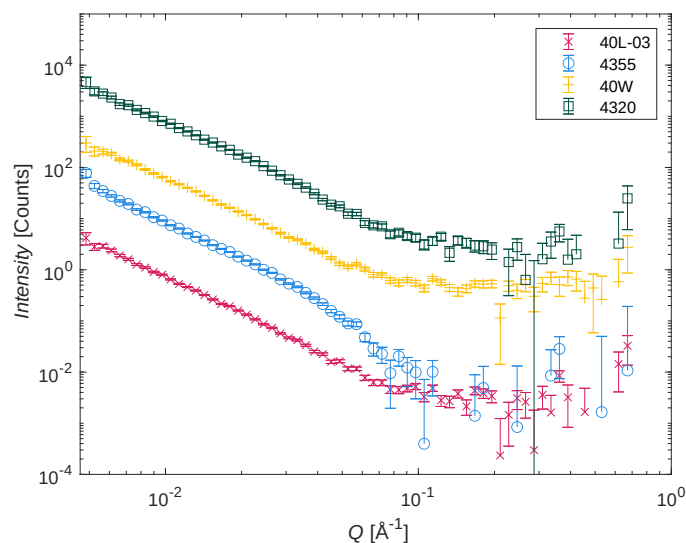


Figure 9.3: Log-log plot of small angle neutron scattering intensities of the 40L, 4355, 40W and 4320 carbon nanotube:polymer systems. Intensities are vertically shifted for easier distinction.

9.3.1 Guinier analysis

A Guinier plot of the four samples with varied polymer melt indices is shown in Fig. 9.4. The Guinier plot shows no linear regime at the low- Q limit for any of the four configurations. Instead, the scattering intensities curve upwards with no sign of flattening. This suggests that the accessed Q -range is insufficient to ascertain the R_g of the probed systems. As a Guinier plot is valid for the region where $QR_g \leq \sqrt{3}$ and the lower Q -limit of the experimental data is $0.0045 \text{ \AA}^{-1}$, this suggests a lower bound of the $R_g = 38.5 \text{ nm}$.

9.3.2 Structural analysis

The four models outlined in Sec. 9.1 are applied to each of the four CNT:P systems with varied polymer composition. Data is fitted in the range $0.0055 - 0.3 \text{ \AA}^{-1}$. This is done to avoid the inclusion of outlier points near the low- Q data limit, such as the extreme case in Fig. 9.7. The fits use a flat background fitted

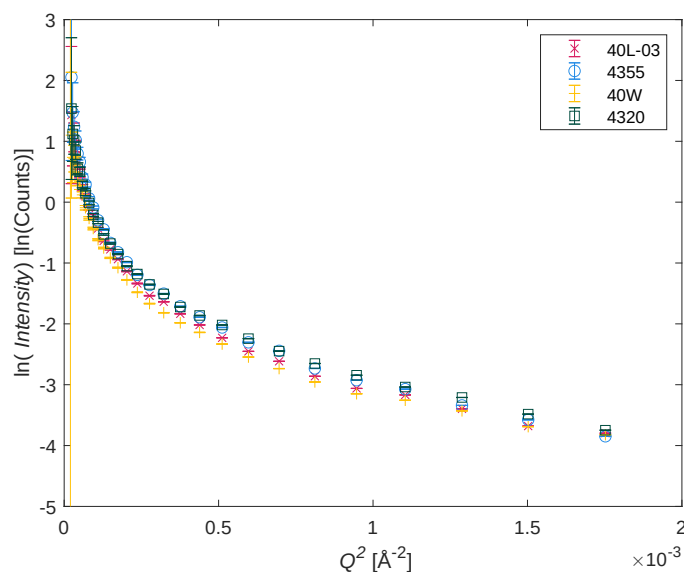


Figure 9.4: Guinier plot of small angle neutron scattering intensities of the 40L, 4355, 40W and 4320 carbon nanotube:polymer systems.

from the $0.1 - 0.3 \text{ \AA}^{-1}$ range. This approach is chosen to minimise the impact of noisy data points towards the high- Q data limit.

Figure 9.5 shows the scattering of 40L-03 and its applied fits, Figure 9.6 shows the scattering of 4355 and its applied fits, Figure 9.7 shows the scattering of 40W and its applied fits and Figure 9.8 shows the scattering of 4320 and its applied fits. The fitted models are extended to $4 \times 10^{-4} \text{ \AA}^{-1}$ to show how each model would predict an extension to a lower Q -range. For each system (Fig. 9.5, Fig. 9.6, Fig. 9.5, Fig. 9.8) all four models appear to closely match the data with small differences arising as the fits reach the high- Q noise limit around $0.1 \text{ \AA}^{-1}$. However, as this regime of the data is inherently noisy, it is difficult to draw conclusions with regard to the suitability of each model. The models differ in the predicted predicted scattering behaviour below the low- Q limit of the data. This will be discussed in conjunction with each applied model.

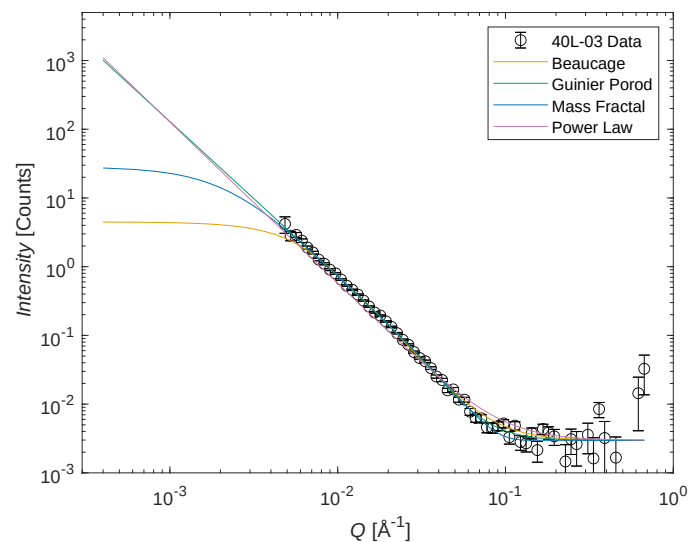


Figure 9.5: Log-log plot of small angle neutron scattering of the carbon nanotube:40L-03 system with Beaucage, Guinier-Porod, Mass Fractal and Power Law fits.

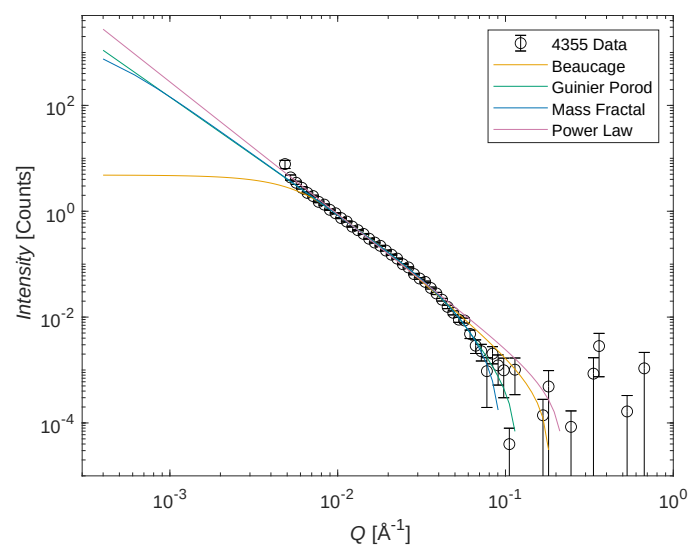


Figure 9.6: Log-log plot of small angle neutron scattering of the carbon nanotube:4355 system with Beaucage, Guinier-Porod, Mass Fractal and Power Law fits.

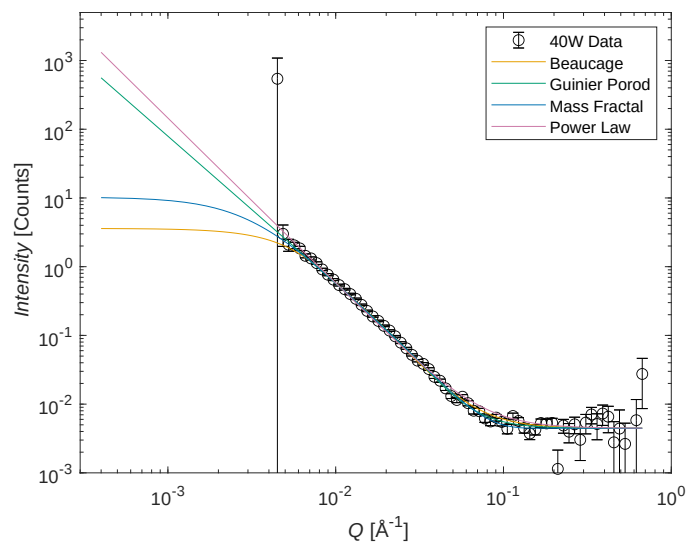


Figure 9.7: Log-log plot of small angle neutron scattering of the carbon nanotube:40W system with Beaucage, Guinier-Porod, Mass Fractal and Power Law fits.

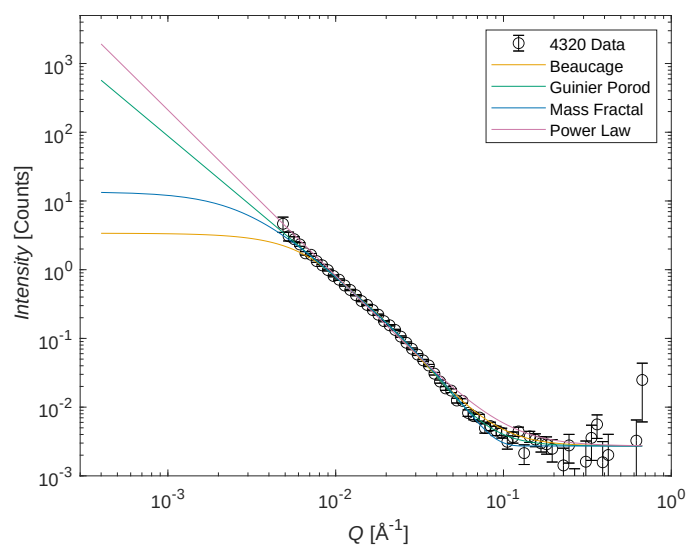


Figure 9.8: Log-log plot of small angle neutron scattering of the carbon nanotube:4320 system with Beaucage, Guinier-Porod, Mass Fractal and Power Law fits.

9.3.3 Beaucage model

Table 9.2 shows fitted values using the Beaucage model. For the Beaucage model, representative correlation and uncertainty plots are shown in Fig. 9.9 and Fig. 9.10, respectively. For the Beaucage model the representative Fig. 9.10 show

Name	40L-03	4355	40W	4320
<i>Scale</i>	1	1	1	1
<i>Background</i> [$\times 10^{-3}\text{cm}^{-1}$]	2.97	-0.361E-04	4.46	2.78
R_g [$\text{\AA}$]	270 ± 10	258 ± 8	280 ± 20	233 ± 8
P	2.74 ± 0.03	2.76 ± 0.02	2.67 ± 0.03	2.78 ± 0.03
B [10^{-6}cm^{-1}]	3.2 ± 0.3	3.5 ± 0.3	3.4 ± 0.4	3.3 ± 0.4
G [cm^{-1}]	4.5 ± 0.4	4.8 ± 0.3	3.6 ± 0.4	3.4 ± 0.2
χ^2	2.2339	3.8697	1.7035	2.5503

Table 9.2: Beaucage fit parameters of 40L, 4355, 40W and 4320 carbon nanotube:polymer systems.

