Electroactive polymeric materials for electronic devices and biosensors

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Conjugated polymers have brought about a revolution in the world of polymers and hence, opened up new possibilities in the utilization of polymers in ways hitherto unknown. As a result of the conjugated bonds present, they are able to carry electrons and therefore mimic metals. One of the objectives of this work is the syntheses of processable conductive polymers in a cost effective manner that would still have desired physical and chemical properties. A series of electroactive polymers have been prepared and most of these are intrinsically conductive. A semiconducting filler, single-walled carbon nanotubes, was added to impart conductivity to the functional polymer, \( \alpha,\omega\)-bi[2,4-dinitrophenyl caproic] [poly(ethylenoxide)-b-poly(2-methoxystyrene)-b-poly(ethylene oxide)] which is non-conducting. Composites of this polymer with polystyrene and SWCNTs were electrospun to form nanofiber mats which had mixed morphologies but
predominantly beaded. The nanofibers ranged in diameter form ~ 65 to ~ 500 nm. These functional nanofibers were incubated in fluorescently (FITC) tagged Immunoglobulin E, IgE and they showed biospecificity towards IgE. The current-voltage characteristics indicated a change in behavior when bound to IgE and otherwise.

The intrinsically conductive polymers of 3-alkylthiophenes were prepared using the Grignard metathesis reaction, oxidative coupling with ferric chloride as well as copolymerization via ATRP with conductive P3DT as the macroinitiator. These environmentally stable polymers show a glass transition mostly between 48 to 50 °C and the $\pi$ to $\pi^*$ transition of the conjugated polymers is evidenced in wavelength of their absorption in the UV/Vis/NIR as the spectra indicated. The particle sizes obtained by light scattering showed average diameter between 28 to 40 nm for the different polymers.

Electrochemical studies on the block copolymer and random polymer series by cyclic voltammetry show the species are redox active in solution. Conductivity of multiwall nanotubes/ P3MT composite series showed conductivity values between $1.3 \times 10^{-7}$ to $2.5 \times 10^{-4}$ S/cm as determined from the bulk resistance measurements of pressed pellets of the composites. The biofunctional polymers investigated are highly promising in the biotechnology/biomedical industry as potential biosensors. The non-biofunctional polymers too are applicable in photovoltaics, optoelectronics, energy storage, solar cells, the semiconductor industry and many more.
ELECTROACTIVE POLYMERIC MATERIALS FOR ELECTRONIC DEVICES AND BIOSENSORS

A DISSERTATION

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

BY

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<td>Multi-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>P3AT</td>
<td>Poly(3-alkylthiophene)</td>
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xviii
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<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>P3DEGT</td>
<td>Poly(3-diethylene glycol monomethyl ether thiophene)</td>
</tr>
<tr>
<td>P3DT</td>
<td>Poly(3-decylthiophene)</td>
</tr>
<tr>
<td>P3MT</td>
<td>Poly(3-methylthiophene)</td>
</tr>
<tr>
<td>P3OT</td>
<td>Poly(3-octylthiophene)</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate Buffer Saline</td>
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<td>Polythiophene</td>
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CHAPTER 1

INTRODUCTION

1.1 Electronically Conductive Polymers, ECPs

Macromolecules or polymers with conjugated backbones have brought about a technological revolution in the electronic industry by forming their own unique class of component devices referred to as, “organic semiconductors.” The organic semiconductors conduct electricity in the partially oxidized state. These can be found in various devices from photonic, to electronic and even devices on the nanoscale. The very fact that they are non-metallic but possess mobile, π- electrons has really made them outstanding. In the mid-nineteenth century, Henry Letheby, a British Physician and Chemist, oxidized aniline on an anode, thus preparing polyaniline and it was found to exhibit electrochromism.¹ A century later in the 1950s, another discovery was made whereby aromatic polycyclic compounds on interaction with halogens, formed charge-transfer complex salts.² These pioneer works laid the foundation for organic compounds that have the ability to move electrons or organic electronics.

The motion of electrons through conjugated systems, in intrinsically conducting polymers is the basis for charge propagation. A salient feature of these polymers is the variability of their conductivity, which is the flexibility of switching them reversibly between their conductive and insulating forms. This attribute is invaluable in components/devices, such as, field effect transistors, thin film transistors, energy storage,
light emitting devices, sensors of various types. Figure 1.1 is a relative comparison of polymer conductivity with conductors, semi conductors and insulators.

![Diagram showing conductivity range of conductive polymers relative to insulators, conductors and semiconductors]

Figure 1.1: Conductivity range of conductive polymers relative to insulators, conductors and semiconductors

In conductive materials (most metals), the conduction band, which is the valence band is partially filled and electrons can move around freely under the influence of an electric field, since many empty levels are available. In insulators, their valence band is completely filled with electrons and the conduction band is separate from the valence band by a large gap. It will take electrons with sufficiently high energy to cross over from the valence band to the conducting band and they cannot be influenced by an electric field. An intermediate between these two phenomena is where the gap between the valence and conduction bands is much smaller than what obtains in an insulator. When energy is applied, these electrons cross over the band gap from valence band to the conducting band. The foregoing is depicted in Figure 1.2. Consequently, they can be influenced by an externally applied electric field and thus, behave like conductors. The
vacated spots in the valence band are known as “holes” and these are mobile charge carriers that behave like positive charge carriers.³

Figure 1.2: Schematic of energy bands in solids

1.2.1 Thiophene

Thiophene or thiofuran is a heterocyclic compound composed of an aromatic, flat, five-member ring. The other two five-member heterocyclic compounds analogous to thiophene are pyrrole and furan (Figure 1.3). Thiophene monomer is the repeating unit in the conductive polymer, polythiophene. The polymer is formed by the linkage of thiophene via its 2- and 5- position.

Figure 1.3: Examples of Heterocyclics: a) Thiophene, b) Pyrrole, c) Furan

1.2.2 Polythiophenes

Polymers have been found to conduct electricity or act as semiconductors. There is an ever increasing focus on the study of polythiophenes, as conducting polymers continue to garner much interest due to their intrinsic electronic properties and
processability. They generally have a high thermal stability with only about 42% weight loss at 900°C as well as excellent electrical conductivity, comparable to copper in the region of $3.4 \times 10^{-4}$ to $1.0 \times 10^{-1}$ S/cm under doping conditions. Polythiophenes have found use in photovoltaics and optoelectronic (light emitting diodes, LEDs) devices as well as organic semiconductors.5-9

Since Alan MacDiarmid and co-workers developed the first conductive polymers, polyacetylene in the 1970s,10 much work has gone into the synthesis of various types of π-conjugated polymers, of which polythiophenes are a group. Expectedly, thiophene analogs, pyrrole and furan have also received attention as conductive polymers as well as other π-conjugated polymers like poly(aniline)$^{11}$ (PANI) and poly(p-phenylene vinylene)$^{12}$ (Figure 1.4).

![Polythiophene, Polyacetylene, Poly(aniline), Poly(p-phenylene vinylene)](image)

For a polymer to be conductive, it must comprise a conjugated system of π electrons in its backbone. The almost infinite π system will extend through all the
monomer units within a polymer chain to enable directional conductivity along the polymer backbone, thereby making the polymers conducting or semiconducting.\textsuperscript{13} Polythiophene, among all the conductive polymers is the most attractive to researchers in the field because of the fact that the polymer possesses excellent solubility in common organic solvents whether doped or un-doped, when there is a long substituent alkyl chain present in its \( \beta \) or 3- position of the thiophene ring.\textsuperscript{14-16} Consequently, hundreds of polythiophene derivatives have been synthesized, which are soluble in organic solvents and also, water.\textsuperscript{17-24}

Syntheses of polythiophene and its derivatives have been carried out via two distinct routes, since its discovery in the early 1980s. The first method is by electrochemical polymerization, which normally requires a higher applied potential than the monomer oxidation potential.\textsuperscript{25,26} Applying a higher potential in the process has a draw back in that unwanted side reactions may occur like cross-linking and perhaps excessive oxidation of the polymers, resulting in polymers of poor quality.\textsuperscript{27} Thin films of poly(3-methylthiophene) with high conductivities have been prepared electrochemically.\textsuperscript{28} The other method of obtaining polythiophene is by chemical synthesis. This type of synthesis is of two types. i) chemical oxidation of thiophenes and its derivatives where ferric chloride is the most common oxidizing agent used \textsuperscript{29,30} and ii) organometallic polycondensation reactions which are mediated by organo- transition metal complexes of various types.

Notable among this class of polycondensation are: a) the Suzuki coupling employing a palladium complex in the presence of a base to catalyze the coupling of 2,5-dihalothiophene with diboronic acid derivatives,\textsuperscript{31} b) the Stille coupling of
dihalothiophenes and di(trialkylstannyl)thiophenes in the presence of a palladium catalyst without a base. Another variation of this is the nickel catalyzed polymerization of 5-bromo-2-thiomagnesium halides to yield a structurally homogenous polymer. The polymer has been synthesized by using the Kumada cross-coupling method by regiospecifically polymerizing 2-bromo-3-alkyl-5-magnesiobromothiophene.

McCullough and co-workers pioneered the Grignard Metathesis (GRIM) method of polymerizing poly(3-alkylthiophenes) which results in polymers with controlled molecular weights, narrow molecular weight distribution (PDI), uniform end groups and highly regioregular stereochemistry. An example of regioregular head-to-tail polythiophene is produced by the reaction of 2-bromo-3-(alkyl)-5-thiophenemagnesium bromide with [1,3-bis(diphenyl-phosphine)propane]nickel(II) chloride. A variation to the McCullough method was to react a dihaloalkane with the highly reactive Rieke’s zinc to form an organometallic intermediate of two isomers containing zinc, as reported by Rieke et al. When tetrakis(triphenylphospine) palladium(0) was added as catalyst, they obtained a regiorandom polythiophene, but when a similar intermediate was treated with [1,3-bis(diphenyl-phosphine)ethane]nickel(II) chloride, a regioregular polythiophene was formed.

1.3 Poly(3-alkylthiophenes), P3ATs

As previously mentioned, polythiophenes are one of the most thoroughly investigated group of conductive polymers, but unsubstituted polythiophenes are not soluble or easily processable. Hence, the addition of pendant alkyl or alkoxy (C>4) chains which are of course flexible in the 3- or 4- position of the thiophene heterocyclic ring (Figure 1.5), allows for ease of solubility of the substituted polythiophene in solvents
like dichloromethane, tetrahydrofuran, chloroform, toluene, benzonitrile, nitrobenzene, xylene and dichlorobenzene.\textsuperscript{41-45}

Figure 1.5: Structure of poly(3-alkylthiophenes)

These substituted polythiophenes are then easily processed in solution to form films. Incorporating alkyl groups in the 3- or 4- position however, makes the thiophene ring lose its symmetry along the polymer backbone.\textsuperscript{46} Two adjacent polymer units are referred to as dyads and there are three possible dyad arrangement in poly(3-alkylthiophenes). They are either head-to-head, head-to-tail or tail-to-tail.\textsuperscript{47} (Figure 1.6)

HH substitution

HT substitution

TT substitution

Figure 1.6: The 3 Dyads of P3ATs
1.3.1 Regiorandom Poly(3-alkylthiophenes)

Oxidative coupling with ferric chloride has been the easiest route to synthesizing regiorandom poly(3-alkylthiophenes). This is the type of polymer where the dyads are not arranged in any particular order.

\[
\text{R} \quad \text{FeCl}_3 \quad \text{CHCl}_3
\]

Figure 1.7: Synthetic pathway for regiorandom poly(3-alkylthiophenes)

A typical oxidative polymerization of 3-alkylthiophene involves the reaction of the monomer with about 4 molar equivalents ferric chloride in anhydrous, deoxygenated chloroform\(^4\) (Figure 1.7). Initiation is via the formation of a thiophene radical cation. (Figure 1.8) Upon the formation of oligomers, the propagation step then proceeds through the carbocation. The growing polymer chain is fully oxidized by the ferric chloride. An electrophilic aromatic substitution occurs when the positively charged polymer chain attacks another monomer species at the 2-position with the formation of a C-C bond. The two hydrogen atoms on these carbon leave as protons and the growing polymer chain is then re-oxidized continuously until reactants are used up.\(^5\)
1.3.2 Regioregular Poly(3-alkylthiophenes)

Since the first completely regioregular poly(3-alkylthiophene) was made by McCullough et al in the early 1990s, there has been a flurry of activities with the syntheses of various derivatives of poly(3-alkylthiophenes) both in the form of the homopolymer and co-polymers.\textsuperscript{50-53} Regioregular polythiophenes (Figure 1.9) are more desired because of their higher conductivities\textsuperscript{54} and higher electron mobilities.\textsuperscript{55} than their regiorandom counterparts. In addition to the advantage of ease of solubility, having a flexible alkyl chain in the 3- position of regioregular polythiophene serves as a means of tuning the electronic properties of the polymer. Morphology is another key factor in the tuning of electronic properties of regioregular polymers.\textsuperscript{56}
Another avenue to alter the physical and electronic characteristics of polythiophenes is end group modification. End capping regioregular polythiophenes with desirable functional groups results in the possibility of co-polymerization with compatible monomers to form diblock and triblock copolymers with interesting architectures. Block co-polymers of 3-alkylthiophenes have been seen to self-organize into periodic, crystalline nanostructures by undergoing phase separation at the nanoscale to form nanofibers or fibrils in particular, and other nanoscale architectures. The self-organization depends on the nature of the block copolymers involved and solvent used.

Figure 1.9a: Cross-coupling polymerization pathway to regioregular polythiophenes: synthetic pathway to perfectly regioregular polythiophenes by McCullough et al.33
1.4 Scientific Merit/Purpose of the Research

The interest in this work was sparked by the need to have inexpensive and easily processable polymeric components for bio-sensing (biotechnology) in particular and the semiconductor industry in general. Poly(3-alkylthiophenes), P3ATs have potential not just because of their intrinsic electronic properties, but because of the alkyl substitution in the 3-position which means better solubility in many organic solvents as well as higher electrical conductivity, when compared to other polythiophenes.

Therefore, we report the syntheses and characterization of some P3ATs homopolymers, block and random co-polymers with hydrophilic moieties (like diethylene glycol monomethyl ether and 2-hydroxy ethyl methacrylate). These polymers can be developed into nanostructures which may be incorporated into sensors or other electronic
devices like solar cells, photovoltaics, optoelectronics, etc. Also reported is the electrospinning of composites of dinitrophenyl (DNP) functionalized poly(2-methoxystyrene), polystyrene and single-walled carbon nanotubes into nanofibers.

Biocompatibility and biofunctionality of the electrospun fibers have been carried out by the incubation of the fibers decorated with the DNP group with the antibody, IgE to check for biospecific and/or bioselective binding characteristics. Electronic activity of the fibers and their potential as nanoscale biosensors have also been investigated.
CHAPTER 2

3-DECYLTHIOPHENE AND 2-HYDROXYETHYL METHACRYLATE BLOCK COPOLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

2.1 Abstract

The use of block copolymers as active components in biosensors and other nanoscale devices has been an area of intense focus in the last decade or so. An example of this is the functionalization of the polymers with appropriate ligands that are capable of binding to high affinity receptors (FceRI) on the surface of mast cells or immunoglobulin E (IgE) for instance. Consequently, we synthesized block copolymers of 3-decylthiophene with 2-hydroxy ethyl methacrylate via atom transfer radical polymerization, ATRP. The macroinitiator, poly(3-decylthiophene) was first made by Grignard metathesis reaction followed by a series of end group modification to yield the bromoester end-capped polymer.

ATRP of 2-hydroxy ethyl methacrylate was carried out in dimethylformamide with CuBr/PMDETA (catalyst/ligand) duo to yield the block copolymers which were then functionalized with 2,4-dinitrophenyl (DNP)-ε-amino-γ-caproic acid. Characterization of the copolymers was done by $^{13}$C and $^1$H NMR, FTIR, Uv-vis and Raman spectroscopy. Thermal analysis was done by differential scanning calorimetry, electrical behavior was studied via cyclic voltammetry. The copolymer solution in chloroform was drop-cast onto silicon substrates to form films whose morphology was
studied using electron and scanning probe microscopy. Biofunctionality studies, done through incubation in fluorescently tagged IgE indicated that there was preferential binding of the protein to the DNP groups, as observed under the fluorescence microscope. The results obtained so far, strongly indicate that these block copolymers have potential use in biosensors, with the incorporation of specific functional groups (ligands) that antibodies recognize and adhere to.

2.2 Atom Transfer Radical Polymerization

2.2.1 Background

Atom transfer radical addition, ATRA, has been a useful tool in the formation of C-C bonds.\textsuperscript{59, 60} The ATRA process involves a halogen atom abstraction by a transition metal species, M\textsuperscript{n}, from an alkyl halide, RX, resulting in the formation of a carbon centered radical (on the alkyl group) and the oxidized species of the transition metal. This is then followed by an intramolecular or intermolecular addition of the radical, to an alkene resulting in the formation of a radical intermediate with the alkene (Scheme 1). When this radical intermediate reacts with the previously formed transition metal species, the target product is formed, as well as the regenerated, reduced transition metal species which is available to promote a new redox process.

Atom transfer radical polymerization, ATRP, is an extension of atom transfer radical addition, ATRA, and it is an efficient method of conducting controlled living radical polymerization. The Matyjazewski research group at Carnegie-Mellon University pioneered this method of controlled “living” polymerization which employs a simple and cost-effective polymerization technique. The radicals formed during the process, exert control over the polymerization process.
Scheme 1: Mechanism of atom transfer radical addition

This is because these radicals can grow ("living") but are deactivated in a reverse reaction to form dormant species. When the radicals are again activated, the polymer chain grows and the cycle is continued to yield a polymer chain that grows steadily and possesses a well defined end group. In other words, control of the process can be enhanced by adding a small quantity of the deactivator, thereby causing a shift in the equilibrium towards the dormant species. Typically, 10% deactivator relative to activator concentration is sufficient and this accounts for the quantity of deactivator formed during the polymerization, which is attributed to irreversible termination. ATRP is typically initiated by an alkyl halide and a transition metal catalyst, which is complexed to a ligand. Additionally, the catalysts used in ATRP are not affected by moisture and trace quantities of oxygen which makes the techniques more preferable.
2.2.2 Examples of Initiators and Ligands used in ATRP

Below (Figure 2.1) are examples of initiators used in ATRP (including alkyl halides)

A. Simple alkyl halide initiators. Examples are shown below.

Figure 2.1: Alkyl halide ATRP initiators. a) bromoacetyl bromide; b) 2-bromopropionyl bromide; c) α-bromoisobutyryl bromide

B. Functional alkyl halide initiators. As the name implies, they possess functional groups like hydroxyl, azide, etc. Some examples of these initiators are shown in Figure 2.2.

Figure 2.2: Functional alkyl halide ATRP initiators. a) 2-hydroxyethyl 2-bromoisobutyrate. b) alkyl functionalized initiator; c) azide functionalized initiator.

C. Specialized ATRP initiators. This class of ATRP initiators, has special architectures, departing from the regular, linear architectures. (Figure 2.3)
D. Ligands for ATRP

In selecting the right ligands for ATRP, careful consideration needs to be made before choosing the ligand that accompanies the transition metal of choice. More details about transition metal catalyst/ligand complex can be found in the report of Tang et al. Examples of ligands used in ATRP are shown in Figure 2.4.
2.2.3 Mechanism of ATRP

There are differing thoughts regarding the reaction pathway for ATRP. However, the process is governed by a dynamic equilibrium between propagating radicals and dormant species mostly in the form of alkyl halide (or a polymeric macroinitiator), depending on starting material. The dormant species become activated by the transition metal ligand species (at a lower oxidation state, e.g. CuI/L) when they react with the rate constant of activation to form growing radicals and deactivators (which comprise the transition metal ligand complex in a higher oxidation state bound to the halide ligand, e.g. CuI-X/L).\(^6\) (Schemes 2 and 3).

