INVESTIGATION OF THE CONDUCTIVE BEHAVIOR OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/POLY(STYRENE SULFONIC ACID) FOR ORGANIC ELECTRONICS

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DEDICATION

To

Eni
Engka
Ghany
DECLARATION

The thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University’s Digital Repository, subject to the provisions of the Copyright Act 1968.

..............................................
Anang Wahid Muhammad Diah
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ABSTRACT

The conductive behaviour of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS), produced by oxidative polymerisation under varying synthetic and doping conditions, and upon structure modification, has been investigated, with the aim of improving the conductivity and processability of PEDOT/PSS films for application in organic photovoltaic (OPV) and organic field electronic transistor (OFET) devices as interfacial conductive layer and gate electrode, respectively.

A capillary electrophoresis (CE) method was developed and showed, for the first time, the separation between the PEDOT/PSS complex and free PSS and allowed estimation of the doping efficiency of PSS. The results show that films with conductivity >1.0 S/cm have higher PEDOT/PSS content indicated by shorter migration times (~8 min) and doping efficiency of >80%.

This work also demonstrates the potential of PEDOT to be modified to contain functional endgroups and form a more complex architecture. PEDOT was successfully endcapped with thiophene-based endcapping agents 2-thiophenemethanol (2TM) and 2-thienylmethyl methacrylate (2TMM). Crosslinked core star (CCS) PEDOT/PSS was also successfully synthesised via the core first method using 2TMM capable of linking PEDOT (via its thiophene moiety) with the non-conductive crosslinked core (via its polymerisable vinyl group).

All PEDOT/PSS films used in this study were generated by spin-coating at 5000 rpm found by formal statistical assessments (correspondence analysis and multi-linear regression analysis) to give the most reproducible results. Conductivity has been found to be affected by the doping efficiency of PSS, the doping condition (in-situ during polymerisation vs post-polymerisation), the combining ratio of EDOT and PSS, the time of reaction, the chain length and the morphology (linear vs CCS) of PEDOT and processability of dispersions. In general, high conductivity was obtain from films generated from highly processable, linear, non-endcapped, high PEDOT/PSS ratios (≤ 1:3) doped in situ dispersions polymerised between 12 and 36 hours. Highest conductivity (5.2 S/cm) was obtained from a linear PEDOT/PSS film resulting from 12 hours reaction. All of the PEDOT/PSS synthesised in house gave conductivity values one to three order of magnitude higher than the commercial sample (Clevious P).

The performance of selected PEDOT/PSS films under un-optimised conditions, are comparable to the commercial PEDOT/PSS when used as an interfacial conductive polymer layer and electrode gate in OPV and OFET devices, respectively.
CHAPTER 1 - INTRODUCTION
1.1. Conducting Polymers

Conducting polymers are macromolecular structures that conduct electricity based upon the movement of electrons along their polymer chain. They are highly $\pi$-conjugated systems in which the $p_z$-orbitals of the chain atoms are involved in conjugation overlap. The $\pi$-conjugated system polymers are by far the most promising functional polymers in view of applications. They are also less expensive and flexible electronic devices.[1] The chain structures of conducting polymers have alternating double and single bonds of carbon to carbon along the polymers, i.e. conjugated bonds. These chains allow the formation of delocalised electronic states and maximise the overlapping of electrons among the $\pi$-molecular orbital. This structure allows charge carrier to move along the polymer backbone and between the adjacent chains. The particular bonding arrangement of the carbon atoms in the polymer backbone is the reason for the characteristic electronic properties of tunable conductivity, electrochromism, electroluminescence and electroactivity. This new class of plastic materials has developed very rapidly, and the initial scientific curiosity about this field has been elevated from academic research to industrial use.

The basis of conducting polymers can be established back in the 1970s, when highly conductive polyacetylene (PA) was discovered by Shirakawa, et al. This discovery of $\pi$-conjugated polymers would begin the future of conducting or semiconducting materials as the materials for the next generation of electronic and optical devices. Excellent processability is one of the most interesting properties of $\pi$-conjugated polymers, and they can be deposited by simple printing techniques, for example. These materials combine the advantageous properties of common polymers, such as low density and flexibility, with those of conventional semiconductors, for example, absorption and emission of light and tuneable conductivities, making them excellent candidates for optoelectronic devices. Nowadays, conducting polymers, such as polypyrrole (PPy), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PAn) (see Figure 1.1) have attracted considerable attention because of changes of their volume and shape resulting from electrochemical doping, characterised by transportation of solvated ions between the interior of the polymer matrix and the surrounding electrolyte solution, electrostatic repulsion, and/or structural distortion through oxidation of $\pi$-conjugated polymers.[2]
Polythiophenes (PThs) and its derivatives are one of the most important and widely studied materials among the growing number of \( \pi \)-conjugated polymers.[3] PThs have recently been used in a wide variety of organoelectronic applications such as field-effect transistors (FETs)[4], polymer light-emitting diodes (PLEDs)[5,6,7], solar cells[8], chemical sensors[9,10,11,12], through-hole plating of printed circuit boards[13], primers for electrostatic spray coating of plastics and antistatic coatings for cathode ray tubes to prevent dust attraction[14,15], photodiodes[16], and photovoltaic devices[17,18].

![Chemical structures of several conducting polymers.](image)

**Figure 1.1** Chemical structures of several conducting polymers.
1.2. Poly(3,4-ethylenedioxythiophene/poly(styrene sulfonic acid) (PEDOT/PSS)

Among the polythiophenes, poly(3,4-ethylenedioxythiophene) or PEDOT (Figure 1.1e), has been attracting specific attention including its methods of synthesis. PEDOT is a highly conducting polymer and a valuable organic electronic material first developed by scientists at the Bayer AG research laboratories in Germany in the 1980s. PEDOT is insoluble in many solvents but can be dispersed in water in the presence of polystyrene sulfonate (PSS) as the charge balancing doping agent during polymerisation. A doping agent or a dopant is a material (e.g. a polymer, solvent, acid, salt) added to improve the processability and electrical properties (e.g. conductivity) of electroactive polymers. In the case of PEDOT/PSS, doping is made possible by the interaction of the \(-\text{SO}_3\text{H}\) functional group of PSS with PEDOT (Figure 1.2) so the unpaired electron on the PEDOT chain will be highly mobile along the backbone making it highly conductive. The resulting PEDOT/PSS dispersion is more stable and processable resulting in a system with good film forming properties, high conductivity (ca. 10 S/cm), high visible light transmissivity, and excellent stability.[19,20] These properties make processable PEDOT a popular choice as a conductive material for the fabrication of electronic devices.

The synthesis of PEDOT aqueous dispersions using PSS as the doping agent has been extensively studied.[19,21] The dispersion can be conveniently prepared by oxidative polymerization of the EDOT monomer in the presence of PSS. This reaction results in PEDOT segments dispersed in aqueous medium by the formation of PEDOT/PSS complexes where the positively charged PEDOT segments are tightly attached (doped) to the higher molecular weight (MW) negatively charged PSS (see Figure 1.2). The PEDOT segments are believed to be short with previous reports indicating 6-18[22], 5-10[23], and 5-15[24,25] repeating units. There are two functions of PSS in the PEDOT/PSS system: 2% of the sulfonic acid functional group of the PSS provides the counter ions or act as dopants to the PEDOT chains and the other 98% is acidic and stabilises the PEDOT/PSS dispersion in water.[22,26] PEDOT and PSS are tied together, so the mobility of unpaired electron on the backbone of PEDOT chain will be high and make it highly conductive (Figure 1.2 A and B). Figure 1.2 C shows the
schematic picture of the PEDOT/PSS film morphology showing the PEDOT/PSS particles (pictured as short bars), surrounded by a thin PSS-rich surface layer.[23]

Figure 1.2 (A) Primary structure, (B) secondary structure of PEDOT/PSS complex, and (C) the schematic representation of the morphology of PEDOT/PSS.[22,23]

PSS is a linear polyelectrolyte with a high negative charge, and PSS content in the system of PEDOT/PSS impacts on some typical properties such as conductivity, transparency, and stability films.[20] Further study reflects that increasing the PSS content logically will reduce the electric conductivity.[22,27] PEDOT/PSS ratio of 1:2.5
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has higher conductivity compared to the PEDOT/PSS ratio 1:6, and the lowest one is PEDOT/PSS ratio 1:20. These values are also associated with the solid contents of the polymer system and correlate to their applications. Therefore PEDOT/PSS ratio 1:2.5 is suitable as antistatic, ratio 1:6 is suitable for OLEDs, and ratio 1:20 is suitable for passive matrix displays.

1.3. PEDOT synthesis

Many routes of synthesis of PEDOT from the monomer EDOT are possible. In the structure of EDOT (Figure 1.3), the oxygen bonded to the 3- and 4-positions of the thiophene ring, minimize unwanted polymerisation reaction at these two β-carbon sites. Moreover, these oxygens act as electron-donating group, which will increase the electron density of the thiophene ring.[28]

![Figure 1.3 Structure of 3,4-ethylenedioxythiophene (EDOT) monomer.](image)

In general, the synthesis of PEDOT derivatives can be divided into three different types of reactions: oxidative chemical polymerisation, electrochemical polymerisation and transition metal-mediated coupling of dihalo derivatives of EDOT.[2,29]

1.3.1. Oxidative chemical polymerisation

Oxidative polymerisation can be carried out using a number of methods and oxidants. The classical method uses iron (III) chloride (FeCl₃).[2] There are five proposed steps of the polymerisation mechanism for oxidative polymerisation of PEDOT: (1) oxidation of EDOT to from cation radical; (2) dimerization of cation radical; (3) deprotonation to form conjugation; (4) further polymerisation from n-mer to (n + 1)-mer; and (5) doping of the neutral PEDOT polymer to the conductive polycation.[28] The reaction is
initiated by an oxidizing agent that reacts with the EDOT monomer to generate the cation radicals that can form dimers. Then the anions of the oxidizing agent scavenge two protons. These steps are repeated continuously to produce the polymer. Some of the positive charge from the thiophene rings will be stabilized by the counter ions of the polymer. The overall oxidative polymerisation steps can be seen in Figure 1.4.

![Figure 1.4](image) The proposed five-step polymerisation mechanism for oxidative polymerisation of PEDOT.[28] In this case, FeCl₃ is the oxidant and Cl⁻ is the dopant.

Chemical polymerisation of EDOT was achieved using the classical oxidant FeCl₃, anhydrous in this case, in acetonitrile.[30] The resulting black powder of PEDOT could be precipitated from the mixture as it is insoluble in acetone, dimethylsulfoxide, N-methylpyrrolidone, methanol, acetic acid, acetonitrile, THF, CHCl₃ and water. Another convenient route using FeCl₃ is also to obtain these materials as stabilised nano- or
microparticles. Numerous groups have used different techniques to synthesise PEDOT nano-objects with the aim of improving the process engineering of this polymer. For instance, Oh and Im, have prepared PEDOT particles in aqueous medium containing micelles of sodium dodecylbenzene sulfonic acid (DBSA) used as templates in the presence of FeCl$_3$/Na$_2$S$_2$O$_8$ as the oxidant mixture. The particles thus obtained were rather ill-defined and showed a tendency to aggregate. In another approach, Mullen and co-workers,[31] also reported the synthesis of PEDOT nanoparticles by emulsion polymerisation in cyclohexane using poly(isoprene)-block-poly(methyl methacrylate) (PI-b-PMMA) as the stabiliser and FeCl$_3$ as the oxidant. Yoon et al,[12] described the original synthesis of PEDOT nanotubes using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) cylindrical micelles as templates.

Oxidative polymerisation can also be carried out using iron (III) p-toluenesulfonate (Fe(OTs)$_3$) as oxidising agent.[2,22] The product, PEDOT, is a black, insoluble, and infusible compound can be converted by oxidative doping to the conductive polycation[22] by, for example, PSS. A variant of this method was developed by de Leeuw, et.al. utilising Fe$_{III}$(OTs)$_3$ in combination with imidazole as base system at elevated temperature. The use of Fe$_{III}$(OTs)$_3$ was advantageous because it did not crystallize and easier to spin coat the solution. The films were dried and baked either on a hotplate, and the polymerisations were done during heating. A black insoluble and infusible PEDOT polymer was obtained in this method.

The third method in oxidative polymerisation of EDOT is the most practical procedure, called Baytron P synthesis which was developed by Bayer AG. PEDOT/PSS film of Baytron P is highly conductive, transparent, mechanically durable, and insoluble in any common solvent after drying.[2] The disadvantage of PEDOT, in general, as an insoluble polymer, can be circumvented by polymerising EDOT in combination with a water-dispersible polyelectrolyte such as PSS. Louwet, et.al.[19] prepared PEDOT/PSS via oxidative polymerisation by mixing EDOT monomers with PSS and Na$_2$S$_2$O$_8$ as the oxidising agent in water and stirring, and adding Fe$_2$(SO$_4$)$_3$. A dark blue-aqueous dispersion of polymer PEDOT/PSS was obtained and purified by ion exchanging with acidic and basic resin. The dark blue dispersion generated transparent and moderate film conductivity (i.e. 0.1 S/cm).
A variation to the Baytron P method is the synthesis of PEDOT in a biocatalysed polymerisation process. Nagarajan, et al.[32] synthesised PEDOT/PSS biocatalytically under much milder pH conditions using soybean peroxidase (SBP). This novel approach, which involves the use of conjugated oligomers terthiophene as the redox initiators, is generic and has vastly expanded the types of materials (thiophenes, pyrroles) that can be polymerised using enzymatic methods and benign conditions. The oxidized terthiophene helps in the oxidation of EDOT and mediated the polymerisation to lead the formation of PEDOT (Figure 1.5).

Figure 1.5 Polymerisation of EDOT catalyzed by SBP using terthiophene as a redox mediator.[32]

1.3.2. Electrochemical polymerisation

The second type polymerisation of the electron-rich thiophene-based monomers to form PEDOT is called an electrochemical oxidation.[2] PEDOT synthesis is not chemically but potentiostatically activated in solutions containing the monomer EDOT. Several derivates of EDOT also have been synthesised electrochemically. In situ measurements of PEDOT films grown this way are presented in some literatures.[33] Heywang and
Jonas [34] synthesised conductive PEDOT with a resistance of \(~100\) ohm maintained over 25 h at 100 °C in water vapour. Pei, et al, [30] used a platinum wire counter electrode and Ag/AgCl reference electrode, and showed that PEDOT has a thin, transparent and rather homogeneous film on the working electrode.

Sankaran and Reynolds,[35] studied the electropolymerisation efficiency in more detail by comparing the amount of electroactive polymer deposited with a set number of repeated scans as a function of electrodeposition medium. The result showed that the electrodeposition rate of EDOT proceeds more rapid than that for 4-octydioxeno[2,3-c]thiophene (EDOT-C\textsubscript{8}), which is more rapid than 4-tetradcyldioxeno[2,3-c]thiophene (EDOT-C\textsubscript{14}) in all of the solvent/electrolyte systems studied. This can be attributed to solubilisation of the oligomers forming at the electrode surface by the long alkyl chains. Furthermore, the deposition was found to be most efficient in CH\textsubscript{3}CN-based electrolytes and least efficient in CH\textsubscript{2}Cl\textsubscript{2}. This is as expected as CH\textsubscript{2}Cl\textsubscript{2} is generally a good solvent for alkyl-derivatized thiophene polymers. In a practical sense, 0.1 M LiClO\textsubscript{4}/CH\textsubscript{3}CN was found to serve as the best electrodeposition medium for the EDOT and alkyl-substituted EDOT polymers. Electropolymerisation of EDOT has been performed in aqueous sodium dodecylsulfate (SDS) solutions on Pt electrode, but this solution lowers its oxidation potential. PEDOT films electrosynthesised in this medium present well-defined structures.[36] Similar electrochemical polymerisation of substituted (alkylated, alkoxyalted, alkylsulfonated, etc.) thiophenes can be achieved as well as combinations of different monomers.[35,37]

Overall, there are a number of advantages to electrochemical polymerisation: it requires only a small amount of monomer; a short time to polymerise; and the product can be both electrode-supported and free-standing films.[2] This polymerisation method results in a highly transmissive PEDOT film formed at the anode. A wide range of electrolytes are suitable for EDOT polymerisation, including polyelectrolytes.[38] This last point is worth noting, since it allows access to a wide range of thiophene-based copolymers with a correspondingly wide range of possible properties.
1.3.3. Transition metal-mediated coupling of dihalo derivatives of EDOT

The third method to synthesise PEDOT is a transition metal-mediated coupling of dihalo derivatives of EDOT. Many polymers based on thiophene structures have been prepared using transition metal-catalysed coupling of activated organometallic derivatives.[2] This methodology has been applied by Yamamoto et al to the direct formation of neutral PEDOT.[39,40] They synthesised PEDOT by Ni-promoted dehalogenation polymerisation of the corresponding dichloro monomer. 2,5-Dichloro-3,4-EDOT was synthesised by chlorination of EDOT with N-chlorosuccinimide (2.2 mol per 1 mol of EDOT) at 0°C in THF.[39] The dehalogenation polymerisation of 2,5-dichloro-3,4-EDOT was carried out by using a mixture of bis(1,5-cyclooctadiene)nickel(0), 2,2’-bipyridyl, and 1,5-cyclooctadiene (Figure 1.6). Materials with low molecular weight are yielded through this method, and it will be very interesting when monomers with solubilising side groups are synthesised by this method.

![Figure 1.6 Polymerisation EDOT by transition metal][39]

1.4. Modification of PEDOT/PSS

Because of the excellent properties and utility of PEDOT/PSS, a number of research groups have continued to study this area. Although availability of oxygen in 3- and 4-positions are blocked and cannot be polymerised further, their presence increase the electron density in the thiophene ring. Therefore, the conjugated polyythiophene ring can be readily be positively charged by dopants.[28] This contributes to the interest of synthesis of new materials based on the EDOT monomer to improve processability and suitability for device applications.

Alkylation and alkoxylation of EDOT to synthesise alkylated or alkoxyalated PEDOT (Figure 1.7) had been done by some groups. Oxidative polymerisation of alkylated EDOT, EDOT-C8 and EDOT-C14,[35] resulted in derivates of PEDOT which have
better solubility. They are also electroactive and conducting polymer films on electrode surfaces and their performance, compared to PEDOT, have been investigated further.

Modification of PEDOT structure by alkoxylation had also been done by Schottland, et al.[41] They synthesised, using FeCl₃, several alkoxy substituted EDOT with different chain lengths from n-C₆H₁₃ to n-C₁₆H₃₃. The importance of this study is on the length of chain to determine the effect of chain length on the solubility of the products. The optimum polymerisation conditions (with 1.5 equivalents of FeCl₃) for n-C₁₄H₂₉ and n-C₁₆H₃₃ resulted in 65% and 68% of the products being soluble in CH₂Cl₂ respectively. These polymers gave approximately the same GPC results (MW: 12.900 and 14.300 with a polydispersity of 1.45 and 1.65). Kumar and Reynolds [37] synthesised a fully soluble polymer which could be isolated in 80% yield from polymerisation of EDOT-C₁₄H₂₉ using one equiv of FeCl₃ in dry CHCl₃. The polymer was completely soluble in CHCl₃, CH₂Cl₂, C₂H₂Cl₄, and THF. Further investigation showed that by increasing the [FeCl₃]/[monomer] ratio to greater than two, a fraction of the polymer becomes insoluble in organic solvents, which may be due to either higher molecular weight or a small amount of crosslinking; but with a ratio greater than or equal to five, the polymer becomes fully insoluble. The characterization of electronic properties has been done on samples prepared with FeCl₃/monomer equal 1, as the polymer is completely soluble. Some other derivates of alkylenedioxythiophene by modification of EDOT also have been synthesised and reported in detail.[42]
A few researches have investigated endcapping of PEDOT. By end-capping, the site for further growth of polymerisation is blocked by pendant functionality. The size of polymer can be controlled directly by varying the ratio of monomer and capping unit.[43] TDA Research, Inc. has synthesised end-capped PEDOT with non-conducting groups.[44] The end-capping monomers containing two methacrylate groups were successfully added to PEDOT via oxidative polymerisation using iron (III) salt as the oxidant in acetonitrile (see Figure 1.8). The products showed that the conductivity increased by increasing the length of PEDOT.

1.5. PEDOT/PSS applications
Modification of PEDOT/PSS not only impacts its chemical and physical properties but also its application. Some typical properties also depend on the PEDOT/PSS ratio. Conductivity and transparency of films are important to meet the requirements for most
applications. PEDOT which have low PSS contents (e.g. 1:2.5) have been associated with high conductivity and are suitable as antistatics. OLED requires small particles and lower conductivities which match with the PEDOT/PSS ratio 1:6. Passive matrix display grades are better at the lower end of the conductivity range which results from PEDOT/PSS ratio 1:20. Increasing the PSS ratio will logically decrease the electric conductivity.[22]

The use of PEDOT/PSS as organic electronics material has been restricted because commercially available PEDOT/PSS dispersions have low conductivity.[23,45,46,47] Therefore, the effort to investigate PEDOT/PSS by modifying the structure in order to enhance the properties, such as the conductivity and solubility, still attract many researchers. Various modifications of PEDOT/PSS has been done to enhance conductivities and their potential use as electrodes.[46] Enhancement of conductivity of PEDOT/PSS films also can be done by adding HCl-methanol treatment,[48] or by adding organic solvent additives and annealing,[49,50] and by using a conductivity enhancement agent such as DMSO or ethylene glycol so the conductivity can reach 900-1000 S/cm.[51] Recent enhancement of the conductivity of PEDOT/PSS films 1880 times that of pristine film was achieved by adding dimethyl sulphate.[52]

Electrical properties of PEDOT/PSS can be modified by incorporation into polymer matrices of inorganic or metallic nanoparticles, such as incorporation of ZnO nanoparticles.[53] Formation of polymer-nanoparticle composites is an attractive method to modify the properties of polymers commonly used in the fabrication of organic electronic devices to improve their performance.[54] The large variety of organic polymers can be combined by this method to be solution-processable with the excellent electronic and optical properties of nanoparticles. By blending PEDOT/PSS and organic solvents, such as N-methylpyrrolidone (NMP), DMSO or ethylene glycol, samples coated will exhibit higher conductivity than pure PEDOT/PSS.[53,55,56]

Various and expanding uses of PEDOT/PSS have been studied in detail for more than three decades, and currently the many applications of PEDOT/PSS films include electroplating for the metallization of insulator [15], cathodes active material in capacitor [57] and also as an anticorrosive additive for paints [58]. This electrically conducting polymer has also been used for antistatic coating [59,60], electrochromics
[61,62], biosensing [63,64,65,66] and drug delivery applications [67]. PEDOT as a conjugated polymer also exhibits greatly significant properties such as absorption and emission of light or electrical and photoconductivity, therefore PEDOT/PSS as blend are also useful for electronic device such as organic light emitting diodes (OLEDs) [68,69,70], organic field effect transistors (OFETs) [71,72,73], and organic photovoltaic devices (OPVs) [45,74,75,76]. As a result, PEDOT/PSS is now a major material for electronic applications.

1.6. Objectives

The long term aim of this research, beyond the scope of this thesis, is the utilisation of PEDOT/PSS as a high performing (better than the commercially available counterpart) polymer layer and a selective sensing material in OPV and OFET devices, respectively.

This thesis focuses on the study of the physical properties, particularly the conductive behaviour of PEDOT/PSS, as dispersion and film, under varying synthetic and doping conditions and upon structure modification, with the aim of improving the conductive performance of PEDOT/PSS.

The results are divided into chapters addressing specific objectives with Chapters 1 and 2 discussing the general introduction and experimental.

Chapter 3 provides a statistical assessment of the reliability of conductivity measurements by the four-point probe method by correspondence analysis and multi-linear regression analysis (MLR) coupled with ANOVA. The statistically determined optimal conductivity measurement conditions have been applied to all PEDOT/PSS films tested in this work.

Chapter 4 discusses the development of a capillary electrophoresis method for PEDOT/PSS allowing the separation of free PSS from PEDOT-doped PSS. This CE method has been used to characterise the PEDOT/PSS dispersions generated in this work.
Chapter 5 focuses on the optimisation of synthetic and doping conditions for PEDOT/PSS by oxidative polymerisation with the aim of enhancing the processability of dispersions and conductivity of the resulting films.

Chapter 6 discusses the capability of the PEDOT end-structure to be modified using thiophene based endcapping agents (e.g. 2-thienylmethyl methacrylate). The aim is the attachment of functional endgroups (e.g. double bond) for subsequent reaction (e.g. polymerisation) such as the reaction presented in Chapter 7.

Chapter 7 builds on Chapter 6 and demonstrates the capability of PEDOT to be used in the synthesis of a more complex polymeric architecture, the crosslinked core star polymer with PEDOT as arms, for potential application in molecular imprinting (beyond the scope of this thesis). This synthetic modification employed 2-thienylmethyl methacrylate, synthesised in this work, as the linking agent between the non-conductive core and PEDOT arm.

Chapter 8 demonstrates the application of the better performing (highly conductive and processable) PEDOT/PSS films as an interfacial conductive polymer layer and electrode gate in OPV and OFET devices, respectively.

Chapter 9 contains the summary of the results and recommendations for future direction of the research.
CHAPTER 2 - EXPERIMENTAL
2.1. Materials and Reagents

Commercial PEDOT/PSS (Clevios, 1:2.5 ratio, P VP Al 4083), with a solid content of 1.3 - 1.7% by weight was purchased from H.C. Starck (Munich, Germany), and stored in a refrigerator at 5°C until it was used.

Poly(styrene sulfonate) (PSS, MW = 70 kDa) and poly(4-vinylpiridine) (PVPy) were purchased from Sigma-Aldrich Australia and used as received.

Poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals Inc, Nebraska USA (Mw = 60K, PDI = 2.1, RR = 91-95%) and Luminescence Technology Corp., Taiwan (Mw = 58-63K, PDI = 3.6, RR = 93- 95%) and stored under nitrogen. (6,6)-Phenyl-C_{61}-butyric acid methyl ester (PCBM) (99.5 % purity) was purchased from Luminescence Technology Corp., Taiwan and stored under nitrogen.

3,4-Ethyleneoxythiophene (EDOT), benzyl chloride, sodium N,N-diethyl dithiocarbamate trihydrate, 2-thiophenemethanol (2TM), 2-thiopheneacetonitrile (2TA) and triethylamine were purchased from Sigma-Aldrich and used as received.

Na$_2$S$_2$O$_8$, Fe$_2$(SO$_4$)$_3$, and ammonium persulfate (APS) were purchased from (Sigma-Aldrich Australia) and were used as received. CaCl$_2$ anhydrous, cuprous chloride (CuCl), sodium hydroxide, sodium tetraborate (Na$_2$B$_4$O$_7$), sodium biphosphate (NaH$_2$PO$_4$), sodium bicarbonate (NaHCO$_3$), ammonium acetate (CH$_3$COONH$_4$) and ammonium bicarbonate (NH$_4$HCO$_3$), from Sigma Aldrich were used as received.

Azobisisobutyronitrile (AIBN) (Dupont) was recrystallised in acetone prior to use.

Ethylene glycol dimethacrylate (EGDMA) (Sigma-Aldrich Australia) was distilled under reduced pressure prior to use.

Methacryloyl chloride, from Sigma Aldrich, was purified using aluminium oxide (activated, basic) and distillation, respectively, prior to use.

Deuterated dimethyl sulfoxide (d$_6$-DMSO), deuterated chloroform (CDCl$_3$), and deuterated water (D$_2$O) were purchased from Sigma-Aldrich Australia and used as received.

Sulfuric acid (H$_2$SO$_4$) 98%, dimethyl sulfoxide (DMSO), dichloromethane (DCM), isopropyl alcohol (IPA), chloroform, and acetonitrile (ACN) were used as received from supplier. Acetone, ether, tetrahydrofuran (THF), and methanol (MeOH) were used after
distillation. THF was dried over molecular sieves. Anhydrous ethanol was used as received.

Acidic and basic ion-exchange resins (LEWATIT, Bayer AG) were purchased from Sigma-Aldrich Australia.

Dialysis tubes, Membra-Cel Dialysis Membranes MWCO 3500, were purchased from SERVA.

Glass microscope slides were purchased from Livingstone and cut into 12 mm x 15 mm. Indium tin oxide (ITO) coated slides (Rs = 8-12 Ω) were purchased from Delta Technologies Limited. Pre-patterned ITO slides (Rs = 15 Ω/sq, 13 mm x 18 mm x 1.1 mm) ITO coated glass (XY 15S) double ended were purchased from Kintec Company, Hong Kong.

2.2. Preparation of PEDOT/PSS aqueous dispersions via oxidative polymerisation

2.2.1. Conventional method (in-situ addition of PSS)

The general procedure for the synthesis of all PEDOT/PSS aqueous dispersions was as previously described by Louwet, et, al.[19] Typically, 192.3 mg of 3,4-ethylenedioxythiophene was mixed with the appropriate volume of 6 wt % PSS solution to obtain the desired PEDOT/PSS ratio by weight (e.g. 8.00 mL of 6 wt % PSS = 481 mg PSS for a 1:2.5 ratio). 384 mg of Na2S2O8 initiator was then added and the reaction mixture made up to 30.0 mL with RO water. After stirring for 10 minutes, 3 mg of Fe2(SO4)3 was added and the reaction mixture was stirred vigorously for the required time of reaction. The dark blue aqueous mixture is purified by stirring (ion exchanging) with acidic and basic ion exchange resins (~500 mg) for about 10 minutes then dialysed in methanol and water to remove unreacted monomers and oxidation agents. Dialysis allowed removal of excess H+ and help maintain the pH of the dispersions as neutral. Presence of excess acid in the dispersion corrodes the films.

All PEDOT/PSS dispersions products were referred to as PP(1:x)-y, where 1:x is the ratio of PEDOT to PSS by weight, and y is the length of reaction time. For example PP(1:2.5)-24 means PEDOT/PSS in ratio 1:2.5 synthesised for 24 hours.
2.2.2. Post-polymerisation dilution with PSS
PEDOT/PSS aqueous dispersion, in a 1:1 ratio (PP(1:1)-24) was synthesised according to the method outlined in Section 2.2.1 and diluted, post-polymerisation, with more PSS. The dilution was adjusted by adding 0.2 ml, 0.3 ml and 0.4 ml of 6% PSS solution to 1.0 mL of PP(1:1)-24 dispersion resulting in PEDOT/PSS ratios of 1:2, 1:3 and 1:5, respectively. These diluted dispersions are referred to as PP(1:2-d)-24, PP(1:3-d)-24, and PP(1:5-d)-24, respectively.

2.2.3. Post-polymerisation addition of PSS
PEDOT was synthesised in water and acetonitrile according to the procedure outlined in Section 2.2.1 in the absence of PSS. The resulting dried polymers were then mixed with an appropriate amount of PSS to obtain a PEDOT/PSS ratio of 1:2.5 by weight and stirred vigorously overnight (24h) to provide the PEDOT/PSS aqueous dispersions. These PEDOT/PSS aqueous dispersions produced by post-polymerisation addition of PSS are referred to as PP\textsubscript{W}(1:2.5-p)-24 for PEDOT synthesised in water and PP\textsubscript{A}(1:2.5-p)-24 for PEDOT synthesised in acetonitrile.

2.3. Preparation of end-capped PEDOT/PSS aqueous dispersions
2-Thiophenemethanol (2TM), 2-thiopheneacetonitrile (2TA) and 2-thienylmethyl methacrylate (2TMM) were employed as endcapping agents. 2TM and 2TA were commercially sourced and used as received. 2TMM was synthesised as follows.

![Structures of some end-capping agents](image)

**Figure 2.1** Structures of some end-capping agents: 2-thienylmethyl methacrylate (2TMM), 2-thiophenemethanol (2TM) and 2-thiopheneacetonitrile (2TA).
2.3.1. Synthesis of 2-thienylmethyl methacrylate monomer

2-Thienylmethyl methacrylate (2TMM) was synthesised according to the previously published procedure for the synthesis of 3-thienylmethyl methacrylate by Cirpan, et al (2002)[77] and summarised in Figure 2.2. To a 250-mL round bottom flask, 2-thiophenemethanol (5.7 g, 50 mmol), dry triethylamine (7.3 g, 71 mmol), and a small amount of CuCl were dissolved in 35 mL of dry diethyl ether. The mixture was added slowly at 0°C with freshly distilled methacryloyl chloride (5.35 g, 51 mmol) in 35 mL of dry diethyl ether. The mixture was then stirred for 2 hr. The triethylammonium chloride was filtered off through a silica gel column. After solvent evaporation, the residue was stirred overnight in a 1:1 mixture of dichloromethane and 2 M NaOH. The organic layer was separated, washed twice with water, and dried over CaCl₂. After solvent evaporation, the residue was distilled in vacuo over a Vigeux column and purified by column chromatography using n-hexane:ethylacetate (90:10).

![Figure 2.2](image_url) Synthetic route of 2-thienylmethyl methacrylate from 2-thiophenemethanol and 2-methyl-acryloyl (methacryloyl) chloride.