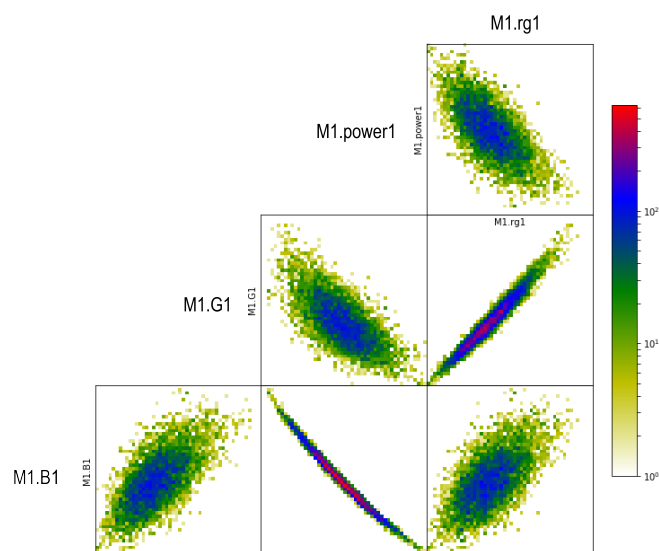


Figure 9.9: Fitting parameters correlations of 40L fitted with the Beaucage model. The shown parameters map as follows to the coefficients in Eq. 9.1: $M1.B1 \hat{=} B$, $M1.G1 \hat{=} G$, $M1.power1 \hat{=} P$ and $M1.rg1 \hat{=} R_g$.

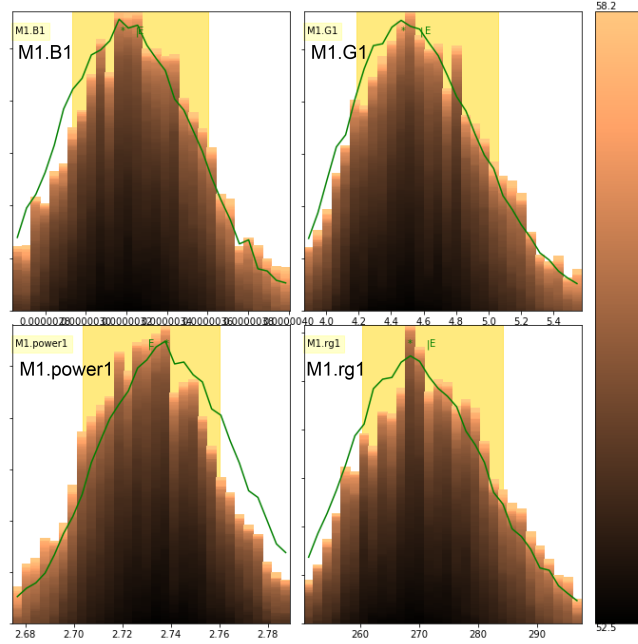


Figure 9.10: Ensemble uncertainties of 40L fitted with the Beaucage model. The shown parameters map as follows to the coefficients in Eq. 9.1: $M1.B1 \hat{=} B$, $M1.G1 \hat{=} G$, $M1.power1 \hat{=} P$ and $M1.rg1 \hat{=} R_g$.

each parameter ensemble uncertainty to be smoothly peaked with the green best value trace matching well. Fig. 9.9 show most cross-correlations to be relatively blob-like whilst also showing clear (anti)-correlations, with $B \times P$ and $G \times R_g$ being strongly correlated due being part of the same term in Eq. 9.1.

Tab. 9.2 show fitted values of R_g vary between 23.3 ± 0.8 nm for the 4320 and 28 ± 2 nm for the 40W. In each case, the fitted value is above the lower threshold determined in Sec. 9.3.1. There does not appear to be any clear relationship between melt index and fitted R_g . Similarly, the fitted Porod exponent P varies between 2.67 ± 0.03 and 2.78 ± 0.03 with the similar values being well in line with the visually similar intensity curves in Fig. 9.2. The lowest Q data points are not included in the fit where the fit can be seen to undershoot the data points slightly. Here, the predicted plot below the lowest Q data range the fitted curves are seen to flatten and enter the Guinier regime immediately before the fitted range.

9.3.4 Guinier-Porod model

Table 9.3 shows the fitted values using the Guinier-Porod model. For the Guinier-Porod model, representative correlation and uncertainty plots are shown in 9.11 and Figure 9.12, respectively. For the Guinier-Porod model the representative

Name	40L-03	4355	40W	4320
Scale [$\times 10^{-5}$]	2.5 ± 0.4	3.2 ± 0.3	3.1 ± 0.6	6.7 ± 0.8
Background [$\times 10^{-3} \text{cm}^{-1}$]	2.97	-0.361	4.46	2.78
R_g [$\text{\AA}$]	14 ± 2	14.8 ± 0.8	16 ± 2	19 ± 1
s	2.24 ± 0.04	2.22 ± 0.02	2.13 ± 0.04	2.04 ± 0.03
P	3.2 ± 1.1	4.1 ± 1.8	3.1 ± 0.6	3.3 ± 0.1

Table 9.3: Guinier-Porod parameters of 40L, 4355, 40W and 4320 CNT:P systems

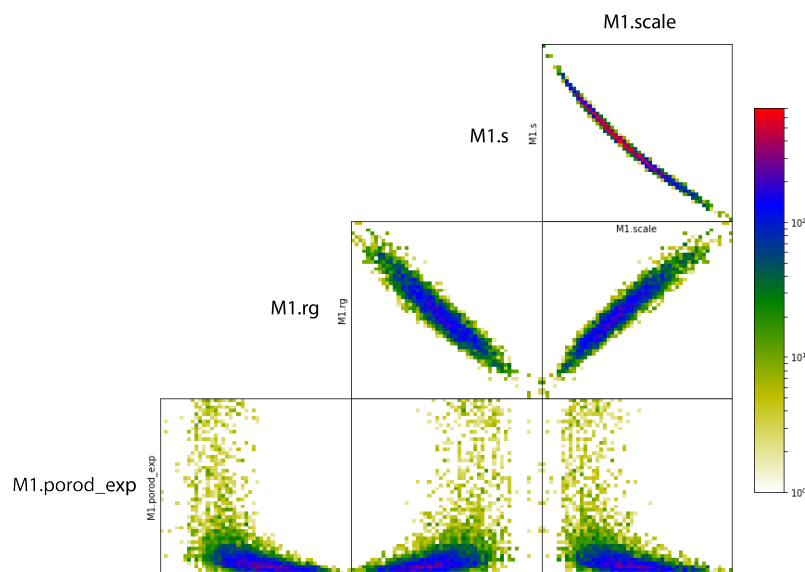


Figure 9.11: Fitting parameters correlations of 40L fitted with the Guinier-Porod model. The shown parameters map as follows to the coefficients in Eq. 9.2: $M1.porod_exp \hat{=} m$, $M1.rg \hat{=} R_g$, $M1.s \hat{=} s$ and $M1.scale \hat{=} G$.

Fig. 9.12 show the Porod exponent to be peaked above 3 with a long tail towards higher values. This tail exists for all four systems in varying magnitudes. The

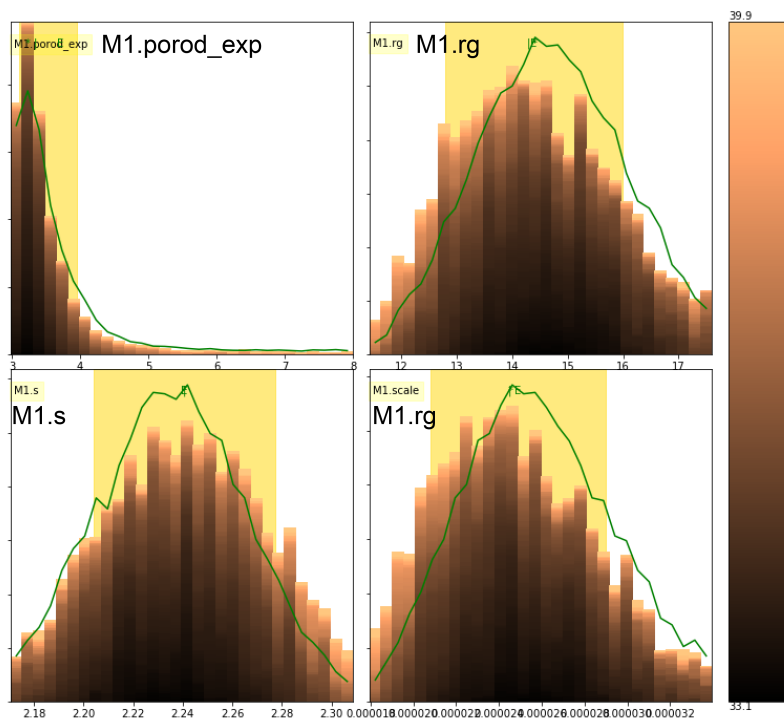


Figure 9.12: Ensemble uncertainties of 40L fitted with the Guinier-Porod model. The shown parameters map as follows to the coefficients in Eq. 9.2: $M1.porod_exp \hat{=} m$, $M1.rg \hat{=} R_g$, $M1.s \hat{=} s$ and $M1.scale \hat{=} G$.

other three fitted parameters smoothly peaked ensemble uncertainties and relatively well matched value traces. Fig. 9.11 show most parameters to be highly cross-correlated, but meaningfully fitted. The long tail of P ensemble is evident in bottom the row representing P .

The fitted radii of the four systems vary between 1.4 ± 0.2 and 1.9 ± 0.1 nm, more than a magnitude less than those of the Beaucage model. Here, a higher fitted R_g is possibly concomitant with increased melt index. However, this would be below the lower R_g limit as determined by the Guinier plot analysis in Sec. 9.3.1. The symmetry dimension variable s varies between 2.04 ± 0.03 at a higher melt index and 2.24 ± 0.04 at a lower melt index which would indicate a 'below 1D' symmetry of the scattering objects. The Porod exponent varies from 3.1 ± 0.6 to 4.1

± 1.8 , however the fitted P values are associated with significant uncertainty as was also reflected in the uncertainty plot, so it is unclear to what degree the fitted values can be taken as meaningfully different. For each of the four systems, the extrapolated Guinier-Porod model is seen to continue with the same slope towards the beyond the low- Q range.

