

# Processing Control of Organic Functional Materials

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**Abstract**— The research involved the hands on work experience of inorganic functional materials (Solar cells), to enhanced the crystalline morphology in organic semiconducting materials, preparing solutions of polymer – P3HT by varying the solvents and the solvent/solute ratio, producing thin films of polymers via drop casting, spin coating and water casting and finally to investigate the reasons for the spherulitic structures present in P3HT – decalin samples at 0.1 mg/ml mass-volume ratio

**Index Terms**— Organic functional materials, semiconducting materials, photovoltaics, solar cells, thin films, polythiophene, decalin, spherulites, electron microscopy, drop casting, spin coating, water casting.

## 1 INTRODUCTION

Recent research in the field of organic materials has shown that plastic electronics has emerged as a potential alternative to inorganic semiconductor materials. This largely due to the availability of new semiconducting materials with low cost-solution processing and this is the reason why materials are very promising for various devices such as light emitting diodes, photodiodes, photovoltaic cells, and sensors. Most of the best performing organic semiconducting polymers derive their high charge mobility from an ability to crystallise. However, the opto-electric properties do change to environmental stimuli with dramatic colour shifts in response to changes in solvents, temperature and the concentration of the solution.

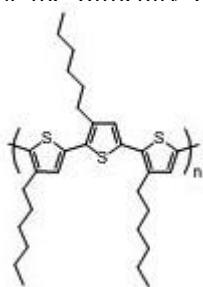
So now, the reason why so much emphasis is on enhancing the crystalline morphology in organic semiconducting materials is because crystallization aids interchain charge transfer by bring the planarized chains together in regular, more intimate contact, and making the material more electrically conductive. Therefore, optimizing crystalline structure remains extremely challenging because of the difficulty of incremental control over crystallization.

ect, we shall investigate how using different annealing temperature, together with different preparation techniques the structural changes the structural

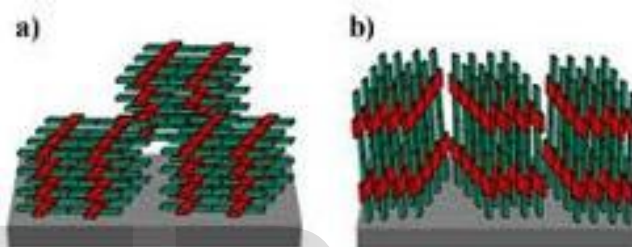
## 2 LITERATURE

### POLYTHIOPHENE

The P3HT, crystallization is dominated by a strong  $\pi$ - $\pi$  interaction perpendicular to the thiophene ring, which is the driving force for the growth of stacked aggregates. When confined to thin films, the  $\pi$ -stacking direction lies in plane, with the molecule adopting an edge-on orientation. These orientations have a higher mobility than those oriented with their  $\pi$ -faces normal to the substrate and the side chains and chain backbone in the plane of the substrate (plane-on). Whereas, Crystals with a plane-on orientation have grain boundaries terminated with insulating alkyl chains on two sides, which reduce charge transfer to neighbouring crystals.



### MORPHOLOGY



**Figure 2** - a) plane-on and b) edge-on orientation of P3HT

The most frequent method used to prepare thin films of P3HT is spin casting. The drawback of this method is the fast evaporation of the solvent during the rotation. This hinders the polymer chains to achieve a more crystalline state and therefore a close packing cannot be achieved. Methods like drop casting with slow evaporation rate of the solvent can typically form more thermodynamically stable products, which in this case mean larger coherent crystalline domains, but have the drawback of irreproducible layer thickness and morphology.

Therefore, it is important to investigate the structure of thin P3HT films and the change in morphology under the influence of different preparation conditions. Typically, these thin films are prepared by drop casting, spin coating or other low cost procedures as-grown films morphologies are not in their most thermodynamically stable state. So in this work, thin P3HT films prepared by different techniques with changes in preparation conditions are analysed.

## 3 EXPERIMENTAL SECTION

### THIN FILMS OF POLYTHIOPHENE

To prepare thin films of P3HT, solution of P3HT with different solvents were prepared by varying the molecular weight and volume of P3HT and the solvents used respectively. P3HT was obtained from Merck Chemicals and different solutions were added to prepare the solutions.