2- Thienylmethyl methacrylate (2TMM) was a colourless liquid, and, evaporated under the pressure 1 mBar at 92°C during vacuum distillation, yield 37.5%. NMR assignments for 2TMM are as follows.[77,78,79]:

\[ ^1H\text{NMR (CDCl}_3, \delta): 1.93 \text{ (s, CH}_3\text{)}, 5.30 \text{ (s, OCH}_2\text{)}, 5.55 \text{ (s, vinyl H), 6.12 \text{ (s, vinyl H), 6.95 \text{ (m, ring H), 7.08 \text{ (m, ring H), 7.26 \text{ (m, ring H).}}) \]  

\[ ^{13}\text{C}\text{NMR (CDCl}_3, \delta): 17.68 \text{ (CH}_3\text{), 60.23 \text{ (CH}_2\text{), 124.64 (CH} = \text{CH}_2 \text{ethylene), 125.55 (C thiophene), 126.22 (C thiophene), 127.49 (C thiophene), 135.47 (C= ethylene), 137.53 (C thiophene), 166.43 (C=O).} \]
The FTIR spectrum of 2TMM exhibited peaks at 3111 cm\(^{-1}\) attributed to the stretching of aromatic =C-H, 2961 and 2945 cm\(^{-1}\) attributed to symmetric stretching of aliphatic – C-H and stretching of the C=O is observed at 1722 cm\(^{-1}\). Appearance of peaks at 1639 cm\(^{-1}\) and 1455 cm\(^{-1}\) are attributed to C=C alkenyl stretching and symmetrical stretching of the C=C in the ring, respectively. Presence of C-O can be identified from the peaks at 1161 and 1012 cm\(^{-1}\). The aromatic C-H can be observed at 946 and 709 cm\(^{-1}\), whilst C-S stretching appeared at 855 and 814 cm\(^{-1}\).

2.3.2. Synthesis of endcapped PEDOT/PSS dispersions
Endcapping of PEDOT with thiophene base monomers 2TMM, 2TM and 2TA was achieved, using EDOT:PSS ratio of 1:2.5, according to the procedure given in Section 2.2.1, with the addition of varying concentrations of end capping agents: 10%, 20%, 30%, 40% and 50% by weight with respect to the EDOT monomer (193.2 mg).

The PEDOT/PSS dispersions resulting from these reactions are referred to as PP-e-wt-y, where \(e\) is the endcapping agent, \(wt\) is the concentration of endcapping agent added, and \(y\) is the length of reaction time. Thus, a PEDOT/PSS synthesised using 10% of 2TM reacted for 24 hr is referred to as PP-TM10-24.

2.3.3. Synthesis of endcapped PEDOT
PEDOT was endcapped with 2TMM, 2TM and 2TA according to the procedure outlined in Section 2.2.1 in the absence of PSS, but with the addition of 50% (with respect to EDOT) end-capping agent in 40 mL dichloromethane. The resulting black PEDOT powders are referred to as PnoP-TMM50, PnoP-TM50, and PnoP-TA50.

2.4. Synthesis of Star PEDOT/PSS
2.4.1. Star PEDOT/PSS via arm-first method
The reactive PEDOT arm was synthesised by endcapping PEDOT with 30% and 50% (with respect to the EDOT monomer) 2TMM containing a polymerisable double bond according the procedure outlined in Section 2.2.1 and 2.3.2 for 24 hours. To these 2TMM endcapped PEDOT/PSS dispersions, 10 mg of ethylene glycol dimethacrylate
(EGDMA) crosslinker and 7.7 mg of ammonium persulfate (APS) initiator were added. The reaction mixtures were stirred for 24 hours. The dark blue aqueous dispersions were stirred in acidic and basic ion exchange resins, filtered then centrifuged to remove residues. The reaction mixtures were further purified by dialysis (MW 3500 cut off) using water and methanol.

2.4.2. Star PEDOT/PSS via core-first method

The non-conductive vinyl-functionalised core was prepared by stirring 2TMM (93 mg) with EGDMA crosslinker (940 mg) using initiator AIBN (9.5 mg) in 3 ml acetonitrile at 60°C for 24 hours after purging with nitrogen gas. The product was purified by stirring and washing with hexane and methanol.

The star PEDOT/PSS was synthesised following the procedure outlined in Section 2.2.1 except that 19.3 mg (10% of the mass of EDOT) of the reactive EGDMA core was added to the reaction mixture. The reaction was repeated using 10 mg EGDMA core (5% of the mass of EDOT). In both cases, the EDOT:PSS ratio was kept at 1:2.5 and reacted for 24 hours. The star PEDOT/PSS obtained via this method are referred to as ScP10P(1:2.5)-24 for 10% core by weight and ScP5P(1:2.5)-24 dispersions for 5% core by weight. Star PEDOT/PSS containing 10% EGDMA core was also prepared in 1:1, 1:3 and 1:5 EDOT:PSS ratios and the products are referred to as ScP10P(1:1)-24, ScP10P(1:3)-24, and ScP10P(1:5)-24, respectively.

2.4.3. Star PEDOT via core-first method and post polymerisation addition of PSS

Star PEDOT was synthesised according the procedure outlined in Section 2.4.2 in the absence of PSS in 50 ml methanol. The reaction was kept at 45°C for 7 days. The resulting greenish product, referred to as ScPEDOT, was then added with an appropriate amount of PSS to obtain a ScPEDOT/PSS ratio of 1:6 by weight and stirred vigorously overnight (24h). The ScPEDOT/PSS aqueous dispersion produced by post-polymerisation addition of PSS is referred to as ScPP(1:6-p)-24.
2.5. Preparation of PEDOT/PSS films

All PEDOT/PSS dispersions were concentrated until the viscosity of the dispersions was close to that of commercial (Clevios P). The dispersion viscosity, based on the time it took for 1 drop of the dispersion to travel 3 cm along a glass slide oriented 90° from a flat surface, were all between 8-15 sec/3cm (Clevios P = 11 sec/3 cm).

PEDOT/PSS films were generated according the following procedure. 70 µL of the PEDOT/PSS aqueous dispersion was filtered with a 0.45µm PTFE syringe filter, dropped onto a 12 x 15 mm² glass microscope slide and spun for 40 seconds at 4000 to 5000 rpm. Prior to use, the glass substrate was pre-cleaned with detergent, de-ionized water and acetone, in sequence, and dried with lint-free tissue. The film was then annealed at 140°C in a hot plate for 1 h in open air before conductivity measurements.

Films (from commercial Clevios P) used for statistical analysis (Chapter 3) were spun at different spin-coating speeds: 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm for 40 seconds then annealed at 140°C in a hot plate for 1 h in open air before conductivity measurements.

2.6. Conductivity measurements

Conductivity of the PEDOT/PSS films was measured using a four point probe attached to a Keithley Model 2400 Source Meter and Fluke 79 III True RMS multimeter. The I-V curve was generated by measuring the voltage resulting from the passage of current between 0.1 µA to 0.8 µA. For each film, representative I-V measurements were obtained three times at different locations (see Figure 2.3). For each of these locations, the thickness was measured 6 times using an Alpha Step-500 profilometer by the following technique. Typically, a stylus was placed in contact with the surface of the film, and then gently dragged, at a speed of 20 µm/s and 200 µm scan length, perpendicular to a mechanically scratched surface of the film. The vertical deflection measured the change in step height and thickness of the film.
Figure 2.3 (A) Schematic diagram of the four-point probe method; two probes are used to measure the current (I) and the other two probes are used to measure the voltage (V) passing through the film; (B) a hypothetical film showing three locations used for I-V measurements using the four point probe. Each location is 6 mm wide; a is the width of the film (and substrate) and b is the length of the film (and substrate).

The conductivity of the film was determined firstly by calculating the slope of the current-voltage curve as the resistance (R) of the film. The sheet resistance (Rₛ) was calculated according to equation 3.2 (see Chapter 3) using the geometric correction factor (k) obtained from the Haldor Topsoe table[80], based on the width a and the length b of the film (substrate) and the spacing s between the probes. For the films under study a = 12 mm, b = 15 mm, s = 1.5 mm, k = 4.2209. The resistivity, ρ, is calculated according to equation 3.3 (see Chapter 3) and is the reciprocal of conductivity.

2.7. Capillary electrophoresis

CE experiments were carried out on a 3D-CE instrument (Agilent Technologies, Waldbronn, Germany) with the 3D-CE Chemstation controller collecting the data for analysis. The DAD was set to 230 nm and the spectrum was also collected between 190 and 320 nm. Uncoated fused silica capillaries of 50 cm total length (50 μm i.d., 360 μm o.d.) and 41.5 cm to the detection window were purchased from Molex (Phoenix, AZ). The detection window was created by removing the polymide coating as mentioned in previous reference.[81] New fused silica capillaries were conditioned by performing the following washes: 0.5 M NaOH for 30 min, and water for 10 min. In between runs, the
capillary was initialized with 1 min of 0.5 M NaOH, 0.5 min of water, 1 min acetonitrile, and 4 min of separation buffer by flushing at 950 mbars. The temperature of the capillary cassette was maintained constant at 20°C. The samples were prepared in purified water and injected at a sample concentration of 0.5 g L⁻¹ by hydrodynamic injection (50 mbar, 4s). Water was purified with a Milli-Q system from Millipore (Bedford, MA). A separation voltage of +15 kV was applied. Sodium tetraborate (Na₂B₄O₇), sodium biphasate (NaH₂PO₄), ammonium acetate (CH₃COONH₄), and sodium bicarbonate (NaHCO₃) were used and added in the sample as an electrophoretic marker.

The amount of free (undoped) PSS in PEDOT/PSS dispersions with migration time of ~14 min was quantified to estimate the degree of doping, i.e. initial PSS concentration minus free PSS. A calibration curve (Figure 2.4) was constructed from various concentrations of PSS solutions against their peak areas. The amount of free PSS in the PEDOT/PSS dispersions was estimated using the Solver function of Excel.

![Figure 2.4 CE calibration curve showing the correlation of peak area and concentration of PSS.](image)
2.8. FTIR studies
FTIR spectra were recorded as neat samples on a Shimadzu FTIR-8400 spectrophotometer. The polymer samples were prepared by evaporating the water in the dispersion followed by drying at 40°C in a vacuum oven.

2.9. NMR studies
$^1$H NMR, $^{13}$C NMR, $^{13}$C distorsionless enhancement by polarization transfer including the detection of the quaternary nuclei (DEPTQ) NMR, and heteronuclear single quantum coherence (HSQC) NMR were measured in chloroform (CDCl$_3$), for the monomers and polymers which are soluble in organic solvent, in deuterated water (D$_2$O) and in deuterated dimethyl sulfoxide (d$_6$-DMSO) for PEDOT/PSS dispersions on a Bruker Biospin Ascend TM 400 Spectrometer. Chemical shifts (δ) are given in ppm relative to CDCl$_3$ (7.26 ppm, $^1$H; 77.0 ppm, $^{13}$C), chemical shifts (δ) are given in ppm relative to D$_2$O (4.8 ppm, $^1$H), and chemical shifts (δ) are given in ppm relative to d$_6$-DMSO (2.5 ppm, $^1$H; 39.5 ppm, $^{13}$C).

2.10. UV spectrophotometric analysis
The UV absorption spectra of PEDOT/PSS films were taken using a Cary 6000i UV-Vis-NIR Spectrophotometer (Varian, Inc) over the wavelength range of 200 to 400 nm. The films were prepared in the same manner as those used for conductivity measurements and spun-coated onto quartz substrates.

2.11. Particle size measurements
Particle size distributions were determined by dynamic light scattering (DLS) performed on a Zetasizer Nano Series from Malvern Instruments (Worcestershire, UK). Typically, 0.1-0.2 mg of dried PEDOT/PSS sample was mixed with 2-3 mL of filtered MilliQ water. The dispersions were ultrasonicated for 30 min and immediately filtered (0.45 μm) before measurements. Figure 2.5 is representative of the raw DLS data from triplicate measurements of PP(1:2.5)-24 dispersion showing size distribution of particles by volume. Where more than one peak is reported, peak numbers are assigned starting from the highest particle size. In all cases, multiple peaks are distinctly separated and are never overlapping.
2.12. **Zeta potential measurements**

Zeta potential is known as the surface potential at the plane of shear between the particle and solvent under the flow[82], and commonly used to characterise the surface charge of particles.[83] Zeta potential measurements of PEDOT/PSS dispersions were performed using a Zetasizer Nano Series from Malvern Instruments (Worcestershire, UK) fitted with maintenance-free folded capillary cell (DTS 1060). Very dilute colloidal dispersions of polymers were prepared using ~1.0 mg PEDOT/PSS composite in 1.5 mL of 20 mM sodium borate buffer solution pH 9.2. The dispersions were shaken overnight and ultrasonicated for 30 min; and immediately filtered (0.45 μm) before measurements. Measurements were performed at 25 °C, 10 sec for equilibrium time, and in triplicate measurements for each sample.

2.13. **Thermogravimetric analysis**

Thermo gravimetric analysis (TGA) of PEDOT/PSS polymers was performed on a Diamond TG/DTA Perkin Elmer. The sample was placed in an aluminium pan at the heating rate 10°C/min from 30°C to 600°C under N₂ atmosphere. Al₂O₃ was used as the reference material.

The surface morphology of the sample PEDOT/PSS films were analysed using a microscope optic “Axioskop 40 Pol” from ZEISS, or scanning electron microscopy (SEM) in XL 30 SEM model and Oxford ISIS EDS instructions, operating at 15 kV. For SEM analysis, the samples were gold coated prior analysed using SPI Sputter Coating Unit EM IX-Ray, SPI MODULE sputter coater.

2.15. Statistical Analysis using SPSS program

All data calculated during conductivity measurements were classified as predictor variables: current (I), voltage (V), thickness (t), resistance (R), sheet resistance ($R_s$), and resistivity ($\rho$); and dependent variable: conductivity ($\sigma$). Correspondence analysis and multiple linear regression (MLR) modelling methods were performed by the SPSS statistical program IBM SPSS Statistics 20.

2.16. Fabrication and testing of an organic photovoltaic (OPV) device

The fabrication steps of an organic photovoltaic cell and its characterisation are as follows.[84]

2.16.1. Fabrication

A typical OPV cell device in this project consists of a thin film (~100 nm) of photoactive material sandwiched between two electrodes. The devices are built onto a glass substrate in layers. The glass slides were purchased with pre-patterned ITO with 5 mm$^2$ active area. The pre-patterned ITO slides allow for six pixels of 3x15 mm defined by chemical etching to be made on each slide. The slide-surface was pre-coated with a protective photoresist to keep the active surface from contamination. The first step in the fabrication process is the removal of this protective layer by sonicating the slides in a 5% NaOH solution before rinsing them in an aqueous detergent solution for 30 min at ~40°C in an ultrasonic bath (Unisonix FXP10M). The glass slides were then rinsed repeatedly with milli-Q water, sonicated in acetone and in isopropyl alcohol (IPA), and dried with lint-free tissue (Kim Wipes®), then blown-dry in dry nitrogen gas.

All PEDOT/PSS aqueous dispersions were sonicated for 30 minutes to break the aggregation and followed by filtration using 0.45 um PVDF filter. The active layer P3HT/PCBM solution was freshly prepared using P3HT (MW2121B) (having a Mw
~60kDa characteristic) and PCBM purchased from Lumtec with a weight ratio of 1:0.8. The solution was made of 18 mg mixed P3HT/PCBM in 1 mL chloroform in 4 mL vial. The solution was then placed in an ultrasonic bath for between 30 mins and 90 mins to completely dissolve each component and to obtain a homogeneous solution.

Typically, the ITO substrates were secured in the ozone cleaner (UV/Ozone Procleaner TM, BIOFORCE NANO SCIENCES) for a minimum of 15 min prior to use. The general schematic of an OPV device can be seen in Figure 2.6. PEDOT/PSS film was deposited onto the substrate by spin coating 75μL of the PEDOT/PSS dispersion to form a thin film (~50 nm thick). The spin-coater (Laurell WS-400A-6nPP/LITE) was adjusted to 4000 rpm for 1 min. The ITO substrate contacts were cleaned with a dry cotton tip soaked in water to remove PEDOT/PSS covering the ITO contacts, the samples were then were annealed at 140°C for 15 min. The active layer P3HT/PCBM was also deposited on top of the PEDOT/PSS layer by spin coating 65μL of P3HT/PCBM solution at 2000 rpm for 1 min using acceleration 1680 rpm/s in the glove box. Again, the excess polymer covering the ITO contacts was wiped out with a dry cotton tip soaked in chloroform.

![Figure 2.6 Schematic of the OPV device.](image)

The next step is cathode deposition which was performed through a shadow mask. This step was performed by the skilled research personnel of the Centre for Organic Electronic (COE), The University of Newcastle. Typically, calcium (20 nm) was deposited followed by aluminium (100 nm) to the slide and in contact with the bottom electrode to complete the circuit. The resulting solar cell device forms six electrically insulated ITO fingers acting as six separate anodes, means six separate solar cells on each slide, with a common calcium/aluminium cathode. All steps of device fabrication
were performed in a nitrogen atmosphere in a glove box to prevent device degradation by the presence of water and oxygen.

2.16.2. Testing
The performance of an OPV device can be determined by the I-V characteristic testing or I-V curve. The I-V curve data can be used to calculate the power conversion energy (PCE) of the device, and other parameters. The important parameters that can be analysed from this curve are the short circuit current, $I_{sc}$ (or current density, $J_{sc}$) and open circuit voltage ($V_{oc}$). These parameters can be used to calculate the fill factor ($FF$) and PCE of the device.

The I-V curves of all devices were measured using a Newport Solar Simulator in 100mW/cm² under AM1.5 conditions. AM1.5 was used as an industrially standard to characterise the OPV. The AM1.5 used in this project was a Newport-Oriel model 92251A with a Xe lamp and an AM1.5G filter filled with ASTM E 927-05 as a Class A Product, and recorded using a Keithley 2400 source meter unit controlled by National Instruments LabVIEW software. The light intensity was typically 1 sun condition, and measured with a calibrated silicon photodiode.

2.17. Fabrication and testing of an organic field effect transistor (OFET) device

2.17.1. Fabrication
An OFET device with a top-gate bottom-contact architecture was prepared using the following procedure. Pre-patterned ITO substrates were cleaned using the same procedure as in the preparation of an OPV device. A schematic of an OFET device is shown in Figure 2.7. P3HT was dissolved in chloroform at a concentration of 20 mg/mL. A 75 μL of P3HT solution was spin-coated for 60 s at 2000 rpm to deposit an approximately 100 nm thick P3HT layer. The film was then patterned manually using chloroform to expose the source and drain electrodes and enough space for spin-coating PVPy layer, and was then annealed for 5 minutes at 140°C in air. PVPy was dissolved in ethanol at a concentration of 80 mg/mL. The dielectric layer was spin-coated for 60 s at 2000 rpm for deposition of 500 nm film thick, and patterned manually using ethyl
acetate. The P3HT/PVPy layer was then annealed for 5 minutes at 85°C in air. For the final step, 16 μL of PEDOT/PSS dispersion sample was drop-cast on the top of the gate dielectric layer and annealed until dry on a hot plate at 40°C in air.

**Figure 2.7** A schematic diagram of the fabricated OFET device.

### 2.17.2. Testing

Characterisation of the fabricated device was run in air immediately after drying the PEDOT/PSS layer. Analysis of the output characteristic is an effective way to see the workings of a transistor. The output characteristic is an $I$-$V$ curve generated by plotting drain current ($I_D$) as a function of drain-source voltage ($V_{DS}$) for a series of gate-source voltage ($V_{GS}$) values. Output characteristics of the transistors were recorded using two Keithley 2400 SourceMeters controlled by a program written in the National Instruments’ LabVIEW development environment. For a given value of $V_{GS}$ (0.4V to -1.4V), $V_{DS}$ was swept over a specified range (0V to -2V) and both $I_D$ and $I_G$ were recorded. This was repeated for a series of different $V_{GS}$. The $I_G$ (gate current or leakage current) values recorded in this measurement are useful for comparing the $I_D$ to $I_G$ ratio.

The transfer characteristic is a plot of $I_D$ as a function of $V_{GS}$ for a given value of $V_{DS}$. This data was collected in a similar method to the data for the output characteristic, with a LabVIEW program controlling the two Keithley SourceMeters. At a fixed value of $V_{DS}$ (-1.5V), $I_D$ is measured as $V_{GS}$ is swept over a range of values (0.4 to -1.4V), and scan speed is 50 mV/s. $V_{GS}$ is swept both “forwards” and “backwards”. Examining the transfer characteristic is an easy way to approximately determine the current modulation ratio ($I_{ON}/I_{OFF}$) and the $V_{GS}$ value for which able to start turning on the devices.
CHAPTER 3 - STATISTICAL ANALYSIS OF CONDUCTIVITY MEASUREMENTS OF PEDOT/PSS FILMS
3.1. Introduction

Conductivity of PEDOT/PSS films, or other conducting polymers, can be measured using a number of techniques. The most widely used method for measuring electrical properties of conducting films is the four point probe method (see Section 2.6). This method has been used for conductivity measurements of PEDOT/PSS films on top of non-conductive substrates. The films can be prepared by spin-coating the dispersions[55,85,86,87], or by making a pellet of composites[88,89], or by pressing indium or putting silver paste technique[90,91]. The conductivity of PEDOT/PSS films can also be measured using the two point probe method in which only one probe is used to measure the current and voltage.[92] Some other methods to measure the conductivity of PEDOT/PSS films involve the use of impedance spectroscopy[27] and gold-plated flat contacts on insulating material loaded with spring pressure[93].

This chapter deals with the statistical evaluation of the conductivity measurements of PEDOT/PSS films generated on a glass substrate by spin-coating at different speeds using the four point probe method. The ultimate objective is to optimise the experimental conditions (e.g. thickness, spin-coating speed) in order to control the variance and reproducibility of conductivity measurements to obtain comparable and reproducible results and minimise uncertainties that can be introduced by variable technical skills of the experimenter.

The aim of this study is two-fold: (i) to examine the relationship between the conductivity (σ) variable and other variables (current, voltage, resistance, sheet resistance, thickness and resistivity) using exploratory correspondence analysis and multiple and nonlinear regression methods for each spin-coating speed and (ii) to compare the mean conductivity among the different spin coating speeds to identify whether there are differences in conductivity measurements using analysis of variance (ANOVA).

3.2. Conductivity Measurements

When physical conditions such as temperature and mechanical stress remain unchanged, the different voltage between two ends of a conductor is proportional to the current flowing through it. The resistance (R) of the conductor (PEDOT/PSS film in this case)
is the proportionality constant derived from the slope of an I-V curve (equation 3.1) that can be generated by plotting the current \( I \) passed through the film against the resulting voltage \( V \).

\[
V \propto I, \text{ therefore } V = R I \tag{3.1}
\]

The sheet resistance, \( R_s \), of the film is calculated by multiplying resistance with a geometric correction factor \( k \) (equation 3.2). \( k \) is determined based on the Haldor Topsoe geometric correction table [80] considering the width \( a \) and the length \( b \) of the film, and the spacing \( s \) between the probes.

\[
R_s = k R \tag{3.2}
\]

The thickness \( t \) of the film is also measured to determine resistivity \( \rho \) of the film according to equation 3.3. The conductivity \( \sigma \) of the film is the inverse of the resistivity.

\[
\rho = R_s t \tag{3.3}
\]

\[
\sigma = \rho^{-1} \tag{3.4}
\]

From equation 3.1 to equation 3.4, it is clear that the relationship between conductivity \( \sigma \) variable and other variables can be generated in equation 3.5. It can be noted from equation 3.5 that this model is a nonlinear model.

\[
\sigma = I (k V t)^{-1} \tag{3.5}
\]

### 3.3. Data

The PEDOT/PSS films used for this study were prepared using a commercial (Clevios) 1:2.5 (PEDOT/PSS ratio) dispersion at different spin-coating speeds, i.e 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm. The thickness measurements of the resulting films are given in Figure 3.1. It can be seen that at low rotation speed (1000 rpm), the films are thicker and rougher as evidenced from the error obtained from 18 measurements from various areas of the film, whereas at higher rotation speed (4000 rpm and 5000 rpm), the films are thinner and smoother.
Chapter 3–Statistical Analysis of Conductivity Measurement of PEDOT/PSS Films

Figure 3.1 Boxplots of thickness of annealed PEDOT/PSS films prepared from commercial (Clevios) dispersion at various spin-coating speeds measured by profilometry. Median range of films from 1000 rpm is shown to be large (i.e. blue fill) while other rotation speeds have small median ranges.

The UV spectra of the PEDOT/PSS films prepared at different spin-coating speeds are given in Figure 3.2 showing two peaks at ~225 nm and at 240-280 nm attributed to free PSS and PEDOT/PSS complex, respectively[94]. The intensity of these peaks was observed to increase with decreasing spin-coating speed which is consistent with the increase in the average film thickness from 5000 rpm to 1000 rpm. The film spun at 5000 rpm generated the thinnest film (61 ± 5 nm) and exhibited the lowest absorbance while the film spun at 1000 rpm gave the thickest film (600 ± 386 nm) and highest absorbance.

Figure 3.2 UV Spectra of PEDOT/PSS commercial films prepared at different spin-coating speeds and annealed at 140°C.
The morphology of PEDOT/PSS films produced at different spin-coating speeds has also been observed by optical microscopy (see Figure 3.3). With the exception of the film generated at 1000 rpm, all of the other PEDOT/PSS films generally exhibit a homogeneous surface. The surface of the film from 1000 rpm, however, is rough and wavy and some lumps and aggregations are visible due to slow drying of the film.

![Figure 3.3](image)

**Figure 3.3** Surface morphology images of commercial PEDOT/PSS films taken using microscope optic “Axioskop 40 Pol” by ZEISS in 20x magnification at (A) 1000 rpm; (B) 2000 rpm; (C) 3000 rpm; (D) 4000 rpm; and (E) 5000 rpm.

The conductivity of the PEDOT/PSS films was determined according to the procedure outlined in the Experimental chapter (Section 2.6). Thickness of the film was measured as an average of 18 measurements per film (6 in each location, see Figure 2.2) and was used for calculation of resistivity. Sheet resistance and resistivity of the films were determined according to equations 3.2 and 3.3 using the geometric correction factor \( k \) from the Haldor Topsoe Table [80], determined to be 4.2209 for width \( a = 12 \) mm, length \( b = 15 \) mm and and distance between the probes \( s = 1.5 \) mm. The conductivity of the films was calculated as an average of the total locations (3 locations for each of the 5 films tested) measured.

Measurement of the electrical properties of the films show variations in the values of each film from the five films produced. Therefore, they provide conductivity and thickness with a larger error distribution value compared to others (see Table 3.1).
Figure 3.4 Boxplots of conductivities of commercial PEDOT/PSS films from various spin-coating speeds showing median ranges (i.e. blue fill).

Table 3.1 Conductivity and thickness measurement of commercial PEDOT/PSS films at various spin-coating speeds.

<table>
<thead>
<tr>
<th>Speed (rpm)</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5.7 ± 3.8 x 10^{-3}</td>
<td>600 ± 386</td>
</tr>
<tr>
<td>2000</td>
<td>7.5 ± 1.0 x 10^{-3}</td>
<td>111 ± 14</td>
</tr>
<tr>
<td>3000</td>
<td>7.6 ± 0.6 x 10^{-3}</td>
<td>74 ± 11</td>
</tr>
<tr>
<td>4000</td>
<td>9.4 ± 1.0 x 10^{-3}</td>
<td>67 ± 7</td>
</tr>
<tr>
<td>5000</td>
<td>9.6 ± 0.9 x 10^{-3}</td>
<td>61 ± 5</td>
</tr>
</tbody>
</table>

Yan, et al. found that PEDOT/PSS films consisted of a monolayer of primary particles (16 – 44 nm) if they were spin-coated at high speed.[95] The electrical conductivity of the films at high speed is also significantly constant and has small error. It is reasonable that colloidal PEDOT/PSS will be more compact in thin films due to increased spin-coating speed.[96]
3.4. Correspondence Analysis

Prior to the application of any formal statistical procedure designed to make inferences about the behaviour of the data at the population level, it is important to explore what type of behaviours may be exhibited. The type of exploratory data analytic procedure depends on the type of variables being analysed and the complexity of the behaviour being considered. For variables of a categorical nature, or for numerical data that has been intervalised, such as the conductivity measurements presented here, one commonly considered exploratory technique is correspondence analysis. The application of correspondence analysis in the chemometric discipline is well documented. One may consider, for example the early contributions of Mellinger(1987)[97,98], Greenacre (1987)[99], Avila and Myers (1991)[100], Avila, Myers and Palmer (1991)[101], Rhodes and Myers (1991)[102], and Devaux, Qannari and Gallant (1992)[103]. Some further examples of correspondence analysis in the chemistry disciplines can be found by referring to [104] in their assessment of ground water. Correspondence analysis has also been used as part of the evaluation of lake water chemistry[102,105,106], and as part of the evaluation of wine classification techniques[107].

The purpose of performing a multiple correspondence analysis is to determine how well the data from the conductivity measurement of PEDOT/PSS films that has been generated using five different spin-coating speeds is associated with other variables of the experiment. These variables include thickness, resistivity, current and voltage. Hence our analysis involves the simultaneous analysis of multiple categorical data. To the best of our knowledge, this is the first demonstration of correspondence analysis to analyse conductivity measurements.

There are many computational resources that one may consider for performing a correspondence analysis on their data. Many commercially available statistics packages, including Statistical Analysis Software, JMP and Minitab, provide ways in which the analysis can be performed. In this study, computations were performed using the statistical package SPSS.

The numerical dataset was set up to classify data in some ranges by coding. For example, the original numerical data speed was set as 1 to 5 to represent 1000 rpm to
5000 rpm, and film thickness was set as 1 to 5 to represent the value of 0 – 100 nm to more than 800 nm. Coding data was applied to speed, current, voltage, thickness, and resistivity variables (see Table 3.2). After classifying all data using a code, the correspondence analysis was run to obtain a graphical view of the association between the variables in the calculation of conductivity measurements. The graphical view of joint association between speed, current, voltage, thickness, and resistivity variables can be seen in the Figure 3.5.

### Table 3.2 Code classification and variable values of data for correspondence analysis

<table>
<thead>
<tr>
<th>Code</th>
<th>Speed (rpm)</th>
<th>Current (µA)</th>
<th>Voltage (V)</th>
<th>Thickness (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Thickness (nm)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Resistivity (ohm.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>&lt; 0.2</td>
<td>0 – 1</td>
<td>0 – 200</td>
<td>0 – 60</td>
<td>0 – 1</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>0.2 – 0.29</td>
<td>1.1 – 2</td>
<td>201 – 400</td>
<td>61 – 80</td>
<td>1.1 – 2</td>
</tr>
<tr>
<td>3</td>
<td>3000</td>
<td>0.3 – 0.39</td>
<td>2.1 – 3</td>
<td>401 – 600</td>
<td>81 – 100</td>
<td>2.1 – 3</td>
</tr>
<tr>
<td>4</td>
<td>4000</td>
<td>0.4 – 0.49</td>
<td>3 +</td>
<td>601 – 800</td>
<td>101 – 120</td>
<td>3.1 – 4</td>
</tr>
<tr>
<td>5</td>
<td>5000</td>
<td>0.5 – 0.59</td>
<td>-</td>
<td>801 +</td>
<td>120 +</td>
<td>4 +</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>0.6 – 0.69</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>0.7 – 0.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0.8 +</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note:  

a) Code for thickness values for all speed data.  
b) Code for thickness values after excluding data from speed 1000 rpm.

In general, Figure 3.5 shows that speed variable does not play a role of association among the variables in conductivity measurements. Only 1000 rpm speed has a strong association by providing the cluster with high thickness and high resistivity. Speeds between 2000 rpm to 5000 rpm have another cluster and associate each other close to the origin. These speeds have weak associations with other variables, and associate with the medium category of voltage and resistivity. The conductivity and thickness of films generated at 1000 rpm have higher standard deviations compared to the films generated between 2000 rpm to 5000 rpm. The higher spin-coating speeds resulting in lower standard deviations (see Table 3.1). Figure 3.5 shows a nice order of the current variable from low to high, which is the same trend exhibited by the voltage variable. The low current associates strongly with low resistivity, but high current associates only with medium resistivity and does not associate with high resistivity.
Figure 3.5 Two dimensional correspondence plot of the classification of variables included in the conductivity measurements.

Association between variables resulting from the films generated at 2000 rpm to 5000 rpm can be seen clearly after excluding variable speed at 1000 rpm and all data related to this speed. However, thickness of the films generated at 2000 rpm to 5000 rpm could not be separated for correspondence analysis because their thickness have similar class or group data, i.e in low thickness category or in code 1. Therefore, this variable was also excluded at this analysis, and the association plot is shown in Figure 3.6. This graph also supports that speed variable is not a major factor in relation to other variables. In this case, all data speeds are in the origin area. The association of the variables can be seen to be very strong between the low current (1, 2) with the low voltage (1) and the low resistivity (1). Strong association can also be seen between the high current (7, 8) with the high voltage (4) and the medium resistivity (3). Here the speed variable has closer association with the medium level of the current (3, 4, 5, 6), medium voltage (2, 3), and less resistivity (2). In other words, lower current level and lower voltage level associate strongly with lower resistivity level, medium current level and medium voltage level also associate strongly with medium resistivity level, and high current level and high voltage level also associate strongly with high resistivity level.
Figure 3.6 Two dimensional correspondence plot of the classification of variables include in the conductivity measurements after excluding variable speed at 1000 rpm and the thickness classification.