9.3.5 Mass Fractal model

Table 9.4 shows the fitted values using the Mass Fractal model. For the Mass Fractal fit, two types of qualitatively different correlation plots are shown in Figures 9.13 and 9.15. The associated uncertainty plots are shown in Figure and Figure 9.14 and 9.16, respectively. For the Mass Fractal model, Fig. 9.14 and 9.16

<i>Name</i>	40L-03	4355	40W	4320
<i>Scale</i> [$\times 10^{-5}$]	2.32	3.49	1.87	3.74
<i>Background</i> [$\times 10^{-3} \text{ cm}^{-1}$]	2.97	-0.361	4.46	2.78
<i>Radius</i> [$\text{\AA}$]	31 ± 2	35 ± 1	28 ± 3	34 ± 2
<i>D</i>	2.29 ± 0.02	2.23 ± 0.02	2.28 ± 0.05	2.20 ± 0.04
ζ [$\text{\AA}$]	432 ± 2930	2967 ± 2656	306 ± 3156	326 ± 3167
χ^2	1.6331	1.4085	1.2934	1.6783

Table 9.4: Mass Fractal fit parameters of 40L, 4355, 40W and 4320 CNT:P systems.

show the two different qualitative outcomes of the ensemble uncertainties. In the first case, the cut-off length ζ is shown to have a flat distribution of found values indicating the parameter is poorly fitted, whilst the other parameters appear as smoothly peaked distributions with shifted best value traces. In the second case, ζ is seen to have its distribution sharply peaked at singular value with a broad distribution towards higher values. For the other three parameters, a bimodal clustering of ensemble values is seen. In accordance, Fig. 9.13 and Fig. 9.15 show ζ to appear with broadly smeared cross-correlations with the other three parameters

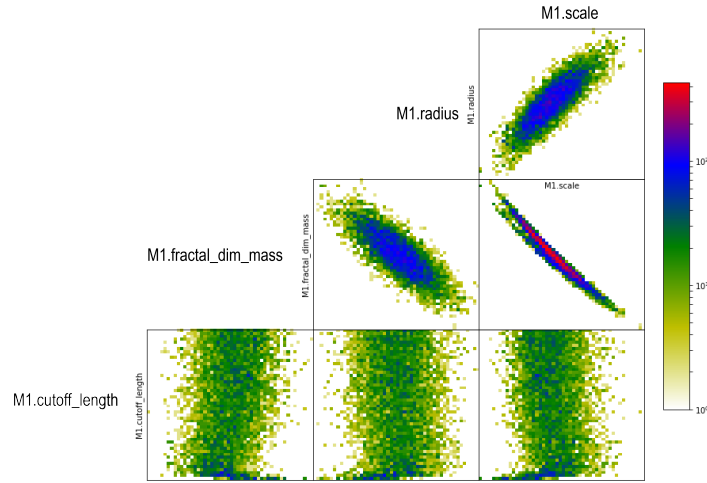


Figure 9.13: Fitting parameters correlations of 40L fitted with the Mass Fractal model. The shown parameters map as follows to the coefficients in Eq. 9.5: $M1.cutoff_length \hat{=} \zeta$, $M1.fractal_dim_mass \hat{=} D$, $M1.radius \hat{=} R$ and $M1.scale \hat{=} scale$.

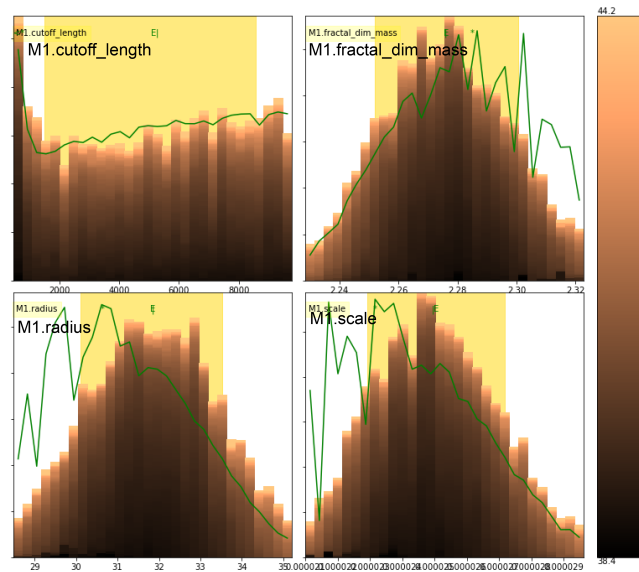


Figure 9.14: Ensemble uncertainties of 40L fitted with the Mass Fractal model. The shown parameters map as follows to the coefficients in Eq. 9.5: $M1.cutoff_length \hat{=} \zeta$, $M1.fractal_dim_mass \hat{=} D$, $M1.radius \hat{=} R$ and $M1.scale \hat{=} scale$.

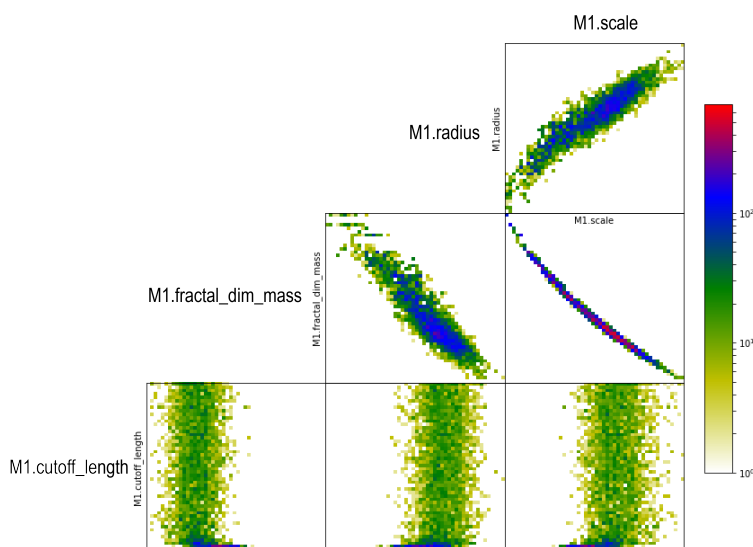


Figure 9.15: Fitting parameters correlations of 40W fitted with the Mass Fractal model showing bimodal ensemble distributions. The shown parameters map as follows to the coefficients in Eq. 9.5: $M1.cutoff_length \hat{=} \zeta$, $M1.fractal_dim_mass \hat{=} D$, $M1.radius \hat{=} R$ and $M1.scale \hat{=} scale$.

with an intense tail. The three other parameters appear as highly correlated.

The fitted cut-off lengths ζ vary from 30.6 ± 316 nm to 296.7 ± 266 nm with large uncertainties. Together with the prior discussed plots, this suggests the cut-off length is not meaningfully described. The fitted radii of the four systems vary from 2.8 ± 0.3 nm to 3.5 ± 0.1 nm with (near) overlapping uncertainties with the similar values being well in line with the visually similar intensity curves in Fig. 9.2. This would be equal to roughly twice the tube diameter (Table 9.1). The Mass Fractal dimension D varies from 2.20 ± 0.04 to 2.29 ± 0.02 and is thus roughly constant across melt index. For three of the four systems, the extrapolated Guinier-Porod exponent is seen to taper off into the Guinier regime below the low- Q data points although at a higher intensity than those of the Beaucage models. The exception is the model for the 4355 where the modelled low- Q continues with the same slope as for the data points. This is likely due to the fitted

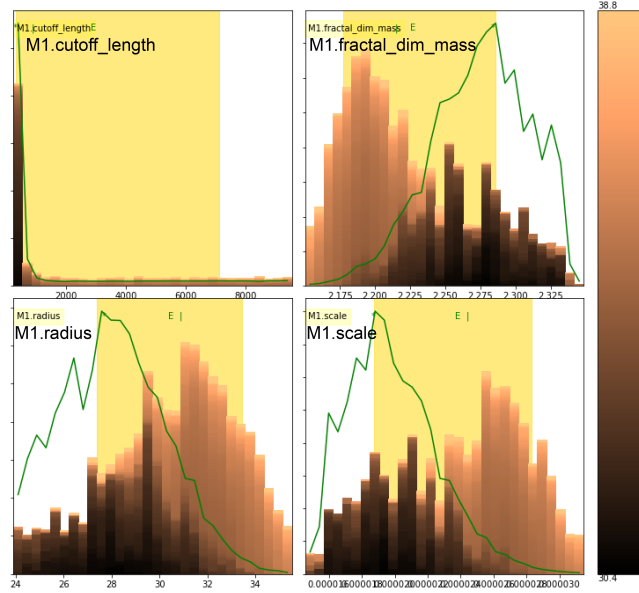


Figure 9.16: Ensemble uncertainties of 40W fitted with the Mass Fractal model showing bimodal ensemble distributions. The shown parameters map as follows to the coefficients in Eq. 9.5: $M1.cutoff_length \hat{=} \zeta$, $M1.fractal_dim_mass \hat{=} D$, $M1.radius \hat{=} R$ and $M1.scale \hat{=} scale$.

ζ of this system which is around 10 times higher than those of the other systems, albeit this is not taken to represent a physically meaningful difference.

9.3.6 Power law model

Table 9.5 shows the fitted values using the Power Law model. For the Power law model, representative correlation and uncertainty plots are shown in Figure 9.17 and Figure 9.18, respectively. For the Power Law model the representative Fig.

Name	40L-03	4355	40W	4320
$A [\times 10^{-5}]$	1.15 ± 0.06	0.88 ± 0.04	0.90 ± 0.05	1.21 ± 0.05
$Background [\times 10^{-3} \text{cm}^{-1}]$	2.97	-0.361	4.46	2.78
$Power$	2.35 ± 0.01	2.50 ± 0.01	2.40 ± 0.01	2.41 ± 0.01
χ^2	1.6331	7.817	4.219	9.0223

Table 9.5: Power Law fit parameters of 40L, 4355, 40W and 4320 CNT:P systems.

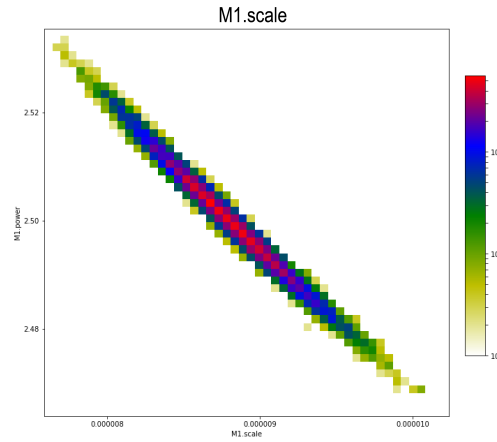


Figure 9.17: Fitting parameters correlations of 4355 fitted with the Power Law model. The shown parameters map as follows to the coefficients in Eq. 9.3: $M1.power \hat{=} P_1$ and $M1.Scale \hat{=} A$.

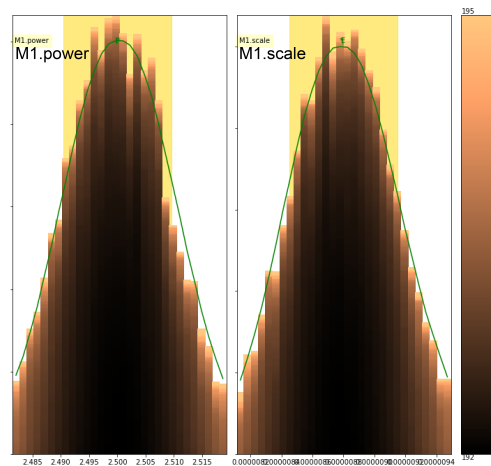


Figure 9.18: Ensemble uncertainties of 4355 fitted with the Power Law model. The shown parameters map as follows to the coefficients in Eq. 9.3: $M1.power \hat{=} P_1$ and $M1.Scale \hat{=} A$.

9.18 shows the two parameters to have smoothly peaked ensemble uncertainties with well-fitting best value trace lines. Fig. 9.17 show the two parameters to be highly (anti)correlated which is expected due to the low amount of fitable parameters in the model.

The fitted Porod exponents vary from 2.35 ± 0.01 to 2.50 ± 0.03 with the similar

values being well in line with the visually similar intensity curves in Fig. 9.2. There is no clear relation between melt index and fitted Porod exponent. For each of the four systems, the extrapolated Power Law model is seen to continue with the same slope towards the beyond the low- Q range.

