

**SYNTHESIS AND PROPERTIES OF WATER SOLUBLE CONDUCTING  
POLY(3-(ALKYLSULFONATE)THIOPHENES)**

by

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B.Sc., Pontificia Universidad Catolica de Chile, 1989

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE  
in the Department  
of  
Chemistry

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SIMON FRASER UNIVERSITY

December 1993

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### **Title of Thesis/Project/Extended Essay:**

SYNTHESIS AND PROPERTIES OF WATER SOLUBLE CONDUCTING

POLY(3-(ALKYLSULFONATE)THIOPHENES )

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## ABSTRACT

Conducting polymers are being developed as materials that combine the characteristics of polymers with useful electronic properties. This work describes the synthesis and properties of water soluble conducting poly(3-alkylsulfonate)thiophenes).

Poly(3-(sodium alkylsulfonate)thiophenes) were synthesized by chemical polymerization of their corresponding sodium-n-(3-thienyl)alkanesulfonates monomers. The "acid" form of each polymer was obtained by ion-exchange chromatography of the sodium salt. Both the sodium salt and the acid form of the polymers were water soluble in their doped and undoped states.

Existence of  $\pi$ -conjugation in these polymer systems was confirmed by their orange-red color and their electronic absorption spectra. The sodium salt and acid forms of the polymers have a  $\pi$  to  $\pi^*$  transition at approximately 450 nm. In addition, the acid form of the polymers have other electronic transitions in the near infrared region due to bipolaron bands.

When polymer solutions of the sodium form were exposed to UV-vis irradiation, blue shifts of their wavelength maxima were observed along with photobleaching of the corresponding solution. Polymer films exhibited a slower photodegradation process than polymer solutions. Acid forms of the polymers photodegraded at lower rates than the sodium salts. Polymer films remained water soluble after irradiation indicating the absence of significant photo-induced crosslinking.

Polymer films of the sodium salt presented conductivities  $< 10^{-6}$  S/cm in their undoped state. After doping, with  $\text{FeCl}_3$  or  $\text{AuCl}_3$ , the conductivities increased to  $10^{-3}$  -  $10^{-2}$  S/cm. Polymer films of the acid form in the undoped

state presented stable conductivities in the order of  $10^{-2}$  S/cm. Upon doping, these conductivities were improved up to  $10^{-1}$  S/cm.

A photoimage of poly(3-(octylsulfonic acid)thiophene) was obtained by photolithography. A film of the polymer was oxidized and subsequently irradiated through a photomask. Following irradiation, the exposed part of the film was insoluble while the unexposed region remained soluble. The latter was dissolved with a suitable solvent thus leaving the conducting polymer pattern.

## DEDICATION

For all of those who believed in me.....

## **ACKNOWLEDGMENT**

I would like to thank the following people for their contribution to this thesis:

My senior supervisor, Dr. Steven Holdcroft for his guidance in the development of my research.

The examining committee, Dr. B. Mario Pinto, Dr. Derek Sutton and Dr. Ross H. Hill for their suggestions and criticisms.

The members of the "Polymer group" for their helpful discussions.

Sharon for her comments and proofreading of this manuscript.

Dawn for her encouragement and support.

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## LIST OF ABBREVIATIONS

AIBN: 2,2'-azo bis(isobutyronitrile)

NIR: near infrared

UV-vis: ultraviolet-visible

## 1. INTRODUCTION

### 1.1 General aspects of conducting polymers

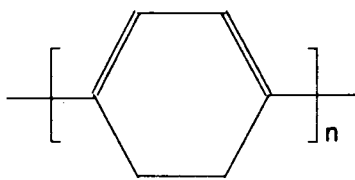
Organic polymers are generally thought of as being electrical insulators. In fact, the insulating properties of polymers are necessary for many applications. Electrical wires, for example, are protected from shorting by coating with insulating polymers. Consistent with this, it was generally viewed that polymers and electrical conductivity were mutually exclusive.<sup>1</sup> The attraction of combining the characteristics of polymers with useful electronic properties led Shirakawa,<sup>2</sup> in 1977, to demonstrate the semiconductivity and metallic properties of a linear conjugated organic polymer, poly(acetylene). Since then, the interest in synthesizing and characterizing members of this new class of organic electronic materials has expanded.<sup>3</sup>

Among the many conductive polymers known, poly(acetylene), poly(aniline), poly(p-phenylene), poly(p-phenylenevinylene), poly(pyrrole), and poly(thiophene) have been intensively studied. The structures of these polymers are shown in figure 1.

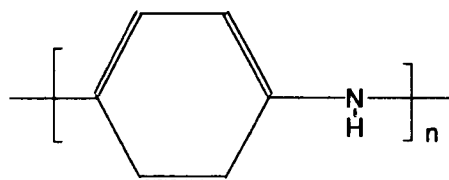
Poly(acetylene) is the prototype of conducting polymers and is the most extensively studied. In this polymer, the carbon atoms are connected by alternating single and double bonds. This conjugated unsaturated system is typical of conducting polymers. To be conductive, an organic polymer material must have an extended  $\pi$ -electron system requiring a sufficient degree of coplanarity along the main chain and, at the same time, the interchain distance should be small enough to allow the transfer of charges between chains.



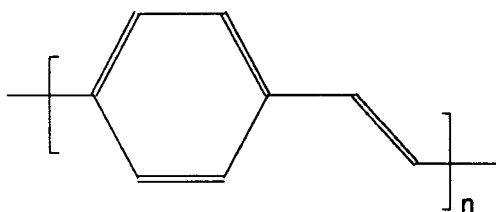
