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**Design, Synthesis, and Characterisation of Curable
Polythiophenes**

By

James G. Montgomery, B.Sc.

A thesis submitted to
The faculty of Graduate Studies and Research
In partial fulfilment of
The requirements for the degree of

Master of Science

The Department of Chemistry
Carleton University
Ottawa, Ontario
September, 5th, 2000
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Acceptance of the thesis

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Submitted by

James G. Montgomery, B.Sc.

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Prof. Z.Y. Wang, Thesis Supervisor

Prof. G. Buchanan, Chair, Department of Chemistry

Carleton University
September, 2000.

Abstract

The objectives of this thesis are to investigate two routes to curable polythiophenes, where the first route entails a chemical crosslinking approach and the second route is that of a photocurable polythiophene.

The first route is the design and synthesis of an imide containing polythiophene, which was characterised by, NMR, IR, UV-Vis spectroscopy, and investigated for the use of a chemically curable polythiophene. The polymer had a molecular weight of 7254 g/mol, a glass transition temperature of 58 °C, and a 5% weight loss at 312 °C in nitrogen.

Secondly, a soluble, electroactive, polythiophene containing a cinnamal moiety was designed and synthesised. This cinnamal group allows the polythiophene to be crosslinked with ultraviolet light whereby the polymer is insoluble in common organic solvents. The polymer had a molecular weight of 3383 g/mol, a glass transition temperature of 68 °C, and a 5% weight loss at 269 °C in nitrogen.

Since the later polymer was shown to undergo crosslinking in both solution and in the solid state, photolithography of this polymer was studied. The electrochromic behaviour of this polymer both before and after crosslinking was also studied. It was found that before crosslinking, the polymer was electroactive, but after crosslinking the polymer was not electroactive.

Acknowledgements

I would like to take this opportunity to thank a few people who were instrumental in graduate studies at Carleton University. Firstly, I would like to thank Dr. Wang for his generous support and guidance. I would also like to thank Dr. Sean Meng, Connie Kuang, Sean Mackinnon, and Jeff Franklin for their friendship throughout the last two years. In addition I would like to acknowledge Marie D'lorio for making available the resources at the NRC. I would also like to thank Anivis Sanchez and Leanne Bedard for their friendship for the last six years.

Last but not least, I would like thank my mother Beverly Montgomery for her Support over that last twenty-four years.

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Symbols and Abbreviations

DMAc	N,N-dimethylacetamide
DMSO	dimethyl sulfoxide
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HRMS	high resolution mass spectrometry
ITO	indium tin oxide
MS	mass spectrometry
M_n	number-average molecular weight
mp	melting point
M_w	weight-average molecular weight
n	number of repeat units
NMP	1-methyl-2-pyrrolidinone
NMR	nuclear magnetic resonance
RT	room temperature
TBAP	tetrabutylammonium perchlorate
TCE	1,1,2,2-tetrachloroethane
T_d	decomposition temperature
T_g	glass transition temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
T_m	melting temperature
UV	ultra violet
Vis	visible
λ_{em}	emission wavelength
λ_{ex}	excitation wavelength

Chapter 1: Polythiophenes

1.1 A brief introduction

Thiophenes are a class of five membered, heterocyclic, aromatic compounds that contain a sulphur atom and closely resemble the corresponding benzene compounds in boiling points and even smell. The accidental discovery of thiophene in coal tar benzene provides a classic anecdote of organic chemistry. This story starts in the later part of the 19th century where colour reactions were of great value in diagnosis. At the time, an important characterisation reaction for benzene involved the production of a blue colour on heating with isatin and concentrated sulphuric acid. In 1882, during a lecture-demonstration by Viktor Meyer before an undergraduate audience, this test failed, no doubt to the delight of everybody except the professor, and especially the professor's lecture assistant. An inquiry revealed that the lecture assistant had run out of commercial benzene who had provided an alternative sample by the decarboxylation of pure benzoic acid. It became apparent that commercial benzene contained an impurity and it was this impurity, not benzene, which was responsible for the colour reaction. In subsequent investigations, Meyer isolated the impurity via its sulphonic acid derivative and showed it to be the first representative of a new ring system, which he named thiophene. The name stems from the Greek word *Theion* for sulphur, and another Greek word *phaino* which means shining, a root first used in phenol because of its occurrence in coal tar.¹ Like

¹ J.A. Joule, K. Mills, G.F. Smith, Heterocyclic Chemistry, 3rd edition, Chapman & Hall, London, 1995.

pyrrole and furan, the atoms of the thiophene ring can be numbered or lettered, but the former system is generally not used in the literature (see figure 1.1).

Figure 1.1 The generic numbering system for thiophenes

Currently, the intensive interest in thiophenes is coupled with the growth in the study of highly conducting polymers. This began in 1977 with the discovery that a change in the electrical conductivity of polyacetylene occurred upon doping with Br_2 , I_2 , and AsF_5 . Some other conjugated polymers that exhibit interesting electrical and electrochemical properties, as a result of their extended π -bonding system are shown in figure 1.2. The electrical conductivity of all these polymers can be increased through oxidation (p doping) and sometimes through reduction (n doping).

Polythiophene and its derivatives have aroused a great deal of interest over the last decade.^{2,3,4,5,6} This is due to the possible advantages that polythiophenes can offer, such as the applications based on the reversibility of the transition between doped and neutral

² Feast, W.J., Tsibouklis, J., Pouwer, K.L., Grouenendaal, L., Meijer, E.W., *Polymer*, 1996, **37**, 5017.

³ Roncali, J. *Chem. Rev.* 1997, **97**, 173.

⁴ Skothei, T., Reynolds, R., Elsenbamer, R., Handbook of Conducting Polymers, Marcel Dekker, New York, 1986.

⁵ Kanatzidis, M.G., *Chem. Eng. News*, 1990, **68** (49), 36.

⁶ Bredas, J.L., Silbey, R., Conjugated Polymers, Kluwer, Dordrecht, The Netherlands 1990.

states, and the ability to modify their electronic and electrochemical properties by manipulation of the monomer structure.⁷

Figure 1.2 Examples of electrically conducting polymers

However, for some time the application of conducting polythiophenes has been limited due to their intractability and insolubility, especially in its doped state. This problem has been remedied by the use of 3-substituted thiophene and aniline derivatives

⁷ Schopf, G., KoBmehl, G., Polythiophenes-Electrically Conductive Polymers, *Adv. Polym. Sci.*, 1997, **129**, 1.

that not only produce processable and conducting polymers, but also allowed the polymers obtained to be fully characterised both chemically and physically. In the quest for commercially viable conducting polymers, polythiophene has always been one of the best candidates because of its high stability in both its doped and undoped states, ease of structural modification, and controllable electrochemical behaviour. The highly processable poly(3-alkyl)thiophenes (P3ATs) and other substituted polythiophenes, in particular, have been the subject of intense research and development over the last ten years which has led to numerous applications in the areas of microelectronics, optoelectronics, and sensors.⁸

As a result of the use of P3AT's in these applications substituted polythiophenes have become an important representative class of conjugated polymers that form some of the most environmentally and thermally stable organic materials. These materials find a variety of applications such as electrical conductors, polymer light emitting device's, electrochromic or smart windows, photoresists, and antistatic coatings.^{9,10}

1.2 Chemical synthesis of polythiophenes

Polythiophenes are principally prepared by two main pathways, that is chemically or electrochemically. One of the first chemical preparations of unsubstituted polythiophene was reported in 1980 by Yamamoto et al., where the author used a metal-catalysed polycondensation of 2,5-dibromothiophene as the polymer forming reaction

⁸ Borroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., MacKay, K., Friend, R.H., Burn, P.L., Holmes, A.B., *Nature*, 1990, **347**, 539.

⁹ Ohmori, Y., Uchida, M., Muro, K., Yoshino, K., *Jpn. J. Appl. Phys.*, 1991, **30**, L1938.

¹⁰ Kim, S.R., Choi, S.A., Kim, K.J., Lee, C. and Rhee, S.B., *Synth. Met.*, 1995, **71**, 2027.

(see figure 1.3).¹¹ This particular reaction treats 2,5-dibromothiophene with magnesium in the presence of nickel(bipyridine)dichloride. The magnesium reacts with either halogen to form 2-bromo-5-magnesiothiophene or 2-magnesiobromo-5-bromothiophene, which is self coupled with the Ni^{II} catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other. This reaction is propagated and eventually a low molecular weight polymer is formed.

Polymerisation of 2,5-dihalothiophene can also be accomplished through the reaction of a generated bromo-Grignard reagent of thiophene with a Ni^{II} catalyst such as $\text{Ni}(\text{dppp})\text{Cl}_2$ (dppp = 1,3-diphenylphosphinopropane), or the 2,5-dihalothiophene can be polymerise by a polycondensation dehalogenation reaction with a nickel(0) catalyst (see figure 1.3). Similarly, polycondensation of 2,5-dihalothiophenes using $\text{Ni}(\text{cod})_2$ (cod = cyclooctadiene), and triphenylphosphine at 60 – 80 °C in N,N-dimethylformamide (DMF) has also been investigated.¹²

Figure 1.3 Examples of the synthesis of polythiophene

Conditions

- 1) Mg, THF, $\text{Ni}(\text{bipy})\text{Cl}_2$
- 2) Mg or Zn, Ni^0 catalyst
- 3) $\text{Ni}(\text{cod})_2/\text{PPh}_3$, DMF, 16 h
- 4) FeCl_3 , CHCl_3

¹¹ Yamamoto, T., Sanechika, T., Yamamoto, A., *J. Polym. Sci., Polym. Lett. Ed.* 1980, **18**, 9.

¹² Yamamoto, T., Morita, A., Miyazaki, T., Maruyama, T., Wakayama, T., Zhou, Z.H., Nakamura, Y., Kanbara, T., Sasaki, S., Kubota, K., *Macromolecules*, 1992, **56**, 1497.

Another metal-catalysed coupling polymerisation of thiophene was first developed for biaryl polymers.^{13,14} Reaction conditions require an inert atmosphere, the use of an aprotic solvent such as N, N-dimethylacetamide (DMAc), a catalytic amount of nickel(0), triphenylphosphine as a ligand, and zinc metal. Zero valent nickel is generated *in-situ* by the reduction of nickel salts (e.g. NiCl_2) with an excess of zinc dust (see figure 1.4). Typically, moderate reaction temperatures are used ($\sim 80^\circ\text{C}$). Moreover, aryl chlorides are commonly used since they are readily available and less expensive than aryl bromides or aryl iodides. Side reactions, such as reductive dehalogenation occur less often for aryl chlorides and can be limited by the use of mild, dry conditions, and a catalyst such as 2,2'-bipyridine.

Figure 1.4 Dehalogenation reaction scheme¹⁵

Yoshino and Sugimoto first reported the chemical oxidative polymerisation of thiophenes in 1986.¹⁶ The monomer is dissolved in chloroform and oxidatively

¹³ Yamamoto, T.; Kashiwaxaki, A.; Kato, K., *Makromol. Chem.* 1985, **6**, 671.

¹⁴ Yamamoto, T.; Osakada, K.; Wakabayashi, T.; Yamamoto, A. *Makromol. Chem.* 1989, **190**, 1649.

¹⁵ Mitsuru, U., Yoshiyuki, M., Takashi, I., *Macromolecules*, 1991, **24**, 2694.