9.3.7 Model comparison

A structural analysis of CNT:P systems with four different polymers with different melt indices using SANS was carried out in Secs. 9.3.2 and 9.3.1. Analysis of the SANS data using different fitting models shows the four systems to have no meaningful differences based on the parameters probe-able by SANS given the current Q -range. A major limitation on the analysis is due to limited Q -range which results in the Guinier regime not being accessible. As such, only a lower bound of 38.5 nm could be imposed on the R_g . This limit is about 2.5 times those found using the Guinier-Porod model indicating this model is not fully suitable to describe the studied CNT:P systems. The R_g values found by the Beaucage model are well above the described lower limit, but as seen in Figs. 9.5, 9.6, 9.7 and 9.8 the models reach their maximum likelihood assuming the Guinier regime begins almost immediately below the lower Q -limit of data, already beginning to diverge from the lower Q data points. This assumed position of the Guinier regime is a weakness with regard to the suitability of the Beaucage model for the given data. Similarly, the cut-off length ζ (Tab. 9.4) found using the Mass Fractal model is seen to not be well determined. The limitations on the other three models due to the limited Q -range leads us to favour the Power Law model as it is a simple model where the Porod exponent P can be determined without influence of an assumed position of the Guinier regime which potentially influences the determination of the Porod exponent and fractal dimension of the Guinier-Porod and Mass Fractal models.

Table 9.6 shows the fitted values of the P using Power Law models, $[\sigma_{dc}/\sigma_{op}]$, the FoM, as well as and melt index for the 4355, 40L-03, 40W and 4320 carbon nanotube:polymer systems. The FoM of each film has been experimentally determined by B. Sturdza. All CNT:P system appear to to be mass fractals based

Polymer	P	Melt index	FoM
40L-03	2.35 ± 0.01	3	1.19
4355	2.50 ± 0.01	5.7	1.22
40W	2.40 ± 0.01	52	1.83
4320	2.41 ± 0.01	150	1.60

Table 9.6: Fitted values of the Porod exponent P , $[\sigma_{dc}/\sigma_{op}]$, the Figure of Merit, as well as and melt index for the 4355, 40L-03, 40W and 4320 carbon nanotube:polymer systems.

on their Porod exponent, with similar packing densities that bear no clear relation to melt index or the device relevant FoM. This suggests that, for the length range probed, the structural information determined by SANS does not show a meaningful link between the melt index of the used polymer and the FoM. A connection could possibly be found by extending the probed Q -range using different neutron sources such as beamline SANS2D at ISIS to access the potentially differing Guinier-regime of the films. Here, the congruence with the extended fits in Figs. 9.5, 9.6, 9.7 and 9.8 serve as predictions of expected behaviour for the different models. Another possibility is that SANS is not able to describe all influences of varying the melt index of the polymer as this is also includes varying processing additives which influence the electronic behaviour of the films or that differences in packing at shorter length scales (~ 1 nm) dominate difference in behaviour.

Due to the Q -range of studied films in the following being similar and the so-far discussed limitations of the other models, only the simple Power Law model will be used to discuss the SANS scattering of CNT:P systems in the following work.

9.4 Process variation of CNT:P films studied via SANS

An adapted version of the following SANS analysis was published by B. Sturdza *et al.*[65].

In this section, SANS studies of the effect of the processing method of the CNT:P films, either via Shear Force Mixing (SFM) or via tip sonication, as well as the number of polymer removal steps is carried out to relate the microstructure as probed by SANS with the effect on device performance as measured the FoM. The processing methods are outlined in Sec. 5.6. The five different compositions are outlined in Table 9.1 under the names SFMx1, SFMx2, TipSonx0, TipSonx1 and TipSonx2. No Tip sonicated sample with 0x polymer steps was manufactured due to experimental time constraints. The TipSonx1, TipSonx2, SFMx1 and SFMx2 scattering curves appear as linear in the Porod (log-log) plot (Figs. 9.19, 9.20) before reaching the noise regime at around $0.1 \text{ \AA}^{-1}$. The SFM films appear with steeper intensity curves. The TipSonx0 scattering curve appears as having two distinct linear regimes with the high- Q regime having a steeper slope. It reaches the background level around $0.1 \text{ \AA}^{-1}$. The background intensity level is higher than of those where polymer has been removed.

9.4.1 Guinier analysis

A Guinier plot of the five samples with varied manufacturing methods is shown in Figure 9.21. The Guinier plot shows no linear regime at the low- Q limit any of the five configurations. Instead, the scattering intensities curve upwards without signs of flattening. As with the study of polymers with varied melt index, the accessed Q -range is insufficient to ascertain the R_g of the probed systems. $QR_g \leq 3$. As the lower range limit of the data is $0.0052 \text{ \AA}^{-1}$, this corresponds to a lower bound

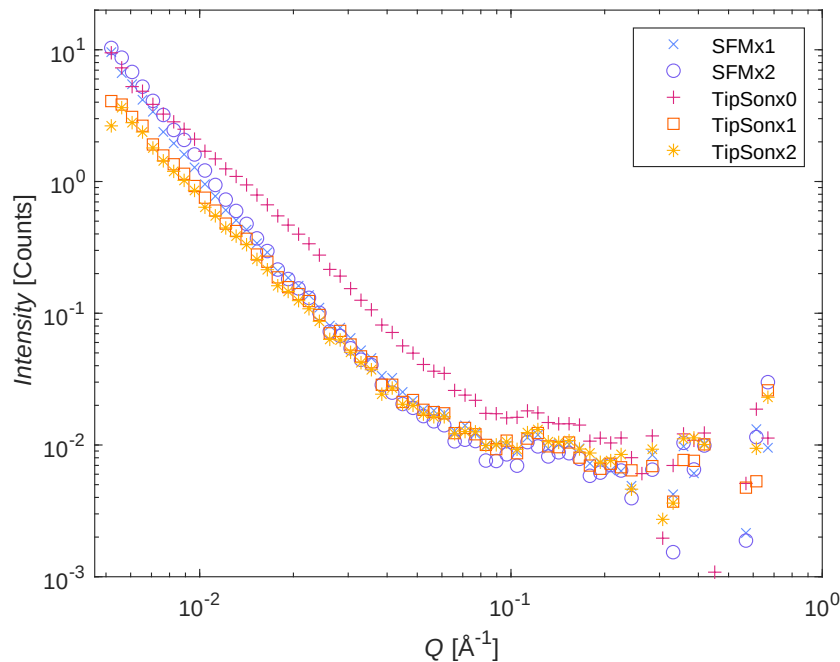


Figure 9.19: Log-log plot of small angle neutron scattering of carbon nanotube:polymer systems manufactured via shear force mixing or Tip sonication with 0, 1x or 2x polymer removal steps. Errorbars omitted for easier comparison, but shown in Fig. 9.20.

of the R_g of 33.3 nm

9.4.2 Structural analysis

The Power Law model (Eq. 9.3) is applied to each of the five compositions. In addition the Two Power Law (Eq. 9.4) is applied to the TipSonx0 due to unsuitability of the (one) Power Law model as will be outlined below. Data is fitted in the range 0.0055 to 0.3 $\text{\AA}^{-1}$ using a flat background fitted from the 0.1 - 0.3 $\text{\AA}^{-1}$. Figure 9.22 show the SANS intensity curves and their applied Power Law fits. Figure 9.23 shows the scattering of the TipSonx0 with one and two Power Law models applied. Table 9.7 shows the fitted values using the Power Law model and Table 9.8 shows the fitted values using the Two Power Model on the TipSonx0 system. Fig. 9.23 shows the one Power Law model applied to TipSonx0 to

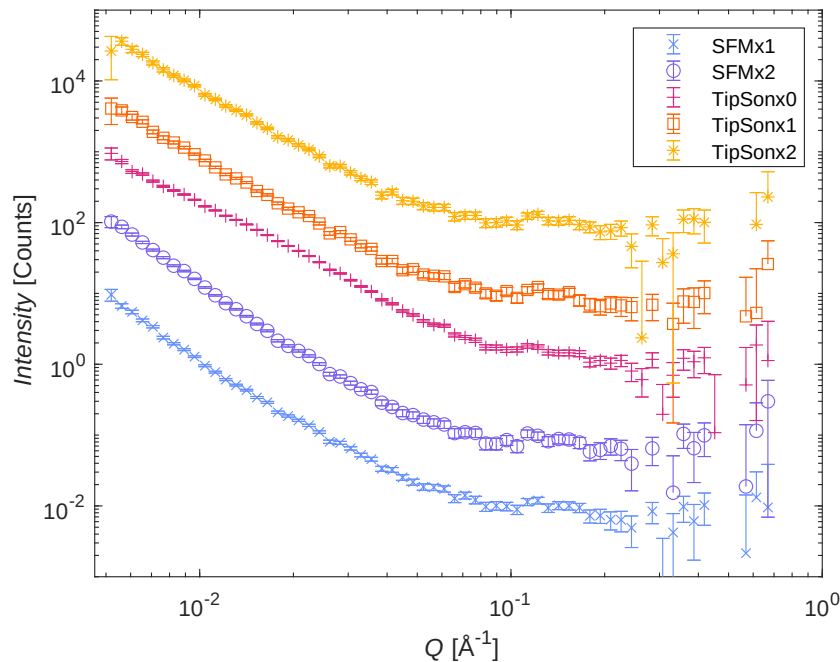


Figure 9.20: Log-log plot of small angle neutron scattering of carbon nanotube:polymer systems manufactured via shear force mixing or Tip sonication with 0, 1x or 2x polymer removal steps. Successive scattering curves are shifted for easier viewing.

Name	SFMx1	SFMx2	TipSonx0	TipSonx1	TipSonx2
$A [\times 10^{-6}]$	3.2 ± 0.2	0.10 ± 0.02	35 ± 1	4.2 ± 0.4	6.5 ± 0.5
Background	0.00851	0.00773	0.01405	0.01003	0.00843
P	2.75 ± 0.02	3.05 ± 0.08	2.37 ± 0.01	2.61 ± 0.02	2.54 ± 0.02
χ^2	2.2791	1.2781	16.198	1.6575	1.4465

Table 9.7: Fit parameters of the shear force mixing and Tip Sonicated systems with 0x, 1x or 2x polymer removal steps using the Power Law Model.

overshoot the intensity of data for both towards the low- Q data range limit and the high- Q noise limit and undershoot in the middle, whereas the Two Power Law fits the data better across those regions. In addition, Tab. 9.7 shows the χ^2 of TipSonx0 to be significantly higher than those of the other systems, whereas for the Two Power Law in Tab. 9.8 the χ^2 is comparable to those of the other system with the One Power Law applied. This suggests a Two Power Law model is the

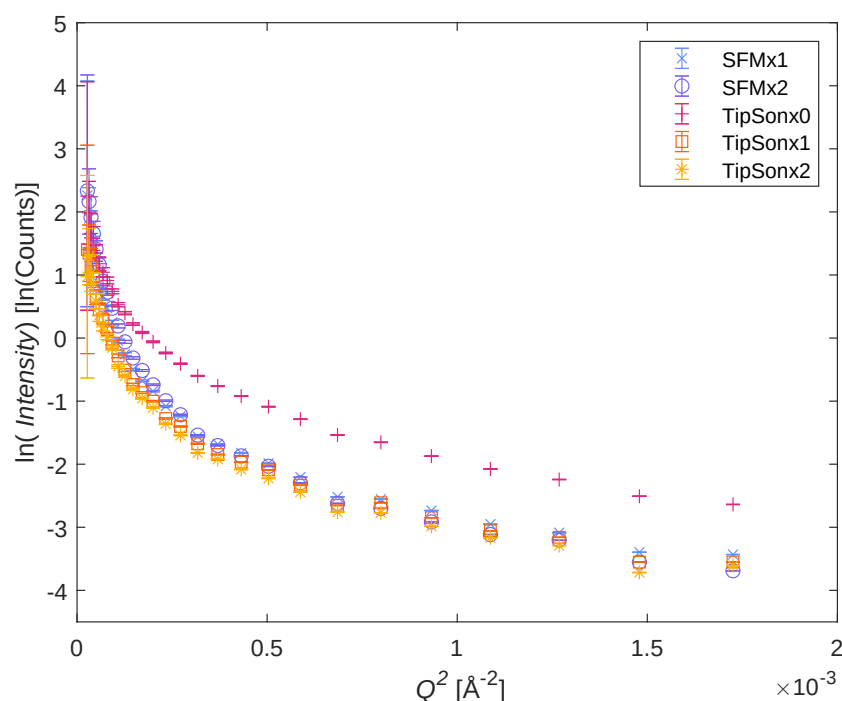


Figure 9.21: Guinier plot of small angle neutron scattering intensities of carbon nanotube:polymer systems manufactured via shear force mixing or Tip sonication with 0, 1x or 2x polymer removal steps.