The association between all variables, including the thickness, for the films generated between 2000 rpm to 5000 rpm was analysed after assigning new codes to the thickness. The thickness of the films 0-200 nm, previously classified by code 1 (see code a in Table 3.2), have been classified with new codes: 1 for 0-60 nm, 2 for 61-80 nm, 3 for 81-100 nm, 4 for 101-120 nm, and 5 for +120 nm (see code b in Table 3.2). The new two-dimension association between the variables shown in Figure 3.7 indicates that thickness is closely associated with the speed variable, and association of other variables remain as shown in Figure 3.6. The closer association between the speed and the thickness is expected because the thickness of the film is primarily determined by the spin-coating speed such that higher spin-coating speeds generated thinner films (see Table 3.1).
In summary, results from correspondence analysis show that only 1000 rpm spin-coating speed is strongly associated with high thickness and high resistivity (i.e. low conductivity) of the films. In depth analysis of speed between 2000 rpm to 5000 rpm shows that the spin-coating speed is still strongly associated with the thickness of the films such that higher spin-coating speed (5000 rpm) generates thinner films and lower spin-coating speed (2000 rpm) generates thicker films. However, 2000 rpm to 5000 rpm still result in significantly higher film conductivity than 1000 rpm.

Formal statistical analysis by multiple linear regression was pursued (see next section) in order to assess if there is significant difference between the conductivity of the films generated from the various spin-coating speeds tested in particular between 2000 to 5000 rpm.
3.5. Multiple linear regression analysis (MLR)

3.5.1. Dataset description for regression

The MLR approach was evaluated by putting current \((I)\), voltage \((V)\), thickness \((t)\), resistance \((R)\), sheet resistance \((R_s)\), and resistivity \((\rho)\) as independent variables or predictors; whereas conductivity \((\sigma)\) of the film as a dependent variable or response. Resistance of a particular current in a particular location was measured by equation 3.1, then the resistance was used to calculate sheet resistance and resistivity of each particular current employed. Thickness of each location on the film was calculated as an average of six measurements on the location. Therefore, every location on each film consists of fifteen data for each predictor and dependent variables.

3.5.2. Regression equation to estimate the value

Each of the five spin-coating speeds of the films (1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm) consisted of six predictor variables \((I, V, t, R, R_s \text{ and } \rho)\), and one response variable \((\text{conductivity, } \sigma)\). Each variable consists of 1125 data.

The datasets were analysed using multiple linear regression, and backward elimination method, minimum acceptable \(F\) to enter = 0.01 and maximum acceptable \(F\) to remove = 0.05. Backward method in SPSS was run by entering all predictor variables into the model. The predictors with minimum contribution to the model were eliminated one by one. This mechanism was repeated until only the useful predictor variables remain.[108] From this conductivity dataset, the following fitted MLR models obtained using the SPSS program for each speed at a significance level of 5%:

\[
\sigma_{1000} = 0.025 - 1.97 \times 10^{4}t - 3.18 \times 10^{9}R_s + 0.02\rho 
\]

(3.6)

\[
\sigma_{2000} = 0.024 - 6.46 \times 10^{4}t - 6.76 \times 10^{10}R_s
\]

(3.7)

\[
\sigma_{3000} = 0.015 - 9.88 \times 10^{11}R - 0.005\rho
\]

(3.8)

\[
\sigma_{4000} = 0.018 + 5.96 \times 10^{3}t - 0.008\rho
\]

(3.9)

\[
\sigma_{5000} = 0.011 + 218.50I - 4.99 \times 10^{5}V + 1.08 \times 10^{5}t + 1.41 \times 10^{9}R - 0.013\rho
\]

(3.10)
The above five regression models show that not all predictors are dominant in estimating the conductivity. Equations 3.6 to 3.9 resulted from dataset films generated at 1000 rpm to 4000 rpm. These equations are built of $t$, $R_s$, and $\rho$ variables which contribute significantly after excluding $I$ and $V$ predictor variables. Both $I$ and $V$ variables have small contributions to the equation models. It is noted that the SPSS program used maximum acceptable $F = 0.05$ to remove the variable. The program accounted only one of $R$ or $R_s$ as a variable, because $R_s$ is multiplication of $R$ by $k$ factor. The exception is in equation 3.10 which resulted from the dataset of films generated at 5000 rpm. The films were smooth, uniform and had less error in conductivity and thickness. In this equation all five predictor variables ($I$, $V$, $t$, $R$, and $\rho$) have contributed significantly to the model to predict conductivity of PEDOT/PSS films.

Correlation between the predictor variables and the dependent variable (conductivity) also can be seen from equations 3.6 to 3.10. For example, equation 3.6 shows that conductivity of the films generated at 1000 rpm is negatively correlated with the thickness ($t$) and sheet resistance ($R_s$), but positively correlated with the resistivity ($\rho$). In the other hand, in equation 3.9, conductivity of the films generated at 4000 rpm is positively correlated with the thickness ($t$), but negatively correlated with the resistivity ($\rho$). In 5000 rpm, conductivity of the films is positively correlated with the current ($I$), thickness ($t$) and resistance ($R$), but negatively correlated with the voltage ($V$) and resistivity ($\rho$).

As defined in equation 3.5, it is clear that the model is non-linear. By fitting to the MLR model, we expect that the residual analysis will confirm the non-linearity relationship. Regression analysis was conducted on all dataset results in the coefficients and significance values of the model. Regression analysis is calculated under the assumption that a good model of relationship forms a straight line. Figure 3.8 exhibits P-P plots of the residuals of the models in (3.6) to (3.10), respectively. The five plots of regression standardised residual resulting from SPSS program analysis show a tendency to divide from the straight line of the dataset ($N = 225$) for films generated at 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm. These results confirm the non-normality of
residuals. However, it can be noted that at the speed 5000 rpm, the residuals tend to lie on the straight line to approximate normality.

![Figure 3.8 Normal P-P Plot of Regression Standardised Residual for Dependent Variable conductivity resulted from SPSS program analysis of dataset (N = 225) for films generated at (A) 1000 rpm, (B) 2000 rpm, (C) 3000 rpm, (D) 4000 rpm, and (E) 5000 rpm. x axis = Observed Cumulative Probabilities; y axis = Expected Cumulative Probabilities.]

Non-normality of residuals is also exhibited in Figure 3.9. This figure also provides a good indication that the MLR regression is working well for 5000 rpm. The figure of normality residuals for each data set shows an increase in normality films from lower speed 1000 rpm (A) to higher speed 5000 rpm (E). Most of the points tend to form and fill the normal shape significantly. The highest speed (5000 rpm) formed approximately normal residual data and more unimodal, representing that the regression is working much better than for other residual data.

The evaluation of MLR equations is important in determining whether the equation can predict and estimate the dependent and predictor variables involved. The evaluation can also consider the coefficient of squared multiple correlation, $R^2$, which is generated by ANOVA.[109] Equations 3.6 to 3.10 represent the predictor variables involved in the
estimation of the dependent variable (conductivity) value. Each equation model also has multiple correlation coefficient value which is attributed as the goodness equation to estimate the conductivity.

![Histogram of Normality distributed residuals for Dependent Variable conductivity resulting from SPSS program analysis of the dataset (N = 225) for films generated at (A) 1000 rpm, (B) 2000 rpm, (C) 3000 rpm, (D) 4000 rpm, and (E) 5000 rpm. x axis = Regression Standardized Residuals; y = axis is Frequency.](image)

**Figure 3.9** Histogram of Normality distributed residuals for Dependent Variable conductivity resulting from SPSS program analysis of the dataset (N = 225) for films generated at (A) 1000 rpm, (B) 2000 rpm, (C) 3000 rpm, (D) 4000 rpm, and (E) 5000 rpm. x axis = Regression Standardized Residuals; y = axis is Frequency.

Each spin-coating speed generated films resulted in an equation for the MLR model. Table 3.3 shows an increase in the value of squared multiple correlation, $R^2$, as well as the value of adjusted squared multiple correlation, $R_a^2$, in relation to an increase in spin-coating speed. The five equation models also have a tendency to increase in the value of adjusted coefficient of multiple determinations, $R_a^2$: 0.873, 0.991, 0.988, 0.995, and 0.999, which also defines by increasing mean of residuals. Equation 3.6 has the smallest value of $R_a^2$, 87.3% whereas equation 3.7, 3.8, 3.9, and 3.10 account for 99.1%, 98.8%, 99.5%, and 99.9%, respectively.
Table 3.3 Table values of $R^2$, $R_a^2$, standard error of the estimate, mean square and significance derived using SPSS for each equation at 5% significance level.

<table>
<thead>
<tr>
<th>Model Eq.</th>
<th>$R^2$</th>
<th>$R_a^2$</th>
<th>Mean of residuals</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>0.875</td>
<td>0.873</td>
<td>-6.61 $10^{-16}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.7</td>
<td>0.991</td>
<td>0.991</td>
<td>-9.15 $10^{-16}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.8</td>
<td>0.989</td>
<td>0.988</td>
<td>-9.98 $10^{-15}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.9</td>
<td>0.995</td>
<td>0.995</td>
<td>8.01 $10^{-14}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.10</td>
<td>0.999</td>
<td>0.999</td>
<td>-1.10 $10^{-13}$</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Increasing $R_a^2$ values mean that there is an increase in the goodness and accuracy of the equation as part contribution of those predictor variables to predict the conductivity value. These $R_a^2$ values also indicate an increase in precision of the measurement of conductivity by increasing spin-coating speed. Films generated at 4000 and 5000 rpm have very high $R_a^2$ which suggest that equations 3.9 and 3.10 can be used accurately and precisely to predict the conductivity of PEDOT/PSS films. This information strengthens the calculation of conductivity using Excel. In particular for the films generated at 4000 and 5000 rpm, the calculation also showed that conductivity and thickness of the films lie within the range of their standard deviation values (see Table 3.1).

3.5.3. Transformation of nonlinear regression model

The regression model is applied by assuming that the predictors and the dependent variable have a linear relationship. However, some datasets do not provide the linear relationship, but rather a curve or nonlinear relationship. The nonlinear model is applied for the condition in which the dataset have a nonlinear relationship.[109] One of the techniques to make a linear relationship is applying a logarithmic transformation, instead of polynomial regression.[108]

Considering equation 3.5, that the above equation is a non-linear equation, but it can be linearized using logarithm transformation to give the new equation.

\[
\log\sigma = \log I - \log k - \log V - \log t
\]  

(3.11)
In this study, all predictor and dependent variables were transformed to logarithmic forms to work on multiple linear regressions. The variables in the dataset then become $\log I$, $\log V$, $\log t$, $\log R$, $\log R_s$, and $\log \sigma$ as predictors, and $\log \sigma$ as the dependent variable. This new dataset was analysed similarly to the original data form by SPSS software using the backward elimination method, with minimum acceptable $F$ to enter = 0.01 and maximum acceptable $F$ to remove = 0.05. From this new transformation dataset, the following regression equations are obtained for each speed at significance 5% level:

\[
\log \sigma_{1000} = 7.576 \times 10^{-7} - \log \rho \\
\log \sigma_{2000} = -2.934 \times 10^{-6} - \log \rho \\
\log \sigma_{3000} = 1.659 \times 10^{-6} - \log \rho \\
\log \sigma_{4000} = 2.734 \times 10^{-7} - \log \rho \\
\log \sigma_{5000} = -5.082 \times 10^{-7} - \log \rho
\] 

The five equation transformation models have similar value of $R^2$ and $R_d^2$ (see Table 3.4). This similarity value means that all equations for transformation model have a straight line relationship between the predictor and the dependent variable. All these equations suggest that the conductivity of PEDOT/PSS films fit to the line of inversion of the value of logarithmic resistivity with different intercepts and error deviation. These equations also prove the calculation of film conductivity shown in equation 3.4 where conductivity is the inverse of the resistivity. All five equation models have the similar value of adjusted coefficient of multiple determinations, $R_d^2$: 1.000, which also defines increasing absolute value mean of residuals.

Considering the new equation (3.11) after logarithm transformation from equation (3.5), we expect that the residual analysis will confirm to the linearity relationship. Regression analysis was conducted on all dataset results in the coefficients and significance values similar to the previous model. Figure 3.10 exhibits P-P plots of the residuals of the models in (3.12) to (3.16), respectively. The five plots of regression standardised residual resulting from SPSS program analysis show a tendency of all data speed at 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm to lie on the straight line of the dataset ($N = 225$) to approximate normality.
Table 3.4 Table values of $R^2$, $R_{a}^2$, mean of residuals and significance of transform dataset derived using SPSS for each equation at 5% significance level.

<table>
<thead>
<tr>
<th>Model Eq.</th>
<th>$R^2$</th>
<th>$R_{a}^2$</th>
<th>Mean of residuals</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.12</td>
<td>1.000</td>
<td>1.000</td>
<td>-2.16 $10^{-12}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.13</td>
<td>1.000</td>
<td>1.000</td>
<td>1.19 $10^{-12}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.14</td>
<td>1.000</td>
<td>1.000</td>
<td>2.78 $10^{-13}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.15</td>
<td>1.000</td>
<td>1.000</td>
<td>-3.96 $10^{-13}$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>3.16</td>
<td>1.000</td>
<td>1.000</td>
<td>3.04 $10^{-13}$</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Figure 3.10 Normal P-P Plot of Regression Standardised Residual for Dependent Variable logarithm conductivity resulted from SPSS program analysis of dataset (N = 225) for films generated at (A) 1000 rpm, (B) 2000 rpm, (C) 3000 rpm, (D) 4000 rpm, and (E) 5000 rpm. x axis = Observed Cumulative Probabilities; y axis = Expected Cumulative Probabilities.

3.5.4. Analysis of variance (ANOVA)

ANOVA in MLR is used to test the null hypothesis ($H_0$) that the population means of $p$-groups ($p > 2$) are all equal. The different value of all mean squares allows another analysis to determine that population or group means differ from others. The one way
ANOVA results can be seen in Table 3.5 for the five groups according to the spin-coating speeds. ANOVA outputs show F ratio 216.594 in significant ($p < 0.0001$) at 5% significant level. The p-value $<0.0001$ in this result means that the $H_0$ is rejected. Hence, because the observed significant value is less than 5% at least one of the predictors has a different mean value compared to the others. Table 3.6 is provided to consider the assumption that all population of speed groups are equal has rejected. This table (Welch version) has F ratio also significant ($p < 0.0001$) at 5% significant level. Therefore, post hoc analysis was run to compare the mean of one population against the means of others. This analysis is used to test whether each variable speed has significant correlation at other speeds to the dependent variable (conductivity).

**Table 3.5** ANOVA one way result for film conductivity measurement generated at five speeds.

<table>
<thead>
<tr>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between groups</td>
<td>0.002</td>
<td>4</td>
<td>0.001</td>
<td>216.594</td>
</tr>
<tr>
<td>Within groups</td>
<td>0.003</td>
<td>1120</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.006</td>
<td>1124</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.6** Robust test of equality of means for film conductivity measurement generated at five speeds.

<table>
<thead>
<tr>
<th>Statistic</th>
<th>df1</th>
<th>df2</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welch</td>
<td>296.999</td>
<td>4</td>
<td>551.729</td>
</tr>
</tbody>
</table>

a. Asymptotically F distributed.

Post Hoc analysis was applied to determine which groups have equal mean data between the five groups using Tukey HSD, Scheffe, LSD, Bonferroni, Gabriel, Tamhane, and Games-Howell methods. The ANOVA results show that three groups can be classified based on means of film conductivity from the five spin-coating speeds.
In general, all methods result in three mean groups at 5% significance level. Spin-coating PEDOT/PSS Clevios at 1000 rpm as the first group, spin-coating at 2000 and 3000 rpm as the second group, and have equal mean, and the third group is for the films spin-coated at 4000 and 5000 rpm (see Table 3.7). This result also strengthens the calculation using Excel (shown in Table 3.1) that conductivity of PEDOT/PSS films generated at 1000 rpm has lowest value, and conductivity films generated at 2000 rpm and 3000 rpm have almost similar value of conductivity. Then films generated at 4000 rpm and 5000 rpm have similar film properties such as roughness, homogeneity, conductivity and thickness.

Table 3.7 Summary of Post Hoc comparisons between the five spin-coating speeds used to generate the films using 5% significance level.

<table>
<thead>
<tr>
<th>Method</th>
<th>Means</th>
<th>Sig. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tukey HSD</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>99.7</td>
</tr>
<tr>
<td>Scheffe</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>99.8</td>
</tr>
<tr>
<td>LSD</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>84.2</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>72.6</td>
</tr>
<tr>
<td>Bonferroni</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>100.0</td>
</tr>
<tr>
<td>Gabriel</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>100.0</td>
</tr>
<tr>
<td>Tamhane</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>99.1</td>
</tr>
<tr>
<td>Games-Howell</td>
<td>$\mu_{2000} = \mu_{3000}$</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>$\mu_{4000} = \mu_{5000}$</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Side-by-side boxplots of all means of conductivity films generated at the five spin-coating speeds can be seen in Figure 3.11. This figure also shows clearly means comparisons between the five speeds and the error values of each speed, and seems to suggest that spin-coating at 1000 rpm has a large mean range value and error, while spin-coating at 2000 rpm and 3000 rpm have means within the same value and range, as well as at 4000 rpm and 5000 rpm also have means value within their range.
Figure 3.11 Side-by-side boxplots reveals conductivity means comparisons between the five spin-coating speeds.

In summary, MLR shows that increasing spin-coating speed from 1000 rpm to 5000 rpm exhibits an increase in linearity of the data of films, which can be seen from the tendency of an increase in adjusted $R^2$ at 5% significance level. Sheet resistance ($R_s$), thickness ($t$), and resistivity ($\rho$) of the film have significant contribution to the calculation of film conductivity at 1000 rpm. Thickness and sheet resistance have significant contribution for determination of conductivity at 2000 rpm, and only resistance and resistivity have significant contribution at 3000 rpm, whereas thickness and the resistivity have significant contribution to determine conductivity at 4000 rpm. All predictors contribute significantly to predict conductivity of the film when it is generated at 5000 rpm.

In terms of the assumption on normality through its residuals, the plots of regression standardised residual from SPSS show a tendency of the dataset from 1000 rpm to 4000 rpm to deviate from the straight line, whereas the dataset from 5000 rpm tends to lie on the straight line to approximate normality of the data. However, all datasets from the five spin-coating speeds tend to lie on the straight line to approximate normality after logarithmic transformation the data.
The ANOVA results show that conductivity of the films can be classified as three groups from the five spin-coating speeds. The groups are generated based on the equality of the means between the films generated from the five spin-coating speeds. Tukey HSD, Scheffe, LSD, Bonferroni, Gabriel, Tamhane, and Games-Howell methods using a 5% significance level proceeded three groups as films generated at 1000 rpm, films generated at 2000 rpm and 3000 rpm, and films generated at 4000 rpm and 5000 rpm.

3.6. Conclusion

Results from correspondence analysis show that only 1000 rpm spin-coating speed is strongly associated with high resistivity (i.e. low conductivity) of the films. While 2000 to 5000 rpm spin-coating speeds are strongly associated with thickness, i.e. higher speed giving thinner films and vice-versa, they are still strongly associated with low resistivity (high conductivity) of the films, i.e. they still give significantly higher film conductivity than 1000 rpm. MLR analysis shows that not all predictor variables (I, V, t, Rs and ρ) in 1000 rpm to 4000 rpm spin-coating speeds are dominant in estimating conductivity of the films (σ). The exception is in 5000 rpm spin-coating speed where all five predictor variables have significant contribution to predict conductivity of PEDOT/PSS films. The plots of regression standardised residual from SPSS show that tendency of the dataset from 1000 rpm to 4000 rpm to deviate from the straight line, whereas the dataset from 5000 rpm tends to lie on the straight line to approximate normality of the data. All datasets from the five spin-coating speeds tend to lie on the straight line to approximate normality after logarithmic transformation the data. The ANOVA results show that three groups can be classified based on means of film conductivity from the five spin-coating speeds, i.e. 1000 rpm, 2000 rpm – 3000 rpm, and 4000 rpm – 5000 rpm.

From a practical point of view, there is no significant difference between the conductivity of films generated using spin coating speeds 2000 and 3000 rpm and the conductivity of films generated using spin coating speeds 4000 to 5000 rpm. Optimal conductivity and high reproducibility, however, is obtained when the films are generated from 5000 rpm. Thus, preparation of films for conductivity measurements of any PEDOT/PSS system, particularly for comparison purposes, must be conducted between 4000 and 5000 rpm spin coating speed to generate the best reproducibility.
CHAPTER 4 - CAPILLARY ELECTROPHORESIS OF PEDOT/PSS DISPERSIONS
4.1. Introduction

Capillary electrophoresis (CE) is a simple technique to analyse samples, with high efficiency, low sample and solvent consumption, and one that has found increased application in analysis and characterization of polyelectrolytes[110], and nanoparticles[111]. Separation of ionic species and charged particles is based on electrophoretic mobility through attraction and repulsion in an electric field.[112] and the technique has been applied in the analysis of PSS[113,114], poly(L-lysine citramide)/poly(L-lysine) complex[115], graphene[81], various latexes[116,117], and carbon nanotubes[118,119].

Separation of particles takes place in a capillary, typically 25-75 μm of inner diameter (i.d.), made of silica. The outer surface of the capillary is coated with a polymer such as polyimide. The configuration of CE is relatively simple, and other parts include a high voltage power supply, buffer or background electrolyte (BGE), sample device, and a selected detection scheme. UV-visible and fluorescence optical detectors are employed and the data are transformed as signals in an electropherogram.[120]

In capillary electrophoresis, the capillary filled with BGE and both ends of the capillary are placed in the reservoir containing the same BGE.[121] The choice of BGE is very important since it will connect to the high electric field applied. Concentration of BGE should be high enough to maintain a constant pH during the analysis and to keep overloading effects to a minimum, and thus allow rapid analysis via the electroosmotic flow (EOF) but preventing the appearance of band broadening through thermal effects.[122] Sample is injected in the inlet (the anode end) while the other end of the capillary is grounded in another buffer vial (see Figure 4.1). The ionic charges of the sample will start to migrate when a high voltage is applied into the two buffer reservoirs, and the differences of their electrophoretic mobility is determined by the charge and mass ratio of the analyte ions.[120]
The properties of PEDOT/PSS complexes can be used to tune the property of films prepared from these materials. For example, smaller particle sizes lead to lower conductivity films that are desirable for OLEDs or passive matrix displays.[22] Alternatively, the conductivity maybe reduced by increasing the PSS content in the reaction mixture. The application-specific properties of PEDOT/PSS aqueous dispersions can only be determined after the preparation and subsequent characterisation of the films. Analysis of the dispersions will, however, improve our understanding of the complexes formed and the conductivity behavior of the film. Spectroscopic analyses have been performed, for example NMR and IR, but the results were inconclusive because of the conductance of PEDOT.[39,57,124] UV-Vis spectrophotometry only provided a spectrum with an absorption maximum at~225 nm that corresponds to PSS in its free and PEDOT-complexed forms.[24,125,126] Gel permeation chromatography (GPC) and MALDI-TOF just measured the oligomeric to polymeric segments about 1000 to 2500 Da, and was never able to observe high molecular weight PEDOT/PSS dispersion.[22] Separation of components is necessary to understand, and possibly predict, the conductive property of the dispersions (and hence films) for further applications.
To the best of our knowledge, this is the first report on the study of the doping efficiency, i.e. separation of free PSS from doped PSS, of PEDOT/PSS using CE and their impact on the film conductivity. There has only been one report on the use of CE for the analysis of PEDOT/PSS. In 1999, Gosh and Inganas filled a 3-cm long capillary of 0.5 cm diameter with 0.2% commercial PEDOT/PSS and 1% polyethylene oxide.[127] There was no separation of components when 40 V was applied with sodium dodecylbenzenesulfonate at both ends of the capillary. One dark coloured band which moved to the anode was attributed to the negatively charged complex.

This chapter reports the CE with photodiode array detection (DAD) of processable PEDOT/PSS aqueous dispersions prepared in house by oxidative polymerisation (see Experimental Section). The separation of free PSS and PEDOT/PSS complex was achieved using a borate buffer and fused silica capillary. The effect of PSS doping with PEDOT on complex electrophoretic mobility, UV detection and spectra, and also the possibility of CE to predict the conductivity of spin coated films are discussed.

### 4.2. Selection of background electrolyte

The stability of PEDOT/PSS dispersion is due to the negatively-charge PSS material as a counter ion or doping agent to the PEDOT segment and to keep it dispersed in aqueous medium. The stability of PSS as a carrier in the CE system is important and the appropriate background electrolyte, i.e. the buffer medium, which is suitable for PSS needs to be chosen. The stability of the system is affected by the ionic strength and pH of the buffer.[2,22,89] Cottet, et al.,[113] has studied the electrophoretic mobility of PSS by CE and obtained excellent results with conditions: fused-silica capillary 47 cm (25 cm to detector) X 50 μm ID at pH 9.2 using 40 mM borate buffer, applied voltage of 20 kV and UV detection at 225 nm. The variation in the electrophoretic mobility of PSS samples also has been studied using a borate buffer at various conditions.[128,129,130]

Optimisation of the conditions of CE for separation of PEDOT/PSS complex and free PSS was studied starting from the performance of pure PSS solution in various applied parameters, such as buffers, pH, solvents and applied potential.
CE of pure PSS solution was run using 5 mM sodium biphosphate buffer at pH 7 to investigate the effect of applied potential on the analysis. The results given in Figure 4.2 showed that when 30 kV was applied, it took ~40 min for the PSS peak to appear whereas 15 kV took ~18 min. Therefore, subsequent experiments on PEDOT/PSS dispersions using various conditions were performed using 15 kV applied potential.

![Figure 4.2](image_url)

**Figure 4.2** Effect of applied potential on the CE analysis of PSS solution. BGE: 5 mM sodium biphosphate, pH 7 and applied potential: (A) 15 kV, and (B) 30 kV. Sample: 0.5 mg/mL of PSS in water.

The separation of PEDOT/PSS complex and free PSS was also optimised using different buffer conditions. Figure 4.3 shows the electropherograms of a PEDOT/PSS dispersion run using three different buffers, ammonium bicarbonate, ammonium acetate and sodium borate at 20 mM and pH 9.2 using 15 kV applied potential. The electropherograms show that the borate buffer showed narrower and more resolved peaks than ammonium bicarbonate and ammonium acetate. The separation using borate buffer gave migration time of ~14-15 min for the last peak assigned as free PSS having negative charge, and narrow spikes at ~9 min having less negative charge than PSS which was attributable to the PEDOT/PSS complex.

The effect of different concentrations of borate was also investigated using commercial PEDOT/PSS Clevios P (PP-A) aqueous dispersions and the results are shown in Figure 4.4. Separation of PEDOT/PSS complex and free PSS with acceptable resolution was achieved when the concentration of borate was > 10 mM. Similar results were obtained using other PEDOT/PSS test samples.
Figure 4.3 Effect of buffer as the BGE on PEDOT/PSS solution by CE at 15 kV of potential applied. BGE: (A) 20 mM NaHCO$_3$ pH 9.2, (B) 20 mM CH$_3$COONH$_4$ pH 9.2, and (C) 20 mM Na$_2$B$_4$O$_7$ pH 9.2. Sample: 0.5 mg/mL of PEDOT/PSS in water.

Thus, the separation buffer of 20 mM borate at pH 9.2 that gave a reasonable migration time of ~14 min for the last eluting peak (PSS) was chosen for the analysis of all test samples. The identity of the PSS peak (see Figure 4.4, peak 2) was confirmed by CE analysis of a standard PSS sample, thus the only other peak that migrated before PSS (see Figure 4.4, peak 1) was assigned to the PEDOT/PSS complex. Note that the flow of an analyte depends on the electroosmotic flow (EOF) of the background electrolyte or buffer. Because the EOF of the buffer was higher and moving in the opposite direction of the electrophoretic migration of the two peaks, the electrophoretic mobility of negatively-charged free PSS (peak 2) is higher intensity than the PEDOT/PSS complex (peak 1). All CE experiments were run with UV detection at 230 nm (based on observed PSS peak).
Figure 4.4 Effect of electrolyte concentration on the separation of a commercial (Clevios P) PEDOT/PSS (1:2.5 by weight) aqueous dispersion (PP-A) by CE. Separation electrolyte: (A) 30 mM, (B) 20 mM (C) 10 mM, and (D) 5 mM sodium borate at pH 9.2. Sample: 0.5 mg/mL of PP-A in water. Identity of peaks: peak 1 is the PEDOT/PSS complex, peak 2 is the free PSS.

In the CE of high MW PSS under 20 mM ionic strength, such as those in this study (MW = 70 kDa and 20 mM sodium borate, pH 9.2), the PSS assume the random coil configuration and their electrophoretic mobility (free draining mobility) is independent of their mass.\[131\] The PEDOT/PSS complexes prepared from high MW PSS are also assumed to be in the same random coil configuration. Because the negative charges in the PSS backbone are neutralized by the positive charges on PEDOT, the complex is expected to have a negative charge lower than that of the free PSS resulting in a lower electrophoretic mobility and thus detected earlier than PSS. An increase in the number of PEDOT segments attached to PSS, due to an increase in doping, will therefore decrease the electrophoretic mobility of complexes.
4.3. CE analysis of various PEDOT/PSS aqueous dispersions

Various PEDOT/PSS aqueous dispersions were subjected to CE analysis and the results are shown in Figure 4.5. The EOF, PEDOT/PSS complexes, and free PSS were detected at ~4, between 4 and 14, and ~14 min, respectively. These PEDOT/PSS aqueous dispersions were all prepared using the same PSS (except for commercial sample PP-A), thus the migration time for uncomplexed PSS were the same. The same migration time was also observed for PSS in the commercial sample PP-A which suggests that the PSS used in the preparation of PP-A is in the same MW range, i.e. 70 kDa.

![Figure 4.5 CE analysis of PEDOT/PSS aqueous dispersions and the average conductivity (in S/cm) of the corresponding films. Samples: 0.5 mg/mL in water of (A) PP-A, (B) PP-B, (C) PP-C, (D) PP-D, (E) PP-E, (F) PP-F, and (G) mixture of the sample PP-A, PP-C and PP-D. Conditions: fused-silica capillary 50 cm (41.5 cm to detector) x 50 μm ID, BGE 20 mM sodium borate at pH 9.2, and applied voltage of 15kV.](image-url)
As shown in Figure 4.5, the electrophoretic mobility of the PEDOT/PSS complexes decreased from sample PP-A to PP-F. Subsequently, PP-A has the longest migration time and PP-F the shortest migration time. Conductivity measurements on the spin coated films were obtained to understand the mobility trend. It is worth noting that the same PSS (MW = 70 kDa) was used in the in-house preparation of all PEDOT/PSS aqueous dispersions, and CE analysis (Figure 4.5) also indicated that the PSS in the commercial sample PP-A is the same as those of the other test samples. Thus, any change in the conductivity of the film could be directly related to the amount of PEDOT complexed to PSS. The conductivity of the films was observed to increase by a factor of ~64 from sample PP-A (9.6 ± 1.0 × 10^{-3} S/cm) to PP-F (6.1 ± 1.2 × 10^{-1} S/cm). This could be attributed to an increase in the number of PSS sites doped with PEDOT segments across samples PP-A to PP-F. The increased in doping reduced the negative charges on the PSS backbone of the complexes, and thus decreased the electrophoretic mobility.

The effect of doping on electrophoretic mobility was studied by changing the ratio of PEDOT and PSS in the reaction mixture. Doping was qualitatively estimated by comparing the peak intensity of the free PSS before and after polymerisation with PEDOT. Doping was anticipated to increase with decreasing PSS amount in the dispersion. The CE results for the 1:5, 1:3, and 1:1 PEDOT/PSS ratios, labeled PP-G, PP-H, and PP-I, respectively, are shown in Figure 4.6. The PSS sample was also analysed in sequence and the result is shown in Figure 4.6 D for comparison. The migration time of the complexes has been observed to decrease from PP-G, PP-H, to PP-I consistent with the decrease in their electrophoretic mobilities as the ratio was increased in favour of the PEDOT amount. Figure 4.6 C also shows negligible amount of free PSS and the highest degree of PSS doping to PEDOT when the PEDOT/PSS ratio was highest (1:1).
Figure 4.6 Effect of doping on the CE analysis of PEDOT/PSS dispersions. Samples: 0.5 mg/ml of (A) PP-G, (B) PP-H, (C) PP-I, and (D) PSS. Ratio PEDOT to PSS in PP-G, PP-H and PP-I are 1:5, 1:3, and 1:1, respectively. BGE: 20 mM sodium borate at pH 9.2.

The occurrence of spikes in the electropherogram was attributed to the detection of aggregated nanoparticles.[81,111] The decrease in the over-all charge due to the increase in doping reduced the electrostatic repulsion and caused the complexes to aggregate. Aggregation was also facilitated by hydrophobic interaction between PEDOT particles at the PSS surface. Sample polydispersity (~0.4 measured from DLS) accounted for the broad peaks and many spikes detected for the less doped (PP-A, PP-B, and PP-C samples) and more doped (from PP-D, PP-E, and PP-F) samples, respectively.

The CE separation of an artificial mixture of the complexes was investigated by mixing samples PP-A, PP-C, and PP-D and the results are shown in Figure 4.5 G. The migration times were similar to those obtained from the individual injections of each sample except for PP-D which contained the most doped PSS. This complex co-
migrated with the PP-C complex and was detected as spikes on top of the PP-C complex peak (mostly at the front). This suggested that the PEDOT chains of these two complexes interacted with each other during electrophoresis. Interestingly, this interaction only caused a shift in the electrophoretic mobility of PP-D but not of PP-C. It could be that the interaction between PP-C and PP-D disrupted the aggregation previously observed in PP-D, resulting in a wider range of electrophoretic mobility of the latter. Further, the intensity of absorbance of the spikes in PP-D also decreased suggesting a decrease in loss of light by scattering (as discussed in Section 4.4 below) and indicative of the formation of smaller aggregates. The formation of large aggregates from the two different complexes (PP-C and PP-D) did not occur.