¹⁶ Sugimoto, R., Takeda, S., Gu, S.H., Yoshino, K., *Chem. Express* 1986, **1**, 635.

polymerised with a Lewis acid such as FeCl_3 , AlCl_3 , MoCl_5 , or RuCl_3 . The Lewis acid method initiates an oxidation of the alkylthiophene to produce radical centres predominantly at the 2- and 5- position of thiophene that propagate to form the polymer (see figure 1.5). The ferric chloride method is generally used to prepare polyalkylthiophenes with molecular weights (M_n) in the range of 30 – 300K and polydispersities ranging from 1.3 to 5.¹⁰ This method is well established and continues to be the most widely used and straightforward means to prepare polythiophene and its derivatives. A major drawback of this method is that the reaction gives varied reproducibility, and can also oxidise substituents on the thiophene ring.¹⁷

Figure 1.5 The mechanism for the oxidative polymerisation of polythiophene

1.3 Regioregular polythiophenes

As previously stated, unsubstituted conjugated polymers are usually insoluble and infusible, thereby presenting a significant disadvantage for their characterisation and possible technological applications. The standard procedure of attaching long, flexible pendant chains to the conjugated backbone can often have deleterious effects on the electrical conductivity of polymers in the oxidised (conducting) states. A significant

¹⁷ McCullough, R.D., in Handbook of Oligo- and Polythiophenes, Wiley, Germany, 1998, p.8.

discovery demonstrated that 3-substituted thiophenes belong to one of the few cases in which substitution of the hydrogen at the 3-position with an alkyl chain does not affect the conductivity of the polymer, but does however impart solubility and consequently enhances processability. There are three generic methodologies that have been developed for the synthesis of regioregular polythiophenes.

These include:

- a) Electrochemical polymerisation.*
- b) Chemical oxidative polymerisation by oxidants such as FeCl_3 and $\text{Cu}(\text{ClO}_4)_2$.*
- c) Chemical polymerisation by catalysed dehalogenation of 2,5-dihalo-3-alkylthiophene, such as nickel catalysed cross-coupling of thiophene Grignard reagents or dihalothiophene monomers.*

In the case of electrochemical polymerisation and oxidative polymerisation, the 3-substituent can be incorporated into the polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH) orientations which in turn result in four triad regio-isomers in the polymer chain, i.e. HT-HT, HT-HH, TT-HT, TT-HH (figure 1.6). Although HT couplings are generally favoured, about 15-20% of HH couplings are often observed.¹⁸

¹⁸ Sze, H., NG, S.C., Synthesis, Characterisation and Applications of Thiophene-Based Functional Polymers, Prog. Polym. Sci. Vol. 23, Pergamon: London, 1998, p. 1167.

Figure 1.6 Possible diads and triads for a polythiophene

The electrical conductivity of functionalised polythiophenes is dependent to a large extent on the stereoregularity achieved during polymerisation. The stereoregularity is determined and controlled by the relative preference for coupling at the α - or β -positions during the polymerisation process (particularly for electrochemical and chemical oxidative couplings). Since the α -position of thiophene is more reactive than the β -position, the coupling of the thiophene unit to form the polymer is expected to occur mainly through the α,α' -positions (see figure 1.7). In this case, a stereoregular polymer is obtained with a fully conjugated backbone that can be easily oxidised and is capable of supporting bipolarons, which are the main form of charge storage in polythiophenes. However, mislinkages through the β -positions (see figure 1.7) result in a “defect” on the

polymer backbone which reduces the conjugation length, raises the oxidation potential and interferes with the formation of bipolarons in the oxidised polymer. Consequently, β -linkages have a detrimental effect on conductivity. The presence of substituents at the β -position of the starting monomer generally results in an increased stereoregularity of the polymer by decreasing the probability of α,β - or β,β -coupling.⁷

On the other hand, as mentioned previously, regioregularity in 3-substituted thiophenes is determined by the preference for HT versus HH coupling in the polymerisation. The presence of HH couplings also represents a "defect" that can result in a significant deviation from coplanarity between adjacent rings (see figure 1.7). This not only results in a reduced conjugation length and bandgap but any deviation from coplanarity also results in an increase in interchain distances arising from poor π -stacking of polymer chains. Therefore, reducing the probability of interchain charge carrier hopping with a consequent in a reduction in conductivity.³

Figure 1.7 A representation of α,α -linkages and α,β -linkages

1.4 Photocrosslinking: an overview

The term photocrosslinking is defined as a process whereby UV or visible light is used to induce the crosslinking of a pre-existing polymer. This means that light irradiation of polymers carrying more than two reactive groups per chain initiates crosslinking to yield a three-dimensional network structure. The reaction may also occur with an added crosslinking reagent, which carries two or more functional groups per molecule.¹⁹

Photocrosslinking requires light absorption in the UV-visible spectral region (typically from 250 to 780 nm) by functional groups in monomers, oligomers, polymers or additives to yield electronically excited singlet and triplet states. This excitation leads to crosslinking directly, or by energy transfer to form reactive intermediates (such as free radicals) which subsequently initiate polymerisation or undergo crosslinking.

Photocrosslinkable polymers can be classified as follows:

- 1) *A polymer bearing functional groups which crosslink by themselves under photoirradiation.*
- 2) *Polymers blended with a photoinitiator.*
- 3) *Polymers mixed with crosslinkers: the functional groups are activated by contact with a crosslinker or the photodecomposition products of a crosslinker.*
- 4) *Polymers synthesised in the presence of polyfunctional monomers via radical or ionic reactions.*

The applicability of the four processes depends on the photocrosslinkable polymeric material itself, the required properties of the photocrosslinked products, and the workability. For example, in photocrosslinking of polyethylene, a photoinitiator such as benzophenone must be added because there are no chromophoric groups in the polyethylene chain and the latter type process has to be applied.¹⁹

¹⁹ Ranby, B., Qu, B., Shi, W., Encyclopedia of Polymeric Materials, 1996, p. 5155.

One of the simplest systems in this group are polymers with cinnamate or chalcone structures as pendant groups in the polymer backbone that undergo photocycloaddition. Poly(vinyl cinnamate) is a well known example of a material that becomes insoluble through photocycloaddition.¹⁹ Crosslinking involves the dimerisation reaction of the UV-activated cinnamate group with a second cinnamate group in the ground state (figure 1.8).^{20,21} The result is the formation of a substituted cyclobutane ring of truxillic ester type (figure 1.8). The crosslinking, from a practical point of view, is reasonably efficient. The density of the crosslinking leading to the insoluble product is very low, and in order to reach the critical hardening point it is sufficient to transform approximately 0.02 % of the cinnamate double bonds into cyclobutane rings.

In addition this cycloaddition reaction takes place by a ground-state antarafacial pathway, and takes disrotatory pathway.

Figure 1.8 The [2 + 2] photocycloaddition reaction of a cinnamate moiety¹⁹

²⁰ Stobbe, H., *Ber.*, 1912, **45**, 3396.

²¹ Stobbe, H., Leffeldt, A. *Ber. B.*, 1925, **58**, 2415.

Some advantages of photocrosslinking are as follows:

- 1) Rapid crosslinking is a one-step process that can form the basis for on-line production units.*
- 2) Crosslinking can be carried out at room temperature for thin coatings and for thicker samples in the melt.*
- 3) The use of solvents can be avoided which gives the process an added environmental value.*

However, the limitations are:

- 1) The thickness of layers which can be photocrosslinked are limited.*
- 2) Problems can occur with pigmented layers that scatter and absorb light.*
- 3) Oxygen inhibition or rate decrease may occur with radical initiating systems.*

1.5 Rationale and objectives

At the present time, there is no photocurable, processable, polythiophenes reported in the literature, despite a commercial need for such a polymeric material in a wide spectrum of applications. The photocured insoluble polythiophene films can be used in device formation, since further layers may be spincoated on top of this layer without causing any damage to the polymer film. Furthermore, such a material could be directly patterned by photolithography on a substrate such as semiconductors, metals, and insulators. In addition, such a material would allow for a versatile process of fabricating electrically conducting polymeric wires, or circuits on solid substrates.

There are at least two routes one can attempt to accomplish the aforementioned goal. That is by either chemical curing, or photochemical curing. When considering a chemical curing process, two approaches to cross-linking could be used (see figure 1.9). The first is to have a latent functional group pendant to the polymer backbone which is inert to polymerisation conditions, but afterwards can react with an epoxide, whereby rendering the polymer insoluble. Or secondly, still having a latent reactive group that is masked by a protecting group and can be removed post-polymerisation to yield the desired moiety. However, there are also disadvantages with such an approach. The process of chemical curing is tedious, it contains numerous steps, and requires both reagents and solvents that are not attractive for a large industrial application.

The second approach involves the photocrosslinking of a pre-existing polymer containing the appropriate photoactive moieties. This approach is a much more elegant avenue, since it eliminates the need for both costly and potentially toxic chemicals. The process is also very simple and can be applied to a large-scale industrial application quite

easily. However, as stated before the photocrosslinkable group must be inert to polymerisation conditions, as well as absorb light at a wavelength that is not interfered with by any other functional groups. Furthermore, since this type of curing is ideally done in the solid state, the efficiency must be enough to render the polymer insoluble. An example of such a group is the cinnamate moiety, which is a well-known example used throughout the literature.

In summary, the objectives of this thesis are to synthesise a 1) soluble, crosslinkable polythiophene, and 2) investigate the physical and electronic properties of the aforementioned polythiophenes for applications as an electrochromic or photolithographic material.

Figure 1.9 Proposed routes to a curable polythiophene

Chapter 2: Chemically crosslinkable polythiophenes

2.1 Design, synthesis, and characterisation of a chemically curable polythiophene

The first approach to achieve the goal of a crosslinkable polythiophene was that of chemical curing. In other words, the goal was to have a nucleophile attached as a latent moiety to the polymer backbone which can then react with a difunctional epoxide whereby curing would occur. More specifically, using a protected amine (such as an imide group), one could incorporate the amine nucleophile into a monomer unit before polymerisation. The imide would then be inert to polymerisation conditions and could be hydrolysed afterwards.

Scheme 2.1 Synthesis of 3-[3-(phthalimido)propyloxy]thiophene

Accordingly, monomer **1a** was designed and synthesised using the method reported by Leclerc et al.,²² whereby 3-methoxythiophene was converted to the appropriate alkoxy derivative with an alcohol under acidic conditions (scheme 2.1). The conversion of 3-methoxythiophene to monomer **1a** in the presence of sodium hydrogen sulphate in toluene afforded monomer **1a** (scheme 2.1). A work-up with water and diethyl ether, followed by purification by column chromatography using silica gel as the stationary phase, and ethyl acetate: hexane as the mobile phase afforded the monomer with only a 14% yield after purification, and a melting point of 82 – 84 °C.

The IR spectrum of the product shows two strong stretches at 1772 and 1705 cm^{-1} , which is indicative of the imide carbonyl stretches. The MS shows the parent molecular ion peak at m/e 288 as expected and the base peak at m/e 160 corresponding to the loss of a $\text{C}_6\text{H}_7\text{OS}$ radical and alpha cleavage of the imide. High-resolution mass spectrometry (HRMS) indicated the correct molecular formula.

The ^1H and ^{13}C NMR chemical shifts are summarised in tables 2.1 and 2.2, and illustrated in figures 2.1, and 2.2 respectively. However, due to the low yield of the reaction, even when using other acids such as KHSO_4 and toluene sulphonic acid, this monomer was deemed not suitable.

²² Leclerc, M., Faid, F., Chayer, M., *Chem. Mater.*, 1997, **9**, 2902.