Scheme 2: Mechanism of metal complex mediated ATRP\(^6\)

\[
\begin{align*}
R-X + \text{Mt}^{+}L_m & \rightleftharpoons \text{Mt}^{+1}L_m-X \\
R^* + \text{Mt}^{+1}L_m-X & \rightarrow R + \text{Mt}^{+}L_m-X
\end{align*}
\]

\[ R = \text{alkyl group} \]
\[ M = \text{transition metal} \]
\[ L = \text{ligand} \]
\[ X = \text{halogen} \]
Scheme 3: Dynamic equilibrium governing ATRP

\[
R \rightarrow X + M_i^{n/L} \xleftrightarrow{R \cdot \xrightarrow{k_{activation}} \xrightarrow{k_{deactivation}}} R^* + X \rightarrow M_{i}^{n+1/L}
\]

The rate at which an ATRP proceeds, depends on the rate constant of propagation as well as the concentration of the monomer and growing radicals. The radical concentration in turn, depends on the equilibrium constant of ATRP and concentration of dormant species, as well as activators and deactivators. The relationship is shown in the equation below:

\[
R_p = k_p [M] [R^*] = k_p K_{ATRP} \left( \frac{[R-X]}{[X-Cu^{II}/L]} \right)
\]

Equation 1: Rate of propagation of an ATRP, where \(R_p\) = rate of propagation, \(k_p\) = rate constant of propagation, \([M]\) = monomer concentration, \([R^*]\) = radical concentration, \(K_{ATRP}\) = equilibrium constant of ATRP, \([R-X]\) = dormant species, \([Cu^{II}/L]\) = activator species.

2.2.4 Poly(3-alkylthiophene) as Macroinitiator for ATRP

Poly(3-alkylthiophenes) belong to the inherently conductive polymer group like polypyrrole, polyfuran and polyaniline because of the conjugated carbon to carbon (C=C) double bond present in their structures. P3ATs are generally highly processable, environmentally stable and possess high electrical conductivity. Successful copolymerization with other vinyl monomers has been done via the ATRP of the appropriately functionalized polythiophene, acting as the macroinitiator for the living radical polymerization process.
2.3 Experimental

Materials

A. Monomers

1) 3-Decylthiophene, Aldrich, 97%
2) 3-Octylthiophene, Aldrich, 97%
3) 2-Hydroxyethyl methacrylate, Aldrich, 97%

Solvents

1) Tetrahydrofuran
2) Toluene
3) Methanol
4) Hexanes

Reagents

1) Methyl magnesium chloride, CH₃MgCl
2) Lithium aluminum hydride, LiAlH₄
3) Phosphorous oxychloride
4) 2-Bromopropionyl bromide
5) Triethylamine
6) N-Methylformaanilide

Other

1) Magnesium sulfate, Aldrich,
2) Sodium acetate, Fisher,
2.3.1 Syntheses of Regioregular poly(3-decylthiophene) and poly(3-octylthiophene)

The regioregular homopolymers were made using the GRIM method, discussed in Chapter 3. The homopolymers then were end-group modified, until the bromoester terminated polymer was achieved.

2.3.2 Synthesis of poly(3-decylthiophene) with ethyl end group

Regioregular poly(3-decylthiophene) 0.4 g (0.02 mmol) was dissolved in 80 ml THF in a two neck flask equipped with a reflux condenser. Ethylmagnesium bromide, (3 ml, 3M) was added and the resulting mixture was refluxed for two hours. It was then cooled to room temperature and 2M HCl (5 ml), was added to neutralize the reaction. The polymer was precipitated in methanol, isolated by centrifugation and then purified by soxhlet extraction in methanol. It was then dried in the oven to obtain the proton end-capped polymer. Yield: 0.37g. $^1$H NMR (CDCl$_3$, TMS) δ (ppm): 0.80 (t 3H), 1.25 (t 3H), 1.26-1.60 (m 16H), 2.60 (m 2H), 2.75 (m 2H), 6.80 (s 1H) $^{13}$C NMR (CDCl$_3$, TMS) δ (ppm): 13.85, 14.20, 21.35, 22.85, 28.1, 29.10, 29.20, 29.5, 29.6, 29.6, 30.85, 32.35, 111.25, 132.4, 134.55, 136.77.

Scheme 4: Synthesis of P3DT with ethyl end group
2.3.3 Synthesis of poly(3-decylthiophene) with carbonyl end group

Poly(3-decylthiophene) (0.4g) with proton end cap was dissolved in 100 ml toluene in a round bottom flask equipped with a nitrogen inlet, bubbler, condenser and drying tube. N-methylformanilide (2 ml, 16 mmol) and phosphorous oxychloride (1.3 ml, 14 mmol) were added and the reaction was stirred at 75°C for 24 hours. It was then cooled to room temperature and afterwards, stirred with a saturated sodium acetate solution for 2 hours and eventually precipitated in methanol. The CHO end functionalized polymer was then isolated by centrifugation, purified by Soxhlet extraction and dried in oven. Yield, 0.38g. 

\[ ^1H\text{ NMR (CDCl}_3,\text{TMS}) \delta (\text{ppm}): 0.80 (t 3H), 1.26-1.60 (m 16H), 2.60 (m, 2H), 2.86 (m 2H), 2.75 (m 2H), 6.80 (s 1H), 8.60 (CHO). \]

\[ ^{13}\text{C NMR (CDCl}_3,\text{TMS}) \delta (\text{ppm}): 13.88, 20.1, 22.5, 28.9, 29.1, 29.3, 29.5, 29.5, 29.65, 31.5, 32.1, 45.35, 111.1, 131.85, 134.2, 136.0, 201.5. \]

Scheme 5: Reaction scheme for synthesis of poly(3-decylthiophene) with carbonyl end group

2.3.4 Synthesis of poly (3-decylthiophene) with hydroxyl end group

CHO end-capped poly(3-decylthiophene) (0.35g, 0.0175 mmol) was dissolved in 100 ml THF in a round bottom flask equipped with a nitrogen inlet and bubbler. LiAlH\textsubscript{4} (1 ml, 1M) was added and the mixture stirred at room temperature for an hour and was then precipitated in methanol. The hydroxyl end capped polymer was isolated by
centrifugation and purified by Soxhlet extraction using methanol after which it was oven
dried. Yield: 0.378 g. $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 0.80 (t 3H), 1.26-1.60 (m 16H),
2.60 (m, 2H), 2.86 (m 2H), 1.82 (m 2H), 3.50 (m 2H), 6.75 (s 1H). $^{13}$C NMR (CDCl$_3$,
TMS) $\delta$ (ppm): 13.88, 21.2, 22.5, 28.9, 29.1, 29.3, 29.5, 29.5, 29.65, 31.5, 32.0, 32.1,
61.8, 110.0, 131.5, 134.0, 136.25.

Scheme 6: Reaction scheme for the synthesis of Poly (3-decylthiophene) with hydroxyl end group.

---

2.3.5. Synthesis of poly(3-decylthiophene) with bromoester end group

Hydroxyl end-capped poly(3-decylthiophene) (0.30 g, 0.015 mmol) was dissolved
in 100 ml THF in a round bottom flask and heated to 50°C. Triethylamine, TEA, (3 ml,
20 mmol) was added and this was followed by the drop-wise addition of 2-
bromopropionyl bromide (2.5 ml, 20 mmol). The reaction was then stirred at room
temperature for 12 hours and precipitated into methanol. The bromoester end-capped
polymer was isolated by centrifugation and subsequently washed in cold methanol, and
dried in the oven. Yield: 0.357 g. $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 0.80 (t 3H), 1.26-1.60
(m 16H), 1.90 (d 3H), 1.97 (m 2H), 2.60 (m, 2H), 2.86 (m 2H), 4.1 (m 1H), 4.40 (m 2H),
6.95 (s1H). $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ (ppm): 13.88, 20.85, 21.2, 22.5, 28.9, 29.1, 29.3,
29.5, 29.5, 28.65, 30.1, 32.1, 33.90, 41.2, 166.7, 62.5, 109.0, 128.5, 130.4, 132.4.
Scheme 7: Synthesis of the bromoester functionalized poly (3-decylthiophene) macroinitiator

\[
\begin{align*}
\text{THF, } \Delta, 50^\circ \text{C} & \quad \text{triethylamine} \\
\text{2-bromopropionyl bromide, rt, 12 hr} & \\
\end{align*}
\]

CH\_2OH end capped P3DT

bromoester end capped P3DT

2.3.6. ATRP of 2-hydroxyethyl methacrylate with P3DT macroinitiator

Atom transfer radical polymerization of 2-hydroxyethyl methacrylate using bromoester terminated poly(3-decylthiophene) as macro-initiator (MI), was carried out firstly with 500:1:3:3 (HEMA: P3DT-MI: CuBr: PMDETA) according to literature\textsuperscript{66} and subsequently modified using different ratios such as 150:2:1:1,

P3DT (0.17 g, 0.025 mmol) functionalized with the bromoester end group macroinitiator was placed into a 25 ml flask, purified CuBr (10.8 mg, 0.075 mmol) and PMDETA (21 µL, 0.075 mmol) were added and the flask was sealed, filled and back-filled with nitrogen three times. DMF (10 ml) was added through a nitrogen purged hypodermic syringe and the resulting mixture was stirred. 2-hydroxyethyl methacrylate (1.61 g, 12.4 mmol) was added to the flask via a purged hypodermic syringe as well and the mixture was transferred to an oil bath maintained at 70°C with constant stirring. The reaction was then allowed to run for 20 hours after which it was terminated by precipitating in methanol. This was followed by Soxhlet extraction in hexanes and the brownish black product was dried in a vacuum oven. Yield: 0.122 g.
2.3.7 Functionalization of P3DT-b-PHEMA with DNP group

The functionalization of the block copolymers with N-2,4-DNP-ε-amino caproic acid was done as reported by Sannigrahi et al.\textsuperscript{67} with some modification. The copolymers (25 mg) was placed in a three-necked flask. To this was added N-2,4-DNP-ε-amino caproic acid (0.7 mg, 2.5 mmol), DCC (7.5 mg, 3.75 mmol) and DMAP (0.1 mg). The flask was placed under dry nitrogen for 2 hours after which 5 ml dry chloroform was introduced into the flask using a nitrogen purged hypodermic syringe. The reaction was then left to run for 12 hours with constant stirring. Thereafter, the reaction mixture was filtered and purified by sequential precipitation from hexanes and methanol and isolated by centrifugation. Scheme 9 shows the synthetic pathway for the reaction.
Scheme 9: Functionalization of P3DT-b-PHEMA with 2,4-DNP-ε-amino-n-caproic acid.

2.3.8 Synthesis of poly(3-octylthiophene) with methyl end groups

The synthesis of regioregular poly(3-octylthiophene) with Br end group was performed in a similar manner to that of poly(3-decylthiophene), after the homopolymerization was done according to the procedure given in chapter 3. Regioregular poly(3-octylthiophene) (0.12g), was dissolved in THF (25ml) in a two-necked flask equipped with a reflux condenser, (Scheme 10). Methylmagnesium bromide, 0.4 ml was added and the mixture was refluxed for two hours. After that, it was cooled to room temperature and 2M HCl was added to neutralize the reaction. The polymer was
precipitated in methanol, isolated by centrifugation and subsequently purified by Soxhlet extraction in methanol to obtain the methyl end functionalized polymer. Yield: 0.101 g.

$^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 0.80 (t 3H), 1.25-1.60 (m 12H), 2.45 (s 3H), 2.60 (m 2H), 6.75 (s 1H). $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ (ppm): 10.35, 14.10, 22.55, 27.25, 29.20, 29.30, 29.6, 31.50, 32.00, 111.55, 131.6, 134.54, 135.35.

Scheme 10: Synthesis of Poly(3-octylthiophene) with methyl end group

2.3.9 Synthesis of poly (3-octylthiophene) with carbonyl end group

P3OT (0.1 g) with methyl end group was dissolved in toluene (50 ml) in a round bottom flask equipped with a nitrogen inlet, bubbler, condenser and a calcium chloride drying tube. N-methylformanilide, (0.11 ml) and phosphorous oxychloride (0.07 ml) were added and the reaction was refluxed at 75°C for 24 hours. After that, the reaction was cooled down to room temperature and stirred with saturated sodium acetate solution for two hours. It was then precipitated in methanol, isolated by centrifugation and purified by Soxhlet extraction in methanol to yield the carbonyl end capped polymer. (Yield, 0.124 g) $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 0.80 (t 3H), 1.25-1.60 (m 12H), 2.62 (t, 2H), 3.60 (s 2H), 6.75 (s 1H), 8.65 (t 1H). $^{13}$C NMR (CDCl$_3$, TMS) $\delta$
Scheme 11: Synthesis of poly(3-octylthiophene) with carbonyl end group

\[
\text{Br} \quad \begin{array}{c}
\text{S} \\
C_2H_{17}
\end{array} \quad \text{n} \\
\text{CHO}
\]

\[
\begin{array}{c}
\text{POCl}_3 \\
toluene, \Delta
\end{array} \rightarrow \\
\text{N-methylformanilide}
\]

\[
P3OT \text{ with methyl end group} \quad \text{CHO end functionalized P3OT}
\]

2.3.10 Synthesis of P3OT with hydroxyl end group

P3OT (0.1 g) with CHO end group was dissolved in THF (25 ml) in a round bottom flask equipped with a nitrogen inlet and bubbler. LiAlH$_4$ (0.5 ml, 1M) was added and the resulting mixture was stirred at room temperature for one hour after which it was precipitated into methanol. The product was isolated by centrifugation and purified via Soxhlet extraction in methanol, to yield the CH$_2$OH end capped P3OT. Yield 0.108g. $^1$H NMR (CDCl$_3$, TMS) δ (ppm): 0.80 (t 3H), 1.25-1.60 (m 12H), 2.62 (t, 2H), 2.72(d 2H), 3.60 (d 1H), 3.65 (m 2H), 6.75 (s 1H), $^{13}$C NMR (CDCl$_3$, TMS) δ (ppm):14.10, 22.55, 27.25, 29.20, 29.30, 29.6, 31.50, 32.00, 32.50, 62.6, 110.25, 133.6, 135.45, 138.35.

Scheme 12: Preparation of hydroxyl (OH) end capped P3OT

\[
\begin{array}{c}
\ast \quad \begin{array}{c}
\text{S} \\
C_2H_{17}
\end{array} \quad \text{n} \\
\text{CHO}
\end{array} \rightarrow \\
\text{LiAlH}_4 \quad \text{THF, rt, 1 hr}
\]

\[
\begin{array}{c}
\ast \quad \begin{array}{c}
\text{S} \\
C_2H_{17}
\end{array} \quad \text{n} \\
\text{OH}
\end{array}
\]

poly(3-octylthiophene) with CHO end group \quad poly(3-octylthiophene) with CH$_2$OH end group
2.3.11 Synthesis of P3OT with bromoester end group

P3OT (0.09 g) with CH$_2$OH end group was dissolved in THF (30 ml) in a round bottom flask and the temperature raised to 50°C by heating. Triethylamine, TEA (0.4 ml) was added, followed by the drop-wise addition of 0.4 ml 2-bromopropionyl bromide. The reaction was then stirred at room temperature for 12 hours and then precipitated into methanol. The product was isolated by centrifugation and washed with cold methanol to yield the bromoester functionalized P3OT. Yield, 0.104 g. $^1$H NMR (CDCl$_3$, TMS) δ (ppm): 0.80 (t 3H), 1.25-1.60 (m 12H), 1.97 (s 3H), 2.62 (t, 2H), 2.82 (d 2H), 4.31 (d 2H), 4.40 (d 1H), 6.75 (s 1H), $^{13}$C NMR (CDCl$_3$, TMS) δ (ppm): 14.10, 20.90, 22.55, 27.10, 29.20, 29.30, 29.6, 31.20, 32.00, 32.30, 41.20, 62.8, 109.75, 130.6, 140.35, 142.44, 167.55.

Scheme 13: Preparation of bromoester end-capped poly(3-octylthiophene)

2.3.12 ATRP of 2-Hydroxyethyl methacrylate (HEMA) with bromoester terminated P3OT as macroinitiator

Bromoester terminated P3OT (25 mg) was placed into a 25 ml flask followed by adding CuBr (78 mg) and PMDETA (94 mg). The flask was then sealed, filled and back-filled with nitrogen three times. DMF (5 ml) was then introduced to the flask via a nitrogen purged hypodermic syringe and the mixture was stirred to eliminate lumpy
CuBr. HEMA (2.14g, 16.5 mmol) monomer was then added to the flask using a purged hypodermic syringe and the flask was immediately transferred to an oil bath maintained at 70°C and stirred for 20 hours. The yield obtained was 18 mg.

Scheme 14: ATRP of HEMA with P3OT macroinitator.

2-hydroxyethyl methacrylate, HEMA
bromoester functionalized poly(3-octylthiophene)

P3OT-b-PHEMA

2.3.13 Functionalization of P3OT-b-PHEMA with DNP groups

The P3OT-b-PHEMA copolymer (17 mg) was placed in a three-necked flask. To this was added N-2,4-DNP-e-amino caproic acid (0.6 mg), DCC (6 mg) and DMAP (0.1 mg). The flask was placed under dry nitrogen for 2 hours after which dry chloroform (5 ml) was introduced into the flask using a nitrogen purged hypodermic syringe. The reaction was then left to run for 12 hours with constant stirring. At the end of the reaction, the product was obtained by filtration and it was purified by sequential
precipitation from hexanes and methanol, and isolated by centrifugation. The reaction schematic is found in Scheme 15.

Scheme 15: Schematic of DNP functionalization of P3OT-b-PHEMA.

2.4 Polymer Processing

2.4.1 Polymer Thin Film Formation

The copolymer (1 mg) was dissolved in chloroform (1 ml) and drop-cast onto a silicon wafer substrate and dried under ambient conditions to form the polymer film.

2.4.2 Biofunctional Property Studies

The polymer film’s interaction with IgE was investigated by incubating the films in a solution of fluorescently tagged anti-DNP IgE in 1% phosphate buffered saline, PBS, for
one hour. It was then rinsed copiously with PBS buffer solution three times and then imaged using a Zeiss Axiovert 200M Fluorescence/Live Cell Imaging Microscope.

2.5 Characterization/Instrumentation methods

2.5.1 Nuclear Magnetic Resonance, NMR

$^1$NMR and $^{13}$C NMR spectra were recorded on Bruker AVANCE III 500 MHz and Bruker AVANCE 400 MHz NMR spectrometers in deuterated chloroform, CDCl$_3$ and dimethyl sulfoxide, DMSO-d respectively. The CDCl$_3$ contained 0.05% v/v tetramethylsilane, TMS, as internal standard while DMSO contained 0.03% v/v TMS. All chemical shifts were referenced to TMS.

2.5.2 Ultraviolet-visible (Uv-vis) Spectroscopy

UV-Vis absorption spectra were measured with a Varian Cary 500 Scan UV-Vis-NIR Spectrophotometer. Stock solutions of polymer samples (1 mg/ 5 ml) were made from spectrophotometric grade chloroform, purchased from Aldrich chemicals.

2.5.3 Fourier Transform Infra Red (FTIR) Spectroscopy

FTIR spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer using sample pellets obtained by pressing polymer samples with KBr.

2.5.4 Differential Scanning Calorimetry

Thermal analysis was done with TA Instrument Q2000 Differential Scanning Calorimeter at a heating rate of 10$^\circ$C/min.

2.5.5 Dynamic Light Scattering, DLS

Light Scattering analysis was carried out with the DynaPro Nanostar from Wyatt Technology at 25$^\circ$C and samples were prepared in HPLC grade chloroform. Prior to use,
the samples were filtered with 0.10 µm Whatman syringe filters. Analysis was done in a quartz cell.

2.5.6 Scanning Electron Microscopy

Agilent Technologies 8500 Field Effect-Scanning Electron Microscope was also used for morphology characterization of the thin films.

2.5.7 Cyclic Voltammetry

The electronic characteristics of the polymers were investigated via cyclic voltammetry with the PARSTAT 2263 Advanced Electrochemical System from Princeton Applied Research in 1 mg/ml of sample in acetonitrile under a nitrogen sealed atmosphere at ambient temperatures. Reference electrode was Ag, AgCl/NaCl saturated. Scanning rate of 50mV/s was used.

2.6 Results and Discussion

Nuclear Magnetic Resonance Spectroscopy

Copolymerization of regioregular poly(3-alkylthiophenes) with vinyl polymers is a way of improving the processability of the vinyl polymers. A method of synthesis, especially with methacrylate polymers that are not easily soluble is to copolymerize them readily soluble polythiophene with long alkyl side chains. This can be achieved by first polymerizing the thiophene block by Grignard metathesis (GRIM) reaction and modifying the end groups to yield a species (such as haloester) that will readily react with the vinyl monomer by acting as a macroinitiator to form copolymers.

This has been done by preparing regioregular poly (3-decylthiophene) via GRIM reaction and this was followed by magnesium-halogen exchange reaction with a Grignard reagent to obtain a proton capped polymer. Formation of this H-capped polymer was
confirmed by $^1$H NMR and the polymer subsequently went through a series of end group modifications until it was finally converted to a bromoester end-capped macroinitiator. ATRP of 2-HEMA was carried out with the P3DT-macroinitiator, Cu catalyst and PMDETA ligand to yield the block copolymers. Functionalization of the block copolymers with N-2,4-DNP-e-amino caproic acid resulted in the DNP functionalized block copolymers. The degree of functionalization estimated from $^1$H NMR data indicated the copolymers was 50%.