**Table 1:** Solution of P3HT with different solvents, mass and volumes.

P3HT( Mass )	0.5 mg	0.56 mg	1.0 mg
P-xylene ( Volume )	5 ml	0.56 ml	0.1 ml
Concentration Ratio	0.1mg/ml	1 mg/ml	10 mg/ml

P3HT( Mass )	0.64 mg	0.63 mg	1.0 mg
Toluene( Volume )	6.4 ml	0.63 ml	0.1 ml
Concentration Ratio	0.1mg/ml	1 mg/ml	10 mg/ml

P3HT( Mass )	0.50 mg	0.64 mg	1.0 mg
Decalin ( Volume )	5 ml	0.64 ml	0.1 ml
Concentration Ratio	0.1mg/ml	1 mg/ml	10 mg/ml

Each of the solutions prepared according to the measurements stated above were first drop casted onto a glass slide (few drops using a glass pipette) at room temperature and was placed inside the fume hood for the solvent to evaporate. P3HT films were annealed by drop casting the solutions on another glass slide placed on hot plate set at 104° C. A small glass beaker was placed on the glass side to reduce the effects of background and air on buffeting of the thin films. This processing method was repeated for all the solution at different concentration and solvents. The glass slides were collected after stabilization of the temperature on sample surface and evaporation of the solvents.

To compare the change in the structure and morphology of the drop-casted P3HT films, the same solutions were spin coated at 1000 rpm( without vacuum )for 90 sec onto glass sides of smaller size. All the glass slides were stored to get an in-depth analysis on their structure and properties using an electron microscope

## 4 RESULTS AND ANALYSIS

### 4.1 THIN FILMS OF POLYTHIOPHENE AND P-XYLENE AT 0.1 MG/ML CONCENTRATION

The glass slides collected were placed under an optical microscope and were taken images using a camera. From the optical microscope images of P3HT and P-xylene at 0.1 mg/ml. we can state that the drying temperature does have an impact on the microscope structures of the P3HT thin films. The drops casted film at R.T.P shows two regions present in the thin films (dark and light regions). The dark and light regions were formed due to the surface pinning effect which results in more materials collecting in a region than the other, these can also be the reason for the ring like structures in these thin films. Therefore, we can state that P3HT has both amorphous and crystalline forms (synthetic polymers) which are invisible from the drop casted film at 104° C. As we are approaching towards the boiling point of the solvent (138° C), most of solvent has evaporated at a fast rate and this would increase surface pinning effects which can lead to an increase in spacing between these dark regions (or more light regions)

Additionally, the spin coated film at 1000 rpm do resemble the films in its dual structure but these films are not continues. This largely depends on the spin coating speed and the concentration of the solution used. For example, if we have to spin coat a dilute solution at a very high speed, as in this case, most of the solution will evaporate while spinning, and will leave us with a discontinuous film.

So, temperature treatment plays an important role on the structural and electronic properties of thin films. In particular, the semi crystalline form is only present in the P3HT samples drop - casted at room temperature and the Spin coated sample but is invisible after annealing above 100°C

### 4.2 THIN FILMS OF POLYTHIOPHENE AND P-XYLENE AT 1 MG/ML CONCENTRATION

Optical microscope images of P3HT and P-xylene with 1 mg/ml concentration were taken. The film drop casted at R.T.P with the 1mg/ml are also having the semi crystalline structure but whereas the casted films at 104° C are quite different from films at RTP. Comparing the film the previous one and this one at 104° C, we have found an increase in spacing between the amorphous regions (between the dark regions) and this is largely due to the difference in aggregation between these films. Finally, in the spin coated films, the semi crystalline form is much more visible than the room temperature drop casted film and the film is also more continuous than the film in the previous section.

### 4.3 THIN FILMS OF POLYTHIOPHENE AND P-XYLENE AT 10 MG/ML CONCENTRATION

The optical microscope images of P3HT and P-xylene at 10 mg/ml. As there is allot of material in this solution. Now, we can start to view the effects of dewetting in these films (some small holes or spaces), especially in the spin coated and the room temperature casted films. These effects are known as the coffee ring effect, were the solid material is dispersed as a residue in a ring like structure. Another noticeable difference would be in the drop casted sample at 104° C, the spacing between the amorphous regions have increased even more and the films much darker than that in fig 4.b) (more material).