Table 2.1 Summary of ^1H NMR data for 3-[3-(phthalimido)propyloxy]thiophene

^1H NMR	H ₁	H ₂	H ₄	H ₅	H ₆	H ₉	H ₁₀	H ₁₁
δ (ppm)	7.05	6.54	3.95	2.09	3.82	7.76	7.65	6.14
Splitting	dd.	dd	t	m	t	dd	dd	dd
(J, Hz)	(1.6, 5.2)	(1.6, 5.3)	(6.0)	(6.2)	(6.9)	(5.4, 3.0)	(5.4, 3.0)	(3.1, 1.6)

Table 2.2 Summary of ^{13}C NMR data for 3-[3-(phthalimido)propyloxy]thiophene

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
δ (ppm)	124.6	119.4	157.6	67.8	28.3	35.5	168.4	132.2	133.9	123.4	97.4

Figure 2.1 ^1H NMR spectrum of 3-[3-(phthalimido)propyloxy]thiophene

Figure 2.2 ^{13}C NMR spectrum of 3-[3-(phthalimido)propyloxy]thiophene

2.2 Synthesis and characterisation of 3-(3-phthalimido)propyloxy-4-methylthiophene and 3-(6-phthalimido)hexyloxy-4-methylthiophene

Scheme 2.2 Synthesis of 3-(3-phthalimido)propyloxy-4-methylthiophene and 3-(6-phthalimido)hexyloxy-4-methylthiophene

Since the yield of monomer **1a** was unacceptable, it was deemed unreasonable to use such a monomer in any future chemistry. Instead monomers **1b** and **1c** were synthesised because it was felt that a methyl group ortho to the bromine atom on the thiophene ring would increase the reactivity of the adjacent methoxy group and therefore increase the reaction yield. As anticipated, a large increase in reactivity was noticed between monomers **1a** and monomers **1b** through **1c**, which was evident by the increase in the reaction yield.

The two imide-containing thiophene monomers were synthesised as outlined in scheme 2.2. The reaction proved to be quite successful with a yield of 72% and 77 %, after purification by column chromatography to yield a brown oil. The IR spectrum of **1b** shows two strong stretches at 1766 and 1705 cm⁻¹, which are indicative of carbonyl stretches. The MS shows the parent molecular ion peak at m/e 301 as expected and the base peak at m/e 160 corresponding to alpha cleavage and the loss of a C₅H₁₁O radical. HRMS indicated the correct molecular formula.

The ^1H and ^{13}C NMR chemical shifts are summarised in tables 2.3 and 2.4, and illustrated in figures 2.3 and 2.4 respectively.

Table 2.3 Summary of ^1H NMR data for 3-(3-phthalimido)propyloxy-4-methylthiophene

^1H NMR	H ₁	H ₃	H ₅	H ₆	H ₇	H ₁₀	H ₁₁	H ₁₂
δ (ppm)	6.78	1.99	4.03	2.21	3.92	7.72	7.85	6.14
Splitting(J, Hz)	dd, (2.2, 1.3)	s	t (6.0)	m (6.6)	t (6.9)	dd (5.4, 3.1)	dd (5.5, 3.0)	dd (3.2)

Table 2.4 Summary of ^{13}C NMR data for 3-(3-phthalimido)propyloxy-4-methylthiophene

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
δ (ppm)	119.8	129.1	12.5	155.8	67.5	28.3	35.5	168.3	132.2	133.9	123.2	96.3

To overcome the potential solubility problem due to a relatively short spacer group, it was decided to increase the aliphatic chain length from three carbons to six, which should impart greater solubility to the polymer. The first step in this procedure was the synthesis of an imide with a longer aliphatic chain and terminal alcohol. This was accomplished as a neat reaction between phthalic anhydride and 6-amino-1-hexanol at 100 °C for one hour while stirring to allow the amic acid to form.

Figure 2.3 ^1H NMR spectrum of 3-(3-phthalimido)propyloxy-4-methylthiophene

Figure 2.4 ^{13}C NMR spectrum of 3-(3-phthalimido)propyloxy-4-methylthiophene

Following the formation of the amic acid, the reaction melt was heated at 200 °C for another three hours in order to drive off all water and complete the condensation of the amic acid ring. The reaction had an overall yield of 95%, and the product had a melting point of 50-53 °C. The IR spectra of N-(6-hydroxyhexyl)phthalimide showed characteristic stretches at 1766 and 1710 cm^{-1} for an imide, as well as a broad stretch at 3462 cm^{-1} assigned to the alcohol functionality. The MS shows the parent molecular ion peak at m/e 247 as expected and the base peak at m/e 160 corresponding to alpha cleavage of the imide and the loss of a $\text{C}_5\text{H}_{11}\text{O}$ radical. HRMS indicated the correct molecular formula, while the ^1H and ^{13}C NMR spectra also show patterns indicative of the molecular structure.

N-(6-Hydroxyhexyl)phthalimide was then used to synthesise compound **1c** using the previously mentioned reaction conditions.²² A tan solid was obtained in 77% yield with a melting point of 59-62 °C. The IR spectrum of the product shows two strong stretches at 1770 and 1713 cm^{-1} which is indicative of the strong imide carbonyl stretches. The MS shows the parent molecular ion peak at m/e 343 as expected and the base peak at m/e 160 corresponding to alpha cleavage and the loss of a $\text{C}_5\text{H}_{11}\text{O}$ radical. HRMS indicated the correct molecular formula. The ^1H and ^{13}C NMR chemical shifts are summarised in tables 2.5 and 2.6, and illustrated in figures 2.5 and 2.6 respectively.

Table 2.5 Summary of ^1H NMR data for 3-(6-phthalimido)hexyloxy-4-methylthiophene

^1H NMR	H ₁	H ₃	H ₅	H ₆	H ₇	H ₈	H ₉	H ₁₀	H ₁₃	H ₁₄	H ₁₅
δ (ppm)	6.8	2.1	3.9	1.42	1.51	1.71	1.78	4.0	7.8	7.7	6.10
Splitting	dd	s	t	m	m	m	m	m	dd	dd	dd
(J, Hz)	(3.2, 1.1)		(3.9)	(6.9)	(6.9)	(6.9)	(6.9)	(6.0)	(5.4, 3.0)	(5.4, 3.1)	(3.2)

Table 2.6 Summary of ^{13}C NMR data for 3-(6-phthalimido)hexyloxy-4-methylthiophene

^{13}C NMR	C1	C2	C3	C4	C5	C6 - C9	C10	C11	C12	C13	C14	C15
δ (ppm)	119.7	129.2	12.6	156.2	69.8	29.1, 28.5, 26.6, 25.7	37.9	168.5	132.2	133.9	123.2	95.9

2.5 ^1H NMR spectrum of 3-(6-phthalimido)hexyloxy-4-methylthiophene **2.6 ^{13}C NMR spectrum of 3-(6-phthalimido)hexyloxy-4-methylthiophene**

2.3 Synthesis and characterisation of an imido based polythiophene

2.3.1 Attempted polymerisation of 3-[3-(phthalimido)propyloxy]thiophene

Monomer **1a** was oxidatively polymerised to give a homopolymer that was insoluble in common organic solvents. Furthermore, a copolymer of the aforementioned monomer with another desirable thiophene was attempted. The first copolymerisation attempted was with 3,4-ethylenedioxythiophene. Two polymers were made, one was a polymer with a 1:1 feed ratio the other polymer with a 1:9 feed ratio. However, neither polymers were soluble in any organic solvents.

2.3.2 Copolymerisation of 3-(3-phthalimido)propyloxy-4-methylthiophene

Monomer **1b** was also polymerised to give an insoluble homopolymer. It too was insoluble when copolymerised with other comonomers such as 3-hexylthiophene and 3,4-ethylenedioxythiophene. To overcome this obstacle, it was decided to increase the aliphatic chain length from three carbons to six, which may impart greater solubility to the polymer.

2.3.3 Oxidative polymerisation of 3-(6-phthalimido)hexyloxy-4-methylthiophene

Scheme 2.3 Synthesis of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

Polymerisations were carried out using stoichiometric ratios of monomers in the presence of four equivalents of FeCl_3 in dry chloroform, at room temperature under an inert atmosphere, for 24 hours. The reaction mixture was poured into an excess of methanol and filtered. The resulting polymer was dedoped by soxlet extraction with methanol to remove all residual iron impurities.

Again, when monomer **1c** was copolymerised with 3,4-ethylenedioxythiophene or 3-hexylthiophene the solubility of all copolymers were negligible in common organic solvents. However, a homopolymer of monomer **1c** prepared using ferric chloride was isolated in 58% yield and was partially soluble in some hot, organic solvents, as can be seen in table 2.7.

2.3.4 Solubility of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

Polymer **1** was a dark, blue-black, powdery solid that displayed partial solubility at room temperature in solvents such as DMF, and solubility in hot solvents such as DMSO, DMF, DMAc, etc.

Table 2.7 Solubility of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

Solvent	Polymer 1	
	Cold	Hot
CHCl ₃	±	±
CH ₂ Cl ₂	±	±
THF	±	±
DMF	±	+
DMAc	±	+
DMSO	±	+
NMP	±	+
TCE	±	±
1,2-dichlorobenzene	±	+

Key: (+) – fully soluble, (-) not soluble, (±) – partially soluble, based on 5 mg in 1 mL of solvent

The limited solubility of polymer **1** in organic solvents is quite puzzling since the polymer has a long flexible, carbon chain attached with a flexible ether linkage. Both functional groups should impart solubility to the polymer by limiting π to π stacking of

the polymer backbone. However the reason for insolubility of copolymers with 3-hexylthiophene is unknown. By adding the long aliphatic group to the polymer backbone, the polymer should be soluble and has been shown numerous times in the literature.^{23,24,25,26} On the other hand, the solubility of copolymers prepared with 3,4-ethylenedioxythiophene is predictable because this monomer is characteristically insoluble when polymerised. This characteristic lack of solubility is a reflection of the large amount of work in the literature trying to prepare soluble derivatives of the moiety.²⁷

Due to the fact that this polymer shows limited solubility in hot, high boiling, organic solvents. It was decided to use a new approach to accomplish the goals described in chapter one. In fact, upon further consideration, using an imide functionality as a protecting group, probably is not the wisest choice. The reason being is as follows: when using the imide group to protect a primary amine, what we are really doing is linking a very rigid, planar group to a thiophene which itself is characteristically planar and rigid. The solubility problem is therefore characteristic of both moieties and intuitively either group should not be joined.

2.3.5 Spectroscopic characterisation

Polymer **1** also exhibits thermochroism when heated above 50-60 °C, where a colour change of purple to orange is observed. UV/Vis spectra show that when heated to

²³ Leclerc, M., Diaz, F.M., Wegner, G., *Makromol. Chem.* 1989, **190**, 3105.

²⁴ McCullough, R.D., Lowe, R.D., Jayaraman, M., Anderson, D., *J. Org. Chem.* 1993, **58**, 904.

²⁵ Hotta, S., Rughooputh, D.V., Heeger, A.J., *Macromolecules*, 1987, **20**, 212.

²⁶ Iraqi, A., Crayston, J., Walton, J., *J. Mater. Chem.*, 1995, **5**, 1831.

²⁷ Kumar, A., Welsh, D., Morvant, M.C., Piroux, F., Abboud, K., Reynolds, J.R., *Chem. Mater.*, 1998, **10**, 896.