4.4. UV spectra of PSS and PEDOT/PSS complexes and films

The UV spectra of representative PEDOT/PSS dispersions subjected to CE separation in Figure 4.5 are given in Figure 4.7 A alongside the UV spectra of the corresponding films (Figure 4.7 B). Similarly, the UV spectra of the PEDOT/PSS dispersions subjected to CE separation in Figure 4.6 and their corresponding films are given in Figures 4.8 A and 4.8 B, respectively. A spectral maximum of ~225 nm was observed in all cases. From the UV spectra of the films (Figures 4.7 B and 4.8 B), it is evident that PSS has a higher absorptivity than PEDOT at ~225 nm.

The UV spectra (see Figure 4.7 A) of the dispersions with higher electrophoretic mobility and no spikes (i.e. PP-A, PP-B, and PP-C in Figure 4.5) were similar to that obtained for PSS. However, the dispersions showing lower electrophoretic mobility and spiking (attributed to higher doping) (i.e. PP-D, PP-E, and PP-F in Figure 4.5) showed markedly higher absorbance intensities from ~190 to ~280 nm. The difference in absorbance between the dispersions showing no spikes in their electropherograms (PSS, PP-A, PP-B and PP-C) from those exhibiting spiking (PP-D, PP-E and PP-F) at ~225 nm could be attributed to the effect of light scattering, resulting to a decrease in transmittance and increase in recorded absorbance, brought about by the aggregation of the PEDOT/PSS particles. DLS analysis of these PEDOT/PSS dispersions under similar conditions as the CE analysis gave high polydispersity indices (~0.4) indicative of particle aggregation. Moreover, more than 80% of the particles of those dispersions not
showing spikes in the electropherograms were in the size range of <160 nm while more than 80% of the particles of those showing spikes were in a higher range of >220 nm. These results are consistent with those observed in the CE where spikes, i.e. due to light scattering, were observed from dispersions of aggregated particles with DLS size (>220 nm) closer to the detection wavelength (223 nm). UV spectra of films prepared from PP-A and PP-D (Figure 4.7 B) did not show appreciable difference in absorbance intensities at ~225 nm. Since minimal aggregation is expected in the film, this suggests that the large increase in absorbance intensity of PP-D compared to PP-A in the CE measurements at the same wavelength (see Figure 4.7 A) is due to the formation of an aggregated complex in the PP-D dispersion.

![Figure 4.7](image)

**Figure 4.7** UV spectra of (A) PEDOT/PSS complexes and PSS from the CE analysis of samples in Figure 4.5, and (B) PEDOT/PSS films (50-70 nm thick) prepared from selected dispersions; the 230-350 nm regions has been enlarged and presented as an inset figure.

The increase in absorbance at 240-280 nm, however, could be attributed to an increase in the amount of PEDOT particles attached to PSS and evident not only in the dispersions but also in the films. The UV spectrum of the EDOT monomer (data not shown) also showed absorbance at 240-280 nm. The film (see inset of Figure 4.7 B), from the PP-A dispersion characterised with no spikes and less doping (according to Figure 4.5), showed lower absorbance intensity at 240-280 nm than the PP-D film prepared from a dispersion characterised with spikes and highly doped with PSS.
The UV spectra for the samples in Figure 4.6 shown in Figure 4.8 strengthen this claim. Note that the complexes for these samples were all detected as spikes in the electropherogram (see Figure 4.6). When the doping was increased (ratio from 1:5, 1:3, to 1:1 of PEDOT/PSS) an increase in the intensity at ~250 nm was also noticed. In addition, the films recorded a decrease in absorbance intensity at ~225 nm with increasing PEDOT: PSS ratio but increasing absorbance at 240-280 nm with increasing PEDOT/PSS ratio.

![UV spectra](image)

**Figure 4.8** UV spectra of (A) PEDOT/PSS complexes from the CE analysis of samples in Figure 4.6, and (B) PEDOT/PSS films (50-70 nm thick) prepared from the corresponding dispersions.

### 4.5. Electrophoretic mobility and conductivity

The electrophoretic mobility of the PEDOT/PSS complexes decreases with increasing level of PSS doping due to the reduction of the free negative charges on the PSS upon interaction with PEDOT. Conversely, PSS doping introduces charge carriers into the electronic structure; increase in PSS doping leads to an increase in the density and mobility of charge carriers and, subsequently, to higher conductivity.[132] From Figure 4.5, it is observed that the electrophoretic mobility of the complexes in the dispersions decreased while the measured conductivity of the corresponding films increased from top to bottom (sample PP-A to PP-F). The samples with spikes in the electropherogram (samples PP-D, PP-E, and PP-F) all yielded films with a conductivity that is at least an order of magnitude higher compared to the commercial sample (PP-A). The samples with no spikes (samples PP-B and PP-C) but with lower complex mobility compared to PP-A sample yielded films of slightly higher conductivity, as expected. The correlation
between the electrophoretic mobility of PEDOT/PSS aqueous dispersions, prepared from PEDOT/PSS ratios of \( \leq 1:6 \), and the conductivity of their corresponding films is summarized in Figure 4.9 and shows that the conductivity of the films increases with decreasing electrophoretic mobility (i.e. shorter migration time) attributed to higher PSS doping. These results demonstrate that CE can be used as a fast screening method to predict film conductivity from the prepared PEDOT/PSS dispersions. The total CE analysis was \(~25\) min for each sample including sample dilution and column conditioning whereas the time needed to prepare the films plus conductivity measurements take several hours.

![Figure 4.9](image)

**Figure 4.9** Correlation between electrophoretic mobility of PEDOT/PSS aqueous dispersions and conductivity of corresponding films. All PEDOT/PSS dispersions were prepared from PEDOT/PSS ratios of \( \leq 1:6 \).

### 4.6. Conclusion

A CE method to analyse PEDOT/PSS aqueous dispersions was developed. This method allowed the separation of free PSS from PEDOT/PSS complex in PEDOT/PSS dispersions based on ionic charges. PEDOT/PSS complex has shorter migration time or lower electrophoretic mobility than PSS because of the reduction of the negative charges of PSS due to doping with PEDOT. Intensity of PSS peak corresponds to the amount of free PSS which is correlated to the doping efficiency of PEDOT/PSS in the dispersion, i.e. the lower the intensity of the free PSS peak, the higher the amount of
PSS doped to PEDOT. Quantitative analysis of doping efficiency from CE is presented in the succeeding Chapters.

The electrophoretic mobility of PEDOT/PSS complexes was related to the doping of PEDOT to PSS where an increase in the amount of PEDOT doped to PSS resulted in an increase in film conductivity. Longer migration time of PEDOT/PSS complexes resulted in lower conductivity of the films, and shorter migration time of the complexes resulted in higher conductivity of the films regardless of the amount of free PSS.

CE can be used as a fast test to predict film conductivity and, perhaps in the future, can be used as a tool to check the quality of the PEDOT/PSS dispersions to ensure uniform conductivity behaviour. CE has been routinely used in subsequent studies presented in the following Chapters for the characterisation of PEDOT/PSS dispersions.
CHAPTER 5 - OPTIMISATION OF THE PROCESSABILITY OF PEDOT/PSS DISPERSIONS AND CONDUCTIVITY OF FILMS
5.1. Introduction

The presence of PSS results in a PEDOT/PSS aqueous dispersion system with good film forming properties, high visible light transmissivity, and excellent stability.[20] PSS content affects the processability of the dispersions and the properties of the resulting films, such as conductivity and transparency. High PSS content reduces the electric conductivity although it improves the processability of the dispersion resulting in highly homogeneous films. For example, films generated from PEDOT/PSS ratio 1:2.5 has higher conductivity than the films generated from PEDOT/PSS ratio 1:6 which is also more conductive than films from PEDOT/PSS ratio 1:20.[22,27] These conductivity values are associated with the solid content of the polymer system and correlated to their applications. Therefore, PEDOT/PSS ratio 1:2.5 is suitable for antistatic applications, ratio 1:6 is suitable for OLEDs, and ratio 1:20 is suitable for passive matrix displays.[22]

This chapter deals with the optimisation of conditions such as time, PEDOT/PSS ratios and PSS dilution effect, for the synthesis of PEDOT/PSS aqueous dispersions in order to achieve processable dispersions that can generate highly conductive films. The properties of the in-house synthesised PEDOT/PSS dispersions have been compared to the commercially-sourced PEDOT/PSS dispersion. This study also involves understanding the relationship between the doping process, processability of the dispersions and conductivity behaviour of the resulting films.

5.2. Comparison of commercial and in-house synthesised PEDOT/PSS dispersions and films

Synthesis of PEDOT/PSS aqueous dispersions via oxidative polymerisation was carried out by mixing the EDOT monomer with an appropriate amount of 6% (by weight) PSS aqueous solution, and the oxidation agents (Na₂S₂O₈ and Fe₂(SO₄)₃) for 24 hours following Louwet’s method.[19] The ratio of PEDOT/PSS used was 1:2.5 by weight and will be referred to herein as PP(1:2.5)-24. Removal of oxidation agents was carried out using acid and basic ion exchange resins. It was observed that this ion exchange process reduced the aggregation of PEDOT/PSS rendering the dispersion more homogeneous.[60] To remove unreacted EDOT, the dispersion was dialysed in
methanol then water using dialysis tube with a molecular weight cut off of 3500. All purified PEDOT/PSS aqueous dispersions had pH values between of 2.5 – 3.0.

The commercial dispersion (Clevios) used for this study was prepared from the same PEDOT/PSS ratio (1:2.5) and will be referred to as PP(1:2.5)-C. This dispersion has a pH of 2.2.

5.2.1. Capillary Electrophoresis of Dispersions

As previously described in Chapter 4, capillary electrophoresis (CE) was used to distinguish the synthesised PEDOT/PSS dispersions and the commercial sample. CE can separate PEDOT/PSS complex from the free (un-doped) PSS based on the difference in electrophoretic mobility between the complexed PSS (lower negative charge) and free PSS (higher negative charge).

The CE electropherograms of PP(1:2.5)-24, PP(1:2.5)-C and PSS aqueous dispersions in 20 mM borate buffer pH 9.2 is shown in Figure 5.1. Both PP(1:2.5)-24 and PP(1:2.5)-C dispersions contain free PSS detected at 14 min. PEDOT/PSS complex from PP(1:2.5)-24 was detected as spikes at 8-9 min, whereas that from PP(1:2.5)-C was detected as a broad peak at 11-12 min. The electrophoretic mobility of the PEDOT/PSS complexes is related to the degree of PSS doping. The electrophoretic mobility of the PEDOT/PSS complex in PP(1:2.5)-24 was slower than PP(1:2.5)-C because the negative charge of the PSS has been reduced due to the interaction of some of its –SO₃⁻ groups with PEDOT. The different migration time between PP(1:2.5)-24 and PP(1:2.5)-C correlated to the size and charge of the complexes due to higher amount of PEDOT segments doped with PSS sites in sample PP(1:2.5)-24 than PP(1:2.5)-C.
5.2.2. Particle size and zeta potential of dispersions

Particle size measurements of PP(1:2.5)-C and PP(1:2.5)-24 were conducted using Dynamic Light Scattering (DLS) after ultrasonically treating the samples for at least 30 min followed by immediate filtration. Data particle size distributions from triplicate subsequent measurements of PP(1:2.5)-C and PP(1:2.5)-24 are summarised in Table 5.1. Both PP(1:2.5)-C and PP(1:2.5)-24 gave two peaks at the first measurement, one at 21 and 29 nm, respectively, attributed to the size of primary particles of PEDOT/PSS which mostly formed aggregates (peak 1) of 219 and 180 nm, respectively, by the time of measurement.

Results of successive triplicate particle size measurements for the same dispersions shown in Table 5.1 indicate the tendency of the particles to form aggregates with increasing time, consistent with published reports.[92] In the case of PP(1:2.5)-24 dispersion, the particle size had variation in size ($247 \pm 67$ nm) during the course of three measurements. However, PP(1:2.5)-C already showed optimal aggregation during the course of three measurements with no significant change in particle size ($223 \pm 4$ nm). The CE results confirmed the bigger size of aggregates of PEDOT/PSS complexes from PP(1:2.5)-24 than those of PP(1:2.5)-C. The electropherograms show complexes from PP(1:2.5)-24 appeared as spikes which could be attributed to the effect of light.
scattering brought about by the aggregation of the PEDOT/PSS particles, whereas the aggregation of the complexes from PP(1:2.5)-C were smaller in size and thus appeared as a broad peak (see Figure 5.1).

Table 5.1 Average* particle size distributions by volume ($D_v$) and zeta-potentials of PP(1:2.5)-C and PP(1:2.5)-24 aqueous dispersions from DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-C</td>
<td>223 ± 4</td>
<td>22 ± 1</td>
<td>-</td>
<td>-57</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>247 ± 67</td>
<td>60 ± 16</td>
<td>28 ± 2</td>
<td>-46</td>
</tr>
</tbody>
</table>

*From 3 measurements.
**Values taken from 3rd measurement after dispersions have settled and equilibrated.

Zeta potential analysis of PEDOT/PSS dispersions was performed on a Zetasizer Nano Series from Malvern Instruments by diluting 1 mg of dried sample in 1.5 mL of 20 mM sodium borate buffer solution pH 9.2, the background electrolyte used in the CE analysis. Zeta potential values for PP(1:2.5)-C and PP(1:2.5)-24 dispersions (Table 5.1) are -57 mV and -46 mV, respectively, indicating that the synthesised PEDOT/PSS dispersion is less stable than the commercial sample and more susceptible to aggregation as shown by its the particle size distribution being bigger than PP(1:2.5)-C. The CE results (Figure 5.1) also suggest that the PEDOT/PSS complex in PP(1:2.5)-24 dispersion has formed big aggregates resulting to spikes. In addition, the PEDOT/PSS complex of PP(1:2.5)-24 exhibited slower electrophoretic mobility than that of PP(1:2.5)-C indicating that its surface charge is less negative than that of PP(1:2.5)-C consistent with their zeta-potential values.

5.2.3. UV spectra of films
UV analysis has been found to provide a spectrum of PEDOT/PSS film with a maximum of ~225-230 nm that corresponds to PSS in its free and PEDOT-complexed forms. Absorbance of PEDOT/PSS complex only could not be detected separately.[24,125,126,133] In Chapter 4, we described the UV absorption of free PSS at ~230 nm and PEDOT/PSS complex at 240-280 nm in their dispersions using CE. The spectra showed that we can detect increase in doping of PEDOT by PSS by observing
the increasing intensity of the peak at 240-280 nm (see Figure 4.7 and 4.8 in Chapter 4). UV analysis of PP(1:2.5)-24 and PP(1:2.5)-C films were carried out to compare the content of PEDOT/PSS complex and free PSS between both films. The UV spectra of the films (see Figure 5.2) indicates the appearance of peak absorbance at ~225 nm due to PSS, and appreciable difference in intensity of absorbance at 240-280 nm due to PEDOT complexed with PSS. While UV analysis of pure PEDOT shows the difficulty of detecting this peak absorbance, the PP(1:2.5)-24 film shows higher intensity of absorbance at 240–280 nm than the PP(1:2.5)-C film. This indicates that the PP(1:2.5)-24 film contains more PEDOT complexed with PSS than the PP(1:2.5)-C film consistent with the CE electropherogram (see Figure 5.1).

![Figure 5.2](image)

Figure 5.2 UV spectra of PP(1:2.5)-24 and PP(1:2.5)-C films in quartz substrate with thickness ~70 nm. The spectrum of PEDOT powder is included for comparison.

5.2.4. Surface morphology of films

The SEM images in Figure 5.3 show the surface morphology of the PP(1:2.5)-C film to be predominantly uniform, but some PSS aggregation formed during drying of the film can be observed[45] appearing as white patches (encircled in Figure 5.3 A). The surface morphology of the PP(1:2.5)-24 film shows a rougher surface than the PP(1:2.5)-C film although PSS aggregation was also observed. The difference in surface morphologies between the two samples can be attributed to the difference in the particle size of the PEDOT/PSS.[56,95,96,134] PP(1:2.5)-24 film, with bigger particle size and more
aggregation, displayed a rougher surface than that of PP(1:2.5)-C containing smaller aggregates.

![SEM images of PP(1:2.5) films](image)

**Figure 5.3** SEM images of (A) PP(1:2.5)-C film; and (B) PP(1:2.5)-24 film. Images were taken in 12000 x magnification. Observed white patches are encircled.

### 5.2.5. Conductivity of films

Films prepared from PP(1:2.5)-C aqueous dispersion exhibited conductivity ($\sigma$), measured using the four point probe method, of $9.6\pm1.1 \times 10^{-3}$ S/cm with the thickness ($t$) of $61\pm5$ nm consistent with reported values which are usually $<1$ S cm$^{-1}$.[23,45,46,47] Although the PP(1:2.5)-C film has good properties, such as high transparency and mechanical flexibility, its conductivity is lower than the films of the in-house prepared PP(1:2.5)-24. The films generated from PP(1:2.5)-24 dispersion have conductivity ($\sigma$) of $2.1\pm0.5$ S/cm with the thickness ($t$) of $251\pm46$ nm. DLS results show the primary particles of PEDOT/PSS in PP(1:2.5)-24 dispersion to be bigger than the primary particles of PP(1:2.5)-C dispersion. A previous study has reported that the smaller particles of PEDOT/PSS resulted in lower conductivity of the films.[22] CE results have confirmed a higher doping between PEDOT and PSS in PP(1:2.5)-24 dispersion than in PP(1:2.5)-C and, presumably, responsible for the higher conductivity of PP(1:2.5)-24 film.

### 5.2.6. Thermal stability of films

Thermal stability of PSS (MW 70kDa), PP(1:2.5)-C and PP(1:2.5)-24 composites (i.e. dry particles and not dispersions) were compared using thermal gravimetric analysis (TGA) and the results are shown in Figure 5.4. The TGA curve of pure PSS indicates four stages of degradation. The first stage is up to $150^\circ$C and accounts for 10% mass
loss from water evaporation. The second stage is quite a stable condition between 150 up to 420°C which is only 3% mass loss and possibly resulted from the removal of residual water [135], and the third stage with high degradation occurs from 420 through 465°C and contributes to the mass loss of about 13.5%. Further degradation continues until 600°C and the total of mass loss is about 31%. The TGA curve of PP(1:2.5)-24, with PSS (70kDa) as the dopant, is slightly different from the TGA of PSS. It seems that the presence of PEDOT doped with PSS decreased the thermal stability of PSS. TGA of pure PEDOT exhibits thermal degradation at 300°C up to 500°C and total mass loss of 95%. Major decomposition of PP(1:2.5)-24 composite started at 360°C attributed to the decomposition of PEDOT particles, and the total mass loss at 600°C was 36%. The TGA curve of PP(1:2.5)-C composite also shows loss of water around 7% up to 150°C, but it decomposed earlier at 260°C. Major decomposition occurred up to 600°C, and the total mass loss of PP(1:2.5)-C composite was 50%. These curves indicate that the PP(1:2.5)-24 composite is more stable than the PP(1:2.5)-C composite. Although, the electropherograms show similar migration time of PSS at ~14 min, the difference in thermal stability of PEDOT/PSS aqueous dispersions suggest that the PSS used in PP(1:2.5)-C may be different as there is a significant difference in the decomposition temperature between PP(1:2.5)-C and the PSS (70kDa) used in the PP(1:2.5)-24 composite. The commercial sample shows more PEDOT decomposition starting at ~300°C whereas the in house sample resembles PSS more.

Figure 5.4 TGA curves of PSS, PEDOT, PP(1:2.5)-C, and PP(1:2.5)-24 composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N₂ atmosphere.
5.2.7. Summary

Overall, the PP(1:2.5)-24 aqueous dispersion can generate very conductive films, ~200 times more conductive than the commercial dispersion PP(1:2.5)-C. This is expected due to the higher doping of PEDOT with PSS in PP(1:2.5)-24 aqueous dispersion than in PP(1:2.5)-C aqueous dispersion as indicated by CE and UV analyses. The particle size distribution of PEDOT doped to PSS in the PP(1:2.5)-24 dispersion showed higher aggregation than PP(1:2.5)-C dispersion and correlated to the higher doping observed in CE resulting in higher conductivity of the films. The zeta potential results also indicated higher stability of PP(1:2.5)-C aqueous dispersion due to less aggregation of the particles than in PP(1:2.5)-24 aqueous dispersion. However, PP(1:2.5)-24 is more thermally stable than the PP(1:2.5)-C composite.

5.3. Processability of PEDOT/PSS aqueous dispersions in various ratios

Synthesis of PEDOT/PSS aqueous solution for 24 hours provided high conductivity PEDOT/PSS films, but the films were less homogeneous and rougher than the commercial PEDOT/PSS. Therefore, the processability of synthesised PEDOT/PSS aqueous dispersions to generate high conductive, more stable and uniform films needs to be improved. In order to investigate their processability, PEDOT/PSS aqueous dispersions were prepared following three methods: (1) synthesis by varying PEDOT/PSS ratios, (2) synthesis of a non-processable PEDOT/PSS (PP(1:1)-24) and subsequent dilution with more PSS post-polymerisation, and (3) synthesis of pure PEDOT and doping with PSS post-polymerisation.

5.3.1. Method 1: synthesis by varying PEDOT/PSS ratios

Processable PEDOT/PSS dispersions were synthesised by oxidative polymerisation using EDOT and PSS ratios (by weight) of 1:1 (PP(1:1)-24), 1:2.5 (PP(1:2.5)-24), 1:3 (PP(1:3)-24), 1:5 PP(1:5)-24 and 1:6 PP(1:6)-24 for 24 h. Processability of the PEDOT/PSS aqueous dispersions was gauged from the quality of the corresponding films produced. PP(1:1)-24 aqueous dispersion was difficult to process. The films generated from this dispersion (Figure 5.5 A) were rough, not uniform, and hence, its conductivity could not be measured. Less PSS to dope and balance the charge can cause
sedimentation, and PEDOT and PSS could not combine well in the film.\textsuperscript{60} Increasing the ratio of PSS from 1:1 to 1:6 resulted in more processable dispersions, and generated more uniform and smoother films (see Figure 5.5).

Conductivity measurements (70-250 nm films thick) resulted in less conductive films at higher ratio of PSS (Table 5.2). Doubling the ratio of PSS from 1:2.5 to 1:5 (PP(1:2.5)-24 vs PP(1:5)-24) decreased the conductivity 14 times (from 2.10 S/cm to 0.15 S/cm) while increasing the ratio to 1:6 (PP(1:6)-24) decreased the conductivity of the film ~27 times (0.079 S/cm). Higher ratio of PSS provided more free PSS surrounding the PEDOT/PSS complexes and decreased connectivity between the complexes PEDOT/PSS domains in the films and thereby decreased conductivity of the films.\textsuperscript{27,85,125} All in-house prepared PEDOT/PSS films provided higher conductivity than those obtained from commercial dispersion PP(1:2.5)-C. Even the conductivity of PP(1:6)-24 film (0.079 S/cm) is still ~8 times higher than the conductivity of PP(1:2.5)-C film (0.0096 S/cm).

\textbf{Figure 5.5} Morphology images of PEDOT/PSS films synthesised for 24 hrs from different ratios of PSS: (A) PP(1:1)-24; (B) PP(1:2.5)-24; (C) PP(1:3)-24; (D) PP(1:5)-24; and (E) PP(1:6)-24. Images were taken using microscope “Axioskop 40 Pol” from ZEISS in 40x magnification.
Table 5.2 Conductivity and thickness of PEDOT/PSS films synthesised by oxidative polymerisation for 24 hrs reaction from different ratios of PSS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-24</td>
<td>$2.1 \pm 0.5 \times 10^0$</td>
<td>$251 \pm 13$</td>
</tr>
<tr>
<td>PP(1:3)-24</td>
<td>$7.6 \pm 1.0 \times 10^1$</td>
<td>$111 \pm 14$</td>
</tr>
<tr>
<td>PP(1:5)-24</td>
<td>$2.5 \pm 0.5 \times 10^1$</td>
<td>$101 \pm 10$</td>
</tr>
<tr>
<td>PP(1:6)-24</td>
<td>$7.9 \pm 2.3 \times 10^2$</td>
<td>$65 \pm 9$</td>
</tr>
</tbody>
</table>

UV spectra of representative PEDOT/PSS films prepared from different PSS ratios given in Figure 5.6 show peaks attributable to both PEDOT/PSS complex (240-280 nm) and un-doped (free) PSS at ~225 nm. The intensity of the free PSS peak at ~225 nm has been observed to increase with increasing PSS content while the intensity of the peak due to PEDOT/PSS complexes at 240-280 nm increased with decreasing PSS content. These results indicate that reducing the PSS content increased the doping of PEDOT to PSS and increasing the PSS content resulted in more free PSS and lower doping. This is consistent with the conductivity results showing low conductivity of PP(1:6)-24 film due to lower amount of PEDOT doped to PSS and high conductivity of PP(1:2.5)-24 and PP(1:3)-24 films expected to contain higher amounts of PEDOT doped to PSS.

Figure 5.6 UV spectra of PEDOT/PSS films (50-70 nm thick) synthesised for 24 hrs in different ratios of PSS: PP(1:1)-24, PP(1:3)-24, and PP(1:5)-24 compared to a pure PSS film.
Thermal stability of PEDOT/PSS composites (i.e. dried dispersions) from different ratios of EDOT and PSS were determined from TGA experiments and the results are shown in Figure 5.7. All curves indicate loss of water around 5-10% by heating up to 150°C. Whilst PSS was stable up to ~420°C, pure PEDOT started to decompose at <290°C. Doping PEDOT to PSS was found to decrease thermal stability of the composites with the highest amount of PEDOT resulting in the least stable composite (PP(1:1)-24) decomposing at ~290°C followed by PP(1:2.5)-24 then PP(1:5)-24 decomposing at ~360°C and ~375°C, respectively, whereas PSS started to decompose at ~420°C. PP(1:5)-24 containing the highest ratio of PSS also exhibits a thermal degradation profile similar to that of pure PSS. Major decomposition of the synthesised PEDOT/PSS composites occurred up to 600°C with weight losses up to 48% for PP(1:1)-24, 35% for PP(1:2.5)-24 and 31% for PP(1:5)-24. These results indicate that the synthesised PEDOT/PSS composites are more stable than the commercial PP(1:2.5)-C composite.

![Figure 5.7 TGA curves of PEDOT, PP(1:1)-24, PP(1:2.5)-24, PP(1:5)-24, and PSS composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N2 atmosphere.](image)

The PEDOT/PSS dispersions prepared from different PSS ratios were also analysed by capillary electrophoresis (CE). For the synthesised PEDOT/PSS dispersions, the peak attributable to free PSS is expected at ~14 min (see Figure 5.1) while peaks due to the PEDOT/PSS complex can occur between ~7 to ~12 min (see Figure 4.5). The
electropherograms in Figure 5.8 show increasing peak intensity of PSS at ~14 min from PP(1:3)-24 (B) to PP(1:6)-24 (D). PP(1:1)-24 (A) did not show any PSS peak. Quantification of the degree of doping on these samples based on the PSS peak area shows decreasing degree of doping from A (98.7%) through to D (56.0%). These results show that increasing the ratio of PSS during preparation of dispersions resulted in higher amount of free un-doped PSS in the dispersions. Availability of free PSS in the PEDOT/PSS dispersions are responsible for the processability of the films. Therefore, increasing the ratios of PEDOT to PSS from 1:1 (A) to 1:6 (D) resulted in more processable dispersions, and generated more uniform and smoother films (see Figure 5.5).

**Figure 5.8** Electropherograms of PEDOT/PSS aqueous dispersions synthesised in different ratios of PSS for 24h: (A) PP(1:1)-24, (B) PP(1:3)-24, (C) PP(1:5)-24, and (D) PP(1:6)-24. BGE: sodium borate buffer 20 mM, pH 9.2, 15 kV. Conductivity and doping efficiency of corresponding dispersions are included.
Figure 5.8 also shows that the varying ratios of PSS in the synthesis of PEDOT/PSS dispersions are also observed to affect the electrophoretic mobility of PEDOT/PSS complexes. The migration time of the PEDOT/PSS complexes in the dispersions increases from PP(1:1)-24 (A), through to PP(1:6)-24 (D) indicating a decrease in electrophoretic mobility from (A), through to (D). Increasing ratio of PSS decreased the amount of doped PEDOT per unit PSS resulting in higher negative charge of PEDOT/PSS complexes and lower electrophoretic mobility. The lower amount of PEDOT doped to PSS from (B) to (D) is presumably responsible to the decrease in conductivity of PEDOT/PSS film from (B) through to (D).

The particle size distributions and zeta potentials of PP(1:1)-24, PP(1:3)-24, PP(1:5)-24, and PP(1:6)-24 aqueous dispersions are shown in Table 5.3. All dispersions are mostly in the form of aggregates. The zeta potential values indicate an increase in the surface charge of dispersions with increasing concentration of PSS, i.e. zeta potentials of -43, -46, -49 and -50 mV, respectively, indicating increasing stability of dispersions. This is consistent with the CE results (Figure 5.8) showing an increasing amount of free PSS, hence, greater negative charge, from PP(1:1)-24 through to PP(1:6)-24.

Table 5.3 Average* particle size distributions by volume ($D_v$) and zeta-potential values for PP(1:1)-24, PP(1:3)-24, PP(1:5)-24 and PP(1:6)-24 aqueous dispersions from DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_v$, 1 nm</th>
<th>$D_v$, 2 nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:1)-24</td>
<td>180 ± 27</td>
<td>55 ± 6</td>
<td>-43</td>
</tr>
<tr>
<td>PP(1:3)-24</td>
<td>448 ± 73</td>
<td>32 ± 13</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:5)-24</td>
<td>618 ± 102</td>
<td>29 ± 0</td>
<td>-49</td>
</tr>
<tr>
<td>PP(1:6)-24</td>
<td>529 ± 111</td>
<td>107 ± 10</td>
<td>-50</td>
</tr>
</tbody>
</table>

*From 3 measurements.
**Values taken from 3rd measurement after dispersions have settled and equilibrated.

In summary, the processability of PEDOT/PSS aqueous dispersions synthesised via oxidative polymerisation can be improved by increasing the ratio of PSS in the dispersions. Increasing the amount of PSS generated smoother and more uniform films. However, increasing PSS caused a decrease in the conductivity of the films due to lower
doping of PEDOT to PSS as indicated by UV and CE. All dispersions have the tendency to form aggregates and zeta potential distributions showed an increase in the stability of dispersions with an increase in PSS ratio. Thermal stabilities of the synthesised PEDOT/PSS composites are affected by the ratio of PEDOT and PSS in the composites, higher PEDOT content resulted to decrease the thermal stability of the composite.

5.3.2. Method 2: synthesis of non-processable (PP(1:1)-24) dispersion and post-polymerisation addition of PSS

Results of our study showed that the free un-doped PSS content in PEDOT/PSS aqueous dispersions determines its processability and ability to generate smoother and homogeneous films. However, CE analysis in Figure 5.9 also show that with the exception of PP(1:1)-24 (D), the conductivity of the films produced from dispersions (A), (B) and (C), increased with decrease in free PSS content and (C), the least uniform and roughest film gave the highest conductivity. From the observed trend, the PP(1:1)-24 dispersion (D) with no free PSS would have been expected to generate highly conductive film if it was processable. However, PP(1:1)-24 dispersions synthesised for ≤ 6 hrs are still processable with free un-doped PSS as shown in the electropherograms, and their conductivities are still higher than commercial PP(1:2.5)-C.

In this work, PP(1:1)-24 dispersion was diluted with additional PSS post-polymerisation to make it processable and to see if the resulting film will exhibit conductivity comparable to the equivalent PEDOT/PSS dispersion synthesised by in-situ polymerisation. Varying concentrations of PSS solution was added to PP(1:1)-24 dispersion by stirring overnight (24h) resulting in modified PEDOT/PSS ratios of 1:2, 1:3 and 1:5 which will be referred to as PP(1:2-d)-24, PP(1:3-d)-24, and PP(1:5-d)-24, respectively. It was observed that the quality of films, i.e. homogeneity, was enhanced by the addition of more PSS in the dispersion, i.e. PP(1:5-d)-24 film is more uniform than PP(1:2-d)-24, and evident in the images of these films shown in Figure 5.10. PP(1:1)-24 film (A) exhibits a very rough and non-uniform surface but by adding PSS solution, PP(1:2-d)-24 dispersion produced smoother and more uniform film (B). Adding more PSS solution increased the processability of the solution and the films
become smoother as can be seen in PP(1:3-d)-24 and PP(1:5-d)-24 films (see C and D). PP(1:1)-24 aqueous dispersion has a high concentration of PEDOT doped with PSS with minimal free PSS (see Figure 5.9). The hypothesis was that the addition of more PSS into the solution would result in more processable PEDOT/PSS dispersion. Additional PSS solution could also induced additional doping with PEDOT.