Figure 2.5 is the $^1$H NMR spectrum of the formation of the bromoester terminated poly (3-decylthiophene) and Figure 2.6 is the $^1$H NMR spectrum of the DNP-functionalized poly(2-hydroxyl ethyl methacrylate)-b-poly(3-decylthiophene). Both spectra show the peak assignments.
Figure 2.5: 500 MHz $^1$H NMR spectrum of bromoester functionalized P3DT.
Figure 2.6: 500 MHz $^1$H NMR spectrum of DNP functionalized P3DT-b-PHEMA.

**FTIR Spectroscopy**

The infrared spectra for the copolymers (blue) and the DNP-functionalized (red) co-polymers are shown in Figure 2.7. The aliphatic C-H stretching for the P3DT block appears at $\sim 1500$ cm$^{-1}$. The methyl rock, also for P3DT appears at $\sim 600$ cm$^{-1}$ while the aromatic C-H out of plane is found at $\sim 800$ cm$^{-1}$. The C-S bending frequency can be found at $\sim 1700$ cm$^{-1}$. The moderately broad but very intense peak with shoulders between $\sim 1000 - 1300$ cm$^{-1}$ belongs to the -C-O-C – in PHEMA.$^6$8

The symmetric stretching for the -NO$_2$ is found at $\sim 1320$ cm$^{-1}$ for DNP. The aromatic C-H stretching frequencies for P3DT can be seen at $\sim 2800$, 2900 and 2920
cm\(^{-1}\). The sharp peak seen at ~ 1710 cm\(^{-1}\) belongs to carbonyl (C=O) absorption band on PHEMA. The broad band in the triblock co-polymers from ~ 3000 to 3700 cm\(^{-1}\) corresponds to the OH vibrations of the side groups in the PHEMA block. After the block co-polymers were functionalized with DNP-\(\varepsilon\)-amino-\(n\)-caproic acid, the OH peak for PHEMA disappeared, thus confirming its replacement with the DNP functional group.

![FTIR spectra](image)

**Figure 2.7:** FTIR spectra of DNP functionalized PHEMA-b-P3DT and PHEMA-b-P3DT.

**Raman Spectroscopy**

The Raman spectrum for the DNP-functionalized copolymer is found in Figure 2.8. The sharp and intense peak at ~ 500 cm\(^{-1}\) is attributed to the C-C aliphatic chain vibrations on the P3DT blocks. The medium peak found at ~ 950 cm\(^{-1}\) is the C-O-C symmetric vibration while that seen at ~ 1150 cm\(^{-1}\) is assigned to the asymmetric vibration of the same group. Delta 1380 cm\(^{-1}\) is attributed to the CH\(_3\) and delta at 1450 to
1500 cm\(^{-1}\) are for CH\(_2\) and asymmetric CH\(_3\). The C-NO\(_2\) asymmetric peak is between 1340 to 1380 cm\(^{-1}\).\(^{70}\)

![Raman spectrum](image)

Figure 2.8: Raman spectrum of the IgE bound, DNP-PHEMA-b-P3DT copolymers.

**Uv-vis Spectroscopy**

Ultraviolet-visible spectroscopy deals with the electronic transitions of molecules when they absorb or reflect in the ultraviolet-visible spectral region of the electromagnetic spectrum. Uv-vis spectroscopy is based on the Beer Lambert's law which states that the absorbance of a solution is dependent on the concentration of the absorbing species in the solution as well as the path length. Samples of regioregular P3DT homopolymer, copolymers and the DNP- functionalized copolymers were dissolved in chloroform and analyzed by Uv-vis spectroscopy. Figures 2.9 and 2.10 are the Uv-vis spectra of poly (3-decylthiophene) and the PHEMA copolymers. The
homopolymer, poly(3-decylthiophene) shows maximum absorption, $\lambda_{\text{max}}$, at ~ 460 nm (Figure 2.9), while the copolymers have $\lambda_{\text{max}}$ at ~ 445 nm (Figure 2.10).

Figure 2.9: Uv-vis spectrum of regioregular P3DT in chloroform
Figure 2.10: Uv-vis spectrum of the block copolymer PHEMA-b-P3DT with maximum absorption at \(~ 445\) nm

Figure 2.11 is the UV-Vis spectrum of the block copolymers showing the maximum absorption at a wavelength of \(~ 450\) nm which is typical of P3ATs. The \(\lambda_{\text{max}}\) experienced a slight shift to 450 nm from 445 nm for the non-functionalized polymers which corresponds to a bathochromic shift. The shoulder seen just before the maximum absorption is attributed to the DNP functional group present in the block copolymers. This is a confirmation that the polymers are indeed functionalized with the intended DNP groups.
Figure 2.11: Uv-vis spectrum of DNP functionalized block copoly PHEMA-b-P3DT with λ_{max} at ~ 450 nm and a shoulder at ~ 360 nm

**Cyclic Voltammetry**

Cyclic voltammetry, C-V, is the electrochemical measurement of a species in solution. C-V occurs by cycling the potential of a working electrode and measuring the corresponding current. It is pertinent that for cyclic voltammetry to be of use, the species being analyzed has to be redox active within the experimental potential range. Figure 2.12 is the cyclic voltammogram of regioregular poly(3-decylthiophene) dissolved in acetonitrile traced at a scanning rate of 50 mV/s. The species is redox active, as expected for polythiophenes. The oxidation peak for the homopolymer (very broad) is seen at a higher potential of ~ 0.75 V, while its reduction peak shows up ~ -0.5 V.
In Figure 2.13, the copolymer is seen to cycle up to 1.0 V, just like the homopolymer in Figure 2.12. However, there is a very broad oxidation peak seen at ~ 0.25 V while the reduction peak, not so broad is seen at ~ -0.20 V. This redox couple can be ascribed to the oxidation of the PHEMA species.
In the DNP functionalized copolymers (Figure 2.14), cycling is seen up to 1.0 V, just as observed previously for the homopolymer and copolymers. Just as observed in the homopolymer, there's a very broad peak assigned to the oxidation of the copolymers at ~ 0.75 V. Its reduction peak however shows up at a potential of ~ 0.15 V which is of course higher than the reduction peaks of the homopolymer and non-functionalized copolymers. This big difference, is caused by the presence of DNP groups in the copolymers. This type of shift in peak potential, has been reported in literature in a polythiophene bearing a nitrobenzene group.\(^\text{71}\) All the polymers were found to be redox active.

![Cyclic voltammogram of DNP functionalized PHEMA-b-P3DT in acetonitrile](image)

After functionalization, the redox active DNP groups were seen to be present (as indicated by the C-V curve, Figure 2.14) and the polythiophene backbone also remained intact. Additionally, the presence of the DNP functional groups in the block copolymers was also confirmed by spectroscopic analysis. In the FTIR spectrum, the broad peak belonging to the hydroxyl group in PHEMA was no longer there, after functionalization.
In the Uv-vis spectrum, the presence of the DNP functional groups is characterized by the presence of a shoulder peak at a wavelength of \( \sim 360 \text{ nm} \).

**Differential Scanning Calorimetry**

Differential scanning calorimetry, DSC, is a thermal analytical technique which measures the amount of heat required to raise the temperature of a sample relative to a reference, as a function of temperature. Information about physical transformations (or phase transitions) that transpire in a material as it is heated or cooled to a certain temperature is given in a DSC experimental scan. Parameters such as glass transitions and heat capacity can be measured by this thermal technique and it has gained ground in the industry as a quality control tool to determine material purity and investigation of curing in polymers.

Figure 2.15 is the DSC scan of P3DT-b-PHEMA copolymers. Two endotherms are observed. The endotherm, a sharp peak at \( \sim 172\text{°C} \) is assigned to the melting of the PHEMA block, while the small broad peak at \( \sim 257\text{°C} \) is assigned to the thiophene block. This is consistent with the thiophene ring melting temperature seen in the thermogram of the homopolymer, below. No crystallization was seen in the copolymers. The glass transition was not very obvious. It is appears at about 50°C slowly leveling out till the onset of melting of the PHEMA block. The two endotherms observed, confirm the formation of the diblock copolymers.
Figure 2.15: Thermogram of heat-cool-heat, DSC analysis on P3DT-b-PHEMA showing melting endotherm peaking at ~ 172°C

The DSC scan for regioregular poly(3-decylthiophene), Figure 2.16 is seen to show multiple transitions upon heating due to its semi-crystalline nature. In this analysis, the first heating cycle shows a second order transition at ~ 43°C and this is assigned to the glass temperature of the polymer. The small, broad endotherm observed right after the T_g is due to the disordering of the alkyl side chain, which corresponds to its melting temperature observed in the endotherm at ~ 79°C. The higher temperature endotherm at ~ 260°C is the main thiophene ring melting temperature. There is no obvious cold crystallization exotherm that appears in thermogram. The second heating cycle also displays the T_g of the polymer and there is no distinct endotherm that indicates melting.
The DNP functionalized polymers in the thermogram (Figure 2.17) show an endotherm at 184°C, which is just slightly higher than the \( T_m \) seen in the non-functionalized copolymers for the PHEMA block. This is likely due to the presence of DNP groups leading to a more cohesive bond between the two and so, the movement of PHEMA chains, is restricted. This would require more energy to make the PHEMA molecules move. However, there is a slight transition at about 42°C, which corresponds to the \( T_g \) of P3DT, while there is a distinct endotherm at \( \sim 142°C \) which may be the \( T_g \) for the DNP-functionalized PHEMA.
Dynamic Light Scattering

An efficient method of determining the size distribution profile of particles of a polymer in solution is by dynamic light scattering, DLS. It is also used to determine molar mass, among other functions. The average hydrodynamic radius for the homopolymer, poly(3-decylthiophene), in Figure 2.18 is observed to be about 17 nm. The DLS trace also shows a clear bimodal distribution where a small fraction of the P3DT particles have an average radius of ~ 2.5 nm. The estimated molecular weight, $M_w$, by light scattering for the homopolymer is ~ 47 kDa.
Figure 2.18: Dynamic Light Scattering of regioregular P3DT in chloroform

In Figure 2.19, a similar observation to Figure 2.18 is seen where there is a bimodal distribution of the particle radii with the small fraction having average radius of ~2.5 nm, while the majority of the copolymer particles have an average hydrodynamic radius of ~18.6 nm. Hence, the block copolymers of P3DT-b-PHEMA, have an average size of 36 nm in diameter and estimated molecular weight, $M_w$ of 130 kDa.

Figure 2.19: DLS of P3DT-b-PHEMA copolymers in chloroform
Scanning Electron Microscopy

The morphology of the copolymer film as observed by SEM shows a rough surface with pores spread all over (Figure 2.20). This is expected because of the nature of the PHEMA block as it is jelly like. The appearance of the film is comparable with the report of Senthilkumar et al. 80

![Image of Scanning electron micrograph of P3DT-b-PHEMA-DNP drop-cast from a DMSO solution of the polymers. (X5800)](image)

Figure 2.20: Scanning electron micrograph of P3DT-b-PHEMA-DNP drop-cast from a DMSO solution of the polymers. (X5800)

Biofunctionality Studies

The IgE antibody binds onto specific antigens through the FceRI receptors present. These receptors recognize certain moieties to which they are active and when
present, they become attracted and therefore bind to them. In this study, the IgE used was produced against the DNP- group and so, the DNPs on the polymer chains were recognized and binding occurred. Figure 2.21 shows the fluorescence microscope image of IgE bound film of DNP functionalized PHEMA-b-P3DT co-polymers. Here, specific binding of IgE to the DNP groups can be inferred as not all the surface of the film show fluorescence.

![Fluorescence micrograph of a film of PHEMA- b-P3DT functionalized with DNP groups after incubation in FITC-IgE](image)

**Figure 2.21:** Fluorescence micrograph of a film of PHEMA- b-P3DT functionalized with DNP groups after incubation in FITC-IgE

### 2.7 Conclusion

The synthesis of copolymers of poly(3-decylthiophene), P3DT and poly(2-hydroxy ethyl methacrylate), PHEMA decorated with pendant DNP groups on the PHEMA block was successfully done and subsequently characterized. The copolymers
showed the expected trend in the thermal analysis of block copolymers as well as interesting electrochemical features, one of which is the redox potential of the DNP functionalized polymers being shifted away from those of the homopolymer and copolymers. Incubation of the copolymers in IgE for an hour followed by washing with phosphate buffered saline solution and observation under the fluorescence microscope indicated the binding specificity of IgE with the functional copolymers through its FcεRI receptors. These electroactive polymers have great potential as biosensors and diagnostic agents.
CHAPTER 3

COPOLYMERIZATION OF 3-OCTYLTHIOPHENE, 3-DIETHYLENE GLYCOL
MONOMETHYL ETHER THIOPHENE AND 3-METHYLTHIOPHENE

3.1 Abstract

Copolymers of P3ATs, whether block or random copolymers are very versatile polymers and they possess desirable characteristics which enable them to be used in a wide array of electronic and optical devices as well as sensors. They have the ability to carry electrons which is due to the nature of the conjugated carbon-carbon backbone. We have prepared a series of block copolymers and random copolymers of all conjugated poly (3-alkylthiophenones) with non-polar (diethylene glycol monomethyl ether) and polar (alkyl) substituents at the 3-position respectively. The polymerization was carried out by the nickel-catalyzed Grignard metathesis reaction. $^1$H NMR analysis showed that the block copolymers were well defined, with distinct domains.

Thermal analysis was carried out using DSC and from the 3:1 block copolymers, it was observed that the polymers were crystalline to a great extent from the cold crystallization exotherm observed. Cyclic voltammetry measurements indicate redox active species and from light scattering plots, it was observed that the hydrodynamic radii of the copolymers became smaller with decreasing P3DEGT content. AFM image of the drop-cast film of the 1:1:2 P3OT-b-P3DEGT-P3MT triblock copolymers revealed self-organization into crystalline nanostructures, triangular in shape.
3.2 Experimental

Materials

A. Monomers

1) 3-Octylthiophene, Aldrich, 97%

2) 3-Thiophenemethanol, Aldrich 99%

B. Catalyst

1) [1,3-bis(diphenylphosphino)propane]-dichloronickel (II), Aldrich, 99%

C. Solvents

1) Tetrahydrofuran, Aldrich, 99%

2) N, N-Dimethylformamide, Aldrich ,99.8%

3) Dichloromethane, Aldrich, 99.5%

4) Chloroform, Aldrich, 99.5%

5) Hexane, Aldrich, 95%

6) Methanol, Aldrich, 99.8%

7) Diethyl ether, Aldrich, 98%

D. Grignard Reagents

1) Methyl magnesiumbromide solution (3.0M in diethyl ether ), Aldrich

2) Ethyl magnesium bromide solution (3.0M in diethyl ether), Aldrich

3) tert-butyl magnesium chloride solution (2.0M in diethyl ether), Aldrich

E. Other

1) N-Bromosuccinimide (NBS), Aldrich, 99%

2) Diethylene glycol monomethyl ether (DEGMME), Fluka, 99%
3) Phosphorous tribromide, Aldrich, 99%
4) Sodium hydride (dry), Aldrich, 95%
5) Calcium hydride, Aldrich, 99.99%
6) Calcium chloride, Aldrich, 99.99%
7) Magnesium sulfate (anhydrous), Sigma-Aldrich, 99%
8) Sodium bicarbonate, Sigma-Aldrich, 99.7%
9) Sodium sulfate (anhydrous), Sigma-Aldrich, 99%
10) Chromatographic silica gel – Fisher Scientific
11) Double- tipped needle, gauge 20, L 24 in
12) Silicon wafer, 720200, Silicon Quest International

F. Instrumentation

1) Bruker AVANCE III 500 MHz Spectrometer
2) Perkins-Elmer Spectrum 65 FT-IR Spectrometer
3) Varian Cary 500 UV-Vis-NIR Spectrophotometer
4) Zeiss Optical Microscope
5) Veeco Atomic Force Microscope
6) Agilent Field Effect Scanning Electron Microscope
7) DynaPro Nanostar Dynamic Light Scattering
8) TA Instruments Q1000 DSC
9) Parstat 2263 Advanced Electrochemical System
10) Lab UV lamp
Solvent Conditions

1) THF was distilled from sodium/benzophenone ketyl, prior to use under pre-purified nitrogen.

2) DMF was dried overnight with 4 Å activated molecular sieves, decanted and distilled under reduced pressure via a “Cow” adapter. It was then stored over 4 Å activated molecular sieves.

3) 1,2- dichloromethane was dried overnight with calcium hydride. It was then refluxed and distilled over 4 Å activated molecular sieves.

4) Chloroform was dried overnight with Calcium chloride. It was then distilled over 4 Å activated molecular sieves.

3.2.1 Purification of N-bromosuccinimide, NBS

NBS was recrystallization from hot water. The succinimide was placed in an Erlenmeyer flask and boiling water was added. In order to dissolve it completely, it was placed in a boiling water bath until complete dissolution was achieved. Since the target crystal color was white and the solution of NBS in hot water was white, a decolorization agent in the form of activated charcoal (small amount) was added to the hot solution and filtered through a filter paper. This removed the yellow color and the clear solution was heated slightly again, taken out of the water bath and set aside for the crystals to form undisturbed.

3.2.2 Synthesis of 2,5-dibromo-3-octylthiophene

The monomer, 2,5-dibromo-3-octylthiophene was synthesized according to the method of Iraqi et al. A solution of NBS (5.34g, 30 mmol) in DMF (100ml) placed in a pressure equalization addition funnel was added drop-wise in the dark and at -20°C,
over a period of one hour to a solution of 3-octylthiophene (2.76 g, 14 mmol) dissolved in DMF (100 ml) in a 250 ml round bottom flask under a blanket of nitrogen. When the addition of NBS was completed, the mixture was left to stir at room temperature overnight after which it was poured over 600 ml of distilled water. This was followed by extraction with 3x 100 ml dichloromethane after which the organic phases were combined and subsequently washed with 5x 100 ml water. The washing was followed by drying over magnesium sulfate. The solvent was evaporated in vacuo to dryness, leaving behind the product as yellow oil (3.9 g, 80% yield). The monomer was then purified by distillation at reduced pressure. $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 0.91, 0.93, 0.94, 1.27-1.7 (12 H), 2.66, 2.68, 6.98. $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ (ppm): 14.10, 22.66, 28.23, 29.03, 29.19, 29.33, 29.40, 31.72, 107.92, 110.30, 130.96, 143.00

Scheme 1: Dibromination of 3-octylthiophene with NBS

3.2.3 Synthesis of 2,5-dibromo-3-thiophenemethanol

Using the same method described above, 2,5-dibromo-3-thiophenemethanol was prepared by the reaction of 3-thiophenemethanol (5 g, 44 mmol) with NBS (16 g, 90 mmol) under similar conditions to 2,5-dibromo-3-octylthiophene. A pale yellow liquid was obtained. Yield 10.9 g (91%) $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 4.57, 6.94. $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ (ppm): 59.09, 109.11, 111.41, 130.53, 141.49.
Scheme 2: Dibromination of 3-thiophenemethanol using NBS in DMF

\[
\begin{align*}
\text{3-thiophenemethanol} & \quad \text{N-bromosuccinimide} & \quad \text{2,5-dibromo-3-thiophenemethanol} \\
\text{Br} & \quad \text{Br} & \quad \text{Br} \\
\end{align*}
\]

3.2.4 Synthesis of 2,5-dibromo-3-bromomethylthiophene

This synthesis was carried out according to the procedure of Tan et al\(^8\) with slight modification. 2,5-dibromo-3-thiophenemethanol (8.65g, 3.11 x 10\(^{-2}\) mol) was added to a 250ml round bottom flask equipped with a nitrogen inlet and bubbler. To this flask was added 100ml, dry dichloromethane and the flask was sealed under a nitrogen atmosphere. It was then placed in an ice water bath and allowed to stir for 20 minutes after which phosphorous tribromide (3.3 ml (3.5 x 10\(^{-2}\) mol) was added drop wise to the solution via a hypodermic syringe, over a period of 15 minutes. The reaction was then allowed to stir at room temperature overnight and quenched with a 10% solution of bicarbonate of soda. The resulting mixture was transferred to a separation funnel and the organic phase was filtered through a plug of celite followed by rinsing with water and finally drying over magnesium sulfate. The drying agent was filtered off and the solution was dried in vacuo to remove residual solvent and the product was a light yellow liquid. Yield 7.68g, 74%.