60 °C that the $\pi - \pi^*$ transition bathochromically shifts from 406 nm to 437 nm compared to its spectrum at room temperature, while the $n-\pi^*$ transition at 289 nm remains the same (see figure 2.7). This observation is not surprising since this behaviour has been exhibited before with other poly(3-alkoxy-4-methylthiophene)s.^{28,29,30} This purple to orange colour transition is related to a rod-to-coil transition of the conjugated backbone. The rodlike, highly conjugated form is believed to be associated with intermolecular and intramolecular (through chain folding) π -stacks, while upon heating, side-chain disordering disrupts these assemblies to yield nonplanar (less conjugated) polymer chains.²²

Figure 2.7 UV/Vis Spectra of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene] at 25 °C and 60 °C

²⁸ Daoust, G., Leclerc, M., *Macromolecules* 1991, **21**, 455.

²⁹ Roux, C., Bergeron, J.Y., Leclerc, M., *Makromol. Chem.* 1993, **194**, 869.

³⁰ Levesque, I., Leclerc, M. *Chem. Mater.* 1996, **8**, 2843.

The ^1H and ^{13}C NMR spectra of polymer **1** were taken at 350 K and are tabulated in tables 2.8 and 2.9, and illustrated in figures 2.9 and 2.10 respectively. All spectra show the expected results and the same characteristic patterns of monomer **1c**. However, the molecular weight of the polymer is shown to be low by the NMR spectrum where two small peaks at 6.58 ppm and 6.09 ppm can be seen. The peaks are indicative of the terminal protons of the polymer chain at the alpha position's of the thiophene ring and can still be seen in the NMR since their proportion to the other polymeric protons is still small. If the molecular weight of the polymer were substantially larger, these peaks would be not observable.

The ^{13}C NMR spectrum of polymer **1** showed 15 distinguishable peaks for each of the representative carbon atoms. The spectrum can be directly compared with that of monomer **1c**, except that when polymerisation occurs two new quaternary carbons are produced thereby decreasing the intensity of proportional peaks.

Table 2.8 Summary of ^1H NMR data for poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

^1H NMR	H ₁	H ₅	H ₆	H ₇	H ₈	H ₉	H ₁₀	H ₁₃	H ₁₄
δ (ppm)	2.17	3.83	1.31	1.32	1.62	1.78	3.53	8.0	7.7
Splitting (broad)	s	t	m	m	m	m	t	m	m

Table 2.9 Summary of ^{13}C NMR data for poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

^{13}C NMR	C1	C2	C3	C4	C5	C6 - C9	C10	C11	C12	C13	C14	C15
δ (ppm)	117.2	129.2	11.9	151.9	69.8	30.1, 28.9, 27.2, 25.5	36.9	167.2	131.3	133.5	122.9	72.5

The infrared spectrum shows the characteristic stretches at 1772 and 1699 cm^{-1} for the carbonyl functionality of the imide (see figure 2.8). These spectral data clearly indicated the formation of the expected polymer.

Figure 2.8 IR Spectrum of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

Figure 2.9 ^1H NMR spectrum of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

Figure 2.10 ^{13}C NMR spectrum of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

2.3.6 Molecular weight

The molecular weight of a polymer is of prime importance in its synthesis and application. Important aspects, such as thermal and mechanical properties are all dependent on the molecular weight. In general, the physical attributes of the polymer increase with increasing molecular weight until a limit is reached at which point, changes in the molecular weight affect those properties in a limited fashion. The attainment of high molecular weight is dependent upon the accurate control of stoichiometry (i.e., the molar ratio of reactants undergoing polymerisation). The minimum useful molecular weight, is usually in the range of 5, 000 – 10, 000 g/mol but differs for different polymers.³¹

In order to obtain a molecular weight distribution of the polymer, gel permeation chromatography (GPC) was used. The polydispersity index (M_w/M_n) for polymer **1** was 1.63 indicating that the molecular weight distribution is large. For polymer **1**, GPC analysis in DMF at 50 °C relative to polystyrene showed that a low molecular weight product was obtained. The apparent weight average molecular weight for the polymer was 7254 g/mol and number average was 4445 g/mol. However, this result is deceiving because the molecular weight is really of the lowest molecular component of the polymer that is soluble in DMF since the polymer was fractionated before GPC analysis.

Other methods used in determining the average molecular weight of polymers are based on solution properties. These would include methods based on light scattering, and viscosity.^{32,33} The various methods do not yield the same average molecular weights as

³¹ Odias, G., Principles of Polymerisation, 3rd ed., 1991, p. 20.

³² Billingham, N.C., Molar Mass Measurements in Polymeric Science, Kogan Page, London, 1972.

the properties being measured are biased differently towards the different shaped polymer molecules in a polymer sample.

2.3.7 Thermal properties

Polymeric materials are characterised by two major types of transition temperatures, the crystalline melting temperature (T_m) and the glass transition temperature (T_g). Polymer **1** exhibited crystalline behaviour as was indicated by DSC. The DSC trace showed both a T_g at 58 °C and a T_m at 119 °C suggesting a semicrystalline nature. The thermooxidative stability of the polymers was measured by thermogravimetric analysis (TGA) in nitrogen. Thermogravimetric analysis indicated a 5% weight loss in nitrogen at 312 °C.

Figure 2.11 DSC of poly[3-(6-phthalimido)hexyloxy-4-methylthiophene]

³³ Bohdanecky, M., Kovar, J., Viscosities of Polymer Solutions, Elsevier, Amsterdam, 1982.

Chapter 3: A Photocurable polythiophene

3.1 Introduction

Due to the difficulties encountered synthesising polymer **1**, the goals for this thesis were re-evaluated. The development of a photocrosslinkable polymer was deemed favourable for two reasons. One, the number of steps to achieve the required goal would be reduced and the simple elegance of the crosslinking step was beneficial. In order to accomplish the goal, a cinnamate moiety was chosen to be incorporated into a polythiophene backbone. However, a couple of potential problems could arise with the use of such a moiety. First, the double bond may react with ferric chloride. However, it has been shown in our lab that this group is not reactive during the polymerisation conditions required for acrylate. Moreover, if and when a film has been formed and ready for crosslinking, will this group readily react in solid state conditions? The cinnamate moiety has been proven to be less efficient in solid state conditions by Reiser et al., and very reactive in solution.^{33,34} Nevertheless, will our conditions be favourable to such a reaction where a finite number of cinnamate groups must overlap and be excited in order for [2 + 2] cycloaddition to occur?

Scheme 3.1 Introduction of a cinnamate moiety into a polythiophene

³³ Reiser, A., Egerton, P.L., *Macromolecules*, 1979, **12**, 670.

3.1 Design, synthesis, and characterisation of 2-(3-thienyl)ethylcinnamate

Scheme 3.2 Synthesis of 2-(3-thienyl)ethylcinnamate

The conversion of 3-ethanalthiophene in the presence of triethylamine and cinnamoyl chloride at room temperature, afforded monomer **2a**. The reaction was stirred at room temperature until no starting thiophene remained, as determined by TLC. The resulting reaction mixture was filtered to remove the precipitated salt and the filtrate was poured into water. The organic phase was separated and repeatedly washed with water. The organic phase was removed under reduced pressure to yield a light yellow solid in 65% yield after purification by column chromatography with a mp of 34 - 38 °C.

The IR spectrum of the product shows two strong stretches at 1712 and 1632 cm⁻¹, which are attributed to the ester carbonyl and carbon-carbon double bond (alkene) stretches. The C-O stretch can be seen at 1173 cm⁻¹. The MS shows the parent molecular ion peak at m/e 258 as expected and the base peak at m/e 131 corresponding to α cleavage of the carbonyl and the loss of the C₆H₇OS⁺ ion. HRMS indicated the correct molecular formula. The ¹H and ¹³C NMR chemical shifts are summarised in tables 3.1

³⁴ Egerton, P.L., Pitts, E., Reiser, A., *Macromolecules*, 1981, **14**, 95.

and 3.2 respectively and were assigned with the help of COSY, HETCOR and DEPT experiments.

Table 3.1 Summary of ^1H NMR data for 2-(3-thienyl)ethylcinnamate

^1H NMR	H_1	H_2	H_4	H_5	H_7	H_8	H_{10}	H_{11}	H_{12}	H_{13}
δ (ppm)	7.19	6.96	2.95	4.32	6.34	7.62	7.32	7.39	7.27	6.91
Splitting (J, Hz)	dd (4.9,3.0)	dd (4.9,3.0)	t (6.9)	t (7.0)	d (16.0)	d (16.0)	d (6.7)	d (7.2)	t (6.9)	dd (4.9,1.1)

Table 3.2 Summary of ^{13}C NMR data for 2-(3-thienyl)ethylcinnamate

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
δ (ppm)	125.7	128.4	138.1	29.7	64.4	166.9	118.0	144.9	134.4	129.1	128.9	128.2	121.6

Figure 3.1 ^1H NMR spectrum of 2-(3-thienyl)ethylcinnamate

Figure 3.2 ^{13}C NMR spectrum of 2-(3-thienyl)ethylcinnamate

3.2 Design, synthesis, and characterisation of 2-[3-(2,5-dichloro)thienyl]ethylcinnamate

Monomer **2b** was synthesised as an alternative to monomer **2a** since by having a dihalo-monomer the option of using this compound in a different polymer forming reaction is possible. Thus, this monomer could be used in a dehalogenation condensation reaction whereby both the carbonyl and alkene functional groups will be inert to the aforementioned reaction conditions.

The first step in this procedure was the chlorination of 3-ethanolthiophene. This was accomplished by treating 3-ethanol thiophene with 2 equivalents of N-chlorosuccinimide (NCS) in DMF, at 40 °C, for twenty-four hours, which afforded 2,5-dichloro-3-ethanolthiophene in 65% yield. The IR spectrum of 2,5-dichloro-3-ethanolthiophene showed a stretch at 3441 cm⁻¹ that was assigned to the alcohol functionality, and a strong resonance at 1043 cm⁻¹ for the C-O stretch. The MS shows the parent molecular ion peak at m/e 196 as expected, and M + 2 and M + 4 peaks at 198 and 200 with decreasing intensities. HRMS indicated the correct molecular formula. The ¹H and ¹³C NMR spectra also show patterns indicative of the molecular structure.

Scheme 3.3 Synthesis of 2-[3-(2,5-dichloro)thienyl]ethylcinnamate

2,5-Dichloro-3-ethanethiophene was then used to synthesise monomer **2b** using cinnamyl chloride and the same conditions for monomer **2a**. A light yellow oil was obtained in 73% yield after purification by column chromatography. The IR spectrum of the product shows two strong stretches at 1712 and 1633 cm^{-1} , which is indicative of the carbonyl ester and carbon-carbon double bond stretches. The MS shows the parent molecular ion peak at m/e 326 as well as $M + 2$, and $M + 4$ peaks at 328 and 330. HRMS indicated the correct molecular formula. The ^1H and ^{13}C NMR chemical shifts are summarised in tables 3.3 and 3.4 respectively and were assigned with the help of COSY, HETCOR, and DEPT experiments.