**Figure 5.9** CE electropherograms of PEDOT/PSS aqueous dispersions, (A) PP(1:1)-1; (B) PP(1:1)-3; (C) PP(1:1)-6; and (D) PP(1:1)-24. BGE: sodium borate buffer 20 mM, pH 9.2, 15 kV.
Figure 5.10 Images of (A) PP(1:1)-24 film, and after additional PSS solutions: (B) PP(1:2-d)-24, (C) PP(1:3-d)-24, and (D) PP(1:5-d)-24. Images were taken using microscope “Axioskop 40 Pol” from ZEISS in 5x magnification.

Conductivity of the films (60-110 nm thick) generated from the resulting dilution of PP(1:1)-24 dispersion measured by four point probe can be seen in Table 5.4. The data show that PP(1:2-d)-24, with the least amount of PSS added, exhibited higher conductivity (0.53 S/cm) than the dispersions, PP(1:3-d)-24 (0.19 S/cm) and PP(1:5-d)-24 (0.10 S/cm), with higher amounts of PSS added, consistent with previous results showing that higher PSS content tends to decrease the conductivity of the film. In comparison to the films generated from dispersions doped in situ, conductivity of both PP(1:2-d)-24 and PP(1:3-d)-24 films are ~4 times lower than PP(1:2.5)-24 and PP(1:3)-24 films, respectively, while that of PP(1:5-d)-24 is comparable to PP(1:5)-24 film. These suggest that post-polymerisation addition of PSS to PEDOT in PP(1:1)-24 dispersion did not result in optimal doping.
Chapter 5 – Optimisation of the Processability of PEDOT/PSS Dispersions and Conductivity of Films

Table 5.4 Conductivity and thickness of PP(1:2-d)-24, PP(1:3-d)-24, and PP(1:5-d)-24 compared to equivalent films doped in-situ.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2-d)-24</td>
<td>5.3 ± 0.8 10^{-1}</td>
<td>62 ± 10</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>2.1 ± 0.5 10^{0}</td>
<td>104 ± 13</td>
</tr>
<tr>
<td>PP(1:3-d)-24</td>
<td>1.9 ± 0.1 10^{1}</td>
<td>60 ± 11</td>
</tr>
<tr>
<td>PP(1:3)-24</td>
<td>7.6 ± 1.0 10^{1}</td>
<td>110 ± 14</td>
</tr>
<tr>
<td>PP(1:5-d)-24</td>
<td>1.0 ± 0.2 10^{1}</td>
<td>87 ± 8</td>
</tr>
<tr>
<td>PP(1:5)-24</td>
<td>1.5 ± 0.5 10^{1}</td>
<td>101 ± 10</td>
</tr>
</tbody>
</table>

The electropherograms of PP(1:1)-24, PP(1:2-d)-24, PP(1:3-d)-24, PP(1:5-d)-24 aqueous dispersions, and equivalent PEDOT/PSS doped in-situ are given in Figure 5.11. These electropherograms show the peak at 7–8 min due to PEDOT/PSS complexes in PP(1:1)-24 (A) moved to 8–11 min after PSS dilution in PP(1:2-d)-24 (B), PP(1:3-d)-24 (D), and PP(1:5-d)-24 (E) attributed to increasing negative charge of the complexes most likely due to additional doping with PSS added post-polymerisation. Interestingly, the spikes from (A) became broad peaks on (B), (D) and (E) whereas the equivalent (i.e. same amount of PSS) PEDOT/PSS dispersions doped in-situ, PP(1:3)-24 (B) and PP(1:5)-24 (F) can be seen as spikes at 9-10 min. This is an indication that doping still occurs post-polymerisation. The CE electropherograms of PP(1:1)-24 dispersion (A) indicated no peak of un-doped PSS at ~14 min (doping efficiency = 98.7%), while PP(1:2-d)-24 (B), PP(1:3-d)-24 (D), and PP(1:5-d)-24 (E) show higher intensity of undoped PSS peak at ~14 min compared to the equivalent in-situ dispersions. These translated to a lower doping efficiency for PP(1:3-d)-24 (D) and PP(1:5-d)-24 (59.6% and 42.1%, respectively) compared to PP(1:3)-24 (C) and PP(1:5)-24 (F) (78.6% and 56.4%, respectively). It is reasonable that films generated from post-polymerisation doping by PSS dilution of PP(1:1)-24 dispersion have conductivities lower than those observed from films doped in-situ due to the observed lower doping efficiency.
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Figure 5.11 CE electropherogram of: (A) PP(1:1)-24, (B) PP(1:2-d)-24, (C) PP(1:3)-24, (D) PP(1:3-d)-24, (E) PP(1:5-d)-24, and (F) PP(1:5)-24 aqueous dispersions. BGE: sodium borate buffer 20 mM, pH 9.2, 15 kV. Conductivity of corresponding films and doping efficiency are included.

Results of triplicate particle size measurements for the dispersions prepared by post polymerisation addition PSS are shown in Table 5.5. The data show a decrease in the size of aggregates with increasing amount of PSS added. The CE results in Figure 5.11 confirmed the bigger size of PEDOT/PSS aggregates for PP(1:1)-24 (A) showing spikes and shorter migration time than the smaller aggregates manifested as broad peaks with longer migration time of the PSS diluted dispersions (B, D, and E).
Table 5.5 Average* particle size distributions by volume \((D_v)\) and zeta-potential of PP(1:1)-24, PP(1:2.2-d)-24, PP(1:3.4-d)-24, and PP(1:4.6-d)-24 aqueous dispersions from DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Zeta potential*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:1)-24</td>
<td>180 ± 27</td>
<td>55 ± 6</td>
<td>-43</td>
</tr>
<tr>
<td>PP(1:2-d)-24</td>
<td>141 ± 6</td>
<td>34</td>
<td>-43</td>
</tr>
<tr>
<td>PP(1:3-d)-24</td>
<td>135 ± 15</td>
<td>-</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:5-d)-24</td>
<td>99 ± 12</td>
<td>-</td>
<td>-46</td>
</tr>
</tbody>
</table>

*From 3 measurements.
**Values taken from 3rd measurement after dispersion have settled and equilibrated.

The zeta potential values shown in Table 5.5 indicate that additional PSS has contributed to the stability of the dispersions as shown by the small increase in the zeta potential from PP(1:2-d)-24 to PP(1:5-d)-24. This also suggests that additional doping has occurred when PSS was added post-polymerisation.

In summary, post polymerisation dilution with additional PSS to unprocessable PP(1:1)-24 dispersion has been found to improve the processability of the dispersion and generate more uniform and smoother films although the conductivity of the resulting films are still lower than those obtained from the films doped in-situ. CE results suggest that PSS can still be doped post polymerisation as evidenced from the increase in the electrophoretic mobility of the PEDOT/PSS complex after dilution with PSS. Particle size measurements show a decrease in the size of PEDOT/PSS aggregates with increasing amount of added PSS. These additional PSS increased the stability of the dispersions as shown by the small increase in the zeta potential, i.e. more negative with more PSS and suggests that doping still occurred post-polymerisation.

5.3.3. Method 3: synthesis of pure PEDOT and doping with PSS post-polymerisation

The doping process was studied further by observing the effect of post-polymerisation addition of PSS unto PEDOT. PEDOT was synthesised without PSS in acetonitrile (PEDOT\textsubscript{ACN}) and in water (PEDOT\textsubscript{WATER}). These samples, when dried in vacuo, were
shown by SEM images to exhibit different morphology (see Figure 5.1). PEDOT\textsubscript{ACN} shows a mixture of chunks, sheets and particulates while PEDOT\textsubscript{WATER} showed more uniform particulates. The difference in morphology could be due to the difference in the solubility of the EDOT monomer in the reaction system used. EDOT is soluble in acetonitrile but not in water. In addition, the yields obtained from the two systems were also different with water giving higher yield than acetonitrile. This could be attributed to the oxidation agents being soluble in water (but not in acetonitrile) and even if EDOT is insoluble in water, initiation of polymerisation and formation of PEDOT was promoted by stirring the solution. However, although EDOT is soluble in acetonitrile, the oxidation agents are insoluble and polymerisation of EDOT was more difficult.

**Figure 5.12** SEM images of pure PEDOT synthesised (A) in acetonitrile (PEDOT\textsubscript{ACN}); and (B) in water (PEDOT\textsubscript{WATER}). Images were taken at 12000x magnification.

Thermal stability of pure PEDOT composites synthesised in acetonitrile and in water indicated stability and started to decompose at \(~270^\circ\text{C}\) and \(~290^\circ\text{C}\) (see Figure 5.13). There is no degradation of the composites when heated up to \(150^\circ\text{C}\) indicating that PEDOT is not hygroscopic. Major decomposition of PEDOT\textsubscript{ACN} composite occurred up to \(600^\circ\text{C}\) with weight losses up to 63\%, whereas PEDOT\textsubscript{WATER} composite loss of weight up to 57\% (see Figure 5.13). These results indicate that PEDOT\textsubscript{WATER} is more stable than PEDOT\textsubscript{ACN} composite which we can only speculate as related to their morphology. Thermal stability of PEDOT composite however, was observed to increase after doping with PSS.
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Figure 5.13 TGA curves of PEDOT composites synthesised in water (PEDOT\textsubscript{WATER}), in acetonitrile (PEDOT\textsubscript{ACN}), and PP(1:2.5)-24 composite. Samples were placed in aluminium pan at the maximum temperature of 600°C under N\textsubscript{2} atmosphere.

In order to prepare PEDOT/PSS dispersions, PEDOT\textsubscript{ACN} and PEDOT\textsubscript{WATER} were mixed with PSS solution in a 1:2.5 (EDOT:PSS) ratio by weight. The resulting dispersions are referred to here as PP\textsubscript{A}(1:2.5-p)-24 and PP\textsubscript{W}(1:2.5-p)-24. It was observed that the films resulting from spin-coating the dispersions were not homogeneous and some aggregated particles are evident after drying (see Figure 5.14). Both PP\textsubscript{A}(1:2.5-p)-24 (A) and PP\textsubscript{W}(1:2.5-p)-24 (B) films are rough with less uniform surface compared to PP(1:2-d)-24 and PP(1:3-d)-24 shown in Figure 5.5 (B) and (C).

Figure 5.14 Images of (A) PP\textsubscript{A}(1:2.5-p)-24; and (B) PP\textsubscript{W}(1:2.5-p)-24 films. Images were taken using microscope “Axioskop 40 Pol” from ZEISS in 20x magnification.

Conductivity measurements showed PP\textsubscript{A}(1:2.5-p)-24 to be more conductive than PP\textsubscript{W}(1:2.5-p)-24 (see Table 5.6) and both conductivities are still higher by one order of magnitude than the commercial PP(1:2.5)-C film. They are, however, 2 orders of magnitude lower than the PP(1:2.5)-24 film.
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Table 5.6 Conductivity and thickness of PP_A(1:2.5-p)-24 and PP_w(1:2.5-p)-24 films.

<table>
<thead>
<tr>
<th>Sample PEDOT/PSS</th>
<th>Solvent synthesis</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP_A(1:2.5-p)-24</td>
<td>Acetonitrile</td>
<td>3.9±0.9 10^{-2}</td>
<td>81±16</td>
</tr>
<tr>
<td>PP_w(1:2.5-p)-24</td>
<td>Water</td>
<td>2.5±0.2 10^{-2}</td>
<td>97±20</td>
</tr>
</tbody>
</table>

The doping process between PEDOT and PSS solution was also studied using CE. The electropherograms in Figure 5.16 show that PP_A(1:2.5-p)-24 (A) and PP_w(1:2.5-p)-24 (B) have PSS peak at ~14 min of higher intensity than that of PP(1:2.5)-24 (C) which were prepared for the same reaction time (24 hrs) indicating that most of PSS in (A) and (B) were still in un-doped (free) form. The electropherograms of PP_A(1:2.5-p)-24 (A) and PP_w(1:2.5-p)-24 (B) also showed wider peaks of PEDOT/PSS complex at 10-12 min and the intensity was lower than that of PP(1:2.5)-24 (C). The migration time of the PEDOT/PSS complexes from (A) and (B) dispersions are faster than that of (C), also indicating that doping in (A) and (B) were less than in (C). The CE results indicate that post-polymerisation doping was minimal resulting in doping efficiencies of 37.8% and 30.1% for PP_A(1:2.5-p)-24, (A) and PP_w(1:2.5-p)-24, (B), respectively. This is consistent with the conductivity results showing PP_A(1:2.5-p)-24 to be slightly more conductive than PP_w(1:2.5-p)-24 film although the conductivity of both films are lower by two order of magnitude than that obtained from PP(1:2.5)-24 with 89.2% doping efficiency.
Triplicate measurements of the particle size distribution and the zeta potential of PP_A(1:2.5-p)-24 and PP_W(1:2.5-p)-24 aqueous dispersions are shown in Table 5.7. Both particle size distribution and zeta potentials of PP_W(1:2.5-p)-24 and PP_A(1:2.5-p)-24 are comparable even if their morphology were quite different and consistent with the CE results showing similar peak performance at the same migration time for both dispersions.

**Table 5.7** Average* particle size distributions by volume (D_v) and zeta-potential of PP_A(1:2.5-p)-24 and PP_W(1:2.5-p)-24 aqueous dispersions from DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size, nm*</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP_A(1:2.5-p)-24</td>
<td>225 ± 21</td>
<td>-48</td>
</tr>
<tr>
<td>PP_W(1:2.5-p)-24</td>
<td>256 ± 11</td>
<td>-49</td>
</tr>
</tbody>
</table>

*From 3 measurements.

**Values taken from 3rd measurement after dispersion has settled and equilibrated.
In summary, PEDOT/PSS aqueous dispersions obtained by doping with PSS solution post-polymerisation can generate conductive PEDOT/PSS films, even though the conductivity of the films are lower than those resulting from in situ doping (PP(1:2.5)-24). This is expected due to the lower doping of PEDOT with PSS in both PP_A(1:2.5-p)-24 and PP_W(1:2.5-p)-24 films than in PP(1:2.5)-24 film confirmed by CE analysis of their dispersions. The particle size distribution, zeta potentials and thermal stability of these dispersions are similar.

5.4. Synthesis of PEDOT/PSS aqueous dispersions at different time of reactions

PEDOT/PSS of 1:2.5 ratio by weight were synthesised at various times of reaction from 1 to 48 hrs in order to study the effect of time on the processability of the dispersions and conductivity of the resulting films. Figure 5.16 shows that increasing time of reaction resulted in darker PEDOT/PSS dispersions indicating an increase in conversion of EDOT to PEDOT. However, due to solubility problems with EDOT and the nature of the soluble dispersion, i.e. PEDOT attached to PSS, the molecular weights of PEDOT (and conversion) were not measured. Further evidence of increase in polymer conversion was the apparent decrease and/or disappearance of the oily layer on top of the blue dispersions attributed to unreacted EDOT.

Figure 5.16 PEDOT/PSS aqueous dispersions prepared at different times: (A) 1 hr, PP(1:2.5)-1, (B) 3 hrs, PP(1:2.5)-3, (C) 6 hrs, PP(1:2.5)-6, (D) 12 hrs, PP(1:2.5)-12, (E) 24 hrs, PP(1:2.5)-24, (F) 36 hrs, PP(1:2.5)-36, and (G) 48 hrs, PP(1:2.5)-48. Concentration of the solutions is 5 g/L.
Triplicate measurements of particle size distribution presented in Table 5.8 show an increase in aggregation of particles during the preparation of PEDOT/PSS dispersions from 1 hr to 48 hrs. Table 5.8 also shows the zeta potential distributions of PEDOT/PSS dispersions synthesised at various time of reactions. Zeta potential of PP(1:2.5)-C dispersion is included for comparison. Zeta potential was observed to decrease with increasing time of reactions indicating higher amount of PEDOT doped to PSS or bigger PEDOT segment doped to PSS reducing surface charge. The longer time of reaction resulted in attraction more than repulsion between particles in the dispersion resulting in aggregation of particles. We noticed that commercial PEDOT/PSS, PP(1:2.5)-C, is a stable dispersion (-57 mV) indicating that smaller PEDOT is doped to PSS or less of PEDOT doped to PSS consistent with the CE results (see Figure 5.1 A).

Table 5.8 Average* particle size distributions by volume (Dv) and zeta-potentials of PEDOT/PSS aqueous dispersions synthesised at different time of reactions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-1</td>
<td>160 ± 15</td>
<td>9 ± 2</td>
<td>-</td>
<td>-53</td>
</tr>
<tr>
<td>PP(1:2.5)-3</td>
<td>113 ± 5</td>
<td>7 ± 2</td>
<td>-</td>
<td>-50</td>
</tr>
<tr>
<td>PP(1:2.5)-6</td>
<td>193 ± 18</td>
<td>46 ± 8</td>
<td>-</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:2.5)-12</td>
<td>250 ± 55</td>
<td>55 ± 2</td>
<td>30 ± 4</td>
<td>-45</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>247 ± 67</td>
<td>60 ± 16</td>
<td>28 ± 2</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:2.5)-36</td>
<td>386 ± 17</td>
<td>65 ± 4</td>
<td>-</td>
<td>-45</td>
</tr>
<tr>
<td>PP(1:2.5)-48</td>
<td>386 ± 32</td>
<td>-</td>
<td>-</td>
<td>-43</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>223 ± 4</td>
<td>22 ± 1</td>
<td>-</td>
<td>-57</td>
</tr>
</tbody>
</table>

*From three measurements.
**Values taken from 3rd measurement after dispersion has settled and equilibrated.

PEDOT/PSS dispersions synthesised at various time of reactions were also analysed by CE using sodium borate buffer 20 mM pH 9.2 as background electrolyte. The CE electropherograms of PEDOT/PSS (1:2.5) aqueous dispersions synthesised at 1 hr to 48 hrs are shown in Figure 5.17. The CE electropherograms show that PP(1:2.5)-1 (A) has the highest intensity of PSS peak (~14 min) while PP(1:2.5)-48 (G) has the lowest intensity of PSS peak. Quantification of doping using CE shows an increase of doping from (A) to (D) up to 89% and levelled off through to (G). This indicates that the
amount of free PSS decreased with time of reactions due to more PSS doped to PEDOT. Conversely, the intensity of the PEDOT/PSS complexes increased from 1 hr to 48 hrs indicating an increase the amount of PEDOT doped to PSS with increase in reaction time.

The CE electropherograms in Figure 5.17 also show the migration times of PEDOT/PSS complexes to decrease from A to G, indicating decrease in electrophoretic mobility due to decrease of the negative charge in the complex brought about by the increasing growth of PEDOT doped to PSS. In addition, the peaks of PEDOT/PSS complexes appeared as spikes for longer time of reactions, PP(1:2.5)-12 (D) to PP(1:2.5)-48 (G), attributed to the effect of light scattering brought about by the aggregation of the PEDOT/PSS particles or bigger PEDOT segments doped to PSS as discussed in Chapter 4. The complexes from the shorter reactions, PP(1-2.5)-1 to PP(1:2.5)-6 (A to C), were of smaller size with less aggregation and thus appeared as broad peaks, whereas PP(1-2.5)-12 to PP(1:2.5)-48 (D to G) form bigger aggregates and induced light scattering and manifested as spikes. These CE results are consistent with the zeta potentials of dispersions showing shorter time of reactions (A to C) to give higher zeta potentials due
to less or smaller PEDOT doped to PSS resulting in more stable dispersions and less aggregation. Longer time of reactions (D to G) correlated to less free PSS due to higher doping PEDOT and smaller zeta potentials.

The photodiode array detector in the CE instrument also allows analysis of the UV characteristic of PEDOT/PSS samples which set up at 230 nm. For example, the UV spectra from the CE instrument of PEDOT/PSS dispersions (1:2.5 ratios) prepared in various reaction times detected at 230 nm can be shown in Figure 5.18 (A). A spectral maximum of 230 nm was observed in all cases. The increase in absorbance at 240-280 nm observed in PP(1:2.5)-12, PP(1:2.5)-24, PP(1:2.5)-36, and PP(1:2.5)-48, however, could be attributed to an increase in the amount of doping PEDOT to PSS.

![Figure 5.18 UV spectra of PEDOT/PSS dispersions from (A) CE and (B) UV spectrometer.](image)

Analysis of PEDOT/PSS films by UV spectrometer also have been recorded on thin films (50-70 nm thick) obtained on quartz substrates and can be seen in Figure 5.18 (B). All the spectra exhibit peaks absorbance at ~225-230 nm due to PSS. In all spectra, the PSS absorbance at ~225-230 nm varies in intensity due to the thickness of the films. In addition, the films recorded a decrease in absorbance intensity at ~225-230 nm with increasing time of reaction, and followed with an increase absorbance at 240-280 nm. Increasing absorbance at 240-280 nm could be attributed to an increase in the amount of PEDOT particles doped to PSS and this is evident in the films.
Surface morphology images of representative PEDOT/PSS films generated from PEDOT/PSS aqueous dispersions synthesised at various times of reaction can be seen in Figure 5.19. The images show an increase in roughness of the surfaces from PP(1:2.5)-1 film (A) to PP(1:2.5)-48 film (F) indicating an increase of PEDOT particles which are doped to PSS along with an increase of reaction times.[96] Increasing time of reactions was also observed to decrease the processability of the PEDOT/PSS aqueous dispersions.

**Figure 5.19** Surface morphology images of (A) PP(1:2.5)-1, (B) PP(1:2.5)-6, (C) PP(1:2.5)-12, (D) PP(1:2.5)-24, (E) PP(1:2.5)-36, and (F) PP(1:2.5)-48. Images were taken in 40x magnification using microscope optic “Axioskop 40 Pol” from ZEISS.
Conductivity measurements of PEDOT/PSS films generated from PEDOT/PSS dispersions in ratio 1:2.5 by weight synthesised at various time of reactions were observed to be one to three order of magnitude higher than the commercial PEDOT/PSS (PP(1:2.5)-C) film (Table 5.9). Conductivity of the films tends to increase significantly with increasing time of reaction. The conductivity of PP(1:2.5)-1 film could not be measured, even with film thickness of 850 nm, as the four point probe readings were inconsistent. From CE (Figure 5.17 A), PP(1:2.5)-1 film contains minimal PEDOT/PSS complex after 1 hr reaction, and the dispersion still contained high amount of free PSS. The fact that PP(1:2.5)-1 mostly contain free PSS is also demonstrated by the transparent dispersion in Figure 5.16 (A). Increasing the reaction time to 3 hrs resulted in a PP(1:2.5)-3 film which was more conductive and stable than PP(1:2.5)-1 film, but conductivity measurement was still unstable suggesting that the amount of PSS-doped PEDOT in the dispersion is still very small and the dispersion is predominantly free PSS. Conductivity of the films increased in PP(1:2.5)-6 film (9.8 $10^{-3}$ S/cm), in which similar conductivity value was obtained from the commercial PEDOT/PSS, PP(1:2.5)-C film (9.6 $10^{-3}$ S/cm).

Table 5.9 Conductivity and thickness of films generated from PEDOT/PSS (ratio 1:2.5) dispersions synthesised at different time of reactions. The commercial (PP(1:2.5)-C) dispersion is included for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-1</td>
<td>-</td>
<td>62 ± 10</td>
</tr>
<tr>
<td>PP(1:2.5)-3</td>
<td>-</td>
<td>251 ± 13</td>
</tr>
<tr>
<td>PP(1:2.5)-6</td>
<td>$9.8 \pm 0.9 \times 10^{-3}$</td>
<td>268 ± 27</td>
</tr>
<tr>
<td>PP(1:2.5)-12</td>
<td>$5.2 \pm 0.7 \times 10^{0}$</td>
<td>150 ± 24</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>$2.1 \pm 0.5 \times 10^{0}$</td>
<td>251 ± 13</td>
</tr>
<tr>
<td>PP(1:2.5)-36</td>
<td>$1.4 \pm 0.2 \times 10^{0}$</td>
<td>212 ± 27</td>
</tr>
<tr>
<td>PP(1:2.5)-48</td>
<td>$9.0 \pm 3.0 \times 10^{-1}$</td>
<td>263 ± 53</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>$9.6 \pm 0.11 \times 10^{-3}$</td>
<td>61 ± 5</td>
</tr>
</tbody>
</table>

Optimum conductivity was obtained from the film obtained after 12 hrs reaction time (PP(1:2.5)-12) attributed to the right balance between the amount of PEDOT/PSS complex and free PSS in the dispersion with doping efficiency of 89%. Conductivity of
PP(1:2.5)-12 film reach up 5.2 S/cm or ~545 times higher than that obtained from PP(1:2.5)-C film. The PP(1:2.5)-12 dispersion shown in Figure 5.16 (D) is black attributed to the high amount of PEDOT, and the CE electropherogram shown in Figure 5.17 (D) indicated highly doped PEDOT/PSS and availability of free PSS in the dispersion.

While doping efficiency has been estimated as 75% for PP(1:2.5)-6 based on the amount of free PSS (25%), most of the PSS would only be bound to short and less PEDOT chains as demonstrated by the CE results (Figure 5.17) showing higher electrophoretic mobility for the PEDOT/PSS complex which still carried a highly negative charge. Thus, while the resulting film is easily processable, the conductivity is still low. The longer time of reaction to 24 hrs, 36 hrs and 48 hrs resulted in bigger PEDOT particles doped to PSS (indicated by spikes in electropherograms), but decreased the conductivity of the films due to the decrease in the processability of the dispersions due to a decrease in free PSS. The films are rougher and not uniform (see Figure 5.19 D, E, F).

Thermal stability of these PEDOT/PSS composites (i.e. dried dispersions) from different time of reactions was determined from TGA experiments. The curves only show slight differences between PSS and PEDOT/PSS composites synthesised at short time of reactions. The longer time of reactions resulted in a change in the decomposition profile of the composites compared to PSS and showed faster decomposition of the composites. This indicates the presence of more PEDOT, and most likely doped to PSS, in the dispersions and that PEDOT decomposed earlier than PSS (see Figure 5.20). All curves indicate loss of water of around 5-10% when heated up to 150°C. PP(1:2.5)-24 and PP(1:2.5)-48 composites, expected to contain higher amounts of PEDOT, were the least stable composites and started to decompose at ~370°C followed by PP(1:2.5)-6 then PP(1:2.5)-1 decomposed at ~390°C and ~400°C, respectively, whereas PSS started to decompose at ~410°C. The TGA of the commercial PP(1:2.5)-C composite show the total mass loss up to 50% (see Figure 5.4). These results indicate that all the synthesised PEDOT/PSS composites are more stable than the commercial PP(1:2.5)-C composite.
Overall, increasing the time of reaction of in-situ synthesis of PEDOT/PSS aqueous dispersions resulted in more highly doped PEDOT/PSS complexes and reduced availability of free PSS (un-doped). Increasing time of reaction resulted in more conductive PEDOT/PSS films, reaching an optimum at 12 hrs reaction (for ratio of 1:2.5 of EDOT:PSS) due to the right balance between the amount and the size of the PEDOT/PSS complex and free PSS in the dispersion. CE electropherograms indicated the growth of PEDOT particles doped to PSS with time of reactions, which are consistent with the UV analysis. The optimal conductivity of PEDOT/PSS films was obtained at an optimal 80-90% of doping. Higher zeta potentials were obtained for PEDOT/PSS dispersions with high content of free PSS due to shorter reaction time. Triplicate measurements of the particles size of dispersions show the tendency of particles to increase its aggregation with longer reaction times. Thermal stability of PEDOT/PSS composites was observed to decompose earlier due to an increase in the amount of PEDOT particles attached to PSS in their composite forms. All PEDOT/PSS composites show higher thermal stability than that observed in PP(1:2.5)-C composite.

Figure 5.20 TGA curves of PSS, PP(1:2.5)-1, PP(1:2.5)-6, PP(1:2.5)-24, and PP(1:2.5)-48 composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N₂ atmosphere.
5.5. Conclusion

Processable PEDOT/PSS aqueous dispersions were successfully synthesised via oxidative polymerisation of EDOT monomer both in the presence of PSS solution, and post-polymerisation addition of PSS solution. Processability of PEDOT/PSS dispersions and conductivity of resulting films are affected by the amount of PEDOT doped to PSS and availability of free PSS in the dispersions. PEDOT/PSS aqueous dispersions synthesised in the presence of PSS performed better in terms of conductivity and processability compared to the dispersions prepared by post-polymerisation addition of PSS solution. Conductivity of PEDOT/PSS films synthesised via oxidative polymerisation is one to three order magnitudes higher than the commercial PEDOT/PSS (Clevios) film. Optimum conductivity was exhibited by PP(1:2.5)-12 film which is attributed to the right balance between the amount of PEDOT/PSS complex and free PSS in the dispersion with doping efficiency estimated to be 89%. All PEDOT/PSS composites synthesised via oxidative polymerisation have higher thermal stability than the commercial PEDOT/PSS.
Chapter 5 – Optimisation of the Processability of PEDOT/PSS Dispersions and Conductivity of Films
CHAPTER 6 - END-CAPPING OF PEDOT WITH THIOPHENE-BASED MONOMERS
6.1. Introduction

End-capping of conducting polymers is a possible method for the direct control of the molecular weight, and possibly conductivity of these polymers. This method involves the copolymerisation of the conductive monomer units with small amounts of end-capping monomer. By end-capping, the site for further growth of polymerisation is blocked by pendant functionality. The size of polymer can be controlled directly by varying the ratio of monomer and capping unit.[43] The polymerisation is a function of controlling time of reaction[136] or controlling the feed ratio of the initiator to monomers[137,138].

So far, there are only a few examples of research that have been conducted to modify the end-structure of PEDOT by end-capping with other monomers. For example, TDA Research, Inc. has synthesised end-capped PEDOT oligomers by oxidative copolymerisation of end-capping monomers and EDOT monomers using Fe(III) p-TSA as the oxidation agent in acetonitrile solvent. The statistical average oligomer length was set theoretically by the stoichiometry of EDOT and end-capping monomers. The conducting segments provide the electronic properties, while the non-conducting end-segments are designed to promote dispersion. These end-capped PEDOT oligomers are commercially called Aedotron\textsuperscript{TM} and Oligotron\textsuperscript{TM}. These PEDOT oligomers can theoretically be printed using a lithographic technique by crosslinking the oligomers at the methacrylate groups, or formulating them as an organic solution into inks form for inkjet printing.[139]

The effort to investigate PEDOT/PSS by modification of the structure in order to enhance the properties, such as the conductivity and solubility, attracts many researchers. Various modifications of PEDOT/PSS for more applications have been done to enhance conductivities and their potential use as electrodes.[46] This chapter reports the modification of PEDOT by adjusting the chain length and investigates its effect on the conductivity of the resulting films. The general route of end-capping PEDOT with thiophene-based monomers via oxidative polymerisation can be seen in Figure 6.1. The end-capping thiophene-based monomers used in this project are 2-thiopheneacetonitrile (2TA), 2-thiophenemethanol (2TM) and 2-thienylmethyl methacrylate (2TMM). It is anticipated that the endcapping monomer added in the
polymerisation mixture will compete with the EDOT monomers and stop further polymerisation by end-capping PEDOT.

![Figure 6.1 General route of end-capping PEDOT with thiophene-based monomers via oxidative polymerisation.]

### 6.2. Endcapping with 2-thiophene acetonitrile

Endcapping of PEDOT was attempted using 2TA following Louwet’s method by adding various concentrations of 2TA with EDOT and PSS. This endcapping agent was primarily chosen because of the presence of the nitrile (-CN) group which could easily be identified by FTIR as the band due to -C≡N bond stretching is prominently displayed as a sharp peak at at 2256 cm⁻¹ without overlapping with the other peaks. Spectroscopic analyses (FTIR and NMR) did not show any evidence of the presence of 2TA in the resulting PEDOT/PSS dispersions which indicates that endcapping to control the chain length of PEDOT was not successful. The most likely explanation for this is that 2TA contains a cyano group, -CN, one of the strongly deactivating groups.[140] This functional group can withdraw and decrease the electron density from the thiophene ring and deactivate it during polymerisation.

### 6.3. PEDOT/PSS aqueous dispersions endcapped with 2-thiophene methanol

#### 6.3.1. Synthesis and Characterisation using FTIR and NMR spectroscopy

As with the attempted synthesis of PEDOT endcapped with 2TA, PEDOT end-capped with 2-thiophene methanol (2TM) was synthesised via oxidative polymerisation in the presence of PSS (referred to as PP-TM), i.e. via Louwet’s method, using EDOT:PSS ratio 1:2.5 by weight.
In this study, the concentration of 2TM was varied from 10 – 50% by weight with respect to the EDOT monomer. The presence of excess PSS in the PP-TM dispersions made it difficult to use IR and NMR spectroscopic techniques to characterise the endcapped PEDOT. Thus, it was found necessary to synthesise processable TM-endcapped PEDOT without PSS (from hereon referred to as PnoP-TM) made possible by conducting the reaction in dichloromethane solvent.

PnoP-TM composite was characterised using FTIR and the spectra are depicted in Figure 6.2. Peaks attributed to EDOT have been identified. The IR band at 890 cm\(^{-1}\) due to the C-H bending of the H at carbon 2 of EDOT disappeared demonstrating the successful of formation PEDOT chains.[57,141] The peaks at 2938, 1672 and 1385 cm\(^{-1}\) are due to the –CH aliphatic stretching, C=C stretching of the thiophene ring, and –C-H bending vibration of –CH\(_2\), respectively. The vibrations at 1256 and 1189 cm\(^{-1}\) are possibly due to the stretching mode of ethylenedioxy group or C-O-C bond stretch. Peaks at 841 and 711 cm\(^{-1}\) are assigned to –CH bending and thiophene C-S bond stretching.[32,142,143] Evidence of successful endcapping of PEDOT by 2TM is the broad peak at 3450 cm\(^{-1}\) attributed to –OH stretching[144] in 2TM which has also been observed in PnoP-TM.