\(^1\)H NMR (CDCl\(_3\), TMS) \(\delta\) (ppm): 4.34, 6.99. \(^{13}\)C NMR (CDCl\(_3\), TMS) \(\delta\) (ppm): 24.77, 111.55, 111.92, 130.69, 137.61.
Scheme 3: Synthesis of 2,5-dibromo-3-bromomethylthiophene

\[
\text{Br} \quad \text{O} \quad \text{Br} \quad \text{Br} \quad \text{S} \quad \text{Br} \quad \text{Br}
\] \quad \text{PBr}_3 \quad \xrightarrow{\text{CH}_2\text{Cl}_2} \quad \text{Br} \quad \text{Br}
\]

2,5-dibromo-3-thiophenemethanol \quad 2,5-dibromo-3-bromomethylthiophene

3.2.5 Synthesis of 2,5-dibromo-3-{2-(2-methoxyethoxy)ethoxymethyl} thiophene

2,5-dibromo-3-bromomethyl thiophene was functionalized at the 3- position with diethylene glycol monomethyl ether according to the McCullough method,\textsuperscript{83} with slight variation. Firstly, 2,5-dibromo-3-bromomethyl thiophene (8.04 g, 24 mmol) dissolved in THF (25 ml) was placed in a pressure equalizing addition funnel and sealed with a septum. This was then fitted onto a 250 ml 3-necked flask equipped with nitrogen inlet and bubbler. Diethylene glycol monomethyl ether (3g, 24.9 mmol) and THF(100 ml) were added to the flask using hypodermic syringes. An equimolar amount of sodium hydride (0.67 g, 28 mmol) is required, but was added in slight excess to the reaction flask in small portions. Hydrogen gas evolved as evidenced by the effervescence observed and a gentle flow of nitrogen gas was let into the reaction vessel. The solution appeared cloudy.

The contents of the addition funnel were added drop-wise to the reaction vessel over a 20 minute period at room temperature. The solution then changed to a yellowish color as the thiophene solution was slowly added and eventually became pale colored by the time the thiophene solution was completely added. The reaction was then left to stir overnight after which the mixture was passed through a plug of celite. THF was removed
by rotary evaporation to yield the crude product which was purified by column chromatography using silica gel and a 70:30 mixture of hexane:ethyl acetate as eluant. The UV active spots, observed under a 254nm UV lamp were collected and concentrated with the rotavap to yield the compound, diethylene glycol monomethyl ether thiophene, as a yellow oil. Yield 7.4 g, 83%. $^1$H NMR (CDCl$_3$, TMS) $\delta$ (ppm): 3.37 (s, 3 H), 3.54-3.77 (8 H), 4.4 (s, 2H), 6.99.

Scheme 4: Synthesis of 2,5-dibromo-3-diethylene glycol thiophene monomethyl ether

Poly(3-diethyleneglycol monomethyl ether) thiophene was prepared by adding the monomer (0.36 g, 3 mmol) and THF (20 ml) to a 50 ml, 3-neck round bottom flask equipped with a nitrogen inlet and bubbler, reflux condenser with calcium chloride drying tube and a pressure equalizing addition funnel. [1,3-bis(diphenylphosphino)-
propane]-dichloronickel (II) (27.5 mg, 0.051 mmol), dissolved in THF (5 ml) was placed in the addition funnel, prior to fitting onto the 3-necked flask. Tert-Butyl magnesium chloride (2 ml, 4 mmol) was added in slight excess to the reaction via a hypodermic syringe, while maintaining a temperature of 0°C. Stirring was done for 30 min at 0°C after which the reaction was gradually heated to reflux for 2 hours. The catalyst in the addition funnel was added and reflux continued for 5 hours. The reaction was then terminated by precipitation into methanol. The polymer was isolated by centrifugation and subsequently purified by Soxhlet extractions in methanol and hexanes to give the title polymer, which was deep purple in color. Yield 0.132 g.

Scheme 5: Homopolymerization of 3-diethylene glycol monomethyl ether thiophene

![Diagram](image)

2,5-dibromo-3-diethylene glycol monomethyl ether thiophene

poly(3-diethylene glycol monomethyl ether thiophene-2,5-diyl), P(3DEG)T

3.2.7 Homopolymerization of 2,5-dibromo-3-octylthiophene

The glassware set up for this polymerization was the same as described above for P(3DEG)T. The reaction conditions are also the same. The monomer, 2,5-dibromo-3-
octylthiophene (2g, 5.6 mmol) was dissolved in THF (50 ml) and t-butyl magnesium chloride (3 ml, 6 mmol) was added in excess via a hypodermic syringe. Nickel catalyst (33 mg, 0.056 mmol) was added and reaction was terminated in methanol and worked up as for P(3DEG)T. Yield 0.52g. (Scheme 6) The contents of the reaction vessel appeared yellow in color at the beginning of the reaction while the color changed to orange, upon completion of the reaction.

Scheme 6: Polymerization of 2,5-dibromo-3-octylthiophene

2,5-dibromo-3-octylthiophene

poly(3-octylthiophene-2,5-diyl)

3.2.8 Synthesis of poly(3-octylthiophene)-block-poly(3-diethylene glycol thiophene), P3OT-b-P3DEGT copolymers.

This synthesis was carried out with the guidance of the report by Lee et al\textsuperscript{84} as well as that of Zhang et al.\textsuperscript{85} with some modifications. These procedures serve as references in the synthesis of subsequent P3ATs (both block and random) unless otherwise stated. The synthesis of the block co-polymers involved the preparation of the Grignard inter-mediates of each monomer. The poly(3-octylthiophene) block was then polymerized with the total quantity of nickel catalyst required for both, added into the 3-OT reaction flask. The diethylene glycol intermediate was added to the P3OT vessel by cannula transfer and the reaction was allowed to stir under reflux for 5 hours. The glassware required and set up were the same as those used for the homopolymerization.
The P3OT block was made by reacting the monomer (0.5 g, 1.4 x 10^{-3} mol) with ethyl magnesium bromide initiator (0.19 g, 1.4 x 10^{-3} mol) in dry THF (25 ml).

The combined nickel catalyst (0.0148 g, 2.74 x 10^{-5} mol) was added as at when appropriate in one portion to the P3OT pot. The 3-DEGT intermediate was prepared by reacting the monomer (0.5 g, 1.336 x 10^{-3} mol) with ethyl magnesium bromide initiator (0.18 g, 1.336 x 10^{-3} mol) in dry THF (20 ml). The flask was refluxed for about an hour and thereafter, the contents were transferred by cannula, to the already polymerized thiophene block (P3OT) as stated earlier. The reaction was terminated by precipitation in methanol. This was followed by Soxhlet extraction in methanol, hexanes and finally chloroform. The chloroform fraction was transferred to a rotavap and the 1:1 block copolymers, P3OT-b-P3DEGT were recovered as purple solid. The reaction scheme for the block polymerization is shown in Scheme 7.

3.2.9 Synthesis of 2:1 P3OT-b-P3DEGT block copolymers

The procedure used in the previous paragraph for the polymerization of 1:1 block copolymers was used in 2:1 ratio of copolymers. However, the quantity of monomers used was different. The mass of 3-octylthiophene (3-OT) monomer used was double that of the 3-diethylene glycol monomethyl ether (3-DEGT). 3-OT (0.5 g, 1.4 x 10^{-3} mol) was reacted with 3-DEGT (0.25 g, 6.68 x 10^{-4} mol). The initiator, EtMgBr used for 3-OT polymerization was 0.19 g (1.4 x 10^{-3} mol) while the quantity used for 3-DEGT was 90 mg (6.68 x 10^{-4} mol).
Scheme 7: Schematic of polymerization of poly(3-OT)-b-poly(3-DEG)T block copolymers

For the 3-OT block, 11.5 mg ($2.12 \times 10^{-5}$ mol) of the nickel catalyst was required and the amount of catalyst for the 3-DEGT block was 0.4 mg ($7.0 \times 10^{-6}$ mol). The catalyst required for both was added to the 3-OT vessel in one portion. The volume of THF used for polymerization was 25 ml for 3-OT and 20 ml for 3-DEGT. The 3-DEGT intermediate was added to the polymerized 3-OT reactor by cannula transfer and reaction was allowed to stir for 5 hours under reflux.
3.2.10 Synthesis of 3:1 P3OT-b-P3DEGT block copolymers

From the ratio of the block, three times the mass of 3-DEGT was used in the 3-OT polymerization. 3-OT (0.75 g, 2.12 x 10^-3 mol) requiring equimolar (2.12 x 10^-3 mol) quantity of initiator, EtMgBr (0.28 g) were reacted together and nickel catalyst (11.5 mg, 2.12 x 10^-5 mol) was added at the appropriate time. For the 3-DEGT block, 0.25 g (6.68 x 10^-4 mol) of this was reacted with 90 mg (6.68 x 10^-4 mol) initiator. The amount of catalyst required was 4 mg (7.0 x 10^-6 mol) and it was combined with the catalyst for 3-OT and added in one portion as done for the 2:1 ratio, to the 3-OT reactor.

3.2.11 Synthesis of 1:1:2 P3OT-b-P3DEGT-b-P3MT block copolymers

The reaction was carried out initially in a separate 3-necked flask for each monomer. Starting with 3-OT, 0.30 g (0.85 mmol) was placed in a flask equipped with a stir bar, reflux condenser, calcium chloride drying tube, nitrogen inlet, bubbler and sealed with a septum. Dry THF (10 ml) was injected into the flask using a hypodermic syringe. 3M ethyl magnesium bromide (3 ml, 0.85 mmol) was added via a nitrogen purged syringe and the resulting solution was stirred at 0°C for 30 minutes. Meanwhile, 3-DEGT (0.30 g, 0.8 mmol) was placed in a flask with similar equipment as done previously and dry THF (10 ml) was also injected into the flask. 3M ethyl magnesium bromide solution (0.3 ml, 0.8 mmol) was injected into the sealed flask via a nitrogen purged hypodermic syringe and the flask was subsequently stirred at 0°C for 30 minutes.

Into a third flask with similar components was placed 3-methylthiophene (0.61 g, 2.4 mmol), sealed under nitrogen and dry THF (15 ml) was injected via the usual route. Ethyl magnesium bromide (0.8 ml, 2.4 mmol) was also added and the reaction was stirred
at 0°C for 30 minutes. Each flask was gradually warmed up and reflux was carried out for 1 hour. A combined amount of 3-bis(diphenylphosphino)propane-dichloronickel (II) 22 mg was added to the first flask (P3OT block) and gentle reflux continued. The contents of the 3-DEGT flask after the first hour of reflux, was transferred to the 3-OT flask via a cannula and reflux was continued. Then, the contents of the 3-MT flask, was similarly transferred to the one containing the first two monomers being polymerized, by cannula and the reflux was continued for 6 hours. At the end of the reflux, the reaction was terminated by the addition of methanol and it was filtered to obtain the crude copolymer product. The copolymers were then washed in methanol and hexane by sequential Soxhlet extractions and finally in chloroform from which the final copolymers were obtained after rotary evaporation.

3.3 Nanostructure formation

The various polymers were dissolved in chloroform at a concentration of 1 mg/ml and drop cast onto silicon wafers for morphology characterization of the organic thin films formed. The solutions were then air dried under ambient conditions and microscopic techniques were used to study their morphology.

3.4 Characterization

3.4.1 Nuclear Magnetic Resonance (NMR)

$^1$H NMR and $^{13}$C NMR spectra were obtained using Bruker Avance 500 MHz and Bruker Avance 400 MHz NMR spectrometers in deuterated chloroform, CDCl$_3$. Trimethylsiloxane, TMS, was used as internal reference.
3.4.2 Fourier-Transform Infra Red Spectroscopy (FTIR)

Infra Red analysis was carried out on pellets of the samples formed under pressure in anhydrous potassium bromide, KBr, using the Perkin Elmer Spectrum 65 FTIR spectrometer.

3.4.3 Ultraviolet-visible (Uv-vis) Spectroscopy

Uv-vis studies were performed on 1 mg/ml solutions of the polymers dissolved in chloroform. The instrument used for the analyses was the Varian Cary 500 Scan UV-Vis-NIR spectrophotometer with quartz cuvettes of 1 cm optical length.

3.4.4 Dynamic Light Scattering, DLS

Particle size of the polymers was determined by light scattering on Wyatt Technologies’ Dynapro NanoStar Photon Correlation Spectrometer contained in a Quartz cuvette at a concentration of 1 mg/ml.

3.4.5 Differential Scanning Calorimetry, DSC

The glass transition temperatures, T_g and melting temperatures, T_m were determined by differential scanning calorimetry using the TA Q2000 Differential Scanning Calorimeter with Tzero Aluminum Hermetic pans and lids. Heating rate was 10°C/min using the heat-cool-heat method. The glass transitions were measured at the mid-points of heat capacity changes while the melting point temperatures were taken at the maximum of the enthalpy endothermic peaks.

3.4.6 Electrical Measurements

Electronic properties were investigated by cyclic voltammetry carried out on solutions of polymers in chloroform, under a nitrogen atmosphere at room temperature.
The instrument used was the PARSTAT 2263 Advanced Electrochemical System by Princeton Applied Research.

3.5 Morphology Characterization

The morphology of the thin film was characterized by scanning probe and electron microscopy techniques.

3.5.1 Atomic Force Microscopy, AFM

The Veeco Instruments Atomic Force Microscope was used to image the composite films using the non-contact mode.

3.5.2 Scanning Electron Microscopy, SEM

The morphology of the thin films was investigated by observation under the Agilent Technologies 8500 Field Emission Scanning Electron Microscope

3.6 Results and Discussion

Nuclear Magnetic Resonance, NMR

The copolymerization of hydrophobic monomer of 3-octylthiophene with 3-diethylene glycol thiophene, because of its hydrophilic side chain gave rise to new materials with interesting physical properties, basically a mixture of crystalline and amorphous phases.

The structure of the copolymers was determined by NMR. For the 1:1 block (Figure 3.1), the copolymer composition was determined by the integration of the protons on the thiophene rings. The aromatic proton for the poly(3-octylthiophene) block was seen at ~ 2.50 ppm, while that of the poly(3-diethylene glycol monomethyl ether thiophene) block was observed at ~ 4.5 ppm. Integration of these protons results in agreement with the ratio that was targeted at the beginning of the polymerization which was 1:1.
Figure 3.1: 500 MHz $^1$H NMR spectrum of 1:1 diblock P3OT-b-P3DEGT in CDCl$_3$ at room temperature

Similar results were observed for the 3:1 diblock as well as the 1:1:2 triblock copolymers as seen in Figures 3.2 and 3.3. For the 3:1 block copolymers (Figure 3.2), the aromatic proton is observed at $\sim 2.50$ ppm for the P3OT block and at $\sim 4.50$ ppm for the P3DEGT block. The composition of 3:1 ratio was confirmed by the integration of these peaks. The CDCl$_3$ solvent peaks were observed at $\sim 7.25$ ppm in the three proton NMR spectra discussed.
Figure 3.2: 500 MHz $^1$H NMR spectrum of 3:1 diblock P3OT-b-P3DEGT

Figure 3.3: 500 MHz $^1$H NMR spectrum of 1:1:2 block P3OT-b-P3DEGT-b-P3MT in CDCl$_3$
An interesting characteristic observed in the triblock copolymers was the complete solubility in chloroform. It is noteworthy because the homopolymer of 3-methylthiophene is insoluble in common organic solvents, but with the copolymerization, the resulting block copolymers were soluble in chloroform as well as THF. This is being attributed to the influence of the oxygen atoms in the hydrophilic block as well as the long side chain of the 3-octylthiophene block.

**Fourier-Transform Infra Red Spectroscopy, FTIR**

The C=C stretching mode of the thiophene ring is observed at ~ 1450 cm\(^{-1}\) for the three block copolymers (Figure 3.4). This is in agreement with the report of Brustolin.\(^8^6\) The C=C asymmetric stretching, however is seen at ~ 1680 cm\(^{-1}\) for all three block copolymers.\(^8^7\) The area intensity ratio, \(I_{\text{sym}} / I_{\text{asym}}\) of the bands, \((I_{1450} / I_{1680})\), is an indication of the chain length of the co-polymers.\(^8^8\) It can be seen from the spectra that this ratio is highest for the triblock (a), followed by the 3:1 block copolymer (b). The aromatic C-H out of plane vibration for all three block copolymers is seen at about ~ 800 cm\(^{-1}\). This is characteristic of all 2, 3, 5 –tri-substituted thiophene rings.\(^8^9\) The peak for the 1:1 block copolymer is sharp but not as intense as those for the 3:1 block copolymers and the 1:1:2 triblock copolymers. This is attributed to the concentration of the thiophene rings in all three block copolymers.
The triblock copolymers and 3:1 diblock copolymers expectedly, have more intense peaks due to the higher quantity of thiophene than the 1:1 diblock copolymers. Also, the aromatic C-H stretch at ~ 3050 cm\(^{-1}\) is less pronounced in the 1:1 block copolymers whereas, the 3:1 copolymers and the tri-block have sharp peaks at the frequency for the same reason. In the 1:1 block co-polymers, the methoxy functional group for the diethylene glycol is moderately intense, appearing at ~ 1155 cm\(^{-1}\) but in the 3:1 and 1:1:2 block copolymers, the peaks are present but not as intense.\(^90\) The band at 3400 cm\(^{-1}\) for all three copolymers is attributed to the OH functional group (O-H stretching) of water in the KBr used. The peaks at ~ 700 cm\(^{-1}\) and ~ 610 cm\(^{-1}\) are assigned to the C-S bending and C-S-C ring deformation, respectively.\(^91,92\)
Ultraviolet-visible (Uv-vis) Spectroscopy

The Uv-vis spectra of the block copolymers show a slight broadening of peaks ($\lambda_{\text{max}}$ at ~ 440 nm) when compared to the sharp spectrum of pristine poly(3-octylthiophene), Figure 3.5 where $\lambda_{\text{max}}$ at ~ 450 nm. The Uv-vis of poly (3-octylthiophene) obtained is consistent with that of polythiophene solution that shows a strong absorbance around 450 nm due to the $\pi - \pi^*$ transition of the conjugated polymer chain. In Figures 3.6 and 3.7, the diblock copolymers showed absorption in the Uv-visible region at a maximum wavelength of ~ 450 nm, which is typical of dilute solutions of polythiophenes. In the triblock copolymers (Figure 3.8), a moderate broadening of the maximum absorption peak is observed at about the same wavelength (~ 450 nm) as other copolymers.

Figure 3.5: Uv-vis spectrum of poly(3-octylthiophene) with $\lambda_{\text{max}}$ at ~ 450 nm
Figure 3.6: Uv-vis spectrum of 1:1 P3OT-b-P3DEGT showing $\lambda_{\text{max}}$ at 440 nm

Figure 3.7: Uv-vis spectrum of 3:1 P3OT-b-P3DEGT showing $\lambda_{\text{max}}$ at ~ 440 nm
Figure 3.8: Uv-vis spectrum of 1:1:2 P3OT-b-P3DEGT-b-P3MT $\lambda_{\text{max}} \sim 440$ nm

**Dynamic Light Scattering, DLS**

DLS traces of samples performed in chloroform showed a wide variation in the hydrodynamic radii of the block copolymers. Both are characterized by a bi-modal distribution where a small percentage of the particles in the 1:1 block polymer ratio have a hydrodynamic radius of $\sim 4$ nm while the 3:1 block copolymers have a small percentage of particles with average hydrodynamic radius of $\sim 2.5$ nm. The average radii for the 1:1 feed ratio on Figure 3.9 is $\sim 36$ nm while that of the 3:1 feed ratio in Figure 3.10 is 17 nm. The homopolymer of 3-octylthiophene in Figure 3.11, has an average hydrodynamic radius of $\sim 14$ nm.
Figure 3.9: DLS curve of 1:1 P3OT-b-P3DEGT

Figure 3.10: DLS curve of 3:1 P3OT-b-P3DEGT. Average hydrodynamic radius, 17 nm
The higher average hydrodynamic radius for the particles of the 1:1 block copolymers is most likely due to the P3DEGT block as observed by Lee et al. Higher composition of this polymer (1:1) results in a bigger size of its copolymer particles. In the 3:1 copolymers where the fraction of P3OT block was higher, the particles of the copolymers were much smaller. Polymers with specific molecular weights can also be prepared using the GRIM by employing a nickel (dppp or dppe) catalyst, rather than palladium.