Table 3.3 Summary of ^1H NMR data for 2-[3-(2,5-dichloro)thienvl]ethylcinnamate

^1H NMR	H_2	H_4	H_5	H_7	H_8	H_{10}	H_{11}	H_{12}
δ (ppm)	6.76	2.96	4.37	6.44	7.72	7.56	7.42	7.44
Splitting	s	t.	t.	d.	d.	d	t	t
(J, Hz)		(6.6)	(6.7)	(13.4)	(13.4)	(6.9)	(6.4)	(5.9)

Table 3.4 Summary of ^{13}C NMR data for 2-[3-(2,5-dichloro)thienvl]ethylcinnamate

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
δ (ppm)	126.9	127.6	135.3	28.2	63.6	167.2	118.3	145.8	134.9	129.5	128.5	130.9	123.9

Figure 3.3 ^1H NMR spectrum of 2-[3-(2,5-dichloro)thienyl]ethylcinnamate

Figure 3.4 ^{13}C NMR spectrum of 2-[3-(2,5-dichloro)thienyl]ethylcinnamate

3.3 Synthesis of poly(3-ethylcinnamatethiophene)

3.3.1 Polymerisation of 2-(3-thienyl)ethylcinnamate

Monomer **2a** was used in the next logical step, which is polymerisation. Using ferric chloride as the Lewis acid, monomer **2a** was oxidatively polymerised for 24 hours and worked up as usual. The resulting orange polymer was recovered in 50% yield. The IR spectrum of the polymer shows two strong stretches at 1709 and 1634 cm^{-1} , which are assigned to the ester carbonyl and carbon-carbon double bond (alkene) stretches. The C-O stretch can be seen at 1152 cm^{-1} .

The resulting homopolymer was completely insoluble in any organic solvents even when copolymerised with another monomer such as 3-hexylthiophene. The explanation for the lack of solubility is as follows. For this polymer to become insoluble, it must be undergoing crosslinking. A probable explanation is that when the Lewis acid is added to the reaction, it forms a radical on the thiophene ring. The thiophene then acts as an initiator and activates the double bond to behave like styrene. Thus crosslinking occurs and consequently, insolubility.

This means that our approach must change once again. However, if the crosslinking moiety is not inert to the previous reaction conditions we must change the polymer forming environment. In summary, a new polymerisation condition must be used that does not involve any free radicals or Grignard reagents because both will react with the cinnamate moiety. Consequentially, the dehalogenation condensation reaction was chosen as the polymer forming reaction.

3.3.2 Polymerisation of 2-[3-(2,5-dichloro)thienyl]ethyl cinnamate

Polymer **2** was prepared via nickel(0) catalysed coupling polymerisation of 2-[3-(2,5-dichloro)thienyl]ethylcinnamate shown in scheme 3.4. On the basis of previous results, specifically the synthesis of poly(ether ketone)s by nickel-catalysed coupling polymerisation of aromatic dichlorides,³⁵ the polymerisation of monomer **2b** was carried out in the presence of NiCl₂, zinc, triphenylphosphine (PPh₃), and bipyridine (bpy). Ueda et. al. found that the optimal solvents for polymerisation were DMAc or NMP while the best temperature for the reaction was 85 °C. Polymerisation did not start until 60 °C, while raising the temperature over 100 °C, gave inferior results. The concentration whereby the highest inherent viscosity was reached was found to be 7 mol% of the catalyst based on the monomer.

Scheme 3.4 Synthesis of poly[3-(2-ethane cinnamate)thiophene]

Because one of the main side reactions in the nickel-catalysed coupling of aryl chlorides is the transfer of aryl groups from triphenylphosphine to the metal. This

³⁵ Ueda, M., Ichikawa, F. *Macromolecules*, 1990, **23**, 926.

reaction is suppressed by using bipyridine and excess amounts of triphenylphosphine to NiCl_2 . An equimolar amount of bipyridine to NiCl_2 is the most effective

3.3.3 Solubility of poly[3-(2-ethane cinnamate)thiophene]

Polymer **2** was isolated in 90 % yield to give an orange powdery solid that was soluble in many polar aprotic organic solvents such as chloroform, and dichloromethane. The full results can be seen in table 3.5.

Table 3.5 Solubility of poly[3-(2-ethane cinnamate)thiophene]

Solvent	Polymer 2	
	Cold	Hot
CHCl_3	+	+
CH_2Cl_2	+	+
THF	+	+
DMF	+	+
DMAc	+	+
DMSO	±	+
NMP	+	+
TCE	±	±
1,2-dichlorobenzene	+	+

Key: (+) – fully soluble, (-) not soluble, (±) – partially soluble, based on 5 mg in

1 mL of solvent

3.3.4 Spectroscopic characterisation

The UV/Vis spectrum of polymer **2** which is illustrated in figure 3.5 has absorptions at 283 nm and 416 nm which are the $n\text{-}\pi^*$ transition of the carbonyl group and $\pi\text{-}\pi$ absorption band of the thiophene ring. The bathochromic shift from monomer **2b** indicates that an increase in the length of conjugation has occurred due to polymerisation. The fluorescence spectra of polymer **2** show that at a λ_{ex} of 280 nm, the λ_{em} is 548 nm. However, polymer **2** shows no thermochroism.

Figure 3.5 UV/Vis spectrum of poly[3-(2-ethane cinnamate)thiophene]

The ^1H and ^{13}C NMR spectra of polymer **2** are tabulated in tables 3.6 and 3.7 and illustrated in figures 3.7. and 3.8. All spectra show the expected results and the same characteristic patterns of monomer **2b**.

The ^{13}C NMR spectrum of polymer **2** showed 13 distinguishable peaks for each of the representative carbon atoms. The spectrum can be directly compared with that of starting monomer as monomer **2b** except that when polymerisation occurs, two new quaternary carbons are produced thereby decreasing the intensity of proportional peaks.

Table 3.6 Summary of ^1H NMR data for poly[3-(2-ethane cinnamate)thiophene]

^1H NMR	H_2	H_4	H_5	$\text{H}-$	H_8	H_{10}	H_{11}	H_{12}
δ (ppm)	7.13	3.20	4.47	6.44	7.72	7.54	7.35	7.54

Table 3.7 Summary of ^{13}C NMR data for poly[3-(2-ethane cinnamate)thiophene]

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
δ (ppm)	126.6	127.9	135.3	28.8	63.9	166.8	117.9	145.1	134.8	129.3	128.8	130.3	123.9

The infrared spectrum shows the characteristic stretches at 1709 and 1634 cm^{-1} for the ester and carbon-carbon double bond functionality of the cinnamal moiety. These spectral data clearly indicated the formation of the expected polymers.

Figure 3.6 IR spectrum of poly[3-(2-ethane cinnamate)thiophene]

Figure 3.7 ¹H NMR spectrum of poly[3-(2-ethane cinnamate)thiophene]

Figure 3.8 ^{13}C NMR spectrum of poly[3-(2-ethane cinnamate)thiophene]

3.3.5 Molecular weight

For polymer **2**, GPC analysis in chloroform relative to polystyrene showed that a low molecular weight product was obtained. The apparent weight average molecular weight for the polymer was 3383 g/mol and number average was 1140 g/mol with a polydispersity of 2.4. These molecular weights are very low, however they cannot be compared directly to the results of Yamamoto and Sheares since our detection method uses a UV/Vis detector while the authors' use viscosity and light scattering to characterise molecular weight. These various methods do not yield the same average molecular weights as the properties being measured and are biased differently towards the different shaped polymer molecules in a polymer sample. Assuming that similar structures are being compared, a higher viscosity corresponds to high molecular weights. The inherent viscosity of polymer **2** was 0.1 dL/g in chloroform at 30 °C.

3.3.6 Thermal properties

Polymer **2** exhibited crystalline behaviour as was indicated by DSC. The DSC trace showed a T_g at 68 °C. The thermooxidative stability of the polymer was measured in nitrogen. TGA indicated a 5% weight loss for polymer **2** in nitrogen at 269 °C.

Figure 3.9 DSC curve of poly[3-(2-ethane cinnamate)thiophene] **Figure 3.10 TGA curve of poly[3-(2-ethane cinnamate)thiophene]**

3.4 Photocuring and photolithography

In order to study the degree of curing as a function of time, IR spectroscopy was used to yield information on the amount of time needed to crosslink the cinnamate group. Each IR spectra obtained is an average of 4 scans, each with a resolution of 4 cm⁻¹. The spectra were obtained one after another in order to ensure that the UV curing process was obtained in real time. The C=O stretch at 1727 cm⁻¹ and the C=C ring stretching at 1635 cm⁻¹ were used to calculate conversions. The C=O stretching vibration was used as an internal standard since this peak remains unchanged during the course of the experiment.

The conversion of the carbon-carbon double bond to a carbon-carbon single bond through curing at any time can be calculated by first integrating the unreacted alkene peak at the start of the experiment. At a subsequent time t , the area of the peak can be integrated and the conversion at that time can be determined by the following equation:³⁶:

$$x(t) = \frac{A(0) - A(t)}{A(0)}$$

Where $x(t)$ is the conversion at time t , $A(0)$ is the normalised area (with respect to 1635 cm⁻¹) of the initial alkene peak, and $A(t)$ is the normalised area of the alkene peak at time t .

The infrared spectrum of polymer **2** for three different UV exposure times is shown in Figure 3.11. At the beginning of the curing process, both the carbonyl and alkene peaks are distinct. As the curing process progresses, the size of the alkene peak shrinks in size as more cinnamate groups react to form a crosslinked network. Toward the end of the process the peak at 1635 cm⁻¹ has decreased substantially since most of the

³⁶ Chiou, B.S., Khan, S.A., *Macromolecules*, 1997, **30**, 7322.

functional groups have reacted. Figure 3.12 is a plot of alkane conversion as a function of UV exposure time. During the initial stages of UV curing, the crosslinking is very slow and the increases very rapidly after 30 seconds.

The cinnamate conversion data was also used to determine a reaction order for the photoinitiated [2 + 2] cycloaddition reaction. By assuming a rate expression for the reaction and then using the integral method to analyse the kinetic data, we can obtain the order of the reaction. For the cinnamal system, a first-order reaction was assumed:

$$\frac{dx}{dt} = k(1-x)$$

Where x is the cinnamal conversion, t is the time, and k is the rate constant. This expression can then be integrated from the beginning of the reaction ($t = 0$ sec, $x = 0$) to a time t and a conversion x to give the expression:

$$\ln [(x/1-x)] = kt$$

Figure 3.11 Typical IR spectrum of three different UV exposure times

Figure 3.12 Graph of % conversion as a function of UV exposure time for poly[3-(2-ethane cinnamate)thiophene]

Figure 3.13 Plot of $\ln(1-x)$ as a function of UV exposure time

Therefore a plot of $\ln[1-x]$ as a function of time would result in a straight line with the slope equal to the rate constant. Such a plot is shown in figure 3.13 where we find that the rate constant of the reaction is $4.1 \times 10^{-3} \text{ s}^{-1}$.

The ability of polymer **2** to attain patterns by photolithography can be seen by the SEM images in figure 3.14. The orange-coloured films were spun cast from chloroform at room temperature to give uniform films and irradiated with UV light for 2 minutes covered by a photomask. The images shown in figure 3.15 shown the cured image as the dark area where the image is magnified 50 times larger, the smallest line shown is 16.2 μm

A depth profile of the outlined box in figure 3.13 can be seen in figure 3.16. This image shows that the average size of the hills and valleys of the photo-patterned image in figure 3.16 are approximately 1000 Å in depth, or in other words the height of the cured polymer hill is approximately 1000 Å.

Analysis of the thin films by ellipsometry afforded the film thickness and optical constants before and after curing. The results were 144.97 nm before curing with a refractive index of 1.53, while after curing the film thickness was 152.43 nm with a refractive index of 1.4. The measured standard error (MSE) of the measurements was 4.4 and 5.2 respectively.