Name	TipSonx0
Scale [$\times 10^{-4}$]	1.4 ± 0.7
Background	0.014048
A	0.7 ± 0.4
Q_c [$\text{\AA}^{-1}$]	0.023 ± 0.01
P_1	2.13 ± 0.01
P_2	2.95 ± 0.04
χ^2	2.266

Table 9.8: Fitted values of the TipSonx0 carbon nanotube:polymer system using the Two Power Law Model.

more physically appropriate choice for the system, thus indicating two relevant length scales being probed with the given Q -range.

The ensemble uncertainties and cross-correlations for the given systems are similar to those in Fig. 9.18 and Fig. 9.17. The ensemble uncertainties and cross-

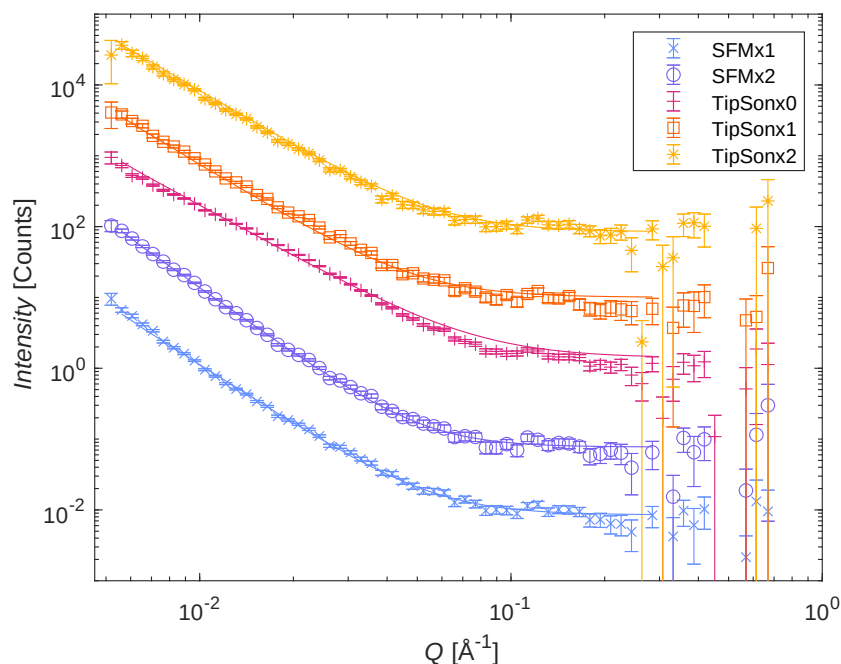


Figure 9.22: Log-log plot of small angle neutron scattering of carbon nanotube:polymer systems manufactured via shear force mixing or Tip sonication with 0, 1x or 2x polymer removal steps. Solid lines represent Power Law model fits (Two Power Law for TipSonx0, One Power Law for the rest).

correlations of TipSonx0 using the Two Power Law model is shown in Figure 9.24 and Figure 9.25, respectively. Fig. 9.24 shows the *scale* and *A* parameters to have broader ensemble distributions where the best value trace (displayed in green) poorly matches the outline of the ensemble values. This is likely due to these two parameters being multiplicative factors in Eq. 9.4. This is also evident in Fig. 9.25 where their cross-correlation show a highly correlated almost line-like shape. The other three 'physical' parameters have smoothly peaked distributions with well tracking best value traces and relatively blob-like cross correlations. Using the Two Power Law regimes, the low- Q Porod exponent of the TipSonx0 is found to be $P_1 = 2.13 \pm 0.01$ and the high- Q exponent to be $P_2 = 2.95 \pm 0.04$ (Tab. 9.8). Using the Power Law model, the Porod exponent of the SFMx1 film is found to be $P = 2.75 \pm 0.02$, the Porod exponent of SFMx2 is found to be

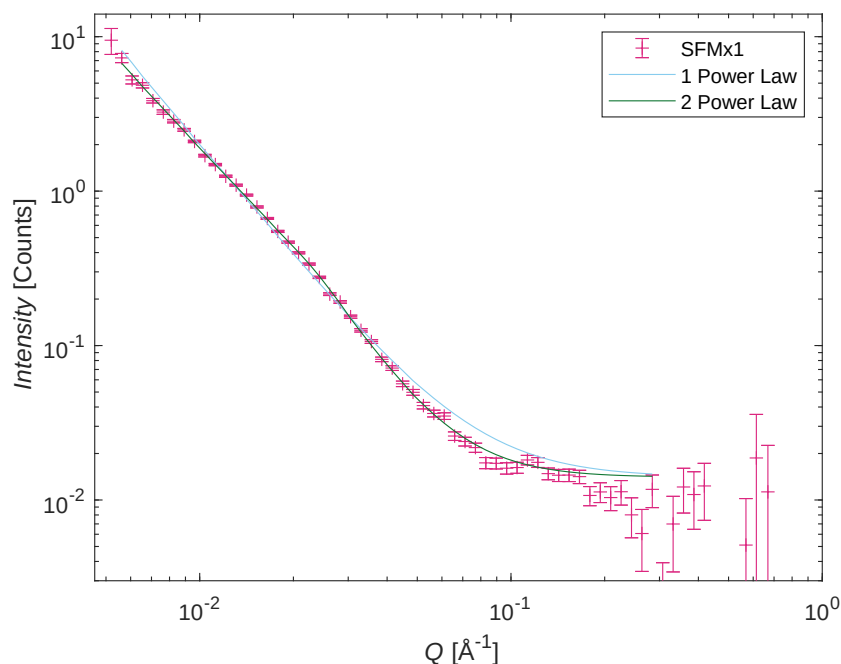


Figure 9.23: Log-log plot of small angle neutron scattering of TipSonx0 with applied (one) Power Law model and Two Power Law model shown with solid lines. (Two Power Law for TipSonx0, One Power Law for the rest).

$P = 3.05 \pm 0.08$, the Porod exponent of TipSonx1 is $P = 2.61 \pm 0.02$ and the Porod exponent of TipSonx2 is $P = 2.54 \pm 0.02$.

A structural analysis of CNT:P systems where polymer had been removed either 0 (tip sonication only), 1 or 2 times using either tip sonication or shear force mixing was carried out in Secs. 9.4.1 and 9.4.2.

We find the TipSonx0 sample to appear as having two linear regimes with different Porod exponents. The low- Q $P_1 = 2.13 \pm 0.01$ is lower than the high- Q $P_2 = 2.95 \pm 0.04$. This could indicate the structural density of the composite system is different at different length scales with the system being denser at smaller length scales. As only a single structural level is present when excess polymer is removed, the two scattering levels could also arise from the excess polymer which

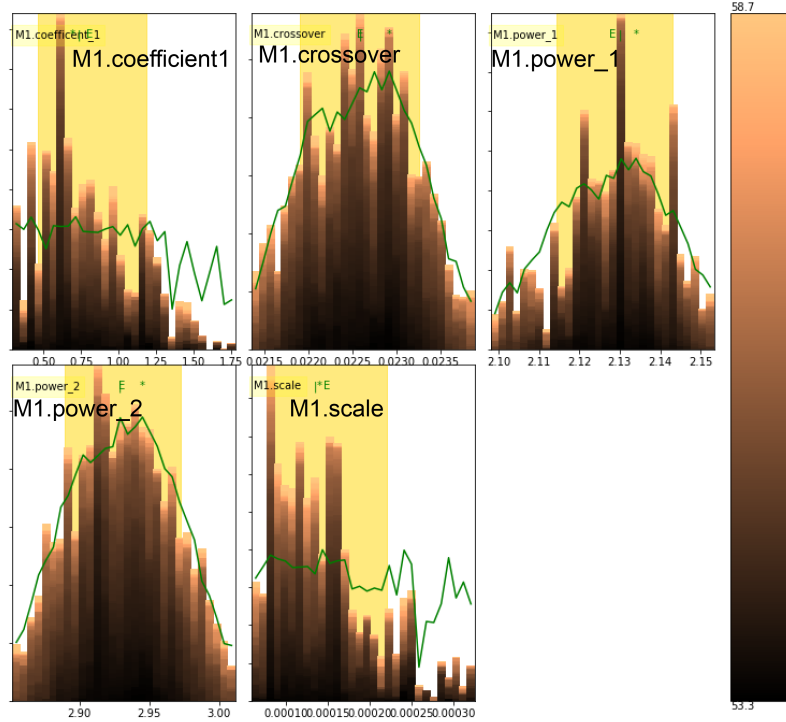


Figure 9.24: Ensemble uncertainties of TipSonx0 using the Two Power Law model. The shown parameters map as follows to the coefficients in Eq. 9.4: $M1.coefficient_1 \hat{=} A$, $M1.crossover \hat{=} A$, $M1.power_1 \hat{=} P_1$, $M1.power_2 \hat{=} P_2$ and $M1.Scale \hat{=} scale$.

is removed. This excess polymer, which is rich in hydrogen, is also assumed to be the cause of the higher background level of the TipSonx0 sample.

Once excess polymer is removed using tip sonication we find Porod exponents of $P = 2.61 \pm 0.02$ for TipSonx1 and $P = 2.54 \pm 0.02$ for TipSonx2. This is close to 2.5, which is the expected value of a randomly branched object [104]. Notably, this is different from both structural levels of the composition with no polymer removed, which indicates that the polymer removal steps do not simply remove matter containing one structural level, but also lead to a change in overall packing density. The Porod exponents change only little and in fact appear to

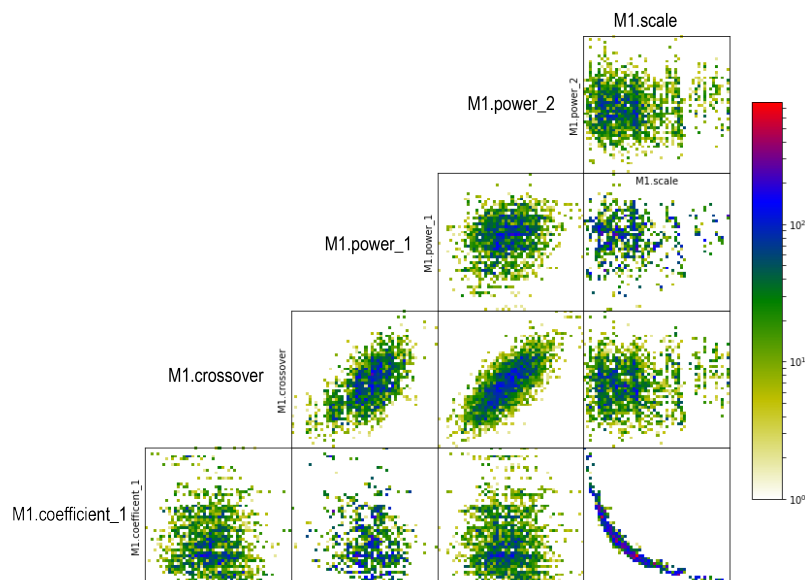


Figure 9.25: Fitting parameter correlations of TipSonx0 using the Two Power Law model. The shown parameters map as follows to the coefficients in Eq. 9.4: $M1.coefficient_1 \hat{=} A$, $M1.crossover \hat{=} A$, $M1.power_1 \hat{=} P_1$, $M1.power_2 \hat{=} P_2$ and $M1.Scale \hat{=} A$.

decrease when polymer is removed a second time, suggesting a limited structural effect of multiple polymer removal steps for tip sonicated samples.