**Cyclic Voltammetry**

Electrochemical measurements were carried out on the block copolymers via cyclic voltammetry in chloroform. Initial potential applied was as low as -2 V, while the maximum was slightly over 1 V. The copolymers analyzed showed reversible activities as they went through the charging and discharging cycles completely, indicating their redox characteristics. In the cyclic voltammogram of the 1:1 block copolymers (Figure
3.12), an oxidation potential peak is observed at ~ -0.2 V and the corresponding cathodic current is $2.5 \times 10^{-6}$ Amps, while the reduction potential is observed approximately -1.5 V and at an anodic current of ~ $1.0 \times 10^{-6}$ Amp.

Figure 3.12: Cyclic voltammogram of 1:1 P3OT-b-P3DEGT in chloroform

In the 3:1 block copolymer (Figure 3.13), the oxidation potential broadens out and peaks at ~ 0.2 V, and the corresponding cathodic current is $2.5 \times 10^{-5}$ Amps, which is expected for that block copolymer ratio while its maximum reduction potential is seen at about the same magnitude as the oxidation peak, but at a cathodic current of $-2.5 \times 10^{-5}$ Amps. A symmetrical curve is observed in Figure 3.14 for the homopolymer, P3OT. The complete trace of its charging and discharging cycles, show the material to be redox active.
Figure 3.13: Cyclic voltammogram of 3:1 P3OT-b-P3DEGT in chloroform

Figure 3.14: Cyclic voltammogram of regioregular P3OT in chloroform
Differential Scanning Calorimetry, DSC

The DSC method carried out in the 1:1 block copolymers (Figure 3.15) is heat-cool-heat and the first transition seen at ~ 44°C is the glass transition for the P3OT block as this value lies within the range of Tgs for P3ATs. The onset of melting of the octyl side chain of P3OT block is approximately 58°C, with a maximum at ~75°C. Tg for the P3DEGT block is not observed. However, the small endotherm at ~ 111.7°C whose onset is at ~ 97°C is attributed to the melting of the P3DEGT block. This is then followed by what appears to be two irreversible endotherms which are most likely due to the release of “stresses” built into the sample through processing, handling or thermal history of the material.

The structural change in the molecule is from rigid to flexible and so, it’s able to move to release the stress. This phenomenon is molecular relaxation and not melting.96 This pseudo melting endotherm is also referred to as “Eutectic melt”. The melting of the P3OT block is seen to start at ~ 135°C and peaks at ~ 150°C. The linear nature of the melting peaks for both polymer blocks may be an indication of their purity. No decomposition is observed as the set temperature was only 200°C. The distinct melting points seen is a confirmation of the formation of the block copolymers.
For the 3:1 block copolymers (Figure 3.16), the transitions observed in the first heating cycle are not as distinct as those seen in the 1:1 but with a much closer look, they are seen to be present, though the peaks, for the most part are broadened except for the melting endotherm of the octyl side chain. The $T_g$ of the P3OT block is about the same as in the 1:1 copolymers and the melting point of the side chain ($\sim 75^\circ C$) is also the same. The line broadens at $\sim 120^\circ C$ and $180^\circ C$, which are attributed to the melting crystals of the P3DEGT block and the P3OT block. A new transition is observed in the first heating cycle though and this is an exotherm at $\sim 243^\circ C$. This phenomenon could be decomposition of the materials while it could also be a crystallization of the metastable phase, right before the melting of the stable phase, since it’s followed by what looks like another melting endotherm that was truncated when the maximum set temperature was
reached. Furthermore, the 3:1 block copolymer DSC thermogram gets more interesting as the cooling cycle reveals an exotherm at ~150 °C, closely followed by a hump. The main exotherm is attributed to the cold crystallization of the block copolymers.

![DSC scan, 3:1 P3OT-b-P3DEGT](image)

Figure 3.16: DSC scan, 3:1 P3OT-b-P3DEGT

In the first heating scan done on the tri-block copolymers (Figure 3.17), a T_g is seen at ~48°C. This is immediately followed by a broad endotherm at ~85 °C, possibly due to the melting of the alkyl side chains. The two distinct endotherms at ~155 °C and ~230 °C however, are ascribed to the melting of all three blocks. The symmetrical nature of the two endotherms is an indication of the purity of the block copolymers. the linear nature of the curve shows the purity of the tri-block co-polymers. No cold crystallization endotherm was observed.
Figure 3.17: DSC scan of 1:1:2 triblock copolymers, P3OT-b-P3DEGT-b-P3MT

**Atomic Force Microscopy, AFM**

Observation of the drop-cast film of 1:1:2 triblock copolymers under the atomic force microscope revealed mostly well organized triangular structures as shown in Figure 3.18. The surfaces of these nanostructures had pores scattered all over. Average height is ~ wide. 500 nm, while the base is over 1 μm long. Also present are smaller structures about 25 nm tall and 50 nm wide.
Figure 3.18: Non-contact mode AFM of 1:1:2 triblock copolymer showing self organization into triangular-shaped nanostructures

**Scanning Electron Microscopy, SEM**

The morphology of the films of the diblock copolymers was studied using the scanning electron microscope. The 1:1 block copolymers had a mixed morphology. A grainy appearance was observed in Figure 3.19a, while a level surface with scattered pores and two distinct colors are seen in Figure 3.19b, indicating a phase separation of the block copolymers at the nanoscale. The 3:1 block copolymers (Figure 3.20) showed mostly a network of interconnected fibrillar structures.
Figure 3.19: SEM micrographs of 1:1 P3OT-b-PDEGT film showing its honeycomb like surface in (a) and phase separated, porous surface in (b) (X3200)

Figure 3.20: SEM of 3:1 block copolymer P3OT-b-P3DEGT showing the sponge-like surface (X1600)
CHAPTER 4

RANDOM COPOLYMERIZATION OF 3-OCTYLTHIOPHENE, 3-DIETHYLENE GLYCOL MONOMETHYL ETHER THIOPHENE AND 3-METHYL THIOPHENE

All conjugated random AB copolymers and random ABC copolymers of 3-alkylthiophenes were polymerized using the Grignard metathesis reaction method. 3-octyl-thiophene and 3-diethylene glycol mono methyl ether thiophene were co-polymerized to form AB random copolymers while a third monomer, 3-methylthiophene was added to form the ABC random copolymers. The method used was also the GRIM method with slight modification.

4.1 Experimental

Materials

A. Monomers

1) 3-Octylthiophene, Aldrich, 97%
2) 3-Thiophenemethanol, Aldrich 99%

B. Catalyst

1) [1,3-bis(diphenylphosphino)propane]-dichloronickel (II), Aldrich, 99%

C. Solvents

1) Tetrahydrofuran, Aldrich, 99%
2) N, N-Dimethylformamide, Aldrich ,99.8%
3) Dichloromethane, Aldrich, 99.5%
4) Chloroform, Aldrich, 99.5%
5) Hexane, Aldrich, 95%
6) Methanol, Aldrich, 99.8%
7) Diethyl ether, Aldrich, 98%

D. Grignard Reagent

Ethyl magnesium bromide solution (3.0M in diethyl ether), Aldrich

E. Other

1) N-Bromosuccinimide (NBS), Aldrich, 99%
2) Diethylene glycol monomethyl ether (DEGMME), Fluka, 99%
3) Phosphorous tribromide, Aldrich, 99%
4) Sodium hydride (dry), Aldrich, 95%
5) Calcium hydride, Aldrich, 99.99%
6) Calcium chloride, Aldrich, 99.99%
7) Magnesium sulfate (anhydrous), Sigma-Aldrich, 99%
8) Sodium bicarbonate, Sigma-Aldrich, 99.7%
9) Sodium sulfate (anhydrous), Sigma-Aldrich, 99%
10) Potassium hydroxide, Sigma-Aldrich, > 85%
11) Whatman pH Paper,

4.2 Preparation of monomers

4.2.1 Preparation of 2,5-dibromo-3-octylthiophene

The monomer, 2,5-dibromo-3-octylthiophene was prepared according to the method reported by Iraqi et al. with slight modification. 3-octylthiophene (2.76 g, 14 mmol) was placed in a 250 ml round bottom flask equipped with a pressure equalizing
addition funnel, nitrogen inlet and bubbler. DMF (100 ml) was added and the solution was stirred immediately. A slight excess of NBS (5.34 g, 30 mmol) was previously dissolved in DMF and this mixture was poured into the addition funnel and carefully mounted onto the round bottom flask. The reaction flask was then cooled in an ice water bath and the mixture of NBS was added drop-wise, over a period of one hour in the dark under a gentle flow of nitrogen. At the end of one hour, the cooling was discontinued and the reaction was allowed to stir overnight at room temperature. The contents of the flask was then poured over ice and transferred to a separation funnel. The aqueous layer was removed and extraction was carried out three times with 100 ml diethyl ether. This was followed by rinsing five times with 100 ml distilled water and the monomer was dried over MgSO₄, then, distilled under reduced pressure before use.

4.2.2 Preparation of 2,5-dibromo-3-thiophenemethanol

The dibromination of 3-thiophenemethanol in this procedure was done according to the method of Watanabe et al. 97 3-Thiophenemethanol (4.844 g, 42.4 mmol) was dissolved in dry dichloromethane (80 ml) in a 200 ml flask. NBS (15.10 g, 85 mmol) was slowly added at room temperature over a period of 30 minutes under a blanket of nitrogen with stirring. The reaction vessel was left to stir for 1.5 hours at the end of which 10 % aqueous KOH (80 ml) solution was added and then rinsed with water several times, until the pH was neutral. The organic layer was dried over MgSO₄ and dried in vacuo. The crude product was re-crystallized from hexanes and needle like streaks were observed in the purified monomer. Yield: 6.4642 g.

4.2.3 Preparation of 2,5-dibromo-3-bromomethylthiophene

Into a 250 ml 2-necked flask was dissolved 2,5-dibromo-3-thiophenemethanol (5.015 g,
18 mmol) in dry methylene chloride (100 ml), according to the procedure of Tan et al.\textsuperscript{82}

A pressure equalizing addition funnel containing Phosphorous tribromide (2 ml, 21 mmol) was mounted on the flask and capped with a septum and the system was sealed under a nitrogen atmosphere. The flask was placed in an ice bath and the mixture stirred for 20 minutes. After that, the funnel containing phosphorous tribromide was slowly opened to release a drop at a time of the reagent into the flask over a period of 15 minutes. Then the ice bath was removed and reaction was allowed to continue at room temperature overnight. It was then quenched by the addition of 10% sodium bicarbonate solution and transferred to a separating funnel. The organic layer was filtered through a fine fritted glass funnel, washed several times with water and dried over magnesium sulfate. The residual solvent was evaporated in vacuo to give the product, yellow oil. Yield 6.25g.

4.2.4 Preparation of 2,5-dibromo-3-diethylene glycol monomethyl ether thiophene

This procedure was carried out according to the report of McCullough et al with slight variation.\textsuperscript{83} 2,5-Dibromo-3-bromomethyl thiophene (5.04 g, 42 mmol) was dissolved in THF (15 ml), added to an addition funnel, stoppered with a septum and set aside. Diethylene glycol monomethyl ether (5.16 g, 43 mmol) was dissolved in 100 ml THF in a 250 ml 3-neck flask equipped with a nitrogen inlet and bubbler. The addition funnel containing the thiophene monomer that was previously set aside was mounted into one of the necks of the flask. Sodium hydride (1.11 g, 46 mmol) was added to the flask portion wise and after the evolution of hydrogen had ceased, the flask was sealed under a nitrogen atmosphere. The addition funnel was set to add the thiophene monomer drop-wise into the flask at room temperature, over a period of 15 minutes.
The reaction was stirred overnight after which the mixture was filtered through a fine fritted funnel and the THF was removed by rotary evaporation. The product was purified by column chromatography by eluting over silica gel using a 70:30 mixture of hexane:ethyl acetate. The UV (254 nm) active spots, as observed by TLC were combined and concentrated in vacuo to yield the pure product, yellow oil.

4.3 Polymerization of 2-component random copolymers

4.3.1 Preparation of 1:1 random copolymers

To make 1:1 random copolymers, equimolar amounts of the two monomers were used with equimolar quantities of ethylmagnesium bromide as the initiator. 3-octyl-thiophene (0.354 g, 1 mmol) was placed in a previously oven-dried 3-necked round bottom flask equipped with a reflux condenser, calcium chloride drying tube, nitrogen inlet and bubbler. Then, freshly distilled THF (10 ml) was added to the flask using a nitrogen purged hypodermic syringe and stirring was initiated. 0.374 g (1 mmol) 3-diethylene glycol monomethyl ether thiophene was also injected into the flask using a nitrogen purged hypodermic syringe followed by the addition of ethylmagnesium bromide (~ 0.7 ml, 2 mmol) via a nitrogen purged hypodermic syringe.

The flask was then placed into an ice water bath to bring the temperature down to about 0°C before the Grignard reagent initiator was added. After the addition of the initiator, the reaction was stirred for 30 minutes and was withdrawn from the ice bath to gradually warm up to room temperature. It was then heated to reflux for 1 hour and the catalyst, [1,3-bis(diphenylphosphino)propane]-dichloronickel (II) (11 mg, 0.02 mmol), was carefully added in one portion. The reaction was then stirred under reflux for 7 hours before quenching with dilute HCl. The product was isolated by filtration and successively
washed in methanol and hexanes via Soxhlet extraction to remove unreacted monomers and catalyst. The product was finally dissolved in chloroform and the solvent removed by rotary evaporation to give a deep purple colored solid.

Scheme 1: Synthetic scheme for two-monomer random poly(3OT-co-3DEGT)

4.3.2 Synthesis of 2:1 Random co-polymers

Using the procedure in section 4.3.1, 2:1 random copolymers of 3-octylthiophene and 3-diethylene glycol monomethyl ether thiophene were prepared. 3-Octylthiophene (0.5 g, 1.4 mmol) was reacted with 3-diethylene glycol thiophene (0.25 g, ~0.7 mmol). THF (10 ml) was also used. The combined volume of initiator, ethyl magnesium bromide used was 0.3 ml, 2.3 mmol. The reaction was catalyzed using 1,3-bis[(diphenyl phosphino)- propane]-dichloro nickel (II) (11.2 mg, 2.1 mmol). The same work up was carried out as done previously (in 1:1 random copolymers) and a purple solid was finally obtained.
4.4 Polymerization of 2-component random copolymers

4.4.1 Experimental

The monomers were prepared as before and the third monomer, 3-methylthiophene was brominated using the method for 3-octylthiophene.

Materials

A. Monomers

1) 3-Octylthiophene, Aldrich, 97%
2) 3-Thiophenemethanol, Aldrich, 99%
3) 3-Methylthiophene, Aldrich, 98%

B. Catalyst

1,3-bis(diphenylphosphino)propane]-dichloronickel (II), Aldrich, 99%

C. Solvents

1) Tetrahydrofuran, Aldrich, 99%
2) N, N-Dimethylformamide, Aldrich, 99.8%
3) Dichloromethane, Aldrich, 99.5%
4) Chloroform, Aldrich, 99.5%
5) Hexane, Aldrich, 95%
6) Methanol, Aldrich, 99.8%
7) Diethyl ether, Aldrich, 98%

D. Grignard Reagents

Ethyl magnesium bromide solution (3.0M in diethyl ether), Aldrich

E. Other

1) N-Bromosuccinimide (NBS), Aldrich, 99%
2) Diethylene glycol monomethyl ether (DEGMME), Fluka, 99%

3) Phosphorous tribromide, Aldrich, 99%

4) Sodium hydride (dry), Aldrich, 95%

5) Calcium hydride, Aldrich, 99.99%

6) Calcium chloride, Aldrich, 99.99%

7) Magnesium sulfate (anhydrous), Sigma-Aldrich, 99%

8) Sodium bicarbonate, Sigma-Aldrich, 99.7%

9) Sodium sulfate (anhydrous), Sigma-Aldrich, 99%

4.4.2 Synthesis of 1:1:1 random copolymers of 3OT-co-3DEGT-co-3MT

The polymerization method for the 1:1:1 random copolymers was the same as that for the 1:1 and 1:2 random copolymers. 2,5-dibromo-3-octylthiophene (0.354 g, 1 mmol) was placed to a reaction flask containing THF (20 ml). To this was added 2,5-dibromo-3-diethyleneglycol monomethyl ether thiophene (0.374 g, 1 mmol) and 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol). The combined volume of EtMgBr initiator used was 0.5 ml, while the combined mass of the Nickel catalyst added was 22 mg. The same work up (described in section 4.3.1) was carried out and the product obtained was purple in color.

4.4.3 Synthesis of 1:1:4 random copolymers of 3OT-co-3DEGT-co-3MT

3-Octylthiophene (0.25 g, 0.7 mmol), 3DEGT (0.25 g, ~ 0.7 mmol) and (3MT 0.73 g, 2.8 x 10^{-3} mol) were reacted together in THF (20 ml). The volume of initiator added was 0.6 ml and the amount of nickel catalyst used was 23 mg. The reaction pathway was similar to section 4.4.2 and about 0.325g of the purple colored product was obtained.
Scheme 2: Synthetic pathway for 1:1:1 and 1:1:4 random copolymers

\[
\begin{align*}
\text{2,5-dibromo-3-OT} & \quad \text{2,5-dibromo-3-DEGT} & \quad \text{2,5-dibromo-3-MT} \\
\text{1) EtMgBr, THF} & \quad \text{2) Ni(dppp)Cl}_2 & \quad \text{reflux}
\end{align*}
\]

poly(3-OT-co-3DEGT-co-3MT)

4.5 Characterization / Instrumentation

Routine characterization, as done in Chapter 3 for the block-copolymers was also performed on the random co-polymers. The techniques are as follows:

4.5.1 Nuclear Magnetic Resonance, NMR

\(^1\text{H} \text{NMR and } ^{13}\text{C} \text{ NMR spectra were obtained using Bruker Avance 500 MHz and Bruker Avance 400 MHz NMR spectrometers in deuterated chloroform, CDCl}_3.\)

Trimethylsiloxane, TMS was used as internal reference.
4.5.2 Fourier-Transform Infra Red Spectroscopy, FTIR

Infra Red analysis was carried out on pellets of the samples formed under pressure in anhydrous potassium bromide, KBr using the Perkin Elmer Spectrum 65 FTIR spectrometer.

4.5.3 Ultraviolet-visible (Uv-vis) Spectroscopy

Uv-vis studies were done on 1 mg/ml solutions of the polymers dissolved in chloroform. The instrument used for the analyses was the Varian Cary 500 Scan UV-Vis-NIR spectrophotometer with quartz cuvettes of 1 cm optical length.

4.5.4 Dynamic Light Scattering, DLS

Particle size of the polymers was determined by light scattering on Wyatt Technologies' Dynapro Nanostar Dynamic Light Scattering Instrument using a quartz cuvette.

4.5.5 Differential Scanning Calorimetry, DSC

The glass transition temperatures, $T_g$, and melting temperatures, $T_m$, were determined by differential scanning calorimetry using the TA Q2000 Differential Scanning Calorimeter with Tzero Aluminum Hermetic pans and lids. Heating rate was 10°C/min using the heat-cool-heat method. Cooling rate was 5°C/min. The glass transitions were measured at the mid-points of heat capacity changes while the melting point temperatures were taken at the maximum of the enthalpy endothermic peaks.

4.5.6 Electrical Measurements

Electronic properties were investigated by Cyclic voltammetry carried out on solutions of polymers in chloroform or dimethylsulfoxide, under a nitrogen atmosphere at room temperature. The instrument used was the PARSTAT 2263 Advanced Electrochemical System by Princeton Applied Research. The reference electrode was saturated Ag,
AgCl/NaCl. Scanning rate was 50 mV/s unless otherwise stated. The system was purged for 60 seconds and equilibrated for 15 seconds.

4.6 Morphology Characterization

The morphology of the thin film was characterized by scanning probe and electron microscopy techniques. They are as follows:

4.6.1 Atomic Force Microscopy, AFM

Veeco Instruments Atomic Force Microscope was used to image the composite films using the non-contact mode.

4.6.2 Scanning Electron Microscopy, SEM

The morphology of the thin films was investigated by observation under the Agilent Technologies 8500 Field Emission Scanning Electron Microscope.

4.7 Results and Discussion

Nuclear Magnetic Resonance Spectroscopy

The $^1$H NMR spectra for the random copolymers and the peak assignments are similar to those of their block copolymers. The methylene protons (adjacent to the ring) as seen in the 1:1 ratio spectrum (Figure 4.1) are about the same, indicating the two monomers were about equally polymerized.
Figure 4.1: 500 MHz $^1$H NMR spectrum of 1:1 random copolymer P(3OT-co-3DEGT) in CDCl$_3$

The 2:1 random copolymers (Figure 4.2) also reflect the feed ratio as the integration of the methylene protons shows there's two times more poly(3-octyl-thiophene) than the copolymer, poly(3-diethylene glycol thiophene).
In the three-component copolymers (Figure 4.3), because the methylthiophene has no methylene proton, the aromatic protons, which all three polymers have in common are considered. As seen in the triblock copolymers (chapter 3), the 3-component random copolymers also indicated a measure of the ratio of its components as observed in the NMR spectrum (Figure 4.3). 3-methylthiophene with a higher feed quantity, had more protons than 3-octylthiophene and 3-diethylene glycol thiophene.