Figure 3.14 SEM pictures of poly[3-(2-ethane cinnamate)thiophene]films on a silicon wafer

Figure 3.15 Micrograph of poly[3-(2-ethane cinnamate)thiophene] films silicon

Figure 3.16 Depth profile of figure 3.15

3.4.1 Electrochemistry

Cyclic voltammograms of a polymer **2** coated ITO electrode was recorded in a one-compartment, three-electrode cell with a Pt-wire counter electrode and an Ag/Ag^+ reference. The electrolyte solution was 0.1 M TBAP in acetonitrile. The cathodic and anodic peaks, at 0.9 V and 1.8 V vs. Ag/Ag^+ , during the first cycle are separated by 0.9 V (see figure 3.17). Figure 3.18 illustrates that the current is linearly proportional to the scan rate indicating that the polymer, and all electroactive sites, is electrode supported. As the potential was varied, the colour of the polymeric film varied, the colour of the film changed from a orange-red colour in the reduced state to a light blue colour in the oxidised state which can be seen in figure 3.19.

Figure 3.17 Cyclic voltammogram of poly[3-(2-ethane cinnamate)thiophene]

Figure 3.18 Scan-rate dependence of the cyclic voltammetry of poly[3-(2-ethane cinnamate)thiophene] scanned at (a) 300, (b) 250, (c) 200, (d), 150, (e) 100, (f) 50 mV/s

Figure 3.19 Images of Oxidised (III), Neutral (II), Reduced (I) poly[3-(2-ethane cinnamate)thiophene] films on ITO

3.4.2 Spectroelectrochemical analysis

In order to probe the electronic structure of the polymers, and to examine the optical changes that occur during redox switching which are important for electrochromic applications, spectroelectrochemical analyses were carried out. Films were spin coated on ITO and 0.1 TBAP/CH₃CN was used as the electrolyte/solvent system, along with Ag as the pseudo-reference and platinum as the counter electrode. The optoelectrochemical spectral series was monitored while scanning from 260 nm (4.77 eV) to 1600 nm (0.78 eV) as the polymer was sequentially stepped between its fully oxidised and fully reduced forms. Polymer **2**, in its neutral form exhibits an electronic bandgap (E_g), defined as the onset for the $\pi - \pi^*$ absorbance, of 413 nm (3.00 eV). As the potential is sequentially increased from 600 mV to 1400 mV, in 100 mV steps, the bandgap red shifts to 777 nm (1.60 eV) as the polymer is oxidised while also absorbing in the vis-NIR region at the expense of the intensity of the $\pi - \pi^*$ transition at 413 nm (eV) which is illustrated in figure 3.20. The oxidation of the polymer leads to the formation of bipolaronic charge carriers and induces a change in the polymer conformation to a quinoidal structure. The bipolarons are characterised by two new low energy transitions which appear in the vis-NIR region at the expense of the intensity of the $\pi - \pi^*$ transition.

Figure 3.20 Optoelectrochemical analysis of poly[3-(2-ethane cinnamate)thiophene] as a function of applied potential

In 0.1 M TBAP/ CH_3CN : (a) 1.4 V, (b) 1.3 V, (c) 1.2 V, (d) 1.1 V, (e) 1.0 V, (f) 0.9 V, (g) 0.8 V, (h) 0.7 V, (i) 0.6 V.

3.4.3 Optical switching studies

Electrochromic switching studies were carried out to monitor absorbance changes with time during repeated potential stepping between reduced and oxidised states to obtain an insight into changes in optical contrast. In an initial experiment, polymer **2** was switched by stepping between the potential of 1.4 V and 0 V, with a switching interval of 5 seconds. Using 0.1 M TBAP/ CH_3CN as the electrolyte, while monitoring the absorbance at 1550 nm. The polymer film repeatedly and reproducibly changed from a light blue oxidised state to a light orange-red reduced state. Furthermore, the $\Delta T\%$ for the 1st switch is 52.3% while the $\Delta T\%$ during the 200th switch is 41.5%. Conversely, the

$\Delta T\%$ on the 204th switch is only 10.9 %. These figures coupled with figures 3.21 through 3.23 show that the lifetime stability of the film is quite poor. The reason being is that after 240th switch the charged polymer actually starts to dissolve into the electrolyte solution. Thus the change in transmittance actually decreases because the film is dissolving into solution rather than actually degrading.

Figure 3.21 Electrochromic switching and optical absorbance change monitored at 1550 nm for the 1st and 4th switch

Figure 3.22 Electrochromic switching and optical absorbance change monitored at 1550 nm for the 200th and 204th switch

Figure 3.23 Electrochromic switching and optical absorbance change monitored at 1550 nm for the 240th and 244th switch

3.4.4 Electrochemistry after curing

Unlike uncured films of polymer **2**, cured films show irreversible electroactivity. After curing the films are electroactive and will oxidise. However, the polymer stays in this redox state and cannot be reduced. This can be seen in figure 3.24 where the cyclic voltammogram shows that after eight scans the electroactivity of a cured film diminishes drastically. What may be happening is that when the films are crosslinked, the interpenetrating network that is formed is too dense for ions to move freely in or out of the film. Hence, once the ions move into the film it will oxidise or reduce. Once the ions move in however, they are trapped and cannot move out which is probably why the process is not reversible.

Figure 3.24 Cyclic voltammogram of polymer 2 after curing

Chapter 4: Experimental

4.1.1 Materials: All materials were purchased from Aldrich Chemical Co. and used as received unless stated otherwise. Dimethylsulphoxide (DMSO), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) and other common organic solvents (Aldrich) were reagent grade and were used as received. 2,2'-bipyridine (99+%) and triphenylphosphine (99%) were purified by recrystallization from hexane and ethanol respectively, followed by drying under vacuum for 12 hours at room temperature. Powdered (325 mesh) zinc was washed with 2% HCl/H₂O, MeOH, anhydrous diethyl ether and dried under vacuum at 150 °C. anhydrous nickel chloride was obtained by drying under vacuum at 220 °C for 24 hours.

4.1.2 Characterisation Methods: ¹H and ¹³C NMR spectra were recorded on either a Varian Gemini-200 or Bruker-400 instrument using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomem Michelson 120 FTIR spectrometer. Low (EI) and high resolution mass spectra were obtained at the University of Ottawa on a VG 7070E and Kratos Concept IIF spectrometers, respectively. UV/Vis/NIR absorption spectra were recorded on a Perkin Elmer UV/Vis/NIR Lambda 900 spectrometer. Fluorescence measurements were made on a Shimadzu RF-1501 spectrofluorophotometer. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Gel permeation chromatography (GPC) was performed using chloroform at ambient temperature at a flow rate of 1.0 mL/min; a UV detector set at 254-nm wavelength was used for detection, and a 5% crosslinked polystyrene-divinylbenzene was used as the column packing. Apparent M_w and M_n were calculated relative to narrowly distributed polystyrene molecular weight standards. Inherent

viscosities were measured in chloroform solution at 25 ± 0.1 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko 220C DSC at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. Thermal stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyser run from 25 °C to 800 °C at a heating rate of 10 °C/min under a nitrogen flow rate of 200 mL/min. Ellipsometry was performed on silicon wafers using a J.A. Wollam Co., M-44 ellipsometer. Samples prepared for photolithography were spin coated at 4000 RPM on silicon wafers using solutions of concentration (0.05g/ 2mL), these films were then exposed to UV light with a Novacure curing station through a KarlSuss MJB3 Mask aligner at the National Research Council Institute for Microstructural Sciences in Ottawa, Ontario. The exposed samples were then developed by soaking in chloroform for 30 seconds. Micrographs were taken on an Olympus optical microscope.

4.2 Monomer synthesis

3-[3-(phthalimido)propoxy]thiophene

1a

A 100 mL, round-bottomed flask, fitted with a dean-stark trap, and nitrogen inlet was charge with 16.6 g (87.0 mmol) of N- (3-hydroxypropyl) phthalimide, 30 mL of toluene and 2.90 g (24.4 mmol) of sodium hydrogensulphate. To this suspension 5.00 g (43.7 mmol) of 3-methoxythiophene was added. The light yellow solution was then set to reflux for 24 hours. The reaction was cooled to room temperature and washed with water. The organic phase was dried and removed under reduced pressure to yield a dark brown oil. This oil was purified by column chromatography using hexane as the eluent to give a light brown solid (1.75 g, 14%). Mp, 82 – 84 °C; IR (neat, cm^{-1}), 3116 (C-H, aromatic), 2940 (C-H, alkene), 1772, 1705 (C=O, imide), 1608, 1462 (C=C, aromatic), 1176 (C-O); ^1H NMR (CDCl_3 , 400 MHz), 2.09 (m, 2H, $^3J = 6.2$ Hz), 3.82 (t, 2H, $^3J = 6.9$), 3.95 (t, 2H, $^3J = 6.0$), 6.14 (dd, 1H, $^4J_{\alpha\beta} = 1.6$, $^4J_{\alpha\alpha'} = 3.1$), 6.54 (dd, 1H, $^3J_{\alpha\beta} = 5.3$, $^4J_{\alpha\alpha'} = 1.6$), 7.05 (dd, 1H, $^4J_{\alpha\beta} = 5.2$, $^4J_{\alpha\alpha'} = 1.6$), 7.65 (dd, 1H, $^3J = 5.4$, $^4J = 3.0$), 7.76

(dd, 1H, $^3J = 5.4$, $^4J = 3.0$); ^{13}C NMR (CDCl_3 , 100 MHz), 28.28, 35.45, 67.82, 97.43, 119.41, 123.41, 124.59, 132.16, 133.93, 157.58, 168.36; MS (EI, m/e, relative intensity %) 288.1 (M^+ , 16.9); HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$ 288.0694, found 288.0612.

3-Methoxy-4-methylthiophene³⁸

A 3-necked, 100 mL, round-bottomed flask was charged with 4.50 g (15.7 mmol) of CuBr, and 15 mL of NMP under an inert atmosphere. To this mixture 36 mL of NaOMe (25% in methanol) was added along with 10.0 g (5.70×10^{-2} mmol) of 3-bromo-4-methylthiophene. The reaction mixture was refluxed for 36 hours and cooled to room temperature. The reaction mixture was then diluted with 200 mL of diethyl ether and filtered by suction. The ethereal phase was washed with water, dried with magnesium sulphate, and removed under reduced pressure to give a light yellow oil (5.5 g, 76%). IR (KBr, cm^{-1}) 3117 (C-H, aromatic), 2940 (C-H, alkene), 1566, 1475 (C=C, aromatic), 1121 (C-O); ^1H NMR (CDCl_3 , 400 MHz), ^1H NMR (CDCl_3 , 400 MHz), 2.08 (s, 3H), 3.81 (s, 3H), 6.14 (d, 1H, $^4J_{\alpha\alpha'} = 3.0$), 6.82 (dd, 1H, $^4J_{\alpha\alpha'} = 3.0$, $^4J = 1.1$); ^{13}C NMR (CDCl_3 , 100 MHz) 12.33, 56.79, 95.35, 119.81, 128.53, 156.74; MS (EI, m/e, relative intensity %) 128 (M^+ , 100); HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{OS}$ 128.0696, found 128.0290.

³⁸ Zotti, G., Gallazzi, M.C., Zerbi, G., Meille, S.V. *Synth. Met.*, 1995, **73**, 217.