So the dewetting effect destroys the homogeneity in these thin films and also there is a continuous increase in spacing with the increment in the annealing temperature. The interesting fact about the increase in spacing has shown that they behave quite differently and future investigation is required.

### 4.4 THIN FILMS OF POLYTHIOPHENE AND TOLUENE AT 1 MG/ML AND 10 MG/ML AND CONCENTRATION

From the images produced, we have found that the microscopic images of the P3HT and toluene solution resemble that of the P3HT and p\_xylene solutions at their respective temperatures and preparation conditions. Therefore, from this investigation, we can generalize that the structure and mor-

phology are not influenced by the solvents used till now.

So further investigate more on this generalization, we shall study the structure and morphology of the P3ht and decalin thin film samples.

#### **4.4 THIN FILMS OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION**

As the drop casted samples were viewed under an optical microscope, we discovered many small square shaped structures present in these thin films. So when they were viewed through crossed polarisers, they appeared to be a cluster of radiating from a central point.. This was very interesting as, none of the other solvents had influenced the structural property of P3HT in this manner.

This highlighted the clear need for more investigation. Therefore, the solution was again drop casted at the same temperature to check its structure and the growth of these square crystals.

#### **4.4 ANOTHER THIN FILM OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION**

We got a clearer view on the crystalline structures from these samples drop casted above. Future investigations lead us to find out that these are the spherulites or spherulitic structure in non branched polymers. Previous researches conducted on spherulites have shown that there are 2 categories of spherulite growth (this is the second growth). Category 2 spherulite growth initiates as thread-like fibres, subsequently forming new grains at the growth front). This branching of the crystallization pattern ultimately leads to a crystal 'sheaf' that increasingly splays out during growth. This grows into, what they call, is a multi-sheave like structure. At still longer times, these multi-sheaves develop two 'eyes' (uncrystallized regions) on each side of the primary nucleation site. Finally, this type of spherulite settles down into a spherical growth pattern, as visible in the thin films dropcasted at 104°C.

#### **4.4 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 1 MG/ML CONCENTRATION**

We discovered that the drop casted decaline samples at 1mg/ml at 104° C had also produced spherulitic structures but there were slight noticeable differences. Investigation the size of the crystal sheaf found in these different concentrations, we have found that the crystal sheaves of the more concentrated solution (1mg/ml) is smaller in size than the less concentrated solution (0.1 mg/ml). This can be largely due to the nucleating sites present in these thin films. The more concentrated solution has more nucleating sites in the thin films than the dilute solution, so these results in more spherulite sheaves in their microstructure pushing against each other and this could be the reason for the decrease in size noticed.

#### **4.5 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 10 MG/ML CONCENTRATION**

From the images, we have found that the concentration of the solution can influence the formation of the spherulites. Also, the more concentrated solution does not form spherulites. This is largely to do with most of the P3HT not completely dissolving with decaline, as when the films were cross polarised, we could find, what looked like small holes, the dewetting effects suggesting that there is too much material in this solution. This can prevent the polymer chains from bending and folding on to themselves forming the spherulite structures, So from all this investigation, we have found that the spherulitic structures are visible in 0.1mg/ml and 1mg/ml solutions. This can also have something to do with the boiling point and the molecular structure of decalin. With decalin having a very high boiling point, it can give enough time for the P3HT thin films to aggregate, resulting in the sufficient bending and holding of the polymer chain to form these spherulites, as in the 0.1mg/ml and the 1 mg/ml. On the contrary, this does not occur in the concentrated solution due to the high solute – solvent ratio; the solute (P3HT) is left stagnated on the glass slides.

As we can draw conclusion on how the spherulite structures were formed, we need to investigate on how to control this spherulite growth, for this we shall use the 0.1mg/ml to find the effects of the drying temperature on the spherulitic structure. We drop casted the solution to get thin films at different temperature by increasing the dry temperature from 50° C to 75° C and 101° C, 150° C to 175° C ( close to the boiling point of decalin ).

#### **4.6 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION AT 55°C**

We have found that drop casting the solution at 55° C does not result into spherulites. We can also see the effects of surface pinhole( 2 regions ) and some dewetting effects. So at this temperature, the solubility of P3HT with decalin is quite low and this can be the reasons for no spherulitic structures.