Figure 4.2: 500 MHz $^1$H NMR spectrum of 2:1 random copolymer P(3OT-co-3DEGT) in CDCl$_3$
Figure 4.3: 500 MHz $^1$H NMR spectrum of 1:1:4 random copolymer P(3OT-co-3DEGT) in CDCl$_3$

**Fourier Transform Infra Red Spectroscopy**

The FTIR spectra of the random copolymers are presented in Figure 4.4. The peak assignments are similar to those of the block copolymers as discussed in Chapter 3. The broad peaks from 3100 to 3600 cm$^{-1}$ are attributed to residual moisture, in the KBr. Notable peaks are the frequencies between 800 to 820 cm$^{-1}$ which characterize the 2,3,5-tri-substituted thiophene rings as mentioned previously. The thiophene ring stretching for all four copolymers can be seen at ~ 1450 cm$^{-1}$. The aliphatic C-H stretching frequencies can be seen on or slightly shifted from 2900 cm$^{-1}$ for all the copolymers.
Figure 4.4: Infra red spectra of random copolymers, a) 1:1 P(3OT-co-3DEGT), b) 3:1 P(3OT-co-3DEGT), c) 1:1:1 P(3OT-co-P3DEGT:-co-P3MT) & c) 1:1:4 P(3OT-co-P3DEGT:-co-P3MT)

**Uv-vis Spectroscopy**

The Uv-vis spectra for the random copolymers seem to follow different trends. In the 1:1 copolymer (Figure 4.5), the maximum wavelength of absorption is observed at ~425 nm while there’s a shift to a slightly higher wavelength in the 2:1 composition (Figure 4.6). The $\lambda_{\text{max}}$ peaks at ~435 nm indicating a bathochromic shift. In the 1:1:1 and 1:1:4 random copolymers, there’s no remarkable difference in their absorption in the UV region as both have approximately the same maximum wavelength of absorption (Figures 4.7 and 4.8).
Figure 4.5: Uv-vis spectrum of 1:1 random P(3OT-co-3DEGT) with $\lambda_{\text{max}}$ at $\sim 425$ nm

Figure 4.6: Uv-vis spectrum of 2:1 random P(3OT-co-P3DEGT) in chloroform having $\lambda_{\text{max}}$ at $\sim 435$ nm
Figure 4.7: Uv-vis spectrum of 1:1:1 random P(3OT-co-P3DEGT-co-P3MT) in chloroform

Figure 4.8: Uv-vis spectrum of 1:1:4 random P(3OT-co-3DEGT-co-3MT) in chloroform
Dynamic Light Scattering

The light scattering curve for the 1:1 feed random copolymers shows an overwhelming average hydrodynamic radius of \( \approx 18 \) nm for the particles as seen in Figure 4.9. However, a very small fraction of this feed ratio have an average radius of \( \approx 2 \) nm which is almost negligible, considering their low intensity. For the 2:1 feed ratio in Figure 4.10, the average radius is also \( \approx 18 \) nm for most of the particles. Here, a small percentage of the particles have an average radius of \( \approx 2 \) nm with a higher intensity than those of the 1:1 feed ratio. The trend in particle size for the random copolymers is dissimilar to that observed in block copolymers. This may be due to the random distribution of the monomer over the polymer chain.

Figure 4.9: Light scattering of 1:1 random P(3OT-co-3DEGT) in chloroform
Figure 4.10: Light scattering of 2:1 random P(3OT-co-P3DEGT)

**Differential Scanning Calorimetry**

From Figure 4.11, it can be seen that the random co-polymers only have one definite $T_g$ and this is at $\sim 48$ °C. The symmetrical endotherm peak for melting has an onset at $\sim 172$ °C. The experimental method for the analysis was a DSC “Ramp” at a heating rate of 10°C/minute. There was no decomposition observed after the sample melted as the maximum temperature set was just 200°C. Decomposition may happen at a higher temperature.
Figure 4.11: DSC thermogram of 1:1 random P(3OT-co-3DEGT) ramped at 10°C/min

In the 2:1 feed ratio of copolymers (Figure 4.12), the Tₜ observed is about the same as that of the 1:1 feed ratio (i.e. ~48 °C). The DSC experiment done here was heat-cool-heat and the maximum temperature reached was 300°C. In the first heating cycle, there is a small reversible endotherm at ~150 °C, which might be an Eutectic melting peak. The main melting peak at ~238 °C arises from a sharp drop in the baseline, forming a side peak, before the actual melting endotherm. This could be the melting of the metastable modification peak at ~210 °C. The endotherm observed at ~265 °C is a much smaller peak, which is most likely due to the decomposition of the sample. This may be why no crystallization was observed.
The 1:1:1 random copolymer DSC scan in Figure 4.13, can be seen to have similar features to the 2:1 feed ratio of copolymers. From the second heating cycle, the $T_g$ of the copolymers is at $\sim 50^\circ$C. This was missed in the first heating cycle as the starting temperature was $50^\circ$C. The small reversible endotherm, seen in the 2:1 at $\sim 150^\circ$C, is also observed here at $\sim 145^\circ$C. The melting temperature can be seen at $\sim 235^\circ$C and this is closely followed by another endotherm, as a result of the decomposition of the materials.
The DSC method carried out for the 1:1:4 copolymers (Figure 4.14) was also heat-cool-heat. A slightly broad melting endotherm is observed at ~ 225 °C. The Tg is observed at ~ 50 °C. No decomposition is observed and there was no crystallization either. In Figure 4.15, pristine regioregular poly(3-octylthiophene) was ramped at 10°C/minute from 10°C to 200°C. A broad endotherm is seen at ~67°C and this is due to melting of the alkyl side chain (see block copolymer chapter). The glass transition temperature is at ~ 48 °C, while the onset for melting occurred at ~ 195°C. With the glass transition temperatures of the random copolymers similar to the P3OT homopolymer, it is clear that the copolymers mostly exhibit the characteristics of P3ATs.
Figure 4.14: DSC thermogram of 1:1:4 of random P(3OT-co-3DEGT-co-3MT)

Figure 4.15: DSC scan of rr-P3OT ramped at 10°C/min showing T_g at ~ 45°C
Cyclic Voltammetry

The potentiodynamic electrochemical measurement carried out for the 2:1 feed ratio random copolymer was a single vertex measurement. Hence only one peak potential is distinctly seen (as shown in Figure 4.16). The charging and discharging of the copolymer is seen to be reversible as a complete cycle is shown with the maximum potential reached at ~ -0.6 V, while the corresponding current was approximately 6.0 x 10^{-6} Amps. This is an indication of the ability of the copolymers to conduct and act as charge carriers.

Figure 4.16. Cyclic voltammogram of random 2:1 poly(3OT-co-3DEGT)
For the 1:1:1 feed ratio of copolymers (Figure 4.17), the type of measurement done was a two-vertex. So, two peaks are seen at a potential of 0.3 V for the anodic peak with a corresponding anodic current of $-1.2 \times 10^{-4}$ Amps while the cathodic potential peaked at -0.3 V with the corresponding cathodic current at $1.2 \times 10^{-4}$ Amps. The cycle is almost complete save for the termination point and hence, the solution of the random copolymer is deemed quasi-reversible.

![Cyclic voltamogram of 1:1:1 random poly(3OT-co-3DEGT-co-3MT) in chloroform at 25°C under a nitrogen atmosphere.](image)

**Figure 4.17**: Cyclic voltamogram of 1:1:1 random poly(3OT-co-3DEGT-co-3MT) in chloroform at 25°C under a nitrogen atmosphere.

A result similar to the 1:1:1 ratio of polymers is seen with the potentiodynamic measurement of the 1:1:4 feed ratio random copolymers in Figure 4.18. The experimental type was also 2-vertex and the peak anodic potential was 0.25 V while the corresponding
anodic current was $-7.0 \times 10^{-5}$ Amps. The cathodic potential peaked at -0.25 V with the corresponding cathodic current at $7.0 \times 10^{-5}$ Amps. This ratio of random copolymers (1:1:4) also happen to be quasi reversible since the discharge cycle did not completely return to the starting point. From the overall trend observed in the CVs of the random copolymers, it is certain that the random copolymers are electronically active.

Figure 4.18: Cyclic voltammogram of 1:1:4 random P(3OT-co-3DEGT-co-3MT)
Atomic Force Microscopy

The non-contact mode (NCM) atomic force micrograph for the 2:1 random copolymer drop-cast film shows some structural organization into triangular shapes, somehow similar to the 1:1:2 triblock copolymer morphology. The topography and phase images are shown in Figure 4.19 while the profile and 3-D image are shown in Figure 4.20. The length of one of the triangles measured was ~700 nm while its height was only ~20 nm. Figure 4.21 shows the NCM-AFM topography micrograph (a) of 1:1:1 feed ratio of copolymer as well as its 3-dimensional image (b). It appears like a perforated surface (circular holes) while these holes in the 3-D image appear like depressions or craters. The profile of a cross-section of these images is seen in Figure 4.22. A magnified image of the small depression seen in Figure 4.21 is depicted in Figure 4.23.

Figure 4.19: AFM image of a) 2:1 random P(3OT-co-3DEGT) and b) its phase image
Figure 4.20: AFM height profile of 2:1 random p(3OT-co-3DEGT) film and its 3-D image

Figure 4.21: AFM image of 1:1:1 poly(3OT-co-3DEGT-co-3MT) and its 3-D image
Figure 4.22: a) AFM profile of Figure 4.21a, while Figure 4.22b is the profile of 3-D image in Figure 4.21b

Figure 4.23: Magnified AFM image of a feature on Figure 4.21a
Scanning Electron Microscopy (SEM)

Figure 4.24 is the SEM image of 2:1 random copolymers showing a different morphology. Here, the surface appears to be a network of interconnected fibrils separated by pores or holes. The 1:1:1 random copolymer however maintained its morphology in the second drop-cast film as shown in Figure 4.25. For clarification, the sample of polymer imaged by AFM is not the same film shown in Figure 4.25, though they came from the same polymer. The SEM image shows the copolymer film appearing like droplets of water on a non-permeable surface.

Figure 4.24: SEM micrograph of 2:1 random P(3OT-co-3DEGT)
4.8 Conclusion

The block copolymer syntheses and random copolymer syntheses were essentially done by the same polymerization technique. The only difference was in the feed, where the monomers for the random copolymers were added into the pot all at the same time, while the block copolymers involved the polymerization of the main block first, followed by the addition of intermediates of subsequent blocks. The polymers showed similar traits in their characterization mostly, but the thermal properties vary. The melting point for the random copolymers was just a single value while the block copolymers mostly showed the traits of component polymers. Preliminary electrochemical measurements of solutions of these polymers in chloroform, indicated they are electroactive.
CHAPTER 5

ONE-STEP SYNTHESIS OF MWCNT-P3MT COMPOSITES AND THEIR CHARACTERIZATION

5.1 Abstract

Conductive polymers are such that possess properties similar to metals as they are carriers of delocalized π-electrons in their orbitals. Due to this unique character, they are also referred to as “synthetic” metals. Poly(3-alkylthiophenes) belong to the group of inherently conductive polymers which find use in optoelectronics, semiconductors, photo-voltaics, solar cells and sensors. Electrical conductivity in these polymers is brought about by the conjugated carbon-carbon double bonds. The synthetic pathway for the polymerization was via oxidative coupling with ferric chloride catalyst. The polymers were prepared with various ratios of multiwall carbon nanotubes of 1 to 20%.

Characterization was done mostly in solid state as the 3-methyl substituted polymer is known to be insoluble in common solvents except AsF₃. However, we were successful in drop casting the polymers from a suspension in glacial acetic acid onto silicon wafers. The morphology of the films formed was investigated by scanning electron microscopy. It was observed that the composite ratio with the least amount of MWCNT remained a film after drying, while the 5%-MWCNT composite aggregated into a network of interconnected branches while the 10 and 20% composites self-assembled into short fibrils. Thermal behavior of the polymers was investigated through
differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). The glass transition temperature for the composites was 48 °C and melting was observed at temperatures over 150 °C. Decomposition of the composites was observed to have started from about 300 °C. FTIR and FT-Raman spectroscopic methods were also performed on the composite polymers. The G-band for the MWCNTs was observed at ~1580 cm⁻¹, while the D-band was observed at 1350 cm⁻¹.

The electrical properties of the composite polymers was investigated via measurement of their bulk resistance after pressing them into flat discs from which their electrical conductivities were determined as well as Cyclic Voltammetry. The homopolymer, P3MT has a resistance of 3.5 GΩ and the composite with 20% MWCNTs has a resistance of only 260 Ω. Atomic absorption was studied via UV-Vis spectroscopy and this (atomic absorption) was carried out a step further by circular dichroism studies after helical formation was observed while characterizing the morphology of the fibrilar 10 and 20% MWCNT-P3MT composites. This helped to confirm optical activity in the polymer composites, making them suitable for use in the devices, such as optical sensors.

5.2 Introduction

Carbon nanotubes possess a unique array of physical, mechanical, electronic and chemical properties which make them attractive candidates for use as building blocks in many device architectures such as organic semiconductors, field emission materials, chemical sensors, catalyst support, energy storage, etc. The salient features of carbon nanotubes specifically includes high conductivity, high aspect ratio, large surface
and stability which is the reason they are the filler materials of choice in conductive polymer matrices.\textsuperscript{102} Carbon nanotubes have been used as reinforcement in non-conductive polymers to provide strength and also impart electronic properties.\textsuperscript{103} There is therefore no doubt that they help to improve the overall efficiency of conducting polymers.\textsuperscript{104-106} There has been a plethora of reports on the preparation of SWCNT and MWCNT / polymer composites, either covalently linked or otherwise and undoubtedly, chemical modification with functional moieties will lead to new properties and characteristics.\textsuperscript{107-111}

Multiwall carbon nanotubes cross linked with poly[3-(trimethoxy silyl) propyl methacrylate] have been made by surface initiated ATRP followed by hydrolysis and polycondensation to form hybrid nanomaterials.\textsuperscript{112} Synthesis of conducting polypyrrole/MWNT composites by in-situ $\gamma$-radiation-induced chemical polymerization at room temperature has been reported.\textsuperscript{113} There has been an evaluation of a promising secondary power source, emanating from supercapacitors with MWNTs deposited with conducting polymer as active materials, via in-situ polymerization process.\textsuperscript{114} Among the intrinsically conducting polymers, polythiophene has been the most promising candidate for making composites with carbon nanotubes. This is because of its ease of processibility (or structural modification), flexible electrical properties and stability of the doped and undoped states.\textsuperscript{115} Because of these outstanding qualities, substituted PTs, (especially at the 3- or 4- position) are widely researched for use in sensors, electrode materials, microelectronics and optoelectronics.\textsuperscript{116-118} Some examples of alkyl substituted polythiophene composites with carbon nanotubes prepared as components of electronic
devices are 1) heterojunction solar cells of P3HT/n-Si, where embedding double wall nanotubes in the P3HT layer was found to improve device performance drastically,\textsuperscript{119} 2) organic light emitting diodes (OLEDs) having carbon nanotubes incorporated into polythiophene,\textsuperscript{120} 3) solar cell materials made from simple sonication of single wall nanotubes with poly(3-octylthiophene), to name a few. The general methods used to prepare composites of polymer-carbon nanotubes are as follows:

a) Surface functionalization of carbon nanotubes followed by the addition of matrix polymers resulting in covalent linkage.

b) Dispersion of carbon nanotubes by mechanical means into a polymer matrix where no covalent bonds are formed.

c) In-situ polymerization of composite polymer in the presence of carbon nanotubes; no covalent bonds formed.

d) Surface functionalization of carbon nanotubes, followed by polymerization of matrix polymer on the surface of nanotubes.

5.3 Experimental

Materials

1) 3-Methylthiophene, Aldrich, 98%

2) Carbon Nanotube, multi-walled, Aldrich, ≥98%

Catalyst

Iron (III) Chloride, Sigma-Aldrich, 97%

Solvents

1) Chloroform
2) Methanol
3) Hydrazine

Other
1) Ultrasonic bath

5.3.1 Drying of Chloroform

Prior to use, the chloroform used for the synthesis was dried over 4 Å activated molecular sieves overnight. It was then decanted, distilled and stored over 4 Å molecular sieves.

5.3.2 Polymerization of 1% MWCNT-3-MT

The in-situ polymerization of 3-methylthiophene in the presence of multi-wall carbon nanotubes was carried out according to the oxidative method generally used for the synthesis of P3ATs\textsuperscript{30} and the report of Kim and co-workers.\textsuperscript{121} Chloroform (100 ml) was placed in a 250 ml 2-necked flask equipped with a stir bar. To this was added 1 wt % MWCNTs with respect to monomer weight and the mixture was sonicated for 1 hour at room temperature. Thereafter, FeCl\textsubscript{3} (2 g, 12.33 mmol) was added to the well sonicated nanotube mixture with chloroform and sonicated for 30 minutes. 3-Methylthiophene (0.51 g, 5.17 mmol) was dissolved in chloroform (25 ml) and placed in an addition funnel. At the end of the second sonication (with FeCl\textsubscript{3}), the flask was taken out of the sonicator and the addition funnel containing the dissolved monomer was mounted on it. The monomer was then added drop-wise to the MWCNT/FeCl\textsubscript{3} suspension with constant stirring. The reaction lasted 24 hours and it was terminated by precipitation into methanol and filtered under reduced pressure. Methanol was used to wash the crude polymer
composite several times, followed by subsequent washings in 0.1 M HCl, distilled water and finally, acetone. The brownish black product obtained was then dried in a vacuum oven at 40°C. Yield: 0.32 g.

The procedure was repeated using 5, 10 and 20 wt% of MWCNT with respect to the monomer weight. The homopolymer of 3-methylthiophene was also synthesized using this method.

5.3.3 Polymerization of 5% MWCNT-3-MT

3-MT (1.02 g, 10.4 mmol) was dissolved in chloroform (25 ml), and added drop-wise to a well sonicated suspension of 5 wt% MWCNT with respect to the monomer and Ferric chloride (2.08 g). The monomer addition lasted one hour after which reaction was stirred for 24 hours. It was then terminated by the addition of methanol (150 ml) and washed again with methanol, 0.1M HCl and acetone. The final product was placed in a vacuum oven to dry and it was black in color, powdery and lumpy.

5.3.4 Polymerization of 10% MWCNT-3-MT

3-MT monomer (1.02 g, 10.4 mmol) was again dissolved in chloroform (25 ml), while 10 wt% MWCNT with respect to the monomer was sonicated in chloroform (100 ml) for one hour. This, was followed by the addition of ferric chloride catalyst (2.04 g) to the MWCNT flask and further sonication resumed for 30 minutes. Drop-wise addition of the monomer was performed over a period of 30 minutes and the reaction stirred for 24 hours. It was also terminated by the addition of methanol (150 ml) followed by successive rinsing in methanol, 0.1M HCl and acetone. Product was black in color.
5.3.5 Polymerization of 20% MWCNT-3-MT

3-MT (1.02 g, 10.4 mmol) was dissolved in chloroform (25 ml) and placed in an addition funnel while 20 wt% MWCNT with respect to the monomer was sonicated in 100 ml chloroform for one hour. 2.04 g ferric chloride catalyst was then added and sonicated further for 30 minutes. The monomer was then added to the flask in a drop-wise manner over a period of 30 minutes and the reaction stirred for 24 hours before being terminated again with 150 ml methanol. This was followed by rinsing with ethanol, 0.1M HCl and acetone. The product was placed in the oven to dry, yielding a crusty black powder.

5.3.6 Homopolymerization of 3-methylthiophene by oxidative coupling with Ferric chloride

3-methylthiophene (0.5 g, 5 mmol) was dissolved in chloroform (25 ml) in a flask and stirred to form a solution. Ferric chloride (1.00 g, 6.17 mmol) catalyst was placed in another flask and to this was added 25 ml chloroform. The ferric chloride suspension was then sonicated for 30 minutes after which the monomer solution was added drop-wise, to the ferric chloride suspension, with constant stirring over a period of 30 minutes. The reaction stirred at room temperature for 24 hours and polymer was precipitated into methanol, filtered under reduced pressure followed by rinsing with methanol, 0.1M HCl and acetone. The product obtained was dried in a vacuum oven and it was a blue/black solid. The reaction scheme is shown in Figure 5.1.
5.4 Composite Film Formation

Thin films of the polymer samples were made from suspensions of the polymer composites in glacial acetic acid, drop-cast onto silicon wafers.