3-(3-Phthalimido)propyloxy-4-methylthiophene **1b**

A 50 mL, round-bottomed flask, attached with a Hickman-Hinkle trap, was charged with 1.17 g (9.20 mmol) of 3-methoxy-4-methylthiophene, 2.25 g (11.0 mmol) of N-(3-hydroxypropyl)phthalimide, and 1.89 g (15.0 mmol) of sodium hydrogensulphate. The mixture was set to reflux under an inert atmosphere for 36 hours. The reaction mixture was cooled to room temperature, poured into water and diluted with 30 mL of diethyl ether. The organic phase was then washed with water (3 x 30) mL. The dark brown oil recovered was purified by column chromatography using silica gel as a stationary phase. The elution solvent system used is as follows: the stationary phase was first washed with hexane (75 mL), and the product was then eluted with an ethyl acetate-hexane solution (1:1), (2.00 g, 72 %). IR (KBr, cm^{-1}) 3117 (C-H, aromatic), 2934 (C-H, alkene), 1766, 1705, (C=O), 1608, 1462 (C=C, aromatic), 1121 (C-O); ^1H NMR (CDCl_3 , 400 MHz), 1.99 (s, 3H), 2.21 (m, 2H, $^3J = 6.6$), 3.92 (t, 2H, $^3J = 6.9$), 4.0 (t, 2H, $^3J = 6.0$), 6.14 (dd, 1H, $^4J_{\alpha\alpha'} = 3.2$), 6.78 (dd, 1H, $^4J_{\alpha\alpha'} = 2.18$, $^4J = 1.3$), 7.72 (dd, 1H, $^3J = 5.4$, $^4J = 3.1$), 7.85 (dd, 1H, $^3J = 5.5$, $^4J = 3.0$); ^{13}C NMR (CDCl_3 , 100 MHz), 12.45, 28.33, 35.48, 67.54, 96.30, 119.81, 123.23, 129.13, 132.16, 133.94, 155.80, 168.33; MS (EI, m/e.

relative intensity %) 301 (M^+ , 3.3); HRMS calcd for $C_{16}H_{15}NO_3S$ 301.0772, found 301.0774.

N-(6-Hydroxyhexyl)phthalimide

A 100 mL, Erlenmeyer flask was charged with 20.0 g (1.35 mmol) of phthalic anhydride and 15.8 g (135 mmol) of 6-amino-1-hexanol under an inert atmosphere. The dark-brown slurry was then stirred at 100 °C for one hour, and 200 °C for three hours. The dark brown solid was cooled to room temperature, dissolved in ethyl acetate, washed with water, dried with magnesium sulphate, and rotoevaporated to yield a light brown solid (31.6g, 95%). Mp, 50 –53 °C; IR (neat, cm^{-1}) 3462 (OH), 3938 (C-H, aromatic), 2864 (C-H, alkene), 1766, 1711 (C=O, imide), 1606, 1464 (C=C, aromatic), 1051 (C-O); 1H NMR ($CDCl_3$, 400 MHz), 1H NMR ($CDCl_3$, 400 MHz), 1.41 (m, 4H), 1.57 (m, 2H, $^3J = 7.3$), 1.64 (s, 1H), 3.63 (t, 2H, $^3J = 6.5$), 3.69 (t, 2H, $^3J = 7.2$), 7.71 (dd, 1H, $^3J = 5.4$, $^4J = 5.4$), 7.84 (dd, 1H $^3J = 5.4$, $^4J = 3.1$); ^{13}C NMR ($CDCl_3$, 100 MHz), 25.19, 26.52, 28.55, 32.55, 37.86, 62.69, 123.20, 132.14, 133.87, 168.53; MS (EI, m/e, relative intensity %) 247 (M^+ , 6.5); HRMS calcd for $C_{14}H_{17}NO_3$ 247.1208, found 247.1200.

3-(6-Phthalimido)hexyloxy-4-methylthiophene

A 100 mL, round-bottomed flask, was charged with 5.20 g (41.0 mmol) of 3-methoxy-4-methylthiophene, 20.3 g (82.0 mmol) of N-(6-hydroxyhexyl)phthalimide, 5.41 g (45.0 mmol) sodium hydrogensulphate, and 40 mL of toluene. The mixture was placed under a steady stream of Argon to azeotropically distill the toluene/methanol azeotrope into a Dean-Stark trap. After 10 mL of the azeotrope was collected and another 10 mL of fresh toluene was added. This procedure was repeated three times and the reaction was cooled to room temperature. The reaction mixture was diluted with diethyl ether, and washed repeatedly with water. The organic phase was dried with magnesium sulphate and rotoevaporated to yield a brown oil. This oil was then purified by column chromatography using 20% ethyl acetate: hexane as the eluent to yield a light yellow gummy solid. The gummy solid was then washed with methanol for one hour, filtered by suction, and dried to yield a powdery, yellow solid (10.8 g, 77%). Mp, 59 – 62 °C; IR (neat, cm^{-1}) 2939 (C-H, aromatic), 2856 (C-H, alkene), 1770, 1713 (C=O, imide), 1561, 1459 (C=C, aromatic), 1052 (C-O); ^1H NMR (CDCl_3 , 400 MHz), 1.42 (m,

2H, $^3J = 6.8$), 1.51 (m, 2H, $^3J = 6.9$), 1.71 (m, 2H, $^3J = 7.3$), 1.78 (m, 2H, $^3J = 6.5$), 2.07 (s, 3H), 3.69 (t, 2H, $^3J = 7.3$), 3.91 (t, 2H, $^3J = 6.3$), 6.10 (d, 1H, $^4J_{\alpha\alpha'} = 3.20$, 6.79 (dd, 1H, $^4J_{\alpha\alpha'} = 3.2$, $^4J = 1.1$), 7.69 (dd, 1H, $^3J = 5.4$, $^4J = 3.0$), 7.84 (dd, 1H, $^3J = 5.4$, $^4J = 3.1$); ^{13}C NMR (CDCl_3 , 100 MHz), 12.67, 25.73, 26.62, 28.54, 29.07, 37.93, 69.77, 95.91, 119.69, 123.20, 129.24, 132.17, 133.86, 156.21, 168.46; MS (EI, m/e, relative intensity %) 343 (M^+ , 9.7); HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ 343.1242, found 343.1230.

2,3,5-tribromothiophene³⁹

An oven dried, three-necked flask, was fitted with a pressure equalising dropping funnel, argon inlet, and a gas outlet. The reaction flask was charged with 52.55 g (0.630 mol) of thiophene, and 25 mL of chloroform. Over and six hour period, 299.4 g (1.870 mol) of bromine was added carefully. The light yellow solution was stirred overnight, and refluxed for two hours. Potassium hydroxide (160.9 g in 92 mL) dissolved in water, was added carefully to the reaction solution at 0 °C, which was then refluxed for four hours. The suspension was poured into 200 mL of water and filtered by suction. The filtrate was extracted with diethyl ether (4x100) mL, dried with magnesium sulphate and removed under reduced pressure to give a dark orange liquid. The liquid was then purified by column chromatography using hexane as the mobile phase. A slightly yellow solid was obtained after purification (148.6 g, 74 %). Mp, 25 – 27 °C; IR (neat, cm^{-1}) 3098 (C-H, aromatic), 1501, 1408 (C=C, aromatic), 681 (C-Br); ^1H NMR (CDCl_3 , 400

MHz). 6.89; ^{13}C NMR (CDCl_3 , 50 MHz), 110.89, 112.36, 113.85, 132.58; MS (EI, m/e, relative intensity %) 333 (M^+ , 54); HRMS calcd for $\text{C}_4\text{HBr}_3\text{S}$, 333.0670, found 333.0666.

3-Bromothiophene³⁹

A 250 mL, 3-necked, round bottomed flask equipped with a condenser and dropping funnel was charged with 63.5 mL of water, and 26.43 g (0.404 mol) of zinc. While stirring the mixture, 30 mL of acetic acid was added and then refluxed for 5 minutes. With the heat removed, 2,3,5-tribromothiophene was added dropwise over a 30 minute period. The mixture was then refluxed for three hours. The reaction was then cooled to room temperature and poured into water. The organic phase was separated and washed with a 10% sodium carbonate solution. The brown liquid obtained was then vacuum distilled to yield a clear colourless liquid (12.68 g, 58%). IR (neat, cm^{-1}) 3111 (C-H, aromatic), 1494, 1403 (C=C, aromatic), 681 (C-Br); ^1H NMR (CDCl_3 , 400 MHz), 7.04 (d, 1H), 7.24 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz), MS (EI, m/e, relative intensity %) 162 (M^+ , 31.8); HRMS calcd for $\text{C}_4\text{H}_3\text{BrS}$ 161.9138, found 161.9129.

³⁹ Janda, M., Srogl, J., Stibor, I., Nemec, M., Vopatna, P., Synthesis, 1972, 545.

3-Hexylthiophene⁴⁰

A three necked, oven-dried flask, was charged with 2.234 (91.90 mmol) of magnesium and dried with a flame under a steady stream of argon. To the reaction flask at 0°C, 40 mL of dry diethyl ether was added and 12.90 mL (91.90 mmol) of 1-bromohexane in 10 mL of ether was added dropwise via a dropping funnel. This mixture was refluxed for 3 hours and the grey reaction solution was then cooled to 0°C. To the reaction flask, the Ni(dpp)Cl₂ (0.0831 g, 15.30 x 10⁻² mmol), and 6.30 mL (61.30 mmol) of 3-bromothiophene was added dropwise. After refluxing overnight, the reaction mixture was hydrolysed by pouring into a 10% HCl/ice mixture. To the reaction solution 50 mL of diethyl ether was added and the organic phase was washed with water, saturated sodium bicarbonate and dried with magnesium sulphate. The ether was removed under reduced pressure to give a dark brown liquid (8.880 g, 53.00 mmol, 84%). IR (neat, cm⁻¹), 2953 (C-H, aromatic), 2868 (C-H, alkene), 1563, 1444 (C=C, aromatic); ¹H NMR (CDCl₃, 400 MHz), 0.88 (t, 3H, ³J = 6.8), 1.31 (m, 6H, ³J = 6.9), 1.63 (m, 2H, ³J = 7.2), 2.62 (t, 2H, ³J = 7.8), 6.91 (dd, 1H, ⁴J_{αβ} = 1.1, ⁴J_{αα} = 2.1), 6.92 (dd, 1H, ³J_{αβ} = 4.9, ⁴J_{αα} = 1.1), 7.23 (dd, 1H, ³J_{αβ} = 4.9, ⁴J_{αα} = 3.0); ¹³C NMR (CDCl₃, 100 MHz), 14.10, 22.62, 29.02, 30.29, 30.54, 31.70, 119.75, 125.03, 128.30, 143.28; MS (EI, m/e.

⁴⁰ Leclerc, M., Diaz, F.M., Wegner, G., *Makromol. Chem.* 1989, **190**, 3105.

relative intensity %) 343 (M^+ , 9.7); HRMS calcd for $C_{19}H_{21}NO_3S$ 343.1242, found 343.1230.