For the shear force mixed samples, we find Porod values of $P = 2.75 \pm 0.02$ for SFMx1 and $P = 3.05 \pm 0.08$ for SFMx2. These higher Porod exponents suggest that SFM leads to more structurally dense films compared to tip sonication. In addition, there is a notable difference in mesh density when excess polymer is removed for a second time. The increase in exponent to around 3, the boundary between mass and surface fractals, when polymer is removed possibly indicates the packing has become sufficiently dense that scattering arises from a rough fractal-like surface.

The FoM of the CNT:P systems is shown in Tab. 9.9. The FoM of each film has been determined by B. Sturdza. The FoM is plotted against the low- Q Porod

exponent and fitted with a first order polynomial in Fig. 9.26.

	$[\sigma_{dc}/\sigma_{op}]$
SFMx1	1.64
SFMx2	2.07
TipSonx0	0.83
TipSonx1	1.49
TipSonx2	0.84

Table 9.9: Fitted values of $[\sigma_{dc}/\sigma_{op}]$, the Figure of Merit for the SFMx1, SFMx2, TipSonx0, TipSonx1 and TipSonx2 CNT:P systems.

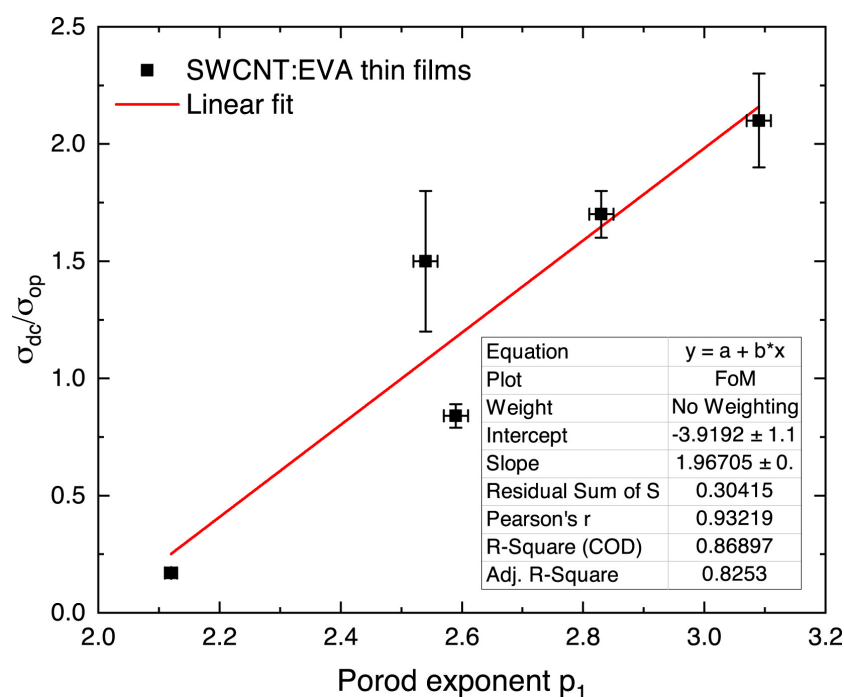


Figure 9.26: Figure of Merit $[\sigma_{dc}/\sigma_{op}]$ as a function of the low- Q Porod exponent extracted from small angle neutron scattering. The red line represents a first order polynomial fit. Figure reused from [65]. CC BY-NC-ND 4.0 DEED

The first order fit in Fig. 9.26 is shown to describe the data well with $R^2 = 0.87$. We interpret this positive correlation between the a higher Porod exponent, signifying a more densely packed system, and a higher FoM σ_{dc}/σ_{op} to be due to an increased number of CNT-CNT junctions, which lowers the electrical resistance

of the film. The change in microstructure induced by different film manufacturing processes as well as polymer removal steps can thus be quantified via the Porod exponent(s) of the SANS data and we are able to link these Porod exponents to a device relevant FoM.

9.5 Discussion

This chapter had a two-fold aim: To investigate the microstructure of select CNT:P systems using SANS and to further the applicability of SANS to CNT:P composite systems. As discussed in Sec. 9.3.7, three of the four applied fitting models were found to not yield physically meaningful results and thus only the results of fits using Power Law functions were taken as physically meaningful.

This does not preclude the Beaucage, Guinier-Porod or *Mass Fractal* models from being applicable to CNT:P composite systems, however. The SANS analysis in this chapter is limited by the Q -range of the data as no Guinier regime is visible in any of the intensity curves. More physically descriptive models could be applied to the studied systems if the Q -range could be extended sufficiently beyond the current lower limit. In this event, the physical parameters (e.g. R_g) extracted by each model could be compared to apparent feature sizes as measured via microscopy techniques such as atomic force microscopy or scanning electron microscopy.

9.6 Chapter conclusions

In this chapter, we use SANS to investigate the microstructure of CNT:P films, ascertain the viability of physical model descriptions and link microstructure to a device-relevant FoM, a combination of electrical conductivity and optical trans-

mission.

All systems appear as fractal-like systems characterised by their scattering following a power law relation in reciprocal space. As an initial explanatory investigation, we investigate CNT:P systems with varied melt indices (4355, 40L-03, 40W and 4320). We apply the Beaucage, Guinier-Porod, *Mass Fractal* as well as scale factor models to their scattering data. Aided by Guinier analysis as well as analysis of the parameter cross-correlation, we find that the probed Q -range of the data is insufficient for meaningfully extract structural information beyond the Porod exponent(s), although we can establish lower bounds for the $R_g = 38.5$ nm.. We do not find the Porod exponents, ranging from 2.35 ± 0.01 to 2.5 ± 0.02 to correlate with the device relevant FoM, suggesting that performance related changes are not determined by the microstructure as probed by SANS.

After establishing power law models as the most appropriate appropriate, we analyse SANS data of CNT:P films made with either SFM or tip sonication with 0x (tip sonication only), 1x or 2x polymer removal steps. We establish a lower bound of $R_g = 33.3$ nm using Guinier analysis. We find the TipSon0x to be described by a two power law model with low- Q $P_1 = 2.13 \pm 0.01$ and high- Q $P_2 = 2.95 \pm 0.04$ could indicate the structural density of the composite system being denser at smaller length scales. We find TipSonx1 and TipSonx2 to have Porod exponents of $P = 2.61 \pm 0.02$ and $P = 2.54 \pm 0.02$, respectively, suggesting scattering arises from randomly branched objects. The small change in Porod exponent between removal steps suggests multiple polymer removals do not change the microstructure as probed by SANS.

For SFM configurations, we find Porod values of $P = 2.75 \pm 0.02$ for SFMx1

and $P = 3.05 \pm 0.08$ for SFMx2. These values are above those of Tip sonicated samples suggesting that SFM contributes to denser structural packing and that additional SFM polymer removal steps have further changed the microstructure. We find that a denser packing, as measured by the Porod exponents, correlates with a higher FoM, which we hypothesise is due to an increase in CNT-CNT junctions.

10 | Conclusion and outlook

This thesis investigates Vacuum Thermally Evaporated (VTE) Small Molecule (SM) Organic Photovoltaic (OPV) thin films as well as Carbon Nanotube:Polymer (CNT:P) electrode layers via Small Angle Neutron Scattering (SANS) as well as Grazing Incidence Wide Angle X-ray Scattering (GIWAXS).

In Chapter 6 we demonstrate for the first time that SANS is a viable technique for the qualitative and quantitative study of evaporated OPV Bulk Heterojunction (BHJ) systems. As an exploratory study, we investigate Donor:C60 (D:C60) in 2:1 mol ratios all evaporated at $T_{sub} = 80\text{ }^{\circ}\text{C}$ with a total molecular deposition rate of $0.15\text{ }\text{\AA}^{-1}$ on a C60 underlayer, with D=[DCV5T-me(3,3), A6T, ZnPc, SubPc, Rubrene]. We categorise the weakly scattering ZnPc:C60 and SubPc:C60 ($T_{sub} = 80\text{ }^{\circ}\text{C}$) systems as being highly intermixed. Applying a *Broad peak* model to the weakly scattering Rubrene:C60 system ($T_{sub} = 80\text{ }^{\circ}\text{C}$), we identify a characteristic feature size of $36 \pm 1\text{ nm}$ between phases of domains that are either Rubrene-rich or C60-rich, but of low purity. The A6T:C60 ($T_{sub} = 80\text{ }^{\circ}\text{C}$) configuration features a smooth upturn in scattering intensity towards the low- Q limit and we apply both the DAB model, describing a two-phase system with a characteristic spacing, and the *Mass Fractal* model, describing a fractal-like aggregating system yielding a characteristic length scale of $L = 21.5 \pm 0.1\text{ nm}$ and coherence length $\xi = 22.0 \pm 0.3\text{ nm}$, respectively. We interpret its lack of peak-like feature as implying a relatively higher domain size polydispersity. The DCV5T-me(3,3):C60 configuration shows scattering with a clear bump and a power law increase in scattering intensity towards the low- Q limit. Using the *Broad peak* model, we identify a two-phase system of a feature size of 19.2 nm . We describe the system as a two-phase system with at least one relatively pure domain as evident by the higher scattering contrast and we interpret the broad peak feature as potentially representing rel-

atively heterogeneously sized C60-rich globular domains previously reported in literature.

To further the quantitative application of SANS, we study the more strongly scattering A6T:C60 and DCV5T-me(3,3):C60 systems and vary the D:A mixing ratios, T_{sub} and molecular deposition rate, i.e. commonly varied processing parameters, of A6T:C60 and apply the Debye-Anderson-Brumberger (DAB) and *Mass Fractal* models. All configurations appear qualitative similar in terms of scattering intensity and we find that

- A higher C60 fraction results in a higher fitted length scale using the DAB model, This potentially suggests C60 more readily phase separates than A6T.
- Increasing the T_{sub} seems to decrease the feature length size when fitted with both DAB and *Mass Fractal* models.
- Increasing the molecular deposition rate appears to increase the characteristic feature size using both the DAB and *Mass Fractal* models. This could potentially be due to a higher deposition rate inducing more spatially distant nucleation sites rather than allowing for molecules to diffuse to more closely spaced sites.

Both the DAB and *Mass Fractal* models are able to provide quantitative descriptions of the A6T:C60 system, with the *Mass Fractal* model fits consistently yielding a higher (0-30%) fitted feature size. This highlights a major difficulty in applying models to SANS data. Even though two models may differ fundamentally in how they physically describe a system, the need to make them practically applicable will often result in heavy mathematical simplifications that result in both models becoming similar in practise.