5.5 Characterization / Instrumentation

The following instrumentation techniques were used to analyze the polymer/CNT composites:

5.5.1 Nuclear Magnetic Resonance, NMR

$^{13}$C CPMAS NMR was carried in the solid state on the homopolymer with a Bruker AVANCE III 500 MHz Spectrometer.

5.5.2 Thermal Analysis

Thermal behavior of the polymer composites was investigated via differential scanning calorimetry, DSC and thermo gravimetric analysis, TGA. DSC was performed with the TA Instruments' Q2000 calorimeter using Tzero aluminum hermetic pans and lids. Heating rate was 10°C/min and the method was the heat-cool-heat cycles. Cooling rate was 5°C/min. The glass transitions were measured at the mid-points of heat capacity changes while the melting point temperatures were taken at the maximum of the enthalpy.
endothermic peaks. Thermo Gravimetric Analysis, TGA, was carried out in air with TA Instruments' Q50 at a heating rate of 20°C/minute with platinum pans.

5.5.3 Raman Spectroscopy

Raman spectra for the polymer composites were recorded using the Thermo Scientific Nicolet Almega XR Raman spectrometer at a wavelength of 488 nm.

5.5.4 FTIR spectroscopy

Infrared analysis was carried out with the Perkin Elmer Spectrum 65 FTIR spectrometer on sample pellets formed under pressure in anhydrous potassium bromide.

5.5.5 Ultraviolet-visible (Uv-vis) Spectroscopy

Uv-vis studies were done on 0.5 mg/ml solutions of the polymers dissolved in chloroform. The instrument used for the analyses was the Varian Cary 500 Scan Uv-vis spectrophotometer with quartz cuvettes of 1 cm optical length.

5.5.6 Electrical Measurements

The resistance of the composites was measured from samples formed into pellets (Figure 5.2) under three metric tons of pressure and dried in a vacuum oven at 50°C overnight. Bulk resistance was measured using the Keithley 6430 sub-femtoamp remote source meter and the Fluke digital multimeter. The conductivity values were obtained from these measurements.

5.5.7 Scanning Electron Microscopy, SEM

The morphology of the thin films was investigated by observation under the Agilent Technologies 8500 Field Emission Scanning Electron Microscope.
5.5.8 Circular Dichroism

Jasco J-710 Spectropolarimeter was used to study optical activity as two of the composites showed some optical characteristics under the electron microscope.

5.6 Results and Discussions

$^{13}$C Nuclear Magnetic Resonance

Since the polymer and its composites are insoluble in common solvents, their structural determination by solution NMR could not be done. Hence, only the homopolymer, P3MT was analyzed by CPMAS solid $^{13}$C NMR. The MWCNT composites were attempted but the instrument would not spin, because the nanotubes were conductive. The methyl carbon appeared at $\sim$ 15 ppm while the thiophene ring carbons appear at $\sim$ 50, 95, 135 and 150 ppm respectively. The NMR spectrum is found in the Appendices.

Thermal analysis

1. Differential Scanning Calorimetry

The homopolymer, poly(3-methylthiophene) has a glass transition at $\sim$ 48 °C (Figure 5.2). A shift in the baseline is seen, forming an exothermic peak at $\sim$ 250 °C and it broadened out thereafter with an endotherm ascribed to the melting of the crystals. Right after this is a very sharp endothermic peak at $\sim$ 380 °C and this is the point where the polymer chains begin to decompose. The second heating cycle shows a small endotherm at $\sim$ 425 °C and this is believed to be the temperature where the degraded polymer vaporizes.
Figure 5.2: DSC thermogram of regioregular P3MT with $T_g$ at $\sim 48 \, ^\circ C$

In the 1%-MWCNT-P3MT composite (Figure 5.3), the $T_g$ observed is similar to the $T_g$ of the homopolymer ($48 \, ^\circ C$) as well as the exothermic peak at $\sim 250 \, ^\circ C$. However unlike the homopolymer, the cooling cycle shows another exothermic peak at $\sim 120 \, ^\circ C$, which is attributed to the cold crystallization of the composite. Additionally, there's a moderately broad endotherm at $\sim 175 \, ^\circ C$, which is attributed to the melting of the polymer. The onset of decomposition is observed before $350 \, ^\circ C$. 
Figure 5.3: DSC thermogram of 1%-MWCNT-P3MT composite with 2 heating cycles where the $T_g$ of the first cycle was observed at $\sim 48 ^\circ C$

The 5% MWCNT composite has two thermograms (Figures 5.4a and 5.4b). Heating in Figure 5.4a was terminated at just over 200 $^\circ C$. In order to extend the heating temperature range, the sample was ramped again to 400 $^\circ C$ as shown in Figure 5.5b. Nevertheless, Figure 5.4a shows a similar exothermic peak to the 1%-MWCNT-P3MT at $\sim 225 ^\circ C$ (with a shoulder at $\sim 180 ^\circ C$). Cold crystallization is observed at $\sim 125 ^\circ C$ and the second heating scan shows a melting endothermic peak at $\sim 175 ^\circ C$ before heating was terminated. The repeat experiment in Figure 5.4b still retained many of the observed transitions in the first run though. These are similar glass transitions and melting points. Also observed is a broad endotherm at $\sim 350 ^\circ C$, just before decomposition set in at $\sim 380 ^\circ C$. 
Figure 5.4a: DSC thermogram of 5% MWCNT-P3MT. Initial heating scan: $T_g \sim 48 ^\circ C$

Figure 5.4b: DSC of 5% MWCNT-P3MT composite, second run. $T_g$ is $\sim 47 ^\circ C$
The 10% MWCNT composite also follows a similar trend to the 1 and 5% composites but no cold crystallization exotherm is observed (Figure 5.5). Melting is observed at ~ 180 °C and at ~ 350 °C, another endotherm is observed which is attributed to decomposition of the polymer.

The 20% MWCNT composite thermogram in Figure 5.6 slightly resembles the 10% MWCNT composite in \( T_g \) and melting point as well but it has a very sharp melting endotherm. The reversible endotherm at ~ 225 °C could be the point at which the poly begins to thermally decompose.

---

Figure 5.5: DSC of 10% MWCNT-P3MT composite. \( T_g \) - 50 °C
Figure 5.6: DSC of 20%-MWCNT-P3MT composite with a $T_g$ of $\sim 50^\circ$C. No crystallization exotherm observed

2. TGA

Figure 5.7 is the TGA thermogram of the 1%-MWCNT-P3MT composite. The plateau of constant weight at the beginning of the heating scan usually seen is not typified here. This means that the sample began to lose weight (99.8% left at $\sim 50^\circ$C) almost immediately after heating started and this may be due to the loss of residual solvent. There is a gradual decrease in weight as sample is heated further and a marked loss in weight is seen between 400°C and 600°C. At 607°C, only about 70% of the sample was remaining and there continued the gradual degradation until heating was terminated at 800°C leaving behind $\sim 60\%$ of the material under analysis.
Figure 5.7: TGA thermogram of 1% MWCNT-P3MT composite

Figure 5.8 shows the TGA for 5% MWCNT-P3MT composite. For this composition, the loss in weight at 50°C compared to the 1%-MWCNT-P3MT is quite negligible as only 0.004% weight loss was observed. As the furnace temperature rose to 400°C, only a tiny amount of weight loss occurred. This may be due to the presence of more MWCNTs in the material than in the 1% MWCNT composite. Between 460°C and 570°C however, there was a sharp drop in weight and the change in sample weight went from ~95 to ~75% left. At 600°C, the 5% MWCNT composite had 5% more weight than the 1% MWCNT composite. At 900°C when heating was terminated, there was ~41% weight loss in sample.
Figure 5.8: TGA thermogram of 5% MWCNT-P3MT composite

Figure 5.9 is the TGA thermogram of the 10% MWCNT composite polymer. At 50°C, there was still 99.87% of sample undecomposed. The decrease in weight is very small compared with the 1% MWCNT load and decomposition onset here was at ~440°C, peaking at 563°C, before slowly losing weight again. The overall weight loss in this composite was ~36% by the time the furnace temperature reached 900°C. At 800°C, the weight change was 32%.
Figure 5.9: TGA thermogram of 10% MWCNT-P3MT composite

Figure 5.10 is the TGA thermogram for 20%-MWCNT-P3MT. Here, the weight loss at 50°C was only 0.04%. The amount of sample used here, is double that used in the 10% MWCNT load. After the temperature reached 200°C, the dip in thermogram became steeper and the material started to decompose at ~ 442°C. This was followed by a much gradual loss of weight as heating continued. By the time the maximum set temperature of 800°C was reached, only about a quarter of the initial weight was lost. Hence, it’s been demonstrated that the more CNTs packed into the polymer, the longer it’s able to withstand high temperatures and hence, have a positive impact on the product life of devices that may contain the composite. The TGA thermogram for the homopolymer, is shown in Figure 5.11.
Figure 5.10: TGA thermogram of 20% MWCNT-P3MT composite

Figure 5.11: TGA curve of regiorandom poly (3-methylthiophene)
Fourier Transform Infra Red Analysis

The aromatic C-H stretching vibration of the pristine poly(3-methylthiophene) is observed at ~ 3050 cm\(^{-1}\) (Figure 5.12) and the peak is conspicuously absent in the multiwall nanotube composites. The fingerprint region for poly(3-methylthiophene) which lies between 600 – 1500 cm\(^{-1}\) is clearly evident from the amount of peaks displayed. For the homopolymer, the aliphatic C-H stretch appears at 2970, 2950 and 2920 cm\(^{-1}\). In the composites, the C-H stretch is observed at a lower energy field. The sharp peak at ~ 1510 cm\(^{-1}\) for the polymer which is the ring stretching is not as prominent for the composites.

![Figure 5.12: Infrared spectra of poly(3-methylthiophene) and composites](image)

In the 10 and 20 wt% composites, there is no peak observed for the methyl rock stretch whereas, the homopolymer and the smaller CNT composites have peaks showing up at 616, 616 and 615 cm\(^{-1}\) respectively. The absence observed in the higher CNT
composites (10 and 20 wt%) coupled with the higher conductivities they show, indicate that the polymer backbone did not become altered during composite formation of these two. The frequency assignments for the polymer and its composites are summarized below in Table 5.1.

Table 5.1 FT-IR peak assignments for the MWCNT-P3MT composites and homopolymer, P3MT, where P stands for the polymer, P3MT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aromatic C-H stretch</th>
<th>Aliphatic C-H stretch</th>
<th>Aromatic C-H out-of-plane</th>
<th>Methyl deformation</th>
<th>Ring stretch</th>
<th>Methyl rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3MT</td>
<td>3050</td>
<td>2970, 2950, 2920</td>
<td>821</td>
<td>1378</td>
<td>1514, 1459</td>
<td>616</td>
</tr>
<tr>
<td>P+ 1%-MWCNT</td>
<td>-</td>
<td>2950, 2910, 2840</td>
<td>817</td>
<td>1384</td>
<td>-</td>
<td>1410, 616</td>
</tr>
<tr>
<td>P+ 5%-MWCNT</td>
<td>-</td>
<td>2950, 2910, 2830</td>
<td>818</td>
<td>1384</td>
<td>1512, 1438</td>
<td>615</td>
</tr>
<tr>
<td>P+10%-MWCNT</td>
<td>-</td>
<td>2950, 2910, 2820</td>
<td>816</td>
<td>1384</td>
<td>-</td>
<td>1400, -</td>
</tr>
<tr>
<td>P+ 20%-MWCNT</td>
<td>-</td>
<td>2950, 2910, 2820</td>
<td>790</td>
<td>1250</td>
<td>-</td>
<td>1520, -</td>
</tr>
</tbody>
</table>

Raman spectroscopy

The Raman spectra for the polymer-carbon nanotube composites (Figure 5.13) were recorded at a wavelength of 488nm. Typically, MWCNTs exhibit a peak at ~ 1580 cm\(^{-1}\) and this corresponds to the G-band or the \(E_{2g}\) mode. This is typical of semiconducting nanotubes and it is ascribed to single crystal graphite. In the spectra for the composites, a small shift is observed in their G-band values. For example, the 10% MWCNT composite has its G-band at ~ 1580 cm\(^{-1}\) while that of the 20% MWCNT composite is slightly less than that value, showing up at ~ 1570 cm\(^{-1}\). The second order D-band is seen at ~ 1350 cm\(^{-1}\) for all the composites which agrees with the expected trend for pristine nanotubes. The second-order G-band frequency showed up for all the
composites at \( \sim 2650 \text{ cm}^{-1} \) as expected. For the 20\% MWCNT composites, the D' band showed up very close to the G-band at \( \sim 1600 \text{ cm}^{-1} \). Both D- and D'-bands are associated with disordered carbon.\textsuperscript{124} The other three composites are missing the D'-band though. Another frequency present in all four is the thiophene ring mode which is at \( \sim 1470 \text{ cm}^{-1} \).

![Raman spectra of the P3MT/MWCNT composites](image)

**Figure 5.13:** Raman spectra of the P3MT/MWCNT composites

**Scanning Electron Microscopy**

The films formed by drop-casting suspensions of the polymer (Figure 5.14) and its composite samples in acetic acid were imaged under the electron microscope and features were observed in the composites containing a higher percentage of multi wall carbon nanotubes not present in the lower percentage composite. The 1\%-MWCNT-P3MT (Figure 5.15) was essentially a film while the 5\% MWCNT composite formed fibrils after drying. This is shown in Figure 5.16.
Figure 5.14: SEM micrograph of drop-cast regioregular P3MT dispersed in acetic acid (X780)

Figure 5.15: SEM image of 1% MWCNT-P3MT composite (X780)
In Figures 5.17 and 5.18, the 10%-MWCNT-P3MT and 20%-MWCNT-P3MT films, did not respectively remain as thin films, but were observed to have self-organized into nanostructures that consisted of mainly fibrils for 10% MWCNT-P3MT composites and fibrils plus a network of interconnected fibers resembling honeycombs for the 20% MWCNT-P3MT composites. Additionally, an interesting feature was observed that was common to both composites. Fibrils were observed that had the twisted, helical shape that is associated with optically active materials. Further work will be carried out to investigate in detail, the nature of the helical fibrils observed. There is the possibility that the helical shape is due to defects in the manufacturing process of the MWCNTs\textsuperscript{125} or as a result of polymer interaction. This observation calls to mind, the report of Lee et al,\textsuperscript{84} where self-assembly of block polythiophenes revealed coiling of the fibrils formed and subsequently found to be optically active. In a preliminary manner, circular dichroism
studies has been carried out on the MWCNT-P3MT composites. The preliminary results can be found in the Appendices and these will be further investigated.

Figure 5.17. a) SEM image of 10% MWCNT-P3MT self organized nanofibrils (X750) b) SEM image of 10% MWCNT-P3MT showing twisted fibrils (X8170), c) SEM image of 10% MWCNT polymer showing helical shape
Conductivity

The DC electrical conductivity of the polymer/MWCNT composites was investigated through the measurement of their bulk resistance by the typical 2-point probe method using the Agilent 34401A digital multimeter and a Fluke digital multimeter. The polymer and its composites (~ 40mg of each) were pressed into disc-like pellets of 1.0cm in diameter and thickness of 0.5mm by means of a manual hydraulic press for 15 minutes. The highest resistance (3.5 GΩ) as expected, came from the homopolymer, poly(3-methylthiophene) while the least resistant (260 Ω) of the composites was that with the highest loading of MWCNTs (20%-MWCNT-P3MT). Table 5.2 shows the
conductivity values at room temperature (25°C). The values were obtained by the equation:

\[ \sigma = \frac{t}{R_b A} \]

Where \( \sigma \) = conductivity in S/cm, \( t \) = thickness of the pellet (cm), \( R_b \) = bulk resistance (\( \Omega \)) and \( A \) = area of the pellet.

Table 5.2: Conductivity values of 1 cm diameter discs of P3MT and composites measured at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>P3MT</th>
<th>1%-MWCNT-P3MT</th>
<th>5%-MWCNT-P3MT</th>
<th>10%-MWCNT-P3MT</th>
<th>20%-MWCNT-P3MT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity S/cm</td>
<td>2 x 10^{-11}</td>
<td>1.3 x 10^{-7}</td>
<td>7.1 x 10^{-7}</td>
<td>1.3 x 10^{-6}</td>
<td>2.5 x 10^{-4}</td>
</tr>
</tbody>
</table>

5.7 Conclusion

Various compositions of MWCNT composites with poly(3-methylthiophene) have been successfully prepared by in-situ polymerization of 3-methylthiophene with ferric chloride catalyst. This was to ensure an even dispersion of the nanotubes into the polymer matrix, rather than mixing or dispersion after the polymer had been prepared. Thermal analysis of the composites by DSC shows their \( T_g \)s to be about the same values indicating there was no chemical bonding between the two species that would have caused a difference in the \( T_g \)s of the homopolymer and its composites. Also, the Raman spectrum, as well as the FTIR spectrum are only suggestive of very weak \( \pi - \pi^* \)
interaction in the composites which indicates the absence of covalent bonds between the multiwall nanotubes and the polymer. TGA analyses show that, overall, the more multiwall carbon nanotubes are present, the more thermally stable the composites are. Additionally, the outstanding electrical conductivities of the polymer/multiwall nanotubes composites make them suitable component materials for semiconductors and other nanoscale electronic devices. Dispersion of the composite in glacial acetic acid gave brittle thin films, just as observed in the film formed from the electropolymerization of the monomer,\textsuperscript{126} but the pliability can be improved by the addition of suitable fillers to render them suitable in the application of solar cells and optoelectronics. This is because when compared with other monomers in the 3-alkylthiophene series, 3-methyl thiophene is the most inexpensive and with the right formulation it can be as useful a polymer, as the other solution processable poly(3-alkylthiophenes).
CHAPTER 6

ELECTROSPINNING OF FUNCTIONAL NANOFIBERS WITH BIOSPECIFIC AND ELECTRONIC CHARACTERISTICS

6.1 Abstract

Electroactive nanofibers decorated with α,ω-bi-(dinitrophenyl caproic acid), abbreviated as DNP pendant groups, have been prepared by electrospinning a solution of α,ω-bi[2,4-dinitrophenyl caproic] [poly(ethyleneoxide)-b-poly(2-methoxystyrene)-b-poly(ethylene oxide)], polystyrene and single-walled carbon nanotubes (SWCNTs). The α,ω-bi[2,4-dinitrophenylcaproic][poly(ethyleneoxide)-b-poly(2-methoxystyrene)-b-poly(ethyleneoxide)] polymers were synthesized by living anionic polymerization and subsequent esterification to obtain the DNP-functionalized polymers. The nanofibers (300 nm) were electrospun onto a silicon wafer substrate at a voltage of 10 kV using dimethylformamide and chlorobenzene as solvents.

The nanofibers were characterized by Raman spectroscopy, fluorescence microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and optical microscopy. The DNP groups, therein, were tethered to the nanofibers via oligo(oxyethylene) spacers. The DNP groups decorating the nanofibers were capable of specifically binding with anti-DNP immunoglobulin E (IgE). The binding specificity of nanofibers containing 1% SWCNTs with anti-DNP IgE was studied via fluorescently
labeled (Fluorescein IsoThioCyanate) FITC-IgE. Electronic activity of the nanofibers was studied by I–V plots from Kelvin sensing. The I–V plots before sensitizing with IgE differed from the I–V plots after incubation in IgE. The results of the studies suggest the possibility of developing functional nanofibers as the active component in biosensors.

6.2 Introduction

The versatility of polymers stem out of the fact that they can be tailor-made for a particular application or purpose. Polymers with intrinsic conductive properties such as polythiophene, polypyrrole, polyaniline, etc have long been used in 1) actuators, 2) batteries, 3) capacitors, 4) photo-voltaics, and 5) transistors. Certain polymeric materials are also known to be easily modified to mimic nature. A number of biocompatible and bio-functional polymers have been synthesized by various groups, since these types of polymers have wide ranging applications in tissue engineering, bio-diagnostics and therapeutics. One way of synthesizing polymers with bioactive properties is by covalent attachment of a short peptide chain to a synthetic polymer. Biofunctional synthetic polymers can also be prepared by conjugation with certain functional groups that antibodies recognize and bind to. An example is the α,ω-2,4-dinitrophenyl (DNP) group that the antibody IgE recognizes via its FceRI receptors. Immunoglobulin E, IgE is a class of antibody found in the skin, lungs and especially, the mucous membranes of mammals. The body’s immune system produces antibodies in response to the invasion of foreign bodies such as bacteria, viruses, fungi, cancer cells, certain plants or food. These antibodies help the body’s immune system to fight the
invading foreign agents by binding on to them. Fabrication of biosensors to determine 
the presence of antibodies such as IgE, is of significant interest.