2-(3-thienyl)ethylcinnamate

2a

A 100 mL, 4-necked, round-bottomed flask, was charged with 5.20 g (31.2 mol) of cinnamoyl chloride, 9.47 g (93.6 mol) of triethylamine, and 2.00 g (15.6 mmol) of 2-(3-thienyl) ethanol, and 25 mL of dry chloroform. This mixture was set to stir overnight at room temperature. The reaction mixture was filtered, and the mother liquor was with water and 10% HCl consecutively. The chloroform was removed to yield a yellow-brown solid. (3.42 g, 85%). Mp, 34 – 38 °C, IR (KBr, cm^{-1}) 3068 (C-H, aromatic), 2958 (C-H, alkene), 1712 (C=O, ester), 1632 (C=C alkene), 1572, 1450 (C=C, aromatic), 1073 (C-O); 1H NMR ($CDCl_3$, 400 MHz), 2.95 [t, 2H, $^3J = 6.9$], 4.32 [t, 2H, $^3J = 7.0$], 6.34 [d, 1H, $^3J_{trans} = 16.0$], 6.91 [dd, 1H, $^3J_{\alpha\beta} = 4.9$, $^4J_{\alpha\beta'} = 1.1$], 6.96 [dd, 1H, $^3J_{\alpha\beta} = 4.9$, $^4J_{\alpha\alpha'} = 3.0$], 7.19 [dd, 1H, $^3J_{\alpha\beta} = 4.9$, $^4J_{\alpha\alpha'} = 3.0$], 7.27 [t, 1H, $^3J = 6.9$], 7.32 [d, 1H, $^3J = 6.7$], 7.4 [d, 1H, $^3J = 7.2$], 7.62 [d, 1H, $^3J_{trans} = 16.0$]; ^{13}C NMR ($CDCl_3$, 100 MHz), 29.68, 64.43, 118.02, 121.64, 125.69, 128.15, 128.34, 128.93, 129.12, 134.44, 138.12, 144.95, 166.92;

MS (EI, m/e, relative intensity %) 258 (M^+ , 1.0); HRMS calcd for $C_{15}H_{14}O_2S$ 258.0714, found 258.0742.

2,5-Dichloro-3-hydroxyethylthiophene

To a 50 mL, round bottomed flask, 0.733 g (5.70 mmol) of 3-hydroxyethylthiophene was combined along with 1.60 g (12.0 mmol) of NCS, and 15 mL of DMF. This solution was stirred in the dark at 40 °C overnight. The reaction solution was poured into water, and extracted with ether. The combined ether phases were then washed repeatedly with 5% HCl, water, saturated sodium chloride, then dried with magnesium sulphate. The ether was removed under reduced pressure to give a light brown liquid (0.73 g, 65%). IR (neat, cm^{-1}) 3341 (OH), 3928 (C-H, aromatic), 2879 (C-H, alkene), 1547, 1432 (C=C, aromatic), 1043 (C-O); 1H NMR ($CDCl_3$, 200 MHz) 1.50 (s, 1H), 2.78 (t, 2H, $^3J = 6.9$), 3.80 (t, 2H, $^3J = 7.2$), 6.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz), 31.65, 62.01, 123.25, 126.41, 127.48, 135.66; MS (EI, m/e, relative intensity %) 196 (M^+ , 49.4); HRMS calcd for $C_6H_6Cl_2OS$ 195.9516, found 195.9520.

2,5-Dichloro-3-hexylthiophene

A 50 mL, round bottomed, four necked flask was charged with 3.755 g (22.40 mmol) of 3-hexylthiophene, 6.263 g (46.90 mmol) of NCS, and 30 mL of DMF. This solution was then stirred in the dark at 40 °C overnight. The reaction solution was poured into water, and extracted with ether. The combined ether phases were then washed repeatedly with 5% HCl, water, saturated sodium chloride, and dried with magnesium sulphate. The ether was removed under reduced pressure to give a light brown liquid. The final product was purified by column chromatography using silica as the stationary phase and hexane as the mobile phase (4.503 g, 85%). IR (neat, cm^{-1}) 2958 (C-H, aromatic), 2861 (C-H, alkene), 1547, 1438 (C=C, aromatic); ^1H NMR (CDCl_3 , 400 MHz) 0.91 [t, 3H, $^3J = 6.4$], 1.32 [m, 6H, $^3J = 6.8$], 1.55 [m, 2H, $^3J = 7.2$], 2.51 [t, 2H, $^3J = 7.7$], 6.66 [s, 1H]; ^{13}C NMR (CDCl_3 , 100 MHz), 14.09, 22.56, 28.01, 28.78, 29.41, 31.55, 121.39, 125.56, 126.93, 139.26; MS (EI, m/e, relative intensity %) 236 (M^+ , 48.5%); HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{S}$ 236.0193, found 236.0184.

2-[3-(2,5-Dichloro)thienyl]ethylcinnamate

An oven dried, 50 mL, round bottomed flask was charged with 7.67 g (3.90 mmol) of 2,5-dichloro-3-hydroxyethylthiophene, 25 mL of dry chloroform, 32.0 mL (234 mmol) of triethylamine, and 13.0 g (78.0 mmol) of cinnamoyl chloride. The reaction mixture was set to stir at room temperature for 24 hours. The yellow-brown reaction mixture was filtered and diluted with 50 mL of diethyl ether. The organic phase was washed water (3 x 60 mL), 5% HCl (3 x 60 mL), saturated sodium chloride, dried with magnesium sulphate and removed under reduced pressure to yield a brown/yellow oil. The product was then purified by column chromatography (1:1, hexane: ethyl acetate) affording a light brown oil. (9.3 g, 73%). IR (neat, cm^{-1}) 3068 (C-H, aromatic), 2952 (C-H, alkene), 1712 (C=O, ester), 1633 (C=C alkene), 1547, 1444 (C=C, aromatic), 1164 (C-O); ^1H NMR (CDCl_3 , 400 MHz) 2.96 (t, 2H, $^3J = 6.6$), 4.37 (t, 2H, $^3J = 6.67$), 6.44 (d, 1H, $^3J_{\text{trans}} = 13.4$), 6.76 (s, 1H), 7.42 (t, 1H, $^3J = 6.4$), 7.44 (d, 1H, $^3J = 6.0$), 7.56 (d, 1H, $^3J = 6.9$), 7.71 (d, 1H, $^3J_{\text{trans}} = 16.0$); ^{13}C NMR (CDCl_3 , 100 MHz), 28.19, 63.59, 118.26, 123.89, 126.79, 127.58, 128.52, 129.46, 130.96, 134.85, 135.25, 145.75, 167.19; MS (EI, m/e,

relative intensity %) 326 (M^+ , 0.4); HRMS calcd for $C_{15}H_{12}Cl_2O_2S$ 325.9935, found 325.9947.

4.3 General procedure for polymerisations

Method 1 (oxidative polymerisation): Polythiophenes were prepared by chemical oxidation of the monomers using iron trichloride according to a procedure similar to that of Sugimoto et al.⁴¹ In a 100 mL three-necked flask, 0.012 mol of iron trichloride was dissolved in 30 mL of dry chloroform under argon to which a solution of 0.003 mol of monomer in 20 mL of chloroform was added dropwise. The mixture was stirred for 24 h at room temperature under a gentle argon stream. The reaction mixture was poured into methanol (1 L), the black precipitate was collected on a Buchner funnel and washed with methanol (yield 50 – 60 %). The polymer was subsequently washed by Soxhlet extractions using methanol/acetone. These treatments induced a “dedoping” of the polymer (the polymer starts to turn red) by removing almost completely the iron chloride species included in the polymer. The polymer was finally dried under reduced pressure at elevated temperatures.

Method 2 (nickel catalysed polymerisation)⁴²: For instance, a 250 mL three-necked flask equipped with a nitrogen inlet, and a gas outlet were added monomer (2.900×10^{-2} mol), nickel (2.175×10^{-3} mol), zinc (8.99×10^{-2} mol), triphenylphosphine (2.900×10^{-2} mol), bipyridine (2.175×10^{-3} mol), and DMAc (12 mL) under nitrogen. The reactions were stirred at 85 °C for 4 h. Sodium Iodide (2.175×10^{-2} mol) was added and the reaction stirred for an additional 2 h. In each case, the very viscous gels produced were

⁴¹ R. Sugimoto, S. Takeda, H. B. Gu, K. Yoshino, *Chem. Express* 1986, **1**, 635.

⁴² J. Wang, V. Sheares, *Macromolecules*, 1998, **31**, 6769.

diluted with four times the original amount of DMAc. The products were precipitated into a large excess of 20% HCl/methanol solution. The dark red solids that remained were washed with methanol, water, and methanol sequentially, collected, and dried under vacuum for 24 h. The yields of the polymers after complete workup were greater than 90%.

Poly[3-(6-phthalimido)hexyloxy-4-methylthiophene], (Method 1)

IR (KBr, cm^{-1}) 2939 (C-H, aromatic), 2856 (C-H, alkene), 1772, 1699 (C=O, imide), 1561, 1459 (C=C, aromatic), 1052 (C-O); ^1H NMR (CDCl_3 , 400 MHz), 1.31 [m, 2H], 1.32 [m, 2H], 1.62 [m, 2H], 1.78 [m, 2H], 2.17 [s, 3H], 3.53 [t, 2H], 3.83 [t, 2H], 7.7 [m, 1H], 8.0 [m, 1H]; ^{13}C NMR (CDCl_3 , 100 MHz), 11.9, 25.5, 27.2, 28.9, 30.1, 36.9, 69.8, 72.5, 117.2, 122.9, 129.2, 131.3, 133.5, 151.9, 167.2.

Poly(3-hexylthiophene), (Method 1)

IR (neat, cm^{-1}), 2953 (C-H, aromatic), 2868 (C-H, alkene), 1563, 1444 (C=C, aromatic); ^1H NMR (CDCl_3 , 400 MHz), 0.88 [t, 3H, $^3J = 6.8$], 1.31 [m, 6H, $^3J = 6.9$], 1.63 [m, 2H, $^3J = 7.2$], 2.62 [t, 2H, $^3J = 7.8$], 6.91 [dd, 1H, $^4J_{\alpha\beta} = 1.1$, $^4J_{\alpha\alpha'} = 2.1$], 6.92 [dd, 1H, $^3J_{\alpha\beta} = 4.9$, $^4J_{\alpha\alpha'} = 1.1$], 7.23 [dd, 1H, $^3J_{\alpha\beta} = 4.9$, $^4J_{\alpha\alpha'} = 3.0$]; ^{13}C NMR (CDCl_3 , 100 MHz), 14.10, 22.62, 29.02, 30.29, 30.54, 31.70, 119.75, 125.03, 128.30, 143.28..

Poly(3-ethylcinnamatethiophene), (Method 2)

IR (KBr, cm^{-1}) 3068 (C-H, aromatic), 2958 (C-H, alkene), 1709 (C=O, ester), 1634 (C=C alkene), 1572, 1450 (C=C, aromatic), 1073 (C-O); ^1H NMR (CDCl_3 , 400 MHz), 3.20 [t, 2H], 4.47 [t, 2H], 6.44 [d, 1H], 6.91 [dd, 1H], 7.13 [dd, 1H], 7.35 [t, 1H], 7.72 [d, 1H],

7.54 [m, 1H]; ^{13}C NMR (CDCl_3 , 100 MHz), 28.8, 63.9, 117.9, 123.9, 126.6, 127.9, 128.8, 129.3, 130.3, 134.8, 135.3, 145.1, 166.8.

Contribution to knowledge

A series of thiophene monomers were synthesised with pendant imide groups that led to insoluble polythiophenes. However, one slightly soluble polymer was characterised and shown to be thermochromic at room temperature and 60 °C, but not suitable for curing experiments since the solubility was too much of a detriment.

Furthermore, two years of research have lead to an extended π -conjugated polymer, specifically a second polythiophene of moderate molecular weight and a low glass transition temperature that is soluble in common organic solvents. This polymer was synthesised by metal coupling of a dihalothiophene with zero valent nickel. However, when a monomer containing a latent cinnamate moiety was synthesised used the ferric chloride route an insoluble product was isolated. This soluble polymer was proven to be photocrosslinkable in the solid state due to its latent cinnamate moiety. The polymer also was proven to be electrochemically reversible yet was not switchable between its oxidised and reduced state when cured.

In summary, to the best of our knowledge the first photocurable, processable, electroactive, polythiophene was synthesised, this work was also published in *Macromolecules*.