![Figure 6.2 FTIR Spectrum of PnoP-TM and the starting monomers: EDOT and 2TM.](image-url)
Both PP-TM and PnP-TM were subjected to NMR experiments. The $^1$H, $^{13}$C DEPTQ (distorsionless enhancement by polarization transfer including the detection of the quaternary nuclei), and HSQC (heteronuclear single quantum coherence) NMR spectra of PP-TM in D$_2$O can be seen in Figure 6.3 with peak assignments corresponding to the given labelled structures. These peak assignments have been compared and deduced from the peaks observed for the monomers summarised in Table 6.1. Figure 6.3 (A) shows the $^1$H NMR spectrum of PP-TM50-24 run in D$_2$O solvent and showed predominantly the peaks of PSS. The peaks at 7.4 - 7.7 ppm (5) and 6.4 - 6.7 ppm (4) correspond to the phenyl -CH in PSS. The peaks at 1.3 – 1.7 ppm (1 and 2) correspond to –CH$_2$- and –CH- of PSS, respectively. The peaks attributed to the formation of PEDOT-TM can be identified from the peaks at 2.8 ppm (e) and 3.6 ppm (7) due to –CH$_2$ of 2TM and –OCH$_2$- of PEDOT, respectively.

Table 6.1 $^1$H and $^{13}$C NMR peak assignments for EDOT and 2TM monomers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C</th>
<th>Code*</th>
<th>H shift (ppm)</th>
<th>C shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDOT</td>
<td>-CH$_2$-</td>
<td>7</td>
<td>4.1</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>-C$_q$-</td>
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<td>141</td>
</tr>
<tr>
<td></td>
<td>-CH-</td>
<td>9</td>
<td>6.4</td>
<td>99</td>
</tr>
<tr>
<td>2TM</td>
<td>-CH</td>
<td>a</td>
<td>7.2</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>-CH</td>
<td>b</td>
<td>6.9</td>
<td>127</td>
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<td></td>
<td>-CH</td>
<td>c</td>
<td>6.9</td>
<td>125</td>
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<td></td>
<td>-C$_q$-</td>
<td>d</td>
<td>-</td>
<td>144</td>
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<tr>
<td></td>
<td>-CH$_2$-</td>
<td>e</td>
<td>4.7</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>-OH</td>
<td>j</td>
<td>4.6</td>
<td>-</td>
</tr>
</tbody>
</table>

*Refer to Figure 6.3.

The DEPTQ $^{13}$CNMR spectrum in Figure 6.3 (B) confirms the carbon assignments in the PP-TM structure. This $^{13}$C DEPTQ-135 spectrum shows the peaks at 40 ppm (2), 125 ppm (5) and 128 ppm (4) corresponding to -CH vinyl and –CH phenyl in PSS, respectively, whilst =CH$_2$ and the quaternary phenyl carbons (–C$_q$) peaks are evident at 42 ppm (1), 140 ppm (6), and 149 ppm (3), respectively. The peaks corresponding to PEDOT and TM end groups have not been visible as they overlap and are lost within the more prominent PSS peaks. However, two peaks can be assigned as –CH$_2$- of 2TM unit appearing at 47 ppm (7) and –OCH$_2$- of PEDOT at 63 ppm (e), respectively. The
HSQC spectrum of PP-TM50-24 confirmed the peak assignments in the $^1$H and $^{13}$C NMR spectra of PP-TM (see Figure 6.3 C). This spectrum supports the $^1$H and $^{13}$C peak assignments for the –CH$_2$– (peak e) of TM unit and –OCH$_2$– (peak 7) of PEDOT.

![Diagram of molecular structures](image)

**Figure 6.3** NMR spectra of PP-TM50-24 in D$_2$O solution: (A) $^1$H NMR, (B) $^{13}$C DEPTQ, and (C) HSQC.
NMR experiments were also run with PnP-TM to investigate the peaks due to PEDOT and TM without PSS. The $^1$H NMR of PnP-TM in Figure 6.4 (A) clearly shows some peaks corresponding to $-\text{CH}_2\text{O}$- of PEDOT at 4.2 ppm (7), and $-\text{CH}$ of the thiophene ring from PEDOT oligomers at around 6.6 ppm (9). Peaks attributed to the $\text{CH}$- of the thiophene ring of 2TM can be seen clearly at 7.5 ppm (a) and 6.8 ppm (b). The $^{13}$C DEPTQ NMR spectrum of PnP-TM50 in Figure 6.4 (B) shows peaks that can be attributed to the end-capping 2TM monomer. The upward peaks at 62 ppm (e) and 67 ppm (7) correspond to the $\text{CH}_2\text{O}$ of end-capping unit (2TM) and $-\text{CH}_2\text{O}$ of PEDOT, respectively. The other downward peaks at 100 ppm (9) and 125-130 ppm (b, c) are due to the $-\text{CH}$- of the thiophene ring of PEDOT and 2TM, respectively.

![Figure 6.4 NMR spectra of PnP-TM50 in DMSO solution: (A) $^1$H NMR; and (B) $^{13}$C DEPTQ.](image)

**Figure 6.4** NMR spectra of PnP-TM50 in DMSO solution: (A) $^1$H NMR; and (B) $^{13}$C DEPTQ.
6.3.2. Capillary electrophoresis of PP-TM dispersions

CE electropherograms show that all PP-TM dispersions have similar PSS peak intensities at ~14 min but they vary in the appearance and migration time of the complexes (between 8-10 min) (see Figure 6.5). The doping efficiency was estimated to be 72.9% for PP-TM50-24 (A), and 68.3% for PP-TM20-24 (B). The electropherogram of PP-TM50-24 (A) shows a broad peak of the complex at 9-10 min, while PP-TM20-24 (B) forms spikes of the complex at slightly lower migration time indicating higher negative charge of (A) than (B). The spikes from PP-TM20-24 (B) can be attributed to the light scattering of bigger particle size of aggregates (read as absorbance), while in PP-TM50-24 (A) has smaller size of aggregate particles. Both PEDOT-TM/PSS complexes have higher electrophoretic mobility or faster migration time (9-10 min) than the PEDOT/PSS complex from PP(1:2.5)-24 (C) dispersion (8-9 min), indicating that the complexes from PP-TM dispersions have more negative charge most possibly due to less doped PSS sites.

The presence of 2TM in the polymerisation system presumably resulted in smaller chains of PEDOT due to the end-capping process based on the amount of 2TM. The higher ratio of 2TM, 50% in (A) resulted in smaller PEDOT-TM segment doped to PSS, and the complex showed as a broad peak in the electropherogram. Decreasing the ratio of 2TMM to 20% in (B) resulted in bigger PEDOT-TM segment doped to PSS, and the complex showed as spikes in the electropherogram. These PEDOT-TM particles doped to PSS are smaller in size than the PEDOT doped to PSS resulting from the reaction without end-capping which also showed as spikes in the electropherogram and slower migration time (C). In the absence of information on PEDOT chain lengths, CE has been used to analyse the effect of end-capping unit to the PEDOT particle size (and hence chain length) by comparing electrophoretic mobilities. The CE electropherograms show that smaller amount of end-capping agent resulted in bigger PSS-doped PEDOT chain decreasing the negative charge of PSS. Hence, the PEDOT/PSS complexes have shorter migration time or lower electrophoretic mobility than the sample prepared without endcapping agent.
6.3.3. Particle size distributions and zeta-potential of PP-TM aqueous dispersions

DLS analysis of PP-TM aqueous dispersions show a trend similar to other PEDOT/PSS samples previously analysed. The DLS results show that majority of particles were in aggregate forms. Increasing concentration of 2TM as in PP-TM50-24 dispersion gave smaller primary particles and aggregates compared to PP-TM20-24 which, most likely, can be attributed to the formation of smaller PEDOT-TM segments in the presence of a higher concentration of 2TM. The bigger cluster particle size in PP-TM20-24 than in PP-TM50-24 is presumably responsible for the appearance of spikes in the CE electropherogram rather than a broad peak from PP-TM50-24 shown in Figure 6.5.
Table 6.2 Average* particle size distributions by volume ($D_v$) and zeta-potentials of PP-TM20-24 and PP-TM50-24 aqueous dispersions compared to PP(1:2.5)-24 and PP(1:2.5)-C dispersions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-TM20-24</td>
<td>561 ± 8</td>
<td>87 ± 11</td>
<td>-</td>
<td>-51</td>
</tr>
<tr>
<td>PP-TM50-24</td>
<td>145 ± 26</td>
<td>31 ± 8</td>
<td>-</td>
<td>-49</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>247 ± 67</td>
<td>60 ± 16</td>
<td>28 ± 2</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>223 ± 4</td>
<td>22 ± 1</td>
<td>-</td>
<td>-57</td>
</tr>
</tbody>
</table>

*From 3 measurements
**Values taken from 3rd measurement after dispersion has settled and equilibrated

Zeta potential values of PP-TM dispersions are quite high (-49 mV and -51 mV) compare to that of PP(1:2.5)-24 dispersion (-46 mV), but lower than PP(1:2.5)-C dispersion (-57 mV) (see Table 6.2). These values indicate high stability of the PP-TM dispersions.[83,145,146]

6.3.4. Conductivity of PP-TM films

Table 6.3 shows the conductivity of PP-TM films compared to PP(1:2.5)-24 and PP(1:2.5)-C films. The conductivity of PP-TM films are higher by one to two order magnitude than that obtained from PP(1:2.5)-C film, but lower than that obtained from PP(1:2.5)-24 film. The conductivity of PP-TM films was observed to decrease with increasing concentration of 2TM. The higher concentration of 2TM produced smaller PEDOT chains (i.e. more efficient endcapping), decreasing the conductivity of the films.

Table 6.3 Conductivity and thickness of PP-TM films in various ratios of end-capping agent and at different time of reactions. Conductivity PP(1:2.5)-24 and PP(1:2.5)-C films are included for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-TM10-24</td>
<td>2.4 ± 1.0 $10^1$</td>
<td>133 ± 6</td>
</tr>
<tr>
<td>PP-TM20-24</td>
<td>1.5 ± 0.4 $10^1$</td>
<td>91 ± 2</td>
</tr>
<tr>
<td>PP-TM30-24</td>
<td>7.5 ± 2.1 $10^2$</td>
<td>92 ± 3</td>
</tr>
<tr>
<td>PP-TM40-24</td>
<td>6.5 ± 1.8 $10^2$</td>
<td>71 ± 2</td>
</tr>
<tr>
<td>PP-TM50-24</td>
<td>6.1 ± 2.0 $10^2$</td>
<td>91 ± 2</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>2.1 ± 0.5 $10^0$</td>
<td>251 ± 13</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>9.6 ± 0.11 $10^{-3}$</td>
<td>61 ± 5</td>
</tr>
</tbody>
</table>
6.3.5. Surface morphology of PP-TM Films

Figure 6.6 shows the surface morphology images of PP-TM20-24, PP-TM50-24, PP(1:2.5)-24, and PP(1:2.5)-C films taken using an optical microscope at 40x magnification. The images show that PP-TM50-24 film (B) is more uniform and homogeneous than PP-TM20-24 film (A), most possibly due to the formation of bigger particles of PEDOT-TM/PSS complex in PP-TM20-24 than in PP-TM50-24. However, PP(1:2.5)-24 (C) shows a rougher surface than that of PP-TM20-24 film indicating the formation of bigger particles size of PEDOT in the absence of an endcapper in PP(1:2.5)-24. PP(1:2.5)-C (D), on the other hand, shows a smoother and more uniform film attributed to small PEDOT particles in this dispersion. Note that these results are confirmed by the CE and DLS results showing PP-TM20-24 to possess bigger size PEDOT/PSS aggregates than PP-TM50-24.

![Surface morphology images of PP-TM20-24, PP-TM50-24, PP(1:2.5)-24, and PP(1:2.5)-C films](image)

**Figure 6.6** Surface morphology images of (A) PP-TM20-24, and (B) PP-TM50-24, (C) PP(1:2.5)-24, and (D) PP(1:2.5)-C films taken using microscope optic in 40x magnification.
6.3.6. **Thermal stability of PP-TM**

Comparison of the thermal stability of PP-TM composites to the commercial PEDOT/PSS, PP(1:2.5)-C and PP(1:2.5)-24 composites are shown in Figure 6.7. All PP-TM composites lost about ~7% of weight at temperatures up to 150°C due to water evaporation. They were stable until 380°C and started to decompose gradually, and these are about similar to the PP(1:2.5)-24 composite, whereas PP(1:2.5)-C composite started decomposition at 320°C. The TGA curves show that the residual mass at 600°C are ~64%, for PP-TM composites which about similar to PP(1:2.5)-24 composite, whereas PP(1:2.5)-C composite is ~51%. These TGA curves show that PP-TM composites are more thermally stable than PP(1:2.5)-C. Variation in the concentration of 2TM in the PP-TM composites did not have a significant effect to the thermal stability.

![TGA curves of PP-TM20-24, PP-TM50-24, PP(1:2.5)-C and PP(1:2.5)-24 composites.](image)

**Figure 6.7** TGA curves of PP-TM20-24, PP-TM50-24, PP(1:2.5)-C and PP(1:2.5)-24 composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N₂ atmosphere.

6.3.7. **Summary**

In summary, 2TM has successfully end-capped PEDOT via oxidative polymerisation as confirmed by FTIR and NMR spectra. PP-TM aqueous dispersions can generate conductive films one to two order magnitudes higher than the commercial PP(1:2.5)-C film, but lower than the non-endcapped PP(1:2.5)-24 film. Different concentrations of
2TM affected the size of PEDOT-TM doped to PSS. The higher concentration of 2TM resulted in smaller size of PEDOT-TM doped to PSS as demonstrated by DLS and CE and lower film conductivity. Conversely, the lower concentration of 2TM resulted in bigger size of PEDOT-TM doped to PSS and higher film conductivity. Thermal stability of PP-TM composites are comparable to PP(1:2.5)-24 composite, and higher than PP(1:2.5)-C composite.

6.4. PEDOT/PSS aqueous dispersions end-capped with 2-thienylmethyl methacrylate

The aim of endcapping PEDOT with 2TMM is two-fold: (1) to adjust the length of the PEDOT chain and investigate the effect of chain length on the conductivity behaviour of films, (2) to introduce a functional endgroup to the polymer, i.e. vinyl polymerisable group, for subsequent reaction as discussed in Chapter 7.

6.4.1. Synthesis and Characterisation using FTIR and NMR spectroscopy

PEDOT end-capped with 2TMM was synthesised via oxidative polymerisation in the presence of PSS, i.e. via Louwet’s method, using EDOT:PSS ratio 1:2.5 by weight. In this study, we varied the ratio of 2TMM 10 – 50% by weight to EDOT monomer. These dispersions from here on are referred to as PP-TMM, for example PP-TMM10-24 is based on 10% of 2TMM and 24 hr reaction.

As with PP-TM, the presence of excess PSS in the PP-TMM dispersions made it difficult to use IR and NMR spectroscopic techniques to characterise the endcapped PEDOT. In order to confirm successful endcapping with 2TMM by spectroscopic techniques, it was necessary to eliminate interfering PSS, thus, 2TMM-endcapped PEDOT without PSS (from hereon referred to as PnoP-TMM) was synthesised by conducting the reaction in dichloromethane.

Figure 6.8 shows the FTIR spectra of PnoP-TMM, EDOT and 2TMM. The FTIR spectrum of PP-TMM (with PSS) is not presented here as only the peaks attributable to PSS were observed and it did not give information on the presence of PEDOT and 2TMM in the system. Despite the difficulty encountered to get a clear FTIR spectrum of
PnoP-TMM, some peaks still can be identified as representative of the functional groups of PEDOT and end-capped 2TMM. The IR band at 890 cm\(^{-1}\) due to the C-H bending of EDOT dissappeared in PnoP-TMM demonstrating successful formation PEDOT chains with C\(_2\)-C\(_2\)-coupling.[57,141] The band at 1491 and 1366 cm\(^{-1}\) are attributed to the stretching modes of C=C and C-C in the thiophene ring, whereas bands at 1214 and 1098 and cm\(^{-1}\) are due to the stretching mode of ethylenedioxy group or C-O-C bond stretching, respectively.[57,141] The vibration at 1451 cm\(^{-1}\) is attributed to –CH\(_3\) from the end-capping unit, while broad band at 1155 cm\(^{-1}\) is attributed to –C-O-C- ester group stretching vibrations from 2TMM, respectively.[77] Peaks at 830 cm\(^{-1}\) is assigned to -C-S bond stretching in the thiophene ring.[32,142,143] Functional groups from the end-capping agent 2TMM especially C=O and C=C stretching are represented as small broad peaks at 1700-1640 cm\(^{-1}\) in this spectrum. Previous FTIR of PEDOT prepared via oxidative polymerisation also gave broad peaks attributed to reduced transparency to the IR light due to its electronic properties.[39,57,124]

![FTIR spectra of PnoP-TMM, EDOT and 2TMM monomers.](image)

**Figure 6.8** FTIR spectra of PnoP-TMM, EDOT and 2TMM monomers.

Both PP-TMM and PnoP-TMM were also subjected to NMR experiments. The \(^1\)H, \(^{13}\)C DEPTQ, and HSQC NMR spectra of PP-TMM in D\(_2\)O can be seen in Figure 6.9 with peak assignments corresponding to the given labelled structures. These peak assignments have also been compared and deduced from the peaks observed for the monomers summarised in Table 6.4.
The $^1$H NMR spectrum of PP-TMM (Figure 6.9 A) shows clearly the peaks due to the aromatic hydrogens of PSS at 7.4 - 7.7 ppm (peak 5) and 6.5 - 6.7 ppm (peak 4). The peaks at 1.3 – 1.7 ppm (peaks 1 and 2) correspond to the $-\text{CH}_2$- and $-\text{CH}$- backbone peaks of PSS, respectively. While the PSS peaks have been very prominent, other peaks that can be attributed to the thiophene moieties have also been observed. The peak at 3.6 ppm (peak 7) has been assigned to $-\text{CH}_2\text{O}$- of PEDOT while the peaks at 1.3 ppm (peak g), and 4.3 ppm (peak e) have been attributed to the $-\text{CH}_3$, and $-\text{CH}_2$- of the endcapping unit 2TMM, respectively.

Table 6.4 $^1$H and $^{13}$C NMR peak assignments for EDOT and 2TMM[77] monomers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C</th>
<th>Code*</th>
<th>H shift (ppm)</th>
<th>C shift (ppm)</th>
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<tbody>
<tr>
<td>EDOT</td>
<td>-CH$_2$-</td>
<td>7</td>
<td>4.1</td>
<td>64</td>
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<tr>
<td></td>
<td>-C$_q$-</td>
<td>8</td>
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<td>141</td>
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<td></td>
<td>-CH-</td>
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<td>2TMM</td>
<td>-CH</td>
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</table>

*Refer to Figure 6.9.

A distortionless enhancement by polarization transfer including the detection of the quaternary nuclei (DEPTQ-135) $^{13}$C NMR spectrum of PP-TMM is also given in Figure 6.9 (B). One of the advantages of a $^{13}$C DEPTQ-135 is that the spectrum can show quaternary carbons present in 180 degrees out of phase, as with $-\text{CH}_2$-, with respect to $-\text{CH}$- and $-\text{CH}_3$ carbons.[147,148] Thus, the peaks at 40 ppm, 125 ppm and 127 ppm have been assigned to $-\text{CH}$- peaks 2, 5 and 4, respectively, whilst 42 ppm has been assigned to $-\text{CH}_2$ peak 1. The peaks at 140 ppm and 149 ppm can only be quaternary and have been assigned as peaks 6 and 3, respectively. Most peaks corresponding to PEDOT and 2TMM end groups have not been visible as they overlap and are lost within the more prominent PSS peaks. However, peaks observed at 20 ppm and two peaks at
63 and 58 ppm could very well correspond to –CH₃ of 2TMM (g), –CH₂- of 2TMM (e) and –OCH₂- of PEDOT (7), respectively.

The peak assignments in the ¹H and ¹³C NMR spectra of PP-TMM have been confirmed by the Heteronuclear Single Quantum Coherence (HSQC) spectrum shown in Figure 6.9 (C). HSQC is 2-dimensional inverse H and C correlation technique which allows determination of the connectivity of carbon and hydrogen by observing their direct coupling. This spectrum supports the ¹H and ¹³C peak assignments for the –OCH₂- of PEDOT (peak 7), -CH₂- of TMM (peak e), and –CH₃ of 2TMM (peak g).

NMR experiments were also run with PnoP-TMM in order to identify peaks belonging to PEDOT and 2TMM that were obscured by the prominent peaks of PSS and demonstrate the success of the endcapping process. The ¹H NMR spectrum in Figure 6.10 (A) clearly shows the –CH₂O- and -CH of the thiophene ring of PEDOT at 4.2 ppm (peak 7) around 6.5 ppm (peak 9). The peaks at 1.9 ppm (g) and 5.3 ppm (e) are attributed to the –CH₃ and -CH₂- of end-capping unit 2TMM, respectively. Other peaks can also be seen at 5.5 ppm (i) and 6.0 ppm (i’) due to =CH₂ of 2TMM whilst the peaks at 7.0 ppm (c) and 7.5 ppm (b) are attributed to the –CH- of the thiophene ring of 2TMM.
Figure 6.9 NMR spectra of PP-TMM50-24 in D$_2$O solution: (A) $^1$H NMR, (B) $^{13}$C DEPTQ, and (C) HSQC.
The $^{13}$C DEPTQ NMR of PnoP-TMM (Figure 6.10 B) has been used to confirm the $^1$H NMR peak assignments with the --CH- and --CH$_3$ peaks oriented downward (negative peaks) and the --CH$_2$- and quaternary C oriented upward (positive peaks). Whilst the peaks attributed to PEDOT are clearly observed in the spectrum, i.e. 100 ppm (peak 9), 128 ppm (peak 8) and 63 ppm (peak 7), the peaks attributable to the endcapping unit TMM are also visible confirming the success of the endcapping process. These peaks have been assigned as follows: 120-130 ppm (peaks b, c), 62 ppm (peak e) and 19 ppm (peak g) corresponding to the thiophene --CH-, --CH$_2$- and --CH$_3$, respectively.

6.4.2. Capillary electrophoresis of PP-TMM aqueous dispersions
The effect of the concentration of end-capping monomer to the length of PEDOT and their doping to PSS in PP-TMM aqueous dispersions were studied by CE. PP-TMM aqueous dispersions were analyzed using 20 mM borate at pH 9.2 as the background electrolyte. PEDOT-TMM doped to PSS complexes and free PSS (undoped form) in PP-TMM aqueous dispersions were detected between 8 to 10 min, and ~14 min,
respectively (see Figure 6.11). Quantification of doping by CE show that higher ratio of 2TMM has lower doping. PP-TMM50-24 (A) dispersion shows a doping efficiency of 50% which is lower than that of PP-TMM20-24 (B) (74%) indicating that higher doping occurred when using less end-capping unit. The electropherograms also show that longer time of reaction from 24 hr to 48 hr had no significant effect to the doping of PEDOT to PSS. Doping efficiency of PP-TMM20-24 (B), synthesised for 24 hr, is similar to that of PP-TMM20-48 (C), synthesised for 48 h, indicating that the reaction of PEDOT with 2TMM and doping to PSS was already optimal for 24 h and additional time was not necessary. This is consistent with the conductivity results of the corresponding films which didn’t show significant difference between PP-TMM20-24 and PP-TMM20-48.

All PEDOT-TMM/PSS complexes (A to C) shown in Figure 6.11 have longer migration time or higher electrophoretic mobility than the PEDOT/PSS complex synthesised without end-capping unit, PP(1:2.5)-24 (D). The presence of 2TMM in the polymerisation system presumably resulted in smaller chains of PEDOT due to the end-capping process. The higher concentration of end-capping agent (A) resulted in smaller PEDOT-TMM segment doped to PSS, and the complex is manifested as a broad peak in the electropherogram. Decreasing the concentration of 2TMM to 20% (B) resulted in bigger PEDOT-TMM segment doped to PSS, and the complex is shown as spikes in the electropherogram closely similar to PP(1:2.5)-24 (D) although still with higher electrophoretic mobility (i.e. slower migration time). These electropherograms of the dispersions correlated to the conductivity of their corresponding films (see Section 6.2.4), e.g. PP-TMM20-24 (PEDOT/PSS complex as spikes) has higher conductivity than PP-TMM50-24 (PEDOT/PSS complex as broad peak).
Figure 6.11 CE analysis of PP-TMM aqueous dispersions: (A) PP-TMM50-24; (B) PP-TMM20-24; (C) PP-TMM20-48; (D) PP(1:2.5)-24; and (E) PP(1:2.5)-C. BGE: sodium borate buffer 20 mM, pH 9.2.

6.4.3. Particles size distributions and zeta potential of PP-TMM dispersions

PP-TMM aqueous dispersions were analysed using DLS to study the particle size and aggregation of particles. Table 6.5 shows data of particle size distribution from triplicate measurements of representative dispersions synthesised for 24 hr and 48 hr. The results indicate that the particles predominantly exist in aggregate form which tends to become larger with increasing analysis time. Aggregation of the particles may occur as part of the doping state of PEDOT in excess of PSS. In general, the size of cluster aggregates decrease with increasing concentration of 2TMM. These results are consistent with the
CE results showing the PP-TMM/PSS complexes from PP-TMM50-24 and PP-TMM50-48 dispersions appearing as broad peaks while PEDOT-TMM/PSS complexes from PP-TMM20-24 and PP-TMM20-48 dispersions appeared as spikes resulting from the light scattering of bigger particle size of aggregates. (see Figure 6.11).

Table 6.5 Average* particle size distributions by volume ($D_v$) and zeta-potential of PP-TMM aqueous dispersions synthesised at various concentrations of end-capping monomer and different time of reactions compare to PP(1:2.5)-24 and PP(1:2.5)-C dispersions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-TMM20-24</td>
<td>187 ± 52</td>
<td>31 ± 2</td>
<td>-</td>
<td>-45</td>
</tr>
<tr>
<td>PP-TMM20-48</td>
<td>229 ± 61</td>
<td>127</td>
<td>-</td>
<td>-47</td>
</tr>
<tr>
<td>PP-TMM50-24</td>
<td>184 ± 42</td>
<td>73</td>
<td>41</td>
<td>-47</td>
</tr>
<tr>
<td>PP-TMM50-48</td>
<td>190 ± 68</td>
<td>40</td>
<td>27</td>
<td>-47</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>247 ± 67</td>
<td>60 ± 16</td>
<td>28 ± 2</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>223 ± 4</td>
<td>22 ± 1</td>
<td>-</td>
<td>-57</td>
</tr>
</tbody>
</table>

*From 3 measurements

**Values taken from 3rd measurement after dispersion has settled and equilibrated.

Zeta potential distributions of PP-TMM dispersions do not differ significantly, all zeta potential values are >-40 mV indicating the dispersions are stable.[83,145,146] These zeta potential values are comparable to that obtained from the zeta potential of PEDOT without end-capping, PP(1:2.5)-24 dispersion (-46 mV), and lower than that of PP(1:2.5)-C dispersion (-57 mV) showing that the commercial PEDOT/PSS is a more stable dispersion (also showed to contain more PSS by CE). Increasing the time of reaction from 24 to 48 hr also does not have a significant effect to the zeta potential meaning that optimal reaction has been achieved after 24 hours (see Table 6.5) which has also been confirmed by CE, i.e. PEDOT/PSS complexes for 24 and 48 hr reaction have similar migration time (9-10 min).
6.4.4. Thermal stability of PP-TMM composites

The thermal stability of PP-TMM composites was analysed by TGA using an aluminium pan with the maximum temperature of 600°C. Figure 6.12 shows the TGA profiles of PP-TMM composites synthesised using 20% by weight of 2TMM (PP-TMM20-24 and PP-TMM20-48) and 50% of 2TMM (PP-TMM50-24 and PP-TMM50-48) compared to the commercial sample, PP-(1:2.5)-C and a sample synthesised without end-capping, PP(1:2.5)-24.

![TGA curves of PP-TMM composites](image)

**Figure 6.12** TGA curves of PP-TMM20-24, PP-TMM50-24, PP-TMM20-48, and PP-TMM50-48 composites compare to PP(1:2.5)-C and PP(1:2.5)-24 composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N₂ atmosphere.

All PP-TMM composites lost about 7% weight at temperature up to 150°C due to water content. They were stable until the temperature reach 370°C and started to decompose gradually similar to PP(1:2.5)-24 composite, whereas PP(1:2.5)-C composite started decomposition at 320°C. The TGA curves show that the residual mass at 600°C are ~63% for PP-TMM composites, which about similar to that obtained from PP(1:2.5)-24 composite, whereas for the commercial composite is ~51%. Variation time of reaction and concentration of 2TMM in PP-TMM composites do not show significant difference to their thermal stabilities.
6.4.5. Conductivity of PP-TMM films

The aim of varying the concentration of 2TMM is to investigate the effect of the chain length of PEDOT, controlled by the end-capping group, on conductivity. Conductivity and thickness of PP-TMM films are listed in Table 6.6. The thickness of the PP-TMM films tested is between 80-120 nm and their conductivity is between 0.077–0.18 S/cm, 12-26 times lower than PP(1:2.5)-24 film (2.1 S/cm), which was generated from the PEDOT/PSS synthesised for 24 hr without end-capping unit, but one to two orders in magnitude higher than PP(1:2.5)-C film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-TMM10-24</td>
<td>1.5 ± 0.6 10^-1</td>
<td>89 ± 18</td>
</tr>
<tr>
<td>PP-TMM10-48</td>
<td>1.7 ± 0.4 10^-1</td>
<td>120 ± 19</td>
</tr>
<tr>
<td>PP-TMM20-24</td>
<td>1.5 ± 0.5 10^-1</td>
<td>86 ± 14</td>
</tr>
<tr>
<td>PP-TMM20-48</td>
<td>1.8 ± 0.3 10^-1</td>
<td>97 ± 8</td>
</tr>
<tr>
<td>PP-TMM30-24</td>
<td>1.4 ± 0.5 10^-1</td>
<td>79 ± 10</td>
</tr>
<tr>
<td>PP-TMM30-48</td>
<td>1.3 ± 0.4 10^-1</td>
<td>85 ± 14</td>
</tr>
<tr>
<td>PP-TMM40-24</td>
<td>1.4 ± 0.3 10^-1</td>
<td>95 ± 10</td>
</tr>
<tr>
<td>PP-TMM40-48</td>
<td>1.0 ± 0.2 10^-1</td>
<td>85 ± 15</td>
</tr>
<tr>
<td>PP-TMM50-24</td>
<td>0.8 ± 0.1 10^-1</td>
<td>83 ± 16</td>
</tr>
<tr>
<td>PP-TMM50-48</td>
<td>1.0 ± 0.2 10^-1</td>
<td>85 ± 15</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>2.1 ± 0.5 10^0</td>
<td>251 ± 13</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>9.6 ± 0.110^-3</td>
<td>61 ± 5</td>
</tr>
</tbody>
</table>

The average conductivity of PP-TMM films has been found to decrease with increasing concentration of 2TMM and suggests that longer PEDOT chains are necessary to obtain optimal conductivity. This is also supported by the fact that the conductivity of PP(1:2.5)-24 is 12-26 times higher than the PP-TMM films. Variation of reaction times from 24 hr to 48 hr using similar concentration of 2TMM did not affect the conductivity
of the films. Quantification of doping efficiency using CE showed increasing doping from 50.1% in PP-TMM50-24 film to 74.2% in PP-TMM50-48 film, and to 89.2% in PP(1:2.5)-24 film.

6.4.6. Surface morphology of films

Figure 6.13 shows the representative surface morphology images of PP-TMM films generated from PP-TMM dispersions synthesised for 24 hr containing 20% 2TMM, PP-TMM20-24 film (A), synthesised for 48 hr containing 20% 2TMM, PP-TMM20-48 film (B), and 50% 2-TMM, PP-TMM50-48 film (C), respectively.

![Figure 6.13 SEM images of surface morphology of (A) PP-TMM20-24 film; (B) PP-TMM20-48 film; (C) PP-TMM50-48 film, (D) PP(1:2.5)-24 film, and (E), PP(1:2.5)-C film. Images were taken at magnification 12000x. Observed white patches are encircled.](image)

The different amount of doping in PP-TMM dispersions did not significantly affect the processability of the dispersions, unlike the conductivity of the films. These SEM images show the surface morphology of PP-TMM films to be similar to the film without end-capping, PP(1:2.5)-24 (D), and rougher than that obtained from PP(1:2.5)-C film (E). The surface roughness of the films generated from PP-TMM dispersions using different concentration of 2TMM at 12000 times magnification also appear to be similar. The morphology images exhibit some white patches on the surface as can be
seen in the commercial and other films. These patches are presumably due to aggregation of PSS,[45] which occurred during drying of PP-TMM films.