Our group has reported the synthesis of α,ω bi[2,4-dinitrophenylcaproic] 
[poly(ethyleneoxide)-b-poly(2-methoxystyrene)-b-poly(ethylene oxide) and a 
poly(pyrrole) based DNP functionalized electroactive polymer. In preliminary 
studies, both polymers were electrospun into nanofibers in order to determine 
processability such that the polymers may be fabricated into components to develop a 
nanoscale sensor. Because of the nature of specific binding of the α, ω-bi[2,4-
dinitrophenylcaproic] [poly(ethyleneoxide)-b-poly(2-methoxystyrene)-b-poly(ethylene 
oxide) to the IgE antibody, it became necessary to fabricate nanofibers based on these 
polymers and to study the potential of such nanofibers as components in biosensors.

Nanofibers have been obtained by various processes among which are 1) template 
synthesis, for example, template synthesis of carbon nanotubule and nanofiber arrays
2) molecular self-assembly; example of which is self-assembled peptide amphiphile 
nanofibers made by Tambralli et al. 3) melt drawing, typically from a viscous polymer 
solution or melt and 4) electrospinning. The latter is the most favored way to produce 
nanofibers. The advantages are the scalability of the process, cost effectiveness and 
control of fiber diameter.

The electrospinning process involves the application of a very high voltage to a 
droplet of polymer solution as it is leaves a spinneret. This process is set into motion by 
the interaction of electrical forces with free charges on the surface or within a polymer 
solution or melt. The charged polymer jet undergoes a series of loops and instabilities as
it travels towards the grounded collector placed some distance away, on which they are deposited as nanofibers. Factors that affect the formation of nanofibers and fiber morphologies include solution viscosity, molecular weight, working distance, applied voltage and solvent volatility.\textsuperscript{155}

The process of electrospinning requires a) a polymer solution of the right viscosity, b) a high voltage DC source with two electrodes (positive and ground), c) a substrate to collect the electrospun fibers and d) a medium to hold the polymer mixture (usually a syringe). The following actions take place during the process of electrospinning: a) droplet generation, b) Taylor's cone formation, c) launching of the jet, d) elongation of straight segment, e) whipping instability and f) solidification into nanofiber.\textsuperscript{156}

Since the DNP functionalized polymer is not electroactive, it became necessary to render it so, by incorporating single walled carbon nanotubes into its matrix. The single walled nanotubes are semiconducting and additionally, they help to strengthen the nanofibers in which they are present.\textsuperscript{103} Consequently, we report our investigation of the preparation of electrospun nanofibers containing of \(\alpha,\omega\)-bi[2,4-dinitrophenylcaproic] [poly(ethylene oxide)-b-poly(2-methoxystyrene)-b-poly(ethylene oxide)], (P2MS, molecular weight: 50,000), polystyrene, polystyrene (molecular weight: 800,000) and single-walled carbon nanotubes, SWCNT. The polymer/SWCNT composites have potential applications as electrode materials due to their high surface to volume ratio and also as biosensors.
6.3 Experimental

Materials:

1) P2MS diblock copolymers
2) Polystyrene, Aldrich
3) Single walled carbon nanotubes, 0.7-1.3 nm, Aldrich.
4) IgE and IgG were provided by the Baird-Holowka Lab, Cornell University.

Solvents:

1) Dimethylformamide, Aldrich, > 98.8%
2) Chlorobenzene, Aldrich, >98.8%.

Other:

1) Silicon wafers,
2) Glassman high voltage source

6.3.1 Preparation of composite mixtures for electrospinning

The complete procedure for the synthesis of the P2MS block copolymer is reported elsewhere by Sannigrahi et al. 67 Four portions, 20 wt% of the P2MS polymer were dissolved in chlorobenzene and DMF. Two portions each of 20 wt% and 40 wt% of polystyrene were also dissolved separately in the two solvents. Four portions of 1 wt % with respect to the P2MS were dispersed in both solvents and stirred overnight for even dispersion. Afterwards, one of the 20 wt% P2MS solution in chlorobenzene was mixed with the 20 wt % polystyrene in chlorobenzene to form a 1:1 ratio. Likewise, a 20wt % solution of P2MS in DMF was mixed with the 20 wt % solution of polystyrene in DMF to form the 1:1 ratio as well. The remaining solutions were mixed to make up the 1:2 ratios respectively in chlorobenzene and DMF. The well dispersed mixture of carbon
nanotubes was then added to the polymer mixtures to make up the composites for electrospinning. The resultant composite mixtures of the DNP-functionalized polymer, polystyrene and SWCNTs were stirred overnight. This is to ensure the dispersion of the CNTs in the polymer matrix as the intention is to use CNTs for both reinforcement and electroactivity.

6.3.2 Electrospinning of functionalized Polymer-CNT composite

A sample of each composite is withdrawn in a syringe and mounted on a retort stand. At a distance of 10cm from the syringe, a silicon wafer is mounted on another stand. The positive clip of the high voltage source is attached to the needle on the syringe while the ground is attached to the silicon wafer. A lamp is positioned behind the set up in order to observe the process as it unfolds. The high voltage source is then powered on and the meter adjusted to 10kV. Nanofibers of the two different polymer compositions in the two solvents were electrospun onto silicon wafers. Figure 6.1, below is the schematic of electrospinning.

![Schematic of electrospinning](image)

Figure 6.1: Schematic of electrospinning
6.3.3 Biocompatibility studies of nanofibers with the IgE Antibody

The electrospun nanofibers were incubated in fluorescently tagged IgE having a concentration of 4μg/ml in PBS-BSA (Phosphate Buffer Saline- Bovine Serum Albumin) solution for one hour. The unbound IgE was then removed from the nanofibers by washing three times with the buffer solution. A control experiment was also carried out using Immunoglobulin G, IgG. IgG is not active towards the DNP functional group and can be used as a control to determine if there is any non-specific adsorption or adhesion of the biomolecules with the nanofibers. The incubated nanofibers were then observed under a Leica confocal microscope where varying levels of fluorescence was manifested in the DNP functionalized fibers incubated in FITC-IgE. Nanofibers in the control experiment (IgG) did not show any fluorescence under the microscope. Schematic binding of the IgE with composite nanofiber is shown in Figure 6.2.

Figure 6.2: Schematic of IgE binding with a composite nanofiber
6.3.4 Current-Voltage (I-V) measurements

In order to determine the electronic behavior of the electrospun fibers, both IgE-bound and unbound nanofibers were put through the four-point collinear probe measurement test. The first test was carried out on the unbound nanofiber composite made up of the DNP-functionalized polymer, polystyrene and SWCNTs which were electrospun as a fiber mat. A small quantity of the fiber mat on a semi-insulating silicon wafer was placed on a S-1150-5, analytical wafer prober with Bausch & Lomb microzoom II microscope. This prober was equipped with four micromanipulators with 10 micron probes, a Keithley 6430 subfemtoamp sourcemeter and an Agilent 34405A digital multimeter. In the four-point probe (also known as Kelvin sensing) method, two probes are connected to the sourcemeter to source the current to stimulate the system. Two other probes are then connected to the multimeter to sense the current sourced. The schematic of the four-point probe arrangement is depicted in Figure 6.3.

Figure 6.3: Schematic of the four-point probe measurement
Probes 1 and 4 are used in sourcing the current and therefore, are attached to the sourcemeter, while probes 2 and 3 are used to measure the potential difference across the outer probes and so, are attached to the Agilent multimeter. Currents, in the nanoamperes range were sourced from the Keithley 6430. The current-voltage values for the unbound nanofibers and bound nanofibers are then plotted to reveal their I-V characteristics.

6.4 Characterization of DNP-Functionalized Nanofibers

Nanofiber dimension and morphology can be characterized by a number of instrumentation methods. Some of these are electron microscopy, scanning probe microscopy, optical microscopy and Raman spectroscopy. The overall appearance and form of nanofibers is of utmost interest in that these can help determine their best uses. Morphological studies include porosity, pore size distribution, fiber diameter, and shape. Mechanical properties of fiber mats like tensile strength and their crystallinity are also of interest. In our study, a Field emission scanning electron microscope and atomic force microscope were used to study the appearance and determine the dimensions of the electrospun nanofibers. Initial observations were made using the Zeiss Optical Microscope and the Keyence Optical Microscope provided more information about the profile of the nanofibers. Raman spectroscopy was used to confirm the presence of the carbon nanotubes at the expected Raman shift range.

6.5 Results and discussion

Representative results from electrospinning of functionalized polymer-CNT composites are described as follows:
Figure 6.4 shows an optical microscope image of 1:1 ratio P2MS to PS nanofibers spun from a chlorobenzene solution. In the image dense nanofibers population with a clear bead-on-a-string morphology were observed. The fibers were well formed and densely populated compared to the fibers obtained using the 1:2 ratio of P2MS:PS in solution. When a 1:2 ratio was used very little fibers formed and most of the polymers were formed beads on the silicon surface. This observation suggests that the necessity to have the high molecular weight polystyrene in order to have effective entanglement required for formation of good fibers but not an excess of it.

Figure 6.5 is also an image of 1:1 ratio of polymers but the solvent here was DMF. Fibers are well defined too and possess mostly beaded morphology. In DMF, the fibers prepared using the 1:1 ratio were had more distinct nanofibers compared to the fibers electrospun using from the 1:2 ratio of the polymers (P2MS:PS), which formed scanty fibers. Figure 6.6 shows an optical image and height profile of nanofibers electrospun from DMF. The 2-D perspective of the nanofibers is given in the Figure
Figure 6.5: Optical microscope image of 1:1 P2MS-PS nanofibers electrospun in DMF

Figure 6.6: Optical microscope image of 1:1 ratio of fibers spun in DMF showing their profile
Figure 6.7 is a Raman spectrum of the SWCNTs within nanofibers spun from DMF. The G-band absorption peak for SWCNTs appears at \( \sim 1580 \text{ cm}^{-1} \), which is typical of semi-conducting SWCNTs, while the second-order D-band is observed at about \( 1350 \text{ cm}^{-1} \).\(^{157,158}\) The second order G' - band frequency is observed at about \( 2690 \text{ cm}^{-1} \) which is very similar to G-band frequencies from SWCNTs reported.\(^{158,159}\) A sharp peak is observed at \( \sim 1900 \text{ cm}^{-1} \) which is attributed to the iTOLA band.\(^{157,159}\) The iTOLA band is the combination of a phonon from the in-plane transverse optical branch iTO, with a phonon from the longitudinal acoustic LA branch (iTO+LA) in the Raman excitation process. The intensity of this peak is ascribed to the bundling of the carbon nanotubes in the polymer matrix as opposed to weak iTOLA band observed in single carbon nanotubes.

![Raman Spectrum of DMF Electrospun Nanofiber Composite](Image)

Figure 6.7: Raman spectrum of DMF electrospun nanofiber composite
Figure 6.8 is a scanning electron micrograph of fibers spun from chlorobenzene and the image shows a tubular core. The fibers appear delicate and spongy with diameters between 250 and 300nm.

Figure 6.9 shows a very high magnification of fibers electrospun from DMF and reveals more compact, but porous fibers with mixed morphologies. The image shows a hollow tubular core separating the beads. Fiber diameters range from about 150 to 350 nm. Figure 6.10 is a confocal microscope image of chlorobenzene spun nanofibers incubated with fluorescently labeled IgE in PBS solution. A lot of fluorescence is seen here and it indicates how well IgE was able to bind to the DNP-groups on the nanofibers prepared using chlorobenzene.

Figure 6.8: SEM of nanofibers electrospun in chlorobenzene
Figure 6.8 is a scanning electron micrograph of fibers spun from chlorobenzene and the image shows a tubular core. The fibers appear delicate and spongy with diameters between 250 and 300nm.

Figure 6.9 shows a very high magnification of fibers electrospun from DMF and reveals more compact, but porous fibers with mixed morphologies. The image shows a hollow tubular core separating the beads. Fiber diameters range from about 150 to 350 nm. Figure 6.10 is a confocal microscope image of chlorobenzene spun nanofibers incubated with fluorescently labeled IgE in PBS solution. A lot of fluorescence is seen here and it indicates how well IgE was able to bind to the DNP- groups on the nanofibers prepared using chlorobenzene.
distinct or prominent as the fluorescence observed for the mats electrospun from chlorobenzene.

Figure 6.11: Confocal microscope image of DMF spun nanofibers showing moderate fluorescence

These observations suggest that the nanofibers electrospun from chlorobenzene have most of the DNP functional groups on the surface of the fibers and thus permit the IgE to bind to the nanofiber surface. The nanofibers prepared using DMF as the solvent results in most of the DNP groups being embedded within the nanofibers and few are available for binding to the IgE. It is well established that solvents play a critical role in electrospinning with regards to the quality of the fibers formed. In our case, it is essential that the DNP functional groups decorate the fibers; so, chlorobenzene is the solvent of choice.
Figure 6.12 is a confocal image (post incubation) of the DNP-functionalized nanofibers, prepared using chorobenzene, with Immunoglobulin G, IgG. IgG is a class of antibodies specific for chemical groups other than DNP. This is a control experiment to determine whether there is non-specific adsorption of biomarkers on the nanofibers. It is observed that the fluorescently tagged IgG did not show any kind of interaction with the functionalized nanofibers and thus it rules out any non-specific adsorption on the fibers. This model system demonstrates that fibers decorated with the DNP specifically bind antibodies specific for DNP and do not bind antibodies non-specifically. Thus, this approach may be used to study material–biomarker (antibody) interactions in a specific manner.

Figure 6.12: Confocal microscope image of FITC IgG incubated nanofibers with no fluorescence
Figure 6.12 is a confocal image (post incubation) of the DNP-functionalized nanofibers, prepared using chorobenzene, with Immunoglobulin G, IgG. IgG is a class of antibodies specific for chemical groups other than DNP. This is a control experiment to determine whether there is non-specific adsorption of biomarkers on the nanofibers. It is observed that the fluorescently tagged IgG did not show any kind of interaction with the functionalized nanofibers and thus it rules out any non-specific adsorption on the fibers. This model system demonstrates that fibers decorated with the DNP specifically bind antibodies specific for DNP and do not bind antibodies non-specifically. Thus, this approach may be used to study material–biomarker (antibody) interactions in a specific manner.

Figure 6.12: Confocal microscope image of FITC IgG incubated nanofibers with no fluorescence
In Figure 6.13, the atomic force micrograph shows a section of the nanofibers. The AFM micrograph complements the SEM images in that the nanofibers prepared were linear with beaded morphologies.

Figure 6.13: AFM micrograph of a section of nanofibers and its profile

Figures 6.14 and 6.15 are I-V curves of DNP-nanofibers with (Figure 6.15) and without (Figure 6.14) bound anti-DNP IgE. The unbound nanofibers (Figure 6.14) show a linear response and when the fibers were bound to specific IgE (Figure 6.15), the I–V characteristic deviates from linearity. It was observed that when a current of 5 nA was introduced to the unbound fibers, the corresponding potential difference was about 0.049 V. When the current was doubled, the difference in potential jumped to 0.105 V, etc. The direct proportion trend observed is attributed to the presence of the SWCNTs, hence, the ohmic nature. As for the nanofibers bound to FITC-IgE, a smaller amount of voltage (between 1.5 and 2 times less than potential difference for unbound fibers) is required to
pass through, when the same magnitude of current is sourced. The relationship between the current and voltage in this case is inverse, which is why the curve is of the form: \( y = g(x) = x^3 \). Thus, as observed, the presence of IgE in solution had an impact on the charge transport behavior of the nanotubes embedded in the nanofiber matrix. The result obtained here is consistent with the current–voltage behavior observed for semiconductors.\(^{160}\)

![Figure 6.14: I-V plot of nanofibers without IgE showing ohmic behavior](image-url)
Fabrication of nanofibers was successfully carried out by solution electrospinning and the nanofibers had pendant DNP functional groups on their surface. The DNP was observed to adhere specifically to immunoglobulin E (IgE). For these nanofibers to be effective in binding with IgE, the fibers need to be electrospun from chlorobenzene. The nanofibers were composed of the functional polymer, \( \alpha,\omega\)-bi[2,4-dinitrophenyl-caproic][poly(ethyleneoxide)-b-poly(2-methoxystyrene)-b-poly(ethylene oxide), polystyrene and 1 wt% SWCNTs. The fibers ranged in diameter from 60 to 250 nm (on the average) with a few fibers have dimensions as high as 700 nm. The interaction of the
DNP functional group with the immunoglobulin E was confirmed by confocal microscope images using fluorescently labeled IgE. The IgE bound nanofibers showed I-V characteristic which was different from the I-V characteristic of unbound nanofibers. When unbound, the nanofibers showed resistive I-V characteristic and on binding to IgE, the nanofibers acted like semiconductors. Therefore, it was concluded that such functional nanofibers may be developed as detectors for biomarkers.
Figure A2-1: 500 MHz $^1$H NMR spectrum of PHEMA-b-P3DT.
Figure A2-2: 500 MHz $^1$H NMR spectrum of ethyl end functionalized P3DT.
Figure A2-3: 500 MHz $^1$H NMR spectrum of poly (3-decylthiophene-2,5-diy).
Figure A2-4: 500 MHz $^1$H NMR spectrum of carbonyl end functionalized P(3DT).
Figure A2-5: 500 MHz $^1$H NMR spectrum of hydroxyl end functionalized P(3DT).
Figure A2-6: 500 MHz $^1$H NMR spectrum of bromoester functionalized P(3OT).
Figure A3-1: 500 MHz $^1$H NMR spectrum of 2,5-dibromo-3-octylthiophene.
Figure A3-2: 125 MHz $^{13}$C NMR spectrum of 2,5-dibromo-3-octylthiophene.
Figure A3-3: 500 MHz $^1$H NMR spectrum of 2,5-dibromo-3-diethylene glycol monomethyl ether thiophene.
Figure A3-4: 125 MHz $^{13}$C NMR spectrum of 2,5-dibromo-3-diethylene glycol monomethyl ether thiophene.
Figure A3-5: 500 MHz $^1\text{H}$ NMR spectrum of 2,5-dibromo-3-thiophenemethanol.
Figure A3-6: 125 MHz $^{13}$C NMR of 2,5-dibromo-3-thiophenemethanol.
Figure A3-7: 500 MHz $^1$H NMR spectrum of 2,5-dibromo-3-bromomethylthiophene.
Figure A3-8: 125 MHz $^{13}$C NMR spectrum of 2,5-dibromo-3-bromomethylthiophene.
Figure A3-9: Chloroform solutions of 1:1 block copolymers and 3:1 block copolymers showing fluorescence under UV lamp at a wavelength of 365 nm.
Figure A4-1: Chloroform solutions of the copolymers placed in the dark showing fluorescence under UV light. Wavelength: 365 nm.
Figure A5-1: $^{13}$C CPMAS NMR of regiorandom P3MT.
Figure A5-2: Uv-vis of regiorandom P3MT in acetic acid, $\lambda_{\text{max}} \sim 750$ nm.

Figure A5-3: Uv-vis of pristine MWCNTs in acetic acid, $\lambda_{\text{max}} \sim 780$nm.
Figure A5-4: Uv-vis spectrum of 1%-MWCNT-P3MT, $\lambda_{\text{max}} \sim 700\text{nm}$.

Figure A5-5: Uv-vis spectrum of 5%-MWCNT-P3MT composite.
Figure A5-6: Uv-vis spectrum of 10%-MWCNT-P3MT composite, $\lambda_{\text{max}} \sim 580$ nm.

Figure A5-7: Uv-vis spectrum of 20%-MWCNT-P3MT composite: maxima at $\sim 440$ nm & $\sim 650$ nm. Vibronic peak at $\sim 900$ nm.
Figure A5-8: Circular Dichroism of 10%-MWCNT-P3MT composite.

Figure A5-9: Circular Dichroism of 20%-MWCNT-P3MT composite.
Figure A6-1: AFM image of representative nanofibers electrospun in chlorobenzene.

Figure A6-2: SEM micrograph of nanofibers electrospun in DMF. Mixed morphology: beaded and cylindrical.
Figure A6-3: Optical image of chlorobenzene spun nanofibers. Morphology: beaded.
Figure A 6-4: Combined I-V curve for representative nanofibers before and after incubation in FITC-IgE.
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