#### **4.7 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION AT 75°C**

We have found that the spherulitic structures are visible at drop casting temperatures above 75° C. This can largely do with the solubility of P3HT with decalin at this temperature. So, we have found that the solubility of P3HT with decalin in thin films can increase with an increase in the drying temperature and this can be the reasons behind the spherulitic structures visible at this temperature and not at 55° C.

By comparing the films casted at 75°C and 104° C, we can see that the crystal sheaves of the casted samples at 75°C are smaller in size that that of the 104° C. This can be due to the temperature effects on the nucleating sites. So as the temperature is increase, the nucleating sites are pushed even further leading to growth of large crystal sheaves.

#### **4.8 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION AT 155°C**

So even at a drying temperature of 155° C, we are able to witness these spherulitic structures clearing showing the need to investigate thin films at a higher drying temperature.

#### **4.9 THIN FILM OF POLYTHIOPHENE AND DECALINE AT 0.1 MG/ML CONCENTRATION AT 175°C**

So as the drop casted temperature approaches the boiling point of decalin, most of the solvent has evaporated leaving no time for the P3HT to aggregate and resulting in these patchy dewetted structures.

So from our investigations, we have found that features of spherulites are clearly visible in the thin films of P3HT and decalin solutions at 0.1mg/ml and 1mg/ml concentration at a drying temperature of 101°C. Also, we found that we can control the size of the crystal sheaves by incrementing the temperature from 75°C but the spherulites are invisible as we approach the boiling point of the solvent due to the fast evaporation rate.

Finally, to probe these thin films casted at different temperatures, UV/visible absorption spectroscopy was used. This technique is usually a way to find the degree of aggregation in many semiconducting polymers.

### **5 ABSORPTION SPECTROSCOPY ANALYSIS**

When studied the behaviour of these thin films casted at different temperature, we observed that the curves produced were suggesting that all these thin films were well aggregated samples. On the contrary, the microscope images proved that the samples casted at 50° C and 177° C did not show spherulitic structures. Therefore, the degree of aggregation of the samples doesn't entirely contribute to the presence of the spherulitic structures and these may rely on other factors like the temperature at which these films were casted.

So, when we compared the UV/vis absorption curves of the 10mg/ml and 0.1mg/ml casted at 104° C. We noted that, the 10mg/ml had a narrowed absorption (at wavelength of 490) showing that these sample have lower aggregation. This discovers supports the microscope images which showed that the spherulite structures were invisible in these films. So we were able to find that the samples of the 10mg/ml drop casted, at the same temperature as the 0.1mg/ml, tend to have lower aggregation which can be the reasons for the spherulitic structures invisible in these samples.

### **5 CONCLUSION**

Through the study of the thin films of P3HT with different

solvents and preparation conditions, we have discovered that the structure and morphology of P3HT are influenced by the properties of solvent used, solvent-solute ratio and the different preparation methods (drop casting, spin coating and water casting). Additional, spherulitic structures were only present with decalin sample at 0.1mg/ml and concentration. We also came to a conclusion that, these spherulitic structures were largely due to the concentration of the solution used and the high boiling point of decalin which gives enough time for these thin films to aggregate and form these spherulitic structures.

Observing the effects of temperature on these spherulitic structures, we discovered that the spherulitic structures are invisible at 55° C and 175° C. Studying the UV/vis spectrum graphs of these thin films have shown that degree of aggregation for these samples are the same suggesting that reasons for the difference in the microscopic structures are largely dependent on the drying temperature and the solubility of P3HT in decalin at that respective temperature.

But whereas, the UV/vis spectrum graphs of the 10mg/ml and 0.1mg/ml samples casted at 104° C. showed the 10mg/ml sample to be at a lower degree of aggregation than the 0.1mg/ml sample showing that the difference in concentration could be the reasons for the spherulites invisible in the higher concentrated solutions.

The investigation conducted on the combination of P3HT and decalin are a strong basis for further understanding on the nature of these films and further like the X-ray diffraction measurements can be conducted on these thin samples with different preparation conditions to gain an in-depth understanding of their properties and behaviours.