6.4.7. UV spectra of PP-TMM films

UV spectra of representative PP-TMM films (80-100 nm thick) have been recorded on quartz substrates and are shown in Figure 6.14. All spectra exhibit absorbance peaks at ~230 nm due to the phenyl group of PSS which decreased markedly in the presence of PEDOT[24,60,125,126,133]. This decrease can be largely attributed to the formation of PEDOT/PSS complexes manifested by an increase of absorbance at 240-280 nm (see inset of Figure 6.14) from PSS to PP(1:2.5)-C to PP-TMM films, and to the PP(1:2.5)-24 film. These results suggest that higher doping of PEDOT to PSS occurred in PP(1:2.5)-24 than PP-TMM and PP(1:2.5)-C, and show comparable doping of PEDOT to PSS in PP-TMM50-24 and PP-TMM20-24. Previous studies have reported that presence of oligomeric PEDOT in the films increased the appearance of the peak at 260 nm which corresponds to =C-H of EDOT.[60]

![Figure 6.14 UV spectra of PSS, PP(1:2.5)-C and PP-TMM films (80-100 nm thick).](image)

6.4.8. Summary

Overall, 2TMM has been successful in end-capping PEDOT via oxidative polymerisation as evident from spectroscopic analyses (UV, FTIR and NMR) and capillary electrophoresis. PP-TMM aqueous dispersions can generate conductive films
one to two order magnitudes higher than the commercial dispersion PP(1:2.5)-C, but lower than that obtained from PEDOT/PSS synthesised without end-capping, PP(1:2.5)-24. The concentration of 2TMM used for the reaction affected the size of PEDOT particles. The higher ratio of 2TMM resulted in smaller size aggregation of PP-TMM as demonstrated by DLS and CE, and decreased their film conductivities. The zeta potentials of PP-TMM dispersions are lower than the commercial PEDOT/PSS indicating lower stability of the dispersion, but they are comparable to PEDOT/PSS dispersion without end-capping. Thermal stability of PP-TMM composites are comparable to PEDOT/PSS dispersion without end-capping, and higher than PP(1:2.5)-C composite.

6.5. Conclusion
Overall, 2TMM and 2TM are successful in end-capping PEDOT via oxidative polymerisation as confirmed by spectroscopic analyses (FTIR and NMR) and capillary electrophoresis. End-capped PEDOT/PSS dispersions can generate conductive films one to two order of magnitudes lower than PP(1:2.5)-24 film but still higher by one to two order of magnitude than the commercial PP(1:2.5)-C film. Higher concentrations of endcapping agents 2TMM and 2TM formed smaller size PEDOT particles doped to PSS as confirmed by DLS and CE resulting in more uniform surface morphology but lower conductivity. Conversely, lower concentrations of endcapping agents 2TMM and 2TM formed bigger size PEDOT particles doped to PSS as confirmed by DLS and CE resulting in rougher surface morphology but higher conductivity. All PP-TMM and PP-TM dispersions formed stable dispersions with zeta potentials lower than the commercial PP(1:2.5)-C dispersion but comparable to the non-endcapped sample PP(1:2.5)-24. All endcapped PEDOT/PSS composites have thermal stability comparable to the non-endcapped PP(1:2.5)-24 composite and higher than the commercially-sourced PP(1:2.5)-C composite.
CHAPTER 7 - SYNTHESIS AND CHARACTERISATION OF CROSSLINKED CORE STAR POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/ POLYSTYRENE SULFONATE
7.1. Introduction

Successful modification of the end-structure of PEDOT by end-capping has been discussed in Chapter 6. This chapter reports our effort to utilise 2TMM, EDOT and 2TMM endcapped PEDOT for the synthesis of crosslinked core star conductive polymers (CCS-CP) (see Figure 7.1). The motivation for this study is the potential for the core of the CCS-CP to be molecularly imprinted. Molecularly imprinted polymers (MIP) contain recognitive sites for a target analyte that can be created by using the target as a template during polymerisation and can be used as a selective sensing material for organic field effect transistor (OFET) devices. Although this study does not extend to the creation of MIPs, the preliminary work presented in this Chapter demonstrates the synthetic feasibility of a MIP-CP via both the arm-first and core-first methods using 2TMM, containing both thiophene and double bond functionality, as a linking agent.

In general, the synthesis of a CCS polymer by the arm-first method starts with the polymerisation of the monomers to produce a macromonomer (the arm) followed by adding the cross-linker to form the core.[149,150,151,152] For the synthesis of the CCS-PEDOT used in this study, the polymerisable PEDOT arm was prepared by oxidative polymerisation[19] in the presence of endcapping agent 2TMM with a polymerisable double bond, and subsequently reacted by conventional free radical polymerisation with a crosslinker (EGDMA) to provide the core. Synthesis of the reactive polymer arm and subsequent addition of a crosslinker results in a star polymer, whereas one-pot copolymerisation of monomer and crosslinker together results in branched polymers or gels.[153] While controlled radical polymerisation (CRP), e.g. RAFT, ATRP, is the preferred method for the preparation of well-defined star polymers, conventional free radical polymerisation has also been used to prepare star polymers, referred to as ‘star-like’ (as they are less defined than those prepared from CRP) polymers by some authors, which we consider appropriate for the purpose of this study. Ho, et al[154] have developed core cross-linked star (CCS) polymers, in one-pot using conventional free radical polymerisation resulting in ‘star-like polymers” using a less reactive methylacrylate (MA) and a more reactive crosslinker (EGDMA). This star like polymers could not be produced in a very concentrated solution due to a threshold monomeric concentration which prevented large amount of monomers reacting in the
system due to macrogelation. Ishizu and Sunahara reported the synthesis of star-like polymers by copolymerisation of polyisoprene macromonomers and divinylbenzene (DVB) in n-heptane, and the star yield was \(<40\%\).[156] Gao and Matyjazewski reported the synthesis of star polymers in high yield (95\%) by conventional radical polymerisation of poly(ethylene oxide) macromonomer and DVB. [157]

The schematic diagram for the preparation of CCS-PEDOT via the arm-first method can be seen in Figure 7.1 (A). In contrast, the core-first method is started by homopolymerising the crosslinker before the growth of arms. The core is synthesised separately from the polymeric arm in the presence of an initiating site or functional group where the polymer arm can grow (2TMM in this work) to generate a star molecule. The schematic diagram to synthesise star PEDOT via core first method can be seen in Figure 7.1 (B). The core-first method allows for the preparation of star with a precise number of arms if one can control the number of initiating sites. This method also provides very high yields and the star polymer product can be easier to purify from the monomer. However, the molecular weight of the arms cannot be calculated directly.

![Figure 7.1 Schematic diagram for the preparation of crosslinked core star PEDOT: (A) via arm-first method and (B) via core-first method.](image-url)
7.2. Synthesis of crosslinked core star PEDOT/PSS via the arm-first method

In Chapter 6, we succeeded in endcapping PEDOT with 2TMM in the presence (PP-TMM) and absence (PnoP-TMM) of PSS. The presence of the polymerisable vinylic (C=C) endfunctional group in PEDOT is essential for the synthesis of the crosslinked EGDMA core attached to the PEDOT arm (Figure 7.1a). Because PnoP-TMM is not soluble in most solvents, CCS PEDOT was generated in aqueous dispersion using the PP-TMM arm starting with 50% 2TMM by weight with respect to the EDOT monomer. The product of this method was a dark blue dispersion and referred to here as Sa50PP(1:2.5)-24.

Figure 7.2 shows the FTIR spectra of Sa50PP(1:2.5)-24, EDOT and TMM. The majority of the peaks in the FTIR spectrum of Sa50PP(1:2.5)-24 is attributable to PSS although some peaks due to PEDOT, e.g. 1522 and 1337 cm\(^{-1}\) attributed to the stretching modes of C=C and C-C in the thiophene ring, are also evident. The prominent functional group of EGDMA, i.e. C=O, was not evident at 1700 cm\(^{-1}\) suggesting that the EGDMA core was not attached to the PEDOT arm.

![Figure 7.2 FTIR spectra of (A) EDOT, (B) PSS and (C) Sa50PP(1:2.5)-24.](image-url)
Figure 7.3 shows the electropherograms of Sa50PP(1:2.5)-24 (A) and PP-TMM50-24 (B). The shapes and migration times of the PEDOT/PSS complex from Sa50PP(1:2.5)-24 appear similar to that from PP-TMM50-24 (PEDOT arm) which suggests that they could be of the same length and composition and that the crosslinked core was not successfully attached to Sa50PP(1:2.5)-24. Their particle sizes (Table 7.1) are also comparable which again suggests that the nature of the two dispersions is not dissimilar. Further, both Sa50PP(1:2.5)-24 and PP-TMM50-24 generated smooth films (Figure 7.4) and Sa50PP(1:2.5)-24 didn’t show any feature that suggests the presence of crosslinked core particles (e.g. Figure 7.12).

**Figure 7.3** CE electropherograms of (A) Sa50PP(1:2.5)-24 and (B), PP-TMM50-24 dispersions. BGE: sodium borate buffer 20 mM, pH 9.2, 15 kV potential applied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa50PP(1:2.5)-24</td>
<td>194 ± 51</td>
<td>77 ± 17</td>
<td>-</td>
<td>-47</td>
</tr>
<tr>
<td>PP-TMM50-24</td>
<td>184 ± 42</td>
<td>73</td>
<td>41</td>
<td>-47</td>
</tr>
</tbody>
</table>

*From 3 measurements
**Values taken from 3rd measurement after dispersion has settled and equilibrated.
Chapter 7 – Synthesis and Characterisation of CCS PEDOT/PSS

Figure 7.4 Morphology images of (A) Sa50PP(1:2.5)-24, and (B) PP-TMM50-24 films. Images were taken in 40x magnification using microscope optic “Axioskop 40 Pol” from ZEISS.

Comprehensive characterisation of the product from the CCS synthesis via arm first method in the presence of PSS could not confirm the presence of the crosslinked EGDMA core. It is very possible that the CCS PEDOT was not successfully formed and could be due to a number of reasons which warrant further investigation, including the presence of oxygen due to inefficient purging with nitrogen gas and, most likely, steric hindrance due to the presence of PSS.

7.3. Synthesis of crosslinked core star PEDOT/PSS via core-first method

7.3.1. Preparation of the PEGDMA-co-TMM core

Highly cross-linked cores containing functional thiophene sites were generated by copolymerisation of divinyl cross-linker ethylene glycol dimethacrylate (EGDMA) and 2TMM using azobisisobutyronitrile (AIBN) as the initiator (see Figure 7.1). The PEGDMA-co-TMM core was synthesised at a ratio of 100:10:1 by weight of cross-linker EGDMA to 2TMM to initiator AIBN.

Successful synthesis of the PEGDMA-co-TMM core was proven using FTIR spectrophotometry shown in Figure 7.5. The FTIR spectrum of the core shows the appearance of the peaks at 2930 cm$^{-1}$ attributed to stretching of aliphatic –C-H. Stretching of C=O and and C-O from EGDMA and, possibly, 2TMM was observed at 1710 cm$^{-1}$ and 1137 cm$^{-1}$, respectively. The peak at 1630 cm$^{-1}$ represents the pendant -
C=C- from EGDMA. The appearance of a peak at 1449 cm\(^{-1}\) is attributed to the C-C stretching from EGDMA and 2TMM. Appearance of 2TMM in the core can be identified specifically from the stretching of C-S from the thiophene ring that can be observed at 1008 cm\(^{-1}\), 821 and 695 cm\(^{-1}\), respectively.[158]

![FTIR spectra](image)

**Figure 7.5** FTIR spectra of core PEGDMA-co-TMM compared to EGDMA and 2TMM monomers.

### 7.3.2. Preparation of CCS PEDOT (with no PSS)

The synthesis of CCS PEDOT in the absence of PSS via core-first method (ScPEDOT) was carried out using Na\(_2\)S\(_2\)O\(_8\) and Fe\(_2\)(SO\(_4\))\(_3\) as the oxidation agents at 45\(^\circ\)C in methanol for seven days. The reaction in organic solvent was slower than in water, most likely because the solubility of the oxidation agents in water is better than in organic solvent. Indication of the progress of reaction was observed from the change in the colour of solution (to blue green), indicating the formation of PEDOT, during polymerisation for seven days as shown in Figure 7.6. The raw product was purified by centrifuge and removal of the precipitate (i.e. unreacted core) by filtration. The light green solution in methanol (i.e. CCS PEDOT) was then dialysed (MWCO Off 3500) in methanol to remove the unreacted EDOT monomer and continued in water to remove the oxidation agents. The dried product was light green powder (17% yield), and soluble in organic solvents such as methanol and chloroform.
Chapter 7 – Synthesis and Characterisation of CCS PEDOT/PSS

Figure 7.6 Progress of synthesis of CCS PEDOT via core first method in methanol after 1, 2, 3, 5, and 7 days of reaction, respectively.

The FTIR spectrum of the light green ScPEDOT sample (see Figure 7.7) closely resembles that of the core PEGDMA-co-TMM indicating successful attachment of the core to PEDOT. Although peaks due to PEDOT are not evident in the spectrum, the change in colour of the solution from colourless to blue green is a strong indication of its formation.

Figure 7.7 The FTIR spectra of ScPEDOT, PEGDMA-co-TMM core and EDOT monomer.

The $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of ScPEDOT shows the formation of CCS PEDOT (see Figure 7.8 A). These peak assignments have been compared and deduced from the peaks observed for the monomers summarised in Table 7.2. The vinylic protons at 5.8 and 6.2 ppm (c) are attributed to the pendant double bonds of the EGDMA core. The vinylic protons from 2TMM were not expected as they should have disappeared due to reaction to form the core. The methyl group from EGDMA (a) and
TMM (o) could be seen as a strong peak at 1.8 ppm whereas protons of –OCH₂- from EGDMA (e) and EDOT (h) can be seen as overlapping peak at 4 ppm.

¹³C NMR spectrum of ScPEDOT can be seen in Figure 7.8 B. The presence of PEDOT is evident from the peaks at 65 ppm, 97 ppm and 138 ppm attributed to –OCH₂- (h), thiophene carbon (f) and (g), respectively. The peaks at 40 ppm, 65 ppm (overlapping with h) and 118 ppm have been assigned to –CH₃ (a), -OCH₂- (e), and =CH₂ (c) of crosslinker EGDMA, respectively. Peaks at 39 ppm and 128-130 ppm have been assigned to –CH₂ (m) and –CH- of the thiophene ring (j and k) of 2TMM, respectively.

Figure 7.8 NMR spectra of ScPEDOT in CDCl₃ solution: (A) ¹H NMR, and (B) ¹³C NMR. Assignment of peaks can be compared to the chemical shifts of the monomers given in Table 7.2.
Table 7.2 $^1$H and $^{13}$C NMR peak assignments for EDOT, 2TMM and EGDMA monomers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C</th>
<th>Code*</th>
<th>H shift (ppm)</th>
<th>C shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDOT</td>
<td>-CH$_2$-</td>
<td>h</td>
<td>4.1</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>-C$_q$-</td>
<td>g</td>
<td>-</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>-CH-</td>
<td>f</td>
<td>6.4</td>
<td>99</td>
</tr>
<tr>
<td>2TMM</td>
<td>-CH</td>
<td>i</td>
<td>7.3</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>-CH</td>
<td>j</td>
<td>7.2</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>-CH</td>
<td>k</td>
<td>6.9</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>-C$_q$-</td>
<td>l</td>
<td>-</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>-CH$_2$-</td>
<td>m</td>
<td>5.3</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>-C=O</td>
<td>n</td>
<td>-</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>-CH$_3$</td>
<td>o</td>
<td>1.9</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>-C$_q$-</td>
<td>p</td>
<td>-</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>=CH$_2$</td>
<td>q</td>
<td>5.6, 6.2</td>
<td>125</td>
</tr>
<tr>
<td>EGDMA</td>
<td>-CH$_3$</td>
<td>a</td>
<td>1.9</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>-C$_q$</td>
<td>b</td>
<td>-</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>=CH$_2$</td>
<td>c</td>
<td>5.6-6.2</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>=CO</td>
<td>d</td>
<td>-</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>-OCH$_2$-</td>
<td>e</td>
<td>4.4</td>
<td>67</td>
</tr>
</tbody>
</table>

*Refer to Figure 7.8.

The SEM images of the PEGDMA core and ScPEDOT can be seen in Figure 7.9. These images show both core and CCS PEDOT to be spherical particles characteristic of crosslinked core particles indicating successful formation of CCS PEDOT. The star polymers are also shown to be bigger (250-350 nm) than the core (150-200 nm) at the same magnification suggesting a change in the nature of the core upon star formation most likely due to the PEDOT arm.

![Figure 7.9 SEM images of (A) core PEGDMA-TMM and (B) ScPEDOT. Images were taken at 24000x magnification.](image-url)
ScPEDOT was doped with PSS 6 times its entire mass (EGDMA core + PEDOT arms) hence, the PEDOT/PSS ratio in the dispersion must be higher than 1:6 by weight. Nevertheless, the product is referred to here as ScPP(1:6-p)-24 aqueous dispersion. Conductivity of the ScPP(1:6-p)-24 film (90-100 nm thickness) is $3.49 \times 10^{-2}$ S/cm, which is lower than the linear PP(1:6)-24 (7.90 $10^{-2}$ S/cm) but comparable to the conductivity of films generated from PEDOT/PSS dispersions doped post-polymerisation (see Sections 5.3.2 and 5.3.3 in Chapter 5).

CE electropherograms of ScPP(1:6-p)-24 aqueous dispersion using background electrolyte 20 mM borate buffer at pH 9.2 is shown in Figure 7.10. The electropherogram shows high intensity of PSS peak at ~14 min attributed to the high amount of free PSS (un-doped) in the dispersion. The spikes appearing between 5 and 13 min (just before PSS) could be attributed to the CCS PEDOT/PSS complex. The very broad range of electrophoretic mobility of the complex is most likely due to the attachment of a random number of arms around the core and random doping to PSS resulting in complexes of variable negative charges.

![Figure 7.10 CE Electropherogram of ScPP(1:6-p)-24 dispersion. BGE: sodium borate buffer 20 mM, pH 9.2, 15 kV potential applied.](image)

### 7.3.3. Preparation of CCS PEDOT/ PSS

CCS PEDOT via core-first method was also prepared in the presence of varying ratios of PSS and using 5% and 10% core by weight with respect to the EDOT monomer and referred to herein as ScxPP(1:y)-24 where x is the core weight and y is the ratio of PSS with respect to EDOT. The resulting black solutions were centrifuged to remove the unreacted core and solid impurities and dialysed (MWCO 3500) with methanol and
water to remove unreacted monomers and the rest of the oxidizing agents. The FTIR and NMR spectra for these star polymers were not obtained because the presence of PSS obscured characteristic peaks from PEDOT and EGDMA rendering the results inconclusive.

Strong evidence for the successful attachment of the TMM-functionalised core to PEDOT/PSS is the morphology of the films shown by the optical images in Figure 7.11. The films obtained from dispersions with different PSS content Sc10PP(1:1)-24, Sc10PP(1:3)-24, and Sc10PP(1:5)-24 show particulate features which can only be due to the presence of the spherical core (see Figure 7.9). The surface features of these films are also significantly different from the optical images of films generated from linear PEDOT/PSS showing smoother surfaces. Increasing the ratio of PSS from 1:1 to 1:5 resulted in more processable dispersions and generated more uniform and smoother films, however, the particulate surface feature is still visible (Figure 7.11C).

![Figure 7.11 Morphology images of star PEDOT/PSS films synthesised for 24 hrs from different ratios of PSS: (A) Sc10PP(1:1)-24, (B) Sc10PP(1:3)-24, and (C) Sc10PP(1:5)-24. Images were taken using microscope “Axioskop 40 Pol” from ZEISS at 40x magnification.](image)

The conductivity of the films can be seen in Table 7.3. As observed from linear PEDOT/PSS systems, the conductivities of the star films were observed to decrease with increasing PSS content although they are still one to two order of magnitude higher than that of the commercial film, PP(1:2.5)-C and slightly lower than the films from the synthesised linear PEDOT/PSS films with the same PSS content. The correlation of conductivity and core content as seen in Sc5PP(1:2.5)-24 and Sc10PP(1:2.5)-24, i.e. doubled with doubling of core content, cannot be confirmed at this stage as the core content of the two star PEDOT/PSS were not determined.
Table 7.3 Conductivity and thickness of star PEDOT/PSS films via core first method compare to the conductivity of PP(1:2.5)-24 and PP(1:2.5)-C films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc5PP(1:2.5)-24</td>
<td>3.3 ± 0.9 10^-1</td>
<td>62 ± 10</td>
</tr>
<tr>
<td>Sc10PP(1:2.5)-24</td>
<td>6.1 ± 1.1 10^-1</td>
<td>60 ± 11</td>
</tr>
<tr>
<td>Sc10PP(1:3)-24</td>
<td>3.1 ± 1.1 10^-1</td>
<td>95 ± 13</td>
</tr>
<tr>
<td>Sc10PP(1:5)-24</td>
<td>2.3 ± 0.7 10^-1</td>
<td>60 ± 11</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>2.1 ± 0.5 10^0</td>
<td>67 ± 9</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>9.6 ± 0.110^-3</td>
<td>61 ± 5</td>
</tr>
</tbody>
</table>

UV analysis of CCS PEDOT/PSS films prepared from different PSS ratios have also been recorded on thin films obtained on quartz substrates and can be seen in Figure 7.12. All UV spectra of representative CCS PEDOT/PSS films show peaks at ~225-230 nm due to PSS [60], and peaks attributable to PEDOT/PSS complex (240-280 nm). The trend of these spectra is similar to those exhibited by linear PEDOT/PSS films prepared from the dispersions in different ratios of PSS (see Figure 5.8). The intensity of the free PSS peak at ~225-230 nm was observed to increase with increasing PSS content while the intensity of the peak due to PEDOT/PSS complexes at 240-280 nm increased with decreasing PSS content. Reducing the PSS content in the films results in an increase in doping of star PEDOT to PSS, and increasing the PSS content resulted in lower doping and more un-doped (free) PSS. These results are consistent with the conductivity of their films which show low conductivity of Sc10PP(1:5)-24 film due to lower amount of PEDOT doped to PSS and higher conductivity of Sc10PP(1:3)-24 film due to higher amounts of star PEDOT doped to PSS.
Representative CE electropherograms of the CCS PEDOT/PSS dispersions in 20 mM borate buffer pH 9.2 are shown in Figure 7.13. The varying ratios of PSS in the CCS dispersions were also observed to clearly affect their electrophoretic mobilities showing a similar trend as observed with linear PEDOT/PSS (see Figure 5.8). The migration time of the CCS PEDOT/PSS complexes in the dispersions increased from Sc10PP(1:1)-24 (A), through to Sc10PP(1:5)-24 (C) indicating a decrease with electrophoretic mobility from (A), through to (C). The amount of star PEDOT doped per unit PSS decreased in higher amounts of PSS resulting in higher negative charge of the complexes and decreased electrophoretic mobility. The higher intensity peak of PSS (from A to C) and the lower amount of star PEDOT doped to PSS are presumably responsible for the increase in the processability of the dispersions and decrease in conductivity of the CCS PEDOT/PSS films (from B to C).
CCS PEDOT/PSS aqueous dispersions were analysed using DLS to study the distribution of particle size. Table 7.4 shows a comparison of the average particle size distribution of various CCS PEDOT/PSS showing the particles mostly in aggregate forms. Increasing PSS ratio tends to increase the aggregation of particles. Lower amounts of PSS resulted in more doping of PEDOT to PSS and resulted in less aggregation of particles, while higher amounts of PSS resulted in less doping PSS but an increase in the size of aggregation. As with conductivity, the correlation of particle size and core content, as seen in Sc5PP(1:2.5)-24 and Sc10PP(1:2.5)-24, i.e. lower core content, bigger size, cannot be confirmed at this stage as the core content of the two star PEDOT/PSS were not determined.
Table 7.4 Average* particle size distributions by volume (Dv) and zeta-potential of CCS PEDOT/PSS at various ratios of PSS compared to PP(1:2.5)-24, and PP(1:2.5)-C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1, nm</th>
<th>Peak 2, nm</th>
<th>Peak 3, nm</th>
<th>Zeta potential** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc5PP(1:2.5)-24</td>
<td>213 ± 53</td>
<td>-</td>
<td>-</td>
<td>-38</td>
</tr>
<tr>
<td>Sc10PP(1:1)-24</td>
<td>180 ± 33</td>
<td>552</td>
<td>-</td>
<td>-45</td>
</tr>
<tr>
<td>Sc10PP(1:2.5)-24</td>
<td>191 ± 29</td>
<td>-</td>
<td>-</td>
<td>-45</td>
</tr>
<tr>
<td>Sc10PP(1:3)-24</td>
<td>263 ± 36</td>
<td>-</td>
<td>-</td>
<td>-46</td>
</tr>
<tr>
<td>Sc10PP(1:5)-24</td>
<td>273 ± 62</td>
<td>-</td>
<td>-</td>
<td>-48</td>
</tr>
<tr>
<td>PP(1:2.5)-24</td>
<td>247 ± 67</td>
<td>60 ± 16</td>
<td>28 ± 2</td>
<td>-46</td>
</tr>
<tr>
<td>PP(1:2.5)-C</td>
<td>223 ± 4</td>
<td>22 ± 1</td>
<td>-</td>
<td>-57</td>
</tr>
</tbody>
</table>

*From 3 measurements.

**Values taken from 3rd measurement after dispersion have equilibrated.

Table 7.4 also shows the zeta potentials measured for the CCS PEDOT/PSS dispersions synthesised using various PSS ratios. The zeta potentials show a trend of increasing value with increasing ratio of PSS in dispersions. Increasing amounts of PSS in the dispersions correlates to higher content of free PSS or less amount of doped PEDOT per unit PSS and increase zeta potential. These zeta potentials also indicated the high stability of Sc10PP(1:5)-24 dispersion and low stability of Sc5PP(1:2.5)-24 dispersion.

Thermal stability of CCS PEDOT/PSS composites was determined from TGA experiments (see Figure 7.14). All curves indicate loss of water around 5-10% by heating up to 150°C. In general, CCS PEDOT/PSS are less stable than PP(1:2.5)-24 but more stable than the commercial sample PP(1:2.5)-C, with no distinct trend observed.
Figure 7.14 TGA curves of star PEDOT/PSS compare to PP(1:2.5)-24, PP(1:2.5)-C composites. Samples were placed in aluminium pan at the maximum temperature of 600°C under N₂ atmosphere.

7.4. Conclusion

Overall, the synthesis of CCS PEDOT/PSS was not successful via the arm first method, and successful via the core first method. The products are confirmed by FTIR and NMR spectra. CCS PEDOT has been successfully synthesised via the core first method in the absence and the presence of PSS. ScPEDOT is a light green solid which is soluble in organic solvent and, by post polymerisation addition of PSS, can generate conductive film one order of magnitude lower than the equivalent linear PEDOT/PSS (1:6) doped in-situ. The lower conductivity of ScPP(1:6-p)-24 resulted from lower doping as confirmed by CE. CCS PEDOT/PSS via the core first method can generate conductive films one to two order of magnitude higher than the commercial PP(1:2.5)-C. This is expected because of the higher doping of the CCS PEDOT with PSS than the PP(1:2.5)-C aqueous dispersion as indicated by CE. The particle size of CCS PEDOT doped with PSS tends to increase with an increasing ratio PSS which also resulted in an increase in the stability of dispersion as shown by the zeta potential values. Thermal stabilities of star PEDOT/PSS composites are comparable to PP(1:2.5-24) and more stable than the PP(1:2.5)-C composite.
CHAPTER 8 - PEDOT/PSS IN ORGANIC PHOTOVOLTAIC AND FIELD EFFECT TRANSISTOR DEVICES
8.1. Organic photovoltaic device

In general, organic photovoltaic cell or organic solar cells have some advantages compared to conventional (inorganic) solar cells. They have the potential to be flexible and transparent films, and can be manufactured using printing processes as well as produced in large area. In addition, organic materials are also easier to apply in various devices, and also important is the substantial economic advantage due to low cost and environmental advantages.\[159,160\] The efficiency of the solar cell defines the competition between the use of inorganic and organic solar cells. High efficiency and long life times can be achieved by inorganic solar cells compare to organic solar cells, but they also are more expensive. Current organic solar cells are not expensive to fabricate, but they have lower efficiency and lifetime. Therefore, achievement of high efficiency and lifetimes are needed in the research of organic solar cell.

The mechanism in organic solar cells has a few different characteristics to inorganic solar cells. Some differences while operating these devices are based on the energy level, dissociation energy, charge carrier mobility, and coefficient light absorptions.\[161\] Nevertheless, the efficiency of the conventional solar cell, such as silicon photovoltaic cell, can reach 20%, whereas the organic solar cell based on the concept bulk hetero junction can operate at 3.0-3.5% efficiency\[162\], Liang could reach 7.4\%\[163\], and the latest result reported an efficiency of 12\%\[164\].

The work on solar cell research and device development has focussed especially on the bulk hetero junction layer, and more investigation to optimise interface between phases of the device is needed. The ideal polymers in bulk hetero junction solar cell should provide a broad absorption and high coefficient across the solar spectrum. They also need high hole mobility, energy level matching fullerene and must be compatible to form a bicontinuous network on the nano scale. These considerations have a large contribution to determining better performance of OPV devices. The active layer in the bulk hetero junction concept consists of two materials as a donor and an acceptor electron. The donor and acceptor electron materials in the active layer represent an ideal bicontinuous composite, which will optimise the all-important interfacial area between the donors and acceptors.\[165\] One material is a conducting polymer that acts as the hole transport, or p-type material, and another material should act to accept and
transport electron (e.g. fullerenes), and is known as n-type material. Both different materials in the active layer of the device are used to improve the optical density. Positive and negative charges are generated simultaneously in this layer. The four fundamental steps in the mechanism: light absorption and exciton generation, exciton diffusion, exciton diffusion and charge transfer, and charge transport and charge collection are represented in Figure 8.1.

Figure 8.1 Schematic diagram of the four steps of the general mechanism for photo energy conversion in solar cells.[165]
Chapter 8 – PEDOT/PSS in Organic Photovoltaic and Field Effect Transistor Devices

The OPV device consists of at least four layers on the top of the substrate. The basic schematic of an organic photovoltaic device is shown in Figure 8.2. At the top of the substrate is indium tin oxide (ITO), which is a popular cathodic material due to its transparency. ITO precoated onto a glass substrate is also commercially available. The conductive polymer layer, which is generally a mix of PEDOT/PSS, can be placed between the cathode and the active layer. Two common materials used in the active layer, among others, are poly(3-hexylthiophene) or P3HT as the donor electron, and (6,6)-phenyl-C$_{61}$-butyric-acid methyl ester or PCBM as the acceptor electron. These materials are popular as model systems in bulk hetero junction for the organic solar cell.[160] The chemical structure of P3HT and PCBM can be seen in Figure 8.3. The last layer is the anode, typically made of aluminium, calcium, silver, or gold, and it is deposited on the top of active layer.

*Figure 8.2* Schematic device structure of an organic photovoltaic cell.

*Figure 8.3* The chemical structures of (A) P3HT, and (B) PCBM.
8.2. Characterising organic photovoltaic device

In characterising a typical bulk heterojunction solar cell, a graph for dark and light current ($I$) versus voltage ($V$), known as current-voltage ($I$-$V$) curves, which define the primary quantities need to validate the performance of a solar cell device, is usually used.[165] The current-voltage curve passes through the origin, when there is no current passing through the device, and no potential is detected. But when the device absorbs light, the curve will shift downward indicating current passing through the device (see Figure 8.4). Some terminologies are used to define organic solar cells. The main parameters measured from the $I$-$V$ curve are the short circuit current density ($J_{sc}$), or sometimes short circuit current ($I_{sc}$) is issued, and open circuit voltage ($V_{oc}$), which can be used to calculate the fill factor ($FF$) and power conversion efficiency (PCE) of the device. Short-circuit current density ($J_{sc}$) is the maximum current produced by the illuminated device area when there is no external load. Open-circuit voltage ($V_{oc}$) is the maximum possible voltage across the device when no current is flowing. $J_{max}$ and $V_{max}$ are the current and voltage at the maximum power point. Fill-factor ($FF$) is the ratio of the maximum power output of the device, and it is a key quantity in measuring solar cell performance. The efficiency ($\eta$) or PCE is calculated by the ratio of the output electrical power (power out, $P_{out}$) to the incident optical power (power in, $P_{in}$). PCE measures the amount of power produced in the device relative to the available power from radiation, and is generally standardized as 100 W/cm$^2$ in solar simulator.[162]

Other terminologies in characterising solar cell efficiency are air mass (AM), and quantum efficiency ($QE$). Air mass defines the quantity of sunlight irradiated at the surface of the earth. A typical value for solar cell measurement is AM 1.5 illumination, which means the sun is at an angle of about 48°. $QE$ is an efficiency of energy or wavelength irradiation in the device. $QE$ can be divided as an external quantum efficiency ($EQE$), the ratio of the number collected carriers to the number of incoming photons, and internal quantum efficiency ($IQE$), the ratio of the number collected carriers to the number of photons absorbed.[161,162]
Energy conversion or power conversion efficiencies ($\eta$) of the OPV device are based on a number of variables: the light absorption of the electron donor-acceptor materials, the transport of excitons from both materials to the donor-acceptor interface, the efficiency of the exciton separation breaking up into electron-hole pairs at the interface, transport of holes across the donating layer to the anode, and transport of electrons across the acceptor layer to the cathode. In addition, it also depends on the quality of contact between the donor layer and the anode, and between the acceptor layer and the cathode.[166]

**8.3. Organic field effect transistor devices**

The use of organic thin films has increased significantly not only for OPV devices, but also in the application of thin film transistors in organic field effect transistors (OFETs). OFETs have attracted attention in many applications such as tags for radio frequency-identification (RFID)[167,168], matrix displays and sensors[65,169,170], and various applications to replace the conventional SiO$_2$ gate dielectric[171,172]. OFET devices have a number of advantages such as low cost fabrication, large-area, flexible, light weight, and lower temperature processing[72,173,174], which mirror those in OPV devices.
A field-effect transistor (FET) is constructed from four components: an electrically conducting material, an insulating material, a semiconducting material, and a substrate.[71] The term organic is due to the use of organic materials as part of components to fabricate the device. There are two main types of architecture of OFETs, based on the source and drain either manufactured before or after depositing the semiconductor, the top-contact and the bottom contact.[72] The transistor architecture used in this study is all using a top-gate bottom-contact. A schematic diagram of the top-gate bottom-contact architecture for the OFETs set up is shown in Figure 8.5. The advantages for using this architecture are that source and drain electrodes (ITO) that have been pre-patterned on glass substrate to achieve a consistent source-drain electrode separation of 20 μm channel are commercially available, have been proven to work well and easy to fabricate other components on top of it.