For DCV5T-me(3,3):C60, configurations evaporated at $T_{sub} = RT$ and $T_{sub} = 140$

°C were manufactured and probed with SANS. The $T_{sub} = RT$ configuration shows no appreciable scattering in the probed Q -range, indicative of a highly intermixed system which is expected based on literature, whilst the $T_{sub} = 140$ °C configuration shows a higher intensity and more well defined broad peak. When fitted with the *Broad peak* model we observe an increase in feature size from 19.2 ± 0.4 nm to 22.3 ± 0.2 nm, indicating that increased T_{sub} results in increased phase separation.

Motivated by the clear scattering features, the study of DCV5T-me(3,3):C60 is further expanded upon in Chapter 7, we use SANS to investigate DCV5T-me(3,3):C60 2:1 mol systems deposited at $T_{sub} = RT, 60, 80, 100, 120, 140$ °C in Chapter 7. We observe the material system transitioning from being highly intermixed at $T_{sub} = RT$ to showing phase separation between DCV5T-me(3,3)-rich and C60-rich domains. We observe an increased phase separation as T_{sub} is increased and we quantify this phase separation by applying the *Broad peak* model. The fitted feature size increases from 17.7 ± 0.6 nm at $T_{sub} = 60$ °C to 23.9 ± 0.3 nm at $T_{sub} = 140$ °C. We find the *Broad peak* fitted centre-to-centre distance between domains in the two-phase system to increase linearly with T_{sub} at a rate of 0.8 ± 0.3 Å/K once phase separation is present. As T_{sub} is increased we also observe an increase in the broad peak intensity, which we hypothesise could be due to increased phase purity or systemic demixing.

The effect of post-annealing DCV5T-me(3,3):C60 deposited at $T_{sub} = RT$ at 80 °C and at 140 °C for 30 min is also investigated. Post-annealing at 80 °C does not induce phase separation between DCV5T-me(3,3) and C60, as shown by the lack of scattering signal, whilst post-annealing at 140 °C does result in a strong scattering towards the low- Q limit indicative of phase separation. The scattering signal is fitted with the DAB model to yield a correlation length of 32.2 ± 0.6 nm.

This is larger than the phase separation between DCV5T-me(3,3)-rich and C60-rich domain fitted feature size of $T_{sub} = 140$ °C using the *Broad peak* model, we interpret the lack of broad peak in the annealed configuration as being indicative a greater degree of polydispersity in domain spacing.

Chapters 6 and 7 demonstrate the viability of SANS to study evaporated SM OPV systems and also showcase several types of physical models that can be used to describe the systems. However, there are limitations to the current work. Both the DAB and *Mass Fractal* models describe the scattering from A6T:C60 configurations, and whilst both describe the same trends in behaviour, the absolute fitted values for inter-domain distances vary. The models can thus still be used for comparative analysis, but correlating absolute microstructural parameters with e.g. device performance becomes more difficult. Similarly, it is difficult to discern whether the increase in the Lorentzian scale factor for DCV5T-me(3,3):C60 configurations with varied T_{sub} is attributable to increased phase purity or film thickness fluctuations, which will affect the both physical and practical applications of increasing T_{sub} . There are several avenues which could be explored in further studies to overcome the current issues, discussed below.

Whilst small angle scattering models for e.g. two-phase microemulsions or for polymers, which incorporate their chain conformations, have been developed, this is not the case for models targeting SM OPV thin films. Theoretical work developing models specifically designed to describe SM packing could further improve the information gleaned from SANS models. However, the application of currently available models could also be improved by improving the quality of the scattering data. This could be done by deriving the absolute scattering from investigated systems. To derive this, more elaborate studies of select systems should

be carried out involving Scattering Length Density (SLD) contrast variation via deuteration or other atomic substitutions of the organic molecules in conjunction with thickness normalisation. The use of auxillary techniques is another way to aid in the interpretation of the data. Using e.g. Scanning Transmission Electron Microscopy, Energy Dispersive X-ray spectroscopy (STEM-EDX) as element-specific microscopy allows for a better heuristic understanding of the system as well as another avenue for numerical analysis.

Continuing the SANS work presented in this thesis allows for new potential avenues for exploring structure-property-performance relationships. We have demonstrated how SANS studies enable quantitative analysis of evaporated SM OPV active layers. With the use of refined modelling, as outlined above, SANS studies could be combined with performance measurements of equivalent OPV devices to challenge assumptions about e.g. optimum D:A domains sizes for device operation. Similarly, software such as BornAgain could be used to compare simulated scattering from idealised systems matching different hypotheses about film formation versus the observed scattering data.

The quality of the experimental data is of course also an area which could be improved upon. Whilst we are able to obtain physically insightful data, the magnitude of scattering, even from systems we describe as showing "strong scattering", is very weak compared to typical polymer films studied via SANS, which have thicknesses on the order of 10^{-3} m compared to the 10^{-6} m of the films studied in this thesis. Increasing the intensity of scattering data could potentially allow for better discernment between models and more accurate derivation of model parameters. Increasing the probed Q -range towards the low- Q limit would also increase the physical information models could provide. For this thesis, a neutron measurement sample holder was developed (see Chapter 5) and successfully used for SANS measurement. We identify the following way in which the holder could

be improved for future studies:

- The design choice of 12 mm x 12 mm substrates were largely determined by limitation of the VTE deposition tool ECHO. However, since the end of the experimental work detailed in this work, a sample cluster deposition tool has opened up at the Oxford Physics department. Due to a larger total area available for deposition, this would allow for larger substrates. This in turn allows for a greater area of the substrates to be coated by film and a larger neutron beam during exposure. This would then increase the total scattering mass and the potential to either reduce the number of stacked substrates or to maintain the same amount of substrates with a shorter counting time, increasing beamtime output. A wider beampath through the holders would allow for larger exit angles without the risk of neutrons hitting the side walls.
- Solar cell devices are affected by photodegradation and chemical degradation from water and oxygen molecules during operation. Whilst the various layers are typically encapsulated to restrict environmental exposure, even industrial grade OPV devices are still subject to small amount of water and oxygen reaching the active layer. Water vapour and oxygen can contribute to chemical degradation of the solar cell stack as well as result in trap states that can adversely affect the performance and lifetime of the devices. This motivates the possibility to study the effect of exposure to gaseous elements *in situ* via neutrons. To make such studies feasible, the design of the individual configuration holders could be configured to allow for a controlled exposure to gas during experimental sessions. We identify several considerations that should be kept in mind.
- In addition to a gas intake and exhaust fitted with flow metres, the boxes

should also be fitted with a pressure relief mechanism for operator safety as to prevent over-pressurised boxes exploding.

- It would also be necessary to spatially separate each substrate to ensure even and consistent flow rates across the exposed films. This would require the adoption of a tray-like system with a gap between each substrate.
- During operation solar cell devices can reach temperatures of 150 °C [105]. Higher temperatures can accelerate physical and chemical degradation and it is thus important to investigate the thermal stability of potential OPV materials. To probe this *in situ* via neutrons, each individual box could be fitted with a resistive heating element as well as a thermocouple to measure the temperature of the box. However, to ensure the neutron holder remains compatible with general neutron beamline set ups, the box bottoms and sides should be covered with insulating ceramics or organic materials as to not affect adjacent boxes or the machinery controlling the sample rack.

In Chapter 8 we thoroughly analyse the *in situ* GIWAXS scattering to study the evaporation of neat DCV5T-me(3,3) and a DCV5T-me(3,3):C60 2:1 mol blend evaporated onto glass substrates held at $T_{sub} = 120$ °C. From the position and relative strength of the Bragg features, we find DCV5T-me(3,3)'s preferred orientation to be that of molecules standing on glass with their long axis primarily aligned along the surface normal with a d -spacing 14.87 ± 0.01 Å in both cases. The blend film shows a greater mosaicity, which we attribute to disruption caused by the C60. We observe a secondary preferred orientation with the molecular long axis parallel to the substrate surface, which we also attribute due to C60 induced interruption. These lying-down crystallites appear slightly elongated compared to the standing crystallites. We only observe a very faint crystalline C60 signal in the blend, and we thus classify the blend as a two-phase system consisting of

crystalline DCV5T-me(3,3) and a disordered mixed DCV5T-me(3,3):C60 phase. We take line cuts along the Yoneda band and identify two $\pi - \pi$ stacking features, designated as π_A and π_B with respective d -spacings of $\pi_A = 3.38 \pm 0.01 \text{ \AA}$ and $\pi_B = 3.67 \pm 0.01 \text{ \AA}$ for the neat film and $\pi_A = 3.39 \pm 0.01 \text{ \AA}$ and $\pi_B = 3.69 \pm 0.01 \text{ \AA}$ for the blend film. The slightly longer d -spacing of the blend is ascribed to interruption from C60. We track the relative scattering intensity of π_A and π_B as the film grows. The neat film maintains a 1:1 ratio throughout the entire deposition, whilst in the blend an initial 1:1 intensity ratio transitions into dominance by the π_B signal. We hypothesise that the relative decrease in $\pi_A - \pi_A$ stacking scattering is the result of increased disorder due to C60 molecules which affects the unit cell internal symmetry.

The scattering does not show signs of Substrate Induced Phases (SIPs) and change in strain during growth appears minimal at less than 1%. We use the relative positions of the split Out-of-Plane (OoP) peak as well as the change in intensity at the anti-Bragg position to try and determine the growth modes of the two films. We tentatively characterise the blend as growing in 3D Volmer-Weber fashion due to approaching split peak positions and absence of anti-Bragg intensity oscillations as well OoP Bragg features appearing at an earlier growth stage than the $\pi - \pi$ stacking features. The growth mode of the pure film is less clear. The Anti-Bragg scattering intensity variation could possibly be caused by imperfect layer-by-layer growth until 1 ML of thickness, followed by island growth. The relative positions of the OoP split peaks as well as timing of the relative emergence of OoP and In-Plane (IP) features as the neat film grows could possibly support this hypothesis, although we stress this analysis is highly tentative. Another puzzling observation is that the primary OoP feature for both the neat film and the blend as having azimuthally off-set analogues at $\sim \pm 10^\circ$. This could potentially be due to an angled preferred orientation, although we are not aware of similar observations

in literature for DCV5T-me(3,3) based films specifically nor organic thin films in general.

The understanding of the investigated system could be furthered by atomic force microscopy measurements of equivalent films made in staggered series of low thicknesses corresponding to a integer (or half/quarter/etc.-integer) number of ML. This would allow for a direct observation of the growth mode. Further insight about the difference in how the scattering from π_A and π_B stacking develops could possibly be done via electron paramagnetic resonance analysis to see how the prevalence of different $\pi-\pi$ bonds change between the neat film and the blend. The cause of the peak triplication is not obvious. A first step in further analysis of this phenomenon would be to repeat the experiments to see if it is reproducible.

The analysis in Ch. 8 showcases the potential of *in situ* studies to improve our understanding of OPV thin films. The change in scattering intensity ratio between the two $\pi-\pi$ features as the film grows, for example, would not be apparent in an *ex situ* study and might be assumed to be a static ratio. As favourable $\pi-\pi$ stacking is of key importance to OPV operation, future studies that seek to optimise OPV device performance could benefit from incorporating *in situ* GIWAXS studies in order to inform decisions about optimum active layer thickness.

In Chapter 9 we apply SANS to CNT:P electrode films. We use an initial study of CNT:P with polymers (4355, 40L-03, 40W and 4320 type Ethylene-Vinyl Acetate (EVA)) of varying melt indices as an opportunity to compare the viability of different models (*Beaucage*, *Guinier-Porod*, *Mass Fractal* as well as scale factor models) that are often used to describe CNT composite systems. Through Guinier analysis as well as a careful examination of the model fit parameters cross-correlations, we find the probed Q -range of the data insufficient for meaningful extraction of structural information beyond the Porod exponent(s), although we

can establish lower bounds for the R_g at 38.5 nm. In the case of polymer melt index variation, we do not find the change in Porod exponents (ranging from 2.35 ± 0.01 to 2.50 ± 0.01) to correlate with favourably higher device performance FoM σ_{dc}/σ_{op} , given by the ratio between the optical and dc conductivities.

We thus proceed with further analysis using only power law models. We use SANS to investigate the effect of film processing method and probe CNT:P films made via either Shear Force Mixing (SFM) or tip sonication with 0x (tip sonication only), 1x or 2x polymer removal steps. We find the TipSon0x configuration to be described by a two-power law model with low- Q $P_1 = 2.13 \pm 0.01$ and high- Q $P_2 = 2.95 \pm 0.04$. We interpret this as the configuration being structurally denser at smaller length scales. The TipSonx1 and TipSonx2 configuration model fits yield Porod exponents of $P = 2.61 \pm 0.02$ and $P = 2.54 \pm 0.02$, respectively, indicative of scattering arises from a randomly branched object. The small change in Porod exponent between removal steps suggests multiple polymer removals do not meaningfully change the microstructure as probed by SANS.

SFM configurations show model fitted Porod exponents of $P = 2.75 \pm 0.02$ for SFMx1 and $P = 3.05 \pm 0.08$ for SFMx2. These values are higher than those of the Tip sonicated samples which suggests that SFM contributes to a denser structural packing and that additional SFM polymer removal steps does impact the microstructure. We find that a denser packing, as measured by higher Porod exponents, to correlate well with a favourably higher FoM σ_{dc}/σ_{op} , which we hypothesise is due to an increase in CNT-CNT junctions.

In the first part of Chapter 9, the predicted intensity of the various investigated models is extended beyond the low- Q limit of the collected data. This in part serves as a prediction for how observed scattering would appear if the Q -range of probed CNT:P systems was extended further towards lower Q . However, it also

serves as a reminder of the complexity of modelling SANS data. We note that in literature, the models applied to CNT composite systems are often quite complex and an abundance of physical parameters is often derived from these model fits. We caution that multiple models can seem to describe the apparent scattering very well whilst yielding what appears as very different physical results even though in reality the scattering data does not contain sufficient information for this level of analysis.

We thus recommend that future small angle scattering studies of CNT:P composite systems should always be initiated by investigating whether a potential model does yield physically meaningful results following the methodical approach described in Ch. 9 including analysis of parameter cross-correlations. In doing so, the physical validity of the results of future studies will be greatly improved. We also recommend future research adopts a "simpler-is-better" approach favouring models with fewer parameters and fewer inbuilt assumptions about the structure. A rule of thumb is that models based on describing the Guinier regime should only be employed when such a regime is identifiable. To take advantage of more complicated models, the Q -range should thus be extended towards lower Q . Future studies could then incorporate e.g. microscopy to map feature sizes, as determined by scattering models, to surface topology phenomena.

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A | Appendix

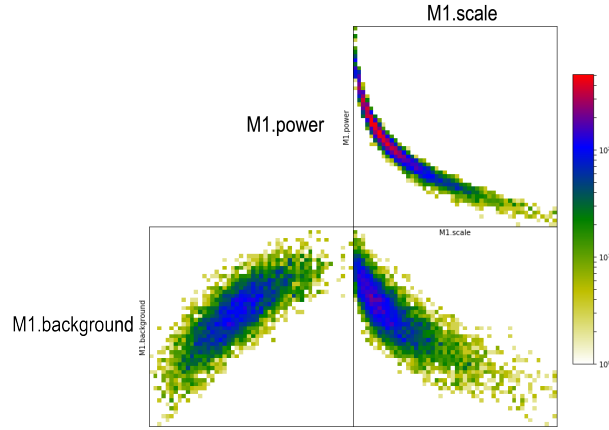


Figure A.1: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol fitted using the Power Law model.

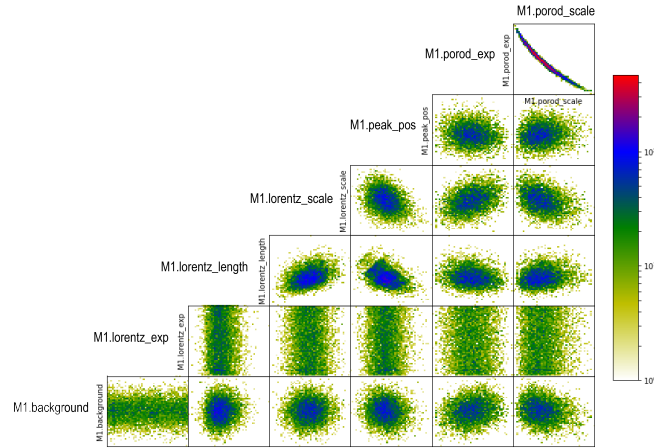


Figure A.2: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 60$ °C fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

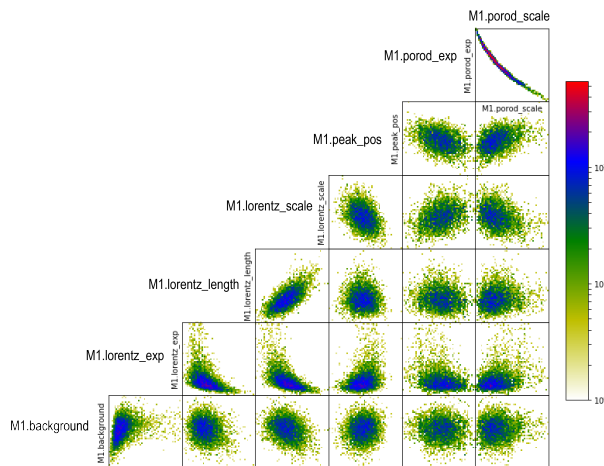


Figure A.3: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 80$ °C fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

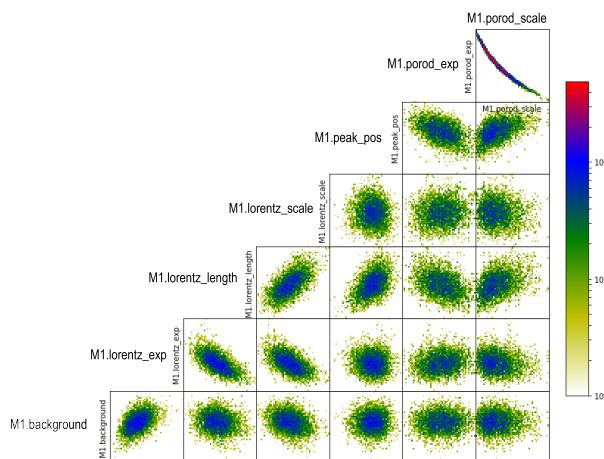


Figure A.4: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 120$ °C fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

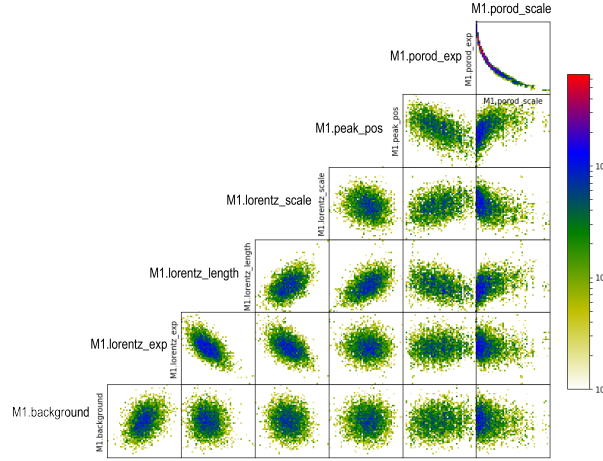


Figure A.5: Fitting parameter cross-correlations of DCV5T-me(3,3):C60 2:1 mol deposited at $T_{sub} = 140$ °C fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

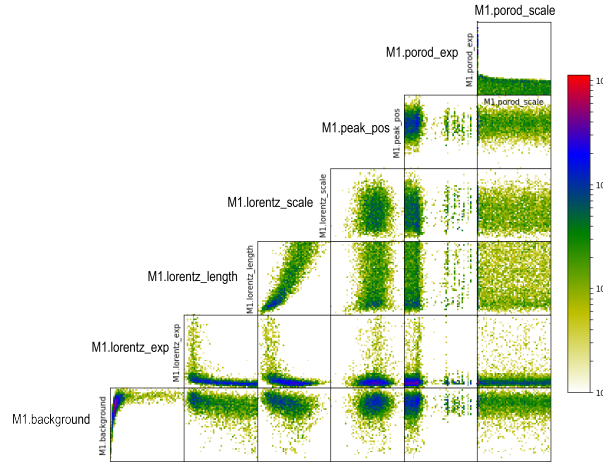


Figure A.6: Fitting parameter cross-correlations of fitted values of the Ann80 DCV5T-me(3,3):C60 2:1 mol sample configuration fitted using the *Broad peak* model. The shown parameters map as follows to the coefficients in Eq. 6.1: $M1.background \hat{=} B$, $M1.lorentz_exp \hat{=} m$, $M1.lorentz_length \hat{=} \xi$, $M1.lorentz_scale \hat{=} C$, $M1.peak_pos \hat{=} Q_0$, $M1.porod_exp \hat{=} n$, $M1.porod_scale \hat{=} A$ and $M1.scale \hat{=} scale$.

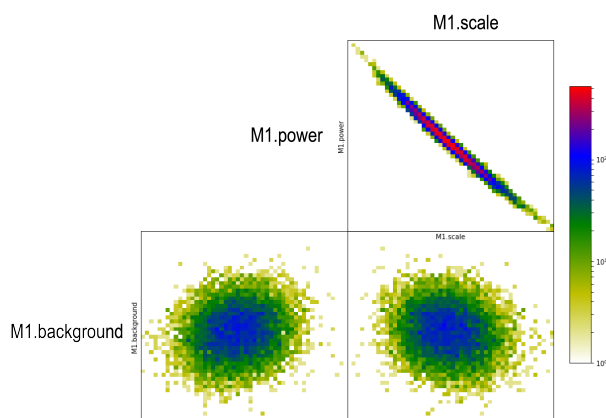


Figure A.7: Fitting parameter cross-correlations of fitted values of the Ann140 DCV5T-me(3,3):C60 2:1 mol sample configuration. The Ann140 configuration was fitted using the *Power law* model.

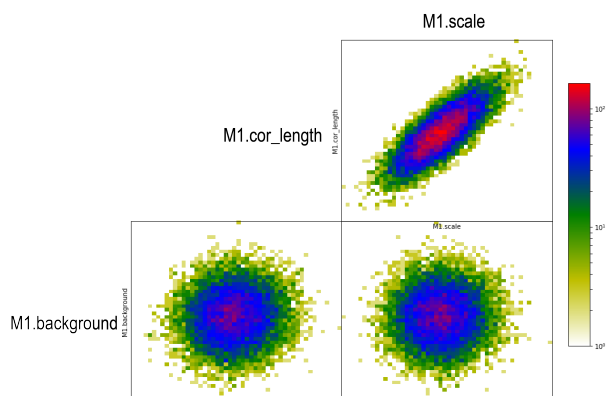


Figure A.8: Fitting parameter cross-correlations of fitted values of the Ann140 DCV5T-me(3,3):C60 2:1 mol sample configuration. The Ann140 configuration was fitted using the *DAB* model.