![Figure 8.5](image-url) A schematic diagram of top-gate bottom-contact architecture of OFET with the relevant current and voltage labelled.

OFETs have been applied for characterizing the charge transport properties or the charge carrier mobility in organic semiconductors. Figure 8.5 shows a diagram of an OFET device with its voltage and currents labelled: gate current \(I_G\), drain current \(I_D\), drain-source voltage \(V_{DS}\), gate-source voltage \(V_{GS}\), and source current \(I_S\). The application of a top-gate configuration OFET device can modulate the current into two terminals, the drain \(I_D\) and the gate \(I_G\). An electric field is produced across the dielectric layer by applying voltage \(V_{GS}\), and the density of charge carriers between source and drain is manipulated in the semiconductor.
Previous studies have reported the use of poly(3-hexylthiophene) (P3HT)/poly(vinylphenol) (PVP) and PEDOT/PSS as the components for semiconducting layer, dielectric layer and the gate electrode, respectively.[175,176,177] P3HT is chosen for the semiconductor layer, because it is one of the popular, well defined polymers for solution processable organic transistors, and has high carrier mobility.[178,179,180] P3HT is an example of a polymer which is soluble in organic solvent and can be deposited onto the pre-patterned substrate as the active area of the device after drying the solution. Conventional inorganic transistors commonly use silicon dioxide as the insulator dielectric layer.[181] Recently, Dastoor, et al have used poly(vinylpyridine) (PVPy) as dielectric layer to replace PVP, and the result showed that PVPy was more effective to block current contributions due to diffusion of protons from the PEDOT/PSS gate and/or doping of P3HT.[182] Due to this reason PVPy is chosen in the fabrication of the OFET devices in this study.

![Figure 8.6](image)

**Figure 8.6** Structure of the molecules (A) poly(vinylphenol), and (B) poly(vinylpyridine)

### 8.4. Characterising organic field effect transistor devices

There are some parameters used to measure and compare the performance of OFETs. Analysing the output characteristic is an effective way to check the transistor performance. The output characteristic is an I-V curve plot of $I_D$ as a function of $V_{DS}$ for a series of $V_{GS}$ values. The device can be considered as a transistor if the characteristic curve shows clearly defined linear and saturation regions as well as $I_D$ modulation with increase in $V_{GS}$. Figure 8.7 shows an output characteristic curve of an OFET device where from drain-source voltage ($V_{DS}$) = 0 V to about -0.5 V, drain current ($I_D$) changes approximately linear with $V_{DS}$ (linear region), and for $V_{DS}$ beyond -0.5 V affects only small change in $I_D$ for changes in $V_{DS}$ (saturation region).
Another parameter used to characterise OFETs is transfer characteristic. The transfer characteristic is a plot of $I_D$ as a function of $V_{GS}$ for a given value of $V_{DS}$. Data is collected using similar method to the data on output characteristic using a LabVIEW program controlling the two Keithley SourceMeters. $I_D$ is recorded as $V_{GS}$ is swept over a range of values in a fixed value of $V_{DS}$. $V_{GS}$ usually sweep both “forwards” and “backwards. Analysing the transfer characteristic is the simplest way for determination of current modulation ratio of the transistor and the $V_{GS}$ value for which able to start turning on the devices.

### 8.5. The role of PEDOT/PSS in OPV and OFET devices

PEDOT/PSS is known as a promising candidate as a future transparent electrode material. It is also commercially the most successful conducting polymer in the application of solar cells, transistors, and other devices. However, commercially PEDOT/PSS has a conductivity below 1 S/cm,[2] and treatments such as adding co-solvents have to be done to enhance the performance of devices.[45,183] The conductive PEDOT/PSS layer in OPV device has a number of functions: it serves as a hole transport layer and it can block the exciton produced in the active layer. This polymer blend also smoothen out the cathode surface, seals it from oxygen and keeps it from diffusing into the active layer.[162] In addition, PEDOT/PSS also can be used as the gate for operating transistors due to its conductivity, robustness and processability.
However, the PEDOT/PSS blend is hygroscopic and found to be highly acidic and a rich source of protons, and the use of PVPy as the dielectric layer in our OFET devices is maintained to minimize this effect.[182]

This chapter will investigate the application of processable in-house synthesised PEDOT/PSS aqueous dispersions as an interfacial conductive polymer layer in P3HT/PCBM based OPV devices and as the gate in P3HT/PVPy based OFET device. The conductivity of our in-house synthesised PEDOT/PSS films measured by the four point probe method is two to three orders in magnitude higher than that obtained from commercially available sources, as already described on the previous chapters. This chapter focuses on the fabrication of OPV and OFET devices, and characterization using current-voltage (I-V) curve methods as the output of OPV and OFET the devices. The performance of the in-house synthesised PEDOT/PSS dispersions, which have higher conductivities, are compared to the commercial PEDOT/PSS dispersion (Clevios P) as the active layer for OPV devices and as the gate for OFET devices.

8.6. OPV device performance fabricated using in-house PEDOT/PSS dispersions

PEDOT/PSS films as a conductive polymer layer in the solar cell device are placed between the cathode and the active layer. The comparison of the properties between synthesised and commercially-sourced PEDOT/PSS aqueous dispersions has already been discussed in the previous chapter (Chapter 5). In terms of processability, all synthesised PEDOT/PSS samples have good film morphology and are homogeneous and uniform. They have different charge mobilities which are related to their conductivity. The more conductive film exhibits slower electrophoretic mobility due to higher doping of PEDOT with PSS in their complexes.[94] Increasing the amount of PSS in the dispersion makes the PEDOT/PSS dispersion more processable, but typically lower conductivity.

The more conductive synthesised PEDOT/PSS films were applied to OPV device fabrication. Table 8.1 shows a summary of the device performance after characterisation. Reading the PCE of all devices, all samples with the exception of
PP(1:2.5)-12, have PCE within the experimental error of the PCE commercial PEDOT/PSS. The tendency of increasing conductivity is not consistent with the increasing of the $J_{sc}$, as well as of the PCE. Increasing the ratio of PSS for samples PP(1:2.5)-12, PP(1:3)-24 to PP(1:5)-24 (1:2.5, 1:3 to 1:5) does not affect the device performance substantially. This means that adjusting the processability of the PEDOT/PSS by adding concentration of PSS can be done without affecting the PCE in this ratio, but with a little change in $V_{oc}$/$J_{sc}$ or $FF$. The main exception is in the performance of device from PP(1:2.5)-12 sample, which is the most conductive film (its conductivity is ~542 times than PP(1:2.5)-C), and generates a device ~10% higher in PCE. The device containing PP(1:2.5)-12 film also showed no real change in $V_{oc}$, but $J_{sc}$ increases by more than 30%, while $FF$ drops by ~30% at the same time. This performance suggests that highest conductivity material has an increase in $J_{sc}$ which must be due to the lowered resistivity of this interfacial layer.

<table>
<thead>
<tr>
<th>PEDOT/PSS</th>
<th>$\sigma$ (S/cm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$</th>
<th>PCE (%)</th>
<th>PCE max. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-C</td>
<td>9.6±1.0E-3</td>
<td>606.8±8.8</td>
<td>-8.14±0.49</td>
<td>0.62±0.06</td>
<td>3.06±0.38</td>
<td>3.54</td>
</tr>
<tr>
<td>PP(1:2.5)-12</td>
<td>5.2±0.7E-0</td>
<td>595.5±3.9</td>
<td>-13.26±1.20</td>
<td>0.42±0.03</td>
<td>3.30±0.36</td>
<td>3.77</td>
</tr>
<tr>
<td>PP(1:3)-24</td>
<td>2.7±0.9E-1</td>
<td>589.6±22.9</td>
<td>-8.35±0.32</td>
<td>0.55±0.04</td>
<td>2.70±0.23</td>
<td>2.93</td>
</tr>
<tr>
<td>PP(1:5)-24</td>
<td>1.5±0.5E-1</td>
<td>597.2±4.4</td>
<td>-8.20±0.28</td>
<td>0.56±0.03</td>
<td>2.72±0.17</td>
<td>2.94</td>
</tr>
</tbody>
</table>

Inconsistency of the OPV performance with increasing conductivity of PEDOT/PSS film can be exhibited from the I-V curve of those devices. Figure 8.8 shows that the I-V curve of both PP(1:2.5)-C and PP(1:2.5)-12 are similar in $V_{oc}$, but their $J_{sc}$ are different and the $FF$ for the device of PP(1:2.5)-12 is also much worse. PP(1:3)-24 and PP(1:5)-24 which have higher concentrations of PSS and lower conductivity than PP(1:2.5)-12 start with about similar density current but lower FF. The worse FF in PP(1:2.5)-12 device is not just because of recombination process of exciton, but higher serial resistance and lower shunt resistance largely affect this performance. More recombination of excitons in the active layer is possibly occuring resulting to a lower
efficiency of the device performance. Notably, the FF of these devices is systematic, with the highest value obtained from the PEDOT/PSS with the lowest conductivity, and the lowest value from the most conductive PEDOT/PSS. This possibly reflect the inability of the higher conductivity PEDOT/PSS to act as an effective electron blocking layer in the device and warrants further investigation.

![Image](image.png)

**Figure 8.8** I-V curves of OPV device using PP(1:2.5)-C, PP(1:2.5)-12, PP(1:3)-24 and PP(1:5)-24 as the interface layer.

In order to ensure that the device performance comes only from the actual device and not from adjacent regions, device masking was employed during testing to avoid drawing current from outside the device area. When masks were applied to the devices, especially those from the commercial material and the most conductive material (PP(1:2.5)-12), the PCE of the device from commercial PEDOT/PSS dropped ~24% its value from 3.06% to 2.34%, but the device from PP(1:2.5)-12 drops ~60% from 3.30% to 1.34% (see Table 8.2 and Figure 8.9). The current generated from the PP(1:2.5)-12 device decreased to about the value of the commercial PEDOT/PSS suggesting that highly conductive PEDOT/PSS must cause a very large perimeter effect to the device. The drawing of current from an outside area is larger in more conductive materials like PP(1:2.5)-12 than in less conductive material.
Consequently, the use of highly conductive PEDOT/PSS as an interface layer in OPV’s maybe counter productive, since the material will be less effective as an electron blocking layer (FF) and will draw current from outside the device area. The observation that these devices draw current from such a large region outside the device (the PCE is tripled) is interesting, and points to the use of high conductivity PEDOT/PSS as transparent electrode material in these devices eliminating the need for ITO.

\[ \text{Figure 8.9} \quad \text{I-V curve of PP(1:2.5)-C and PP(1:2.5)-12 devices with and without masking.} \]

\[ \text{Table 8.2 Photovoltaic parameters of device performance after masking.} \]

<table>
<thead>
<tr>
<th>PEDOT/PSS</th>
<th>$\sigma$ (S/cm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$</th>
<th>PCE (%)</th>
<th>PCE max. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-C</td>
<td>$9.6\pm1.0E-3$</td>
<td>$560.1\pm16.4$</td>
<td>$-6.76\pm0.54$</td>
<td>$0.62\pm0.10$</td>
<td>$2.34\pm0.46$</td>
<td>$2.83$</td>
</tr>
<tr>
<td>PP(1:2.5)-12</td>
<td>$5.2\pm0.7E-0$</td>
<td>$498.2\pm12.6$</td>
<td>$-7.12\pm0.16$</td>
<td>$0.38\pm0.02$</td>
<td>$1.34\pm0.13$</td>
<td>$1.57$</td>
</tr>
</tbody>
</table>
8.7. OFET device performance fabricated using the in-house synthesised PEDOT/PSS as gate

There are several OFETs parameters (see Section 8.4) that can be measured and compared to understand the performance quality of the devices. In this chapter, we compare the output characteristic and transfer characteristic of fabricated devices using different PEDOT/PSS dispersions deposited as the gate.

8.7.1. Morphology of PEDOT/PSS deposit on OFET device

P3HT/PVPy based devices were fabricated using different PEDOT/PSS dispersions added as the gate by drop-casting method. The P3HT/PVPy based device was prepared by spin-coating P3HT solution onto pre-patterned indium-tin-oxide (ITO) source-drain electrode substrates and continued by depositing of the PVPy film as the dielectric insulator. Processability of PEDOT/PSS dispersion is very important to the fabrication of the device. Drop-casting PEDOT/PSS dispersions on top of P3HT/PVPy layer generate different homogeneity of the deposited film. PEDOT/PSS is aqueous solution whereas PVPy is organic processed solution, and this affects the wetting and compactness of the PEDOT/PSS deposited on the top of P3HT/PVPy layer. Most of the PEDOT/PSS dispersions which formed high conductive films as discussed in previous chapters formed rough and non-uniformly deposited films, whereas the dispersions of lower conductivity PEDOT/PSS were able to form smooth and uniform films on top of the P3HT/PVPy layer (see Figure 8.10).
Insets in the Figure 8.10 show clearly that the deposited PEDOT/PSS films that are smooth and uniform similar to the commercial dispersion (A) came from PP(1:2.5)-6 dispersion (B), and PP(1:6)-24 dispersion (F). The representative images suggest that all dispersions which formed rough and non-uniform deposits are from the dispersions having less free PSS, high PEDOT/PSS doping and conductivity two or three order of magnitude higher than that obtained from the commercial PP(1:2.5)-C film ($9.6 \times 10^{-3}$ S/cm). It should be noted that the presence of higher amounts of free PSS in the PEDOT/PSS dispersions decreases conductivity of the resulting films due to less doping of PEDOT to PSS. However, PP(1: 5)-24 which was synthesised using a higher concentration of PSS also did not formed uniform and smooth deposited film (E) which could be due to it being highly doped with bigger PEDOT particles doped to PSS (as indicated by its peak in the electropherogram shown as spikes at 8.5 – 10 min, Figure 5.11). Among the in-house synthesised PEDOT/PSS having lower ratios of PSS (1:2.5), only dispersion PP(1:2.5)-6 synthesised for 6 hr, with conductivity ($9.8 \times 10^{-3}$ S/cm) similar to the commercial PEDOT/PSS film, could be drop-casted to form smooth film. Smoothly deposited films were not obtained from dispersions from longer reactions although they can form very conductive films such as PP(1:2.5)-12 (5.2 S/cm),

Figure 8.10 Images of the representative fabricated P3HT/PVPy devices after depositing of PEDOT/PSS dispersions: (A) PP(1:2.5)-C, (B) PP(1:2.5)-6, (C) PP(1:2.5)-24, (D) PP(1:3)-24, (E) PP(1: 5)-24, and (F) PP(1:6)-24. The insets show the corresponding deposit at 5 times magnification.
PP(1:2.5)-24 (2.1 S/cm) and PP(1:3)-24 (0.76 S/cm). This correlates to the amount of free PSS in their dispersions which can be seen from their electropherogram (see Figure 5.21 Chapter 5), the higher the free PSS content, the more processable the dispersion, the smoother the films.

8.7.2. Output characteristic of OFET devices

The measurement of parameters of OFETs device which have rough and non-uniform PEDOT/PSS deposits showed unstable performance of drain current on the device due to unstable gate current input from the source. Therefore the device did not perform properly and the output characteristic showed a very small range of linear regime and then dropped the drain current and the saturation regime was not stable. They could not generate reversible and reproducible devices. This section focuses on discussion of the output characteristic of the devices forming smooth and uniform films from different PEDOT/PSS as the gate.

Figure 8.11 (A) shows the output characteristics of the P3HT/PVPy/PP(1:2.5)-C device from plotting the recorded drain current ($I_D$) versus $V_{DS}$ for a series of $V_{GS}$ after applying a fixed gate voltage range from 0.4 V to -1.4 V. This device was formulated from the commercial PEDOT/PSS as the gate and the OFET works well as a transistor. The figure also show the readable drain current reaching an optimum at approximately -0.7 V in the linear region and then enters saturation region of the graph. Calculation to the current modulation ratio ($I_{ON}/I_{OFF}$) of some fabricated similar devices showed the highest value of $I_{ON}/I_{OFF}$ at 12.5 (see Table 8.3). Typical PVPy device based transistors have current modulation ratio of 10 to 100, and this device has maximum output current ($I_{ON}$) at -1.2 microampere which is comparable to other conventional OFETs.[182]

Figure 8.11 (B) shows the transfer characteristic of a P3HT/PVPy/PP(1:2.5)-C OFET device. This output was recorded and measured by sweeping across a range of $V_{GS}$ values in forward and backward directions three times for a fixed running of $V_{DS}$ on -1.5 V at a scan rate of 50 mV/s. This figure shows that the transfer characteristic of the P3HT/PVPy based OFET using commercial PEDOT/PSS deposit as the gate is reversible and reproducible. The figure shows a small amount of hysteresis between the forward and the backward of the gate voltage ($V_G$). Subsequent scans of this device showed degradation of the drain current of the device meaning less consistency of the
device but this was still in the order of initial values. Hysteresis of the transistor can result from reasons such as the effect of mobile charges at the channel, charge injection between dielectric and semiconductor, or charge injection between the gate to dielectric.[184] This could be caused by a rough interface between P3HT/PVP and PVPy/PP(1:2.5)-6.[182]

Figure 8.11 (A) Output characteristic of a P3HT/PVPy/PP(1:2.5)-C device; and (B) Transfer characteristic of P3HT/PVPy/PP(1:2.5)-C device measured directly at $V_{DS} = -1.5$ V. Scan speed = 50 mV/s.

Similar conditions were applied to characterise a P3HT/PVPy/PP(1:2.5)-6 device and the output characteristic is shown in Figure 8.12 (A). This device was fabricated using in-house synthesised PEDOT/PSS (1:2.5 ratio) (6 hr reaction). The dispersion generates film conductivities similar to the commercial PEDOT/PSS film, and previous characterisations suggested it contains smaller PEDOT doped with PSS and a high amount of free PSS in the dispersion (25% un-doped form). The PP(1:2.5)-6 deposit as the gate generated current well, and the OFET works as a transistor. The figure shows from $V_{DS} = 0$ V to about -0.4 V, the readable drain current ($I_D$) changes linearly with $V_{DS}$ as the linear region, which is lower than that performed by the commercial PEDOT/PSS gate, and for $V_{DS}$ beyond -0.4 V shows only a small increase in the drain current in the saturation region of the graph. Calculation to the current modulation ratio ($I_{ON}/I_{OFF}$) showed the highest value of $I_{ON}/I_{OFF}$ at 9.6 (see Table 8.3). This device has maximum output current ($I_{ON}$) at -1.2 microampere which is comparable to P3HT/PVPy/PP(1:2.5)-C device OFET.
Table 8.3 Current modulation ratio ($I_{ON}/I_{OFF}$) of PP(1:2.5)-C, PP(1:2.5)-6, and PP(1:6)-24 as the gates for P3HT/PVPy based transistor from 2 measurements.

<table>
<thead>
<tr>
<th>PEDOT/PSS</th>
<th>$I_{ON}/I_{OFF}$</th>
<th>$I_{ON}/I_{OFF}$ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(1:2.5)-C</td>
<td>10.3 ± 3.4</td>
<td>12.5</td>
</tr>
<tr>
<td>PP(1:2.5)-6</td>
<td>9.4 ± 0.4</td>
<td>9.6</td>
</tr>
<tr>
<td>PP(1:6)-24</td>
<td>11.0 ± 2.8</td>
<td>12.9</td>
</tr>
</tbody>
</table>

The transfer characteristic of an OFET of a P3HT/PVPy/PP(1:2.5)-6 device can be seen in Figure 8.12 (B). This output was recorded by sweeping across a range of $V_{GS}$ values in forward and backward directions in three times for a fixed $V_{DS}$ on -1.5 V at a scan rate of 50 mV/s. The transfer characteristic of the P3HT/PVPy/PP(1:2.5)-6 device is highly reversible and reproducible. However, the figure also shows a large amount of hysteresis between the forward and the backward scans of the gate voltage ($V_{G}$) scan direction. The subsequent scans of this device show a small degradation or change in the current levels, but still of the same order meaning stability and reproducibility of the device change is good.

Figure 8.12 (A) Output characteristic of P3HT/PVPy/PP(1:2.5)-6 device; and (B) Transfer characteristic of P3HT/PVPy/PP(1:2.5)-6 device measured directly at $V_{DS} = -1.5$ V. Scan speed = 50 mV/s.

The third device was fabricated with a smooth and uniform gate from PEDOT/PSS (1:6 ratio) dispersion. This dispersion contains 44% of doping PEDOT/PSS and 66% of free PSS. The output characteristic of the resulting P3HT/PVPy/PP(1:6)-24 device is shown in Figure 8.13 (A). This figure shows clearly that the OFET device worked well as a
transistor. The output characterisation curve shows the readable drain current up to the optimum approximately at -0.5 V as the linear region then to be saturation region of the graph. Current modulation ratio ($I_{ON}/I_{OFF}$) of the fabricated P3HT/PVPy/PP(1:6)-24 device can reach the highest value of $I_{ON}/I_{OFF}$ at 12.9 (see Table 8.3), a slightly higher than that obtained from the P3HT/PVPy/PP(1:2.5)-C. The output characteristic of P3HT/PVPy/PP(1:6)-24 device shows the maximum output current ($I_{ON}$) at -0.9 microampere which is less than that performed by two previous devices but this value is still comparable to the commercial PEDOT/PSS OFET.

The transfer characteristic of an OFET of P3HT/PVPy/PP(1:6)-24 device is shown in Figure 8.13 (B). This figure indicates that the transfer characteristic of the P3HT/PVPy based OFET using synthesised in-situ PEDOT/PSS (1:6) deposit as the gate is reversible and reproducible, even better than that performed from P3HT/PVPy/PP(1:2.5)-C device. The figure does not show much hysteresis between the forward and the backward scans of the gate voltage ($V_G$). Furthermore, subsequent scans of this device do not show degradation or change in the current levels meaning that this device has high stability and reproducibility.

**Figure 8.13** (A) Output characteristic of P3HT/PVPy/PP(1:6)-24 device; and (B) Transfer characteristic of P3HT/PVPy/PP(1:6)-24 device measured directly at $V_{DS} = -1.5$ V. Scan speed = 50 mV/s.
8.8. Conclusions

All synthesised PEDOT/PSS dispersions have shown comparable OPV and OFET devices to the commercial PEDOT/PSS dispersion. In particular, in the case of the OPV device, the synthesised PEDOT/PSS dispersions showed similar results to the commercial PEDOT/PSS, except for the most conductive material which has larger “efficiency” when it is not masked. Higher conductivity of PEDOT/PSS films leads to a lower FF but also draws charge from outside the device area. The most important point here is the possibility to produce PEDOT/PSS with higher concentrations of PSS which will generate devices similar to the commercial PEDOT/PSS but with better FF’s.

The application of synthesised in house PEDOT/PSS as the gate for P3HT/PVPy based transistor requires a high amount of un-doped PSS in their dispersions to produced good gate deposits. All fabricated P3HT/PVPy based transistor using synthesised in-house PEDOT/PSS dispersions showed results comparable to the gate from the commercial PEDOT/PSS (Clevios). Current modulation ratio ($I_{ON}/I_{OFF}$) of fabricated P3HT/PVPy based devices using synthesised in house PEDOT/PSS as the gate can reach the value of $I_{ON}/I_{OFF}$ 9.6 to 12.9, whereas the gate from the commercial PEDOT/PSS has 12.5. These values are comparable to the conventional OFET which showed current modulation ratio 10 to 100. They show reversible, stable, and reproducible in transfer characteristic suggesting that the OFETs worked well as transistors. Clearly the amount of free PSS is important in both OPV and OFET applications – in OPV’s the PSS affects the FF of the device, in OFET’s the quality of the gate electrode is affected. The amount of free PSS in the dispersions which governs the processability of the films is a variable that can be adjusted to change the characteristics of these devices towards optimum performance.
CHAPTER 9 - SUMMARY AND RECOMMENDATIONS
9.1. Summary

The conductive behaviour of PEDOT/PSS, as dispersion and film, under varying synthetic and doping conditions and upon structure modification have been investigated with the aim of improving the conductivity and processability of PEDOT/PSS films for application on OPV and OFETs devices as interfacial conductive layer and gate electrode, respectively.

Statistical analysis of conductivity measurements using four point probe shows that spin coating speed correlated strongly with the thickness and conductivity of the films. It is clear from both correspondence analysis and MLR analysis that the use of 1000 rpm spin-coating speed to generate PEDOT/PSS films results in low and non-reproducible conductivity. From correspondence analysis, 2000 to 5000 rpm spin-coating speeds were found to be strongly associated with high conductivity of the films classified by ANOVA, based on means of film conductivity, into two groups, 2000 rpm – 3000 rpm, and 4000 rpm – 5000 rpm. While no significant difference was observed between conductivity of films generated using spin coating speeds 2000 and 3000 rpm, and conductivity of films generated using spin coating speeds 4000 to 5000 rpm, highly reproducible conductivity values were obtained when the films were generated using 5000 rpm. Therefore, all PEDOT/PSS films tested in this study were spun-coat at 5000 rpm.

The CE method developed in this study showed, for the first time, that free PSS (UV absorbance of 230 nm) in PEDOT/PSS dispersions is able to be separated from PEDOT/PSS complex (UV absorbance of 240-280 nm) based on ionic charges. The PEDOT/PSS complex has a shorter migration time or lower electrophoretic mobility than PSS because of the reduction of the negative charges of PSS due to doping with PEDOT. Thus, the higher the doping, the shorter is the migration time. The intensity of the free PSS peak in the CE electropherogram has been used to quantify the doping efficiency of PSS in the dispersion. The results show that electrophoretic mobility of PEDOT/PSS complexes is correlated to the doping of PEDOT to PSS and the conductivity of corresponding films. Figure 9.1 shows the relationship between conductivity of films, electrophoretic mobility (based on migration time) of PEDOT/PSS complex in the dispersion and doping efficiency (based on free PSS).
Films with conductivity > 1.0 S/cm have shorter migration times of 8 min and doping efficiency of >80%. The very high conductivity (5.2 S/cm) of the film generated from the linear PEDOT/PSS dispersion resulting from 12 hours reaction, despite its doping efficiency and migration time being comparable to the film with conductivity of 2.1 S/cm, could be attributed to the right balance between the amount of PEDOT/PSS complex and free PSS in the dispersion (doping efficiency = 89%) rendering the dispersion highly processable.

![Figure 9.1](image)

**Figure 9.1** Relationship between conductivity of films, electrophoretic mobility of PEDOT/PSS complex based on migration time and doping efficiency.

The effect of doping conditions, i.e. in-situ during polymerisation and post-polymerisation (PSS added after polymerisation of PEDOT), was found to affect the processability of dispersions and conductivity of resulting films. PEDOT/PSS doped in situ performed better in terms of conductivity and processability compared to the dispersions doped post-polymerisation.

The PEDOT/PSS dispersions, generated by oxidative polymerisation, formed stable dispersions with zeta potential values between -38 to -53 mV and were found to exist predominantly in aggregate forms, with particle size ranging from 100 to 600 nm,
although primary particles of size between 20 to 60 nm were also obtained. PEDOT/PSS composites are thermally stable and generally decompose at 390°C.

This work also demonstrates the potential of PEDOT to be modified to introduce functional endgroups and generate a more complex architecture. PEDOT was successfully endcapped with thiophene-based endcapping agents 2-thiophenemethanol (2TM) and 2-thienylmethyl methacrylate (2TMM). Further, crosslinked core star (CCS) PEDOT/PSS, with potential application in molecular imprinting, was successfully synthesised via the core first method using 2TMM, both with thiophene and polymerisable vinyl functionalities, to link PEDOT (as arm) with the non-conductive core.

Table 9.1 is a summary of the conductivity values obtained from films generated from all PEDOT/PSS dispersions, linear and CCS, synthesised in house for this work. CCS PEDOT/PSS films give variable conductivity values, with a high (0.53 S/cm) and dispersions ranging from moderate to highly processable. Among the linear PEDOT/PSS films, the endcapped samples expected to have shorter PEDOT chain lengths, gave low conductivity even if the dispersions were highly processable. Post-polymerisation doping also gave variable conductivity values, from a low of .025 S/cm (doping efficiency = 42%, 1:5 PEDOT/PSS) to a high of 0.53 (doping efficiency = 80%, 1:2 PEDOT/PSS), from moderately to highly processable dispersions. In general, dispersions containing high PEDOT/PSS ratios (≤ 1:3) gave highly conductive films because of high concentration of PEDOT/PSS complex and low free PSS in the dispersion and enhanced at reaction times between 12 and 36 hours with the right balance between the amount of PEDOT/PSS complex and free PSS in the dispersion.

All of the PEDOT/PSS samples synthesised in house gave conductivity values one to three order of magnitude higher than the commercial sample (Clevios P). Clevios P has a high content of free PSS, lower doped PEDOT (CE migration time = 11 min), particle size of 220 nm and thermal stability lower than the synthesised PEDOT PSS.
Table 9.1 Summary of conductivity values of tested films synthesised for this work.

<table>
<thead>
<tr>
<th>Sample/Conditions</th>
<th>Conductivity (S/cm)</th>
<th>Processability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varying reaction time (hour) PEDOT/PSS ratio of 1:2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.0098</td>
<td>high</td>
</tr>
<tr>
<td>12</td>
<td>5.2 ± 0.7</td>
<td>high</td>
</tr>
<tr>
<td>24</td>
<td>2.1 ± 0.5</td>
<td>high</td>
</tr>
<tr>
<td>36</td>
<td>1.4 ± 0.2</td>
<td>moderate</td>
</tr>
<tr>
<td>48</td>
<td>0.9 ± 0.3</td>
<td>moderate</td>
</tr>
<tr>
<td>Varying PSS ratios 1:3</td>
<td>0.76 ± 0.10</td>
<td>high</td>
</tr>
<tr>
<td>1:6</td>
<td>0.08 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Post-polymerisation doping</td>
<td>0.025 to 0.53</td>
<td>Moderate to high</td>
</tr>
<tr>
<td>Endcapping</td>
<td>0.061 to 0.18</td>
<td>high</td>
</tr>
<tr>
<td>CCS Core first method</td>
<td>0.23 to 0.61</td>
<td>Moderate to high</td>
</tr>
<tr>
<td>Commercial sample (Clevios P)</td>
<td>0.0096</td>
<td>high</td>
</tr>
</tbody>
</table>

This study also demonstrates the performance of selected PEDOT/PSS films, under un-optimised conditions, to be comparable to the commercial PEDOT/PSS when used as an interfacial conductive polymer layer and electrode gate in OPV and OFET devices, respectively. In particular, in the case of the OPV device, the higher conductivity of PEDOT/PSS films leads to a lower $FF$ but also draws charge from outside the device area. All fabricated P3HT/PVPy based transistor using synthesised in-house PEDOT/PSS dispersions showed results comparable to the gate from the commercial PEDOT/PSS (Clevios) shown by their current modulation ratio. They show reversible, stable, and reproducible in transfer characteristic suggesting that the OFETs worked well as transistors.

9.2 Recommendations for future work

Considering the results obtained in this study, a number of interesting further studies can be pursued. Firstly, the performance of highly conductive PEDOT/PSS for the application in the OPV and OFET devices can be optimised. For both devices, PEDOT/PSS with processability comparable to commercially-sourced dispersions but
still highly conductive can be tested. This could be achieved, for example, by increasing the PSS content to enhance processability and the addition of a secondary dopant to increase conductivity. It is to be noted that both devices do not require very highly conductive PEDOT/PSS and the conductivity of films generated from PEDOT/PSS synthesised in this work is sufficient.

The capability of PEDOT to form the non-conductive crosslinked core star architecture can be pursued. The core can be molecularly imprinted (i.e. creation of a molecular mould) and the molecularly imprinted star PEDOT doped with PSS can be used as a sensing gate for OFET (see Figure 9.2). This work has shown that the conductivity of CCS PEDOT/PSS in its un-optimised form is comparable to the linear PEDOT/PSS prepared using high PEDOT/PSS ratios. An ideal result will be a change in the current modulation ratio in the presence or upon removal of an analyte selectively bound to the molecularly imprinted gate.

![Figure 9.2](image.png) Schematic of the potential application of CCS PEDOT/PSS as a sensing gate for OFET devices.

It is also possible that the molecularly imprinted core can be attached to the dopant PSS instead of PEDOT. The PEDOT/CCS-PSS can be applied as a gate for OFET as with the CCS PEDOT/PSS. I have done some preliminary synthetic work in this area and have demonstrated the feasibility of introducing the crosslinked core to PSS by controlled radical polymerisation. I have used the CCS PSS to dope PEDOT which have resulted to conductivities (0.4 S/cm) which is comparable to the linear PEDOT/PSS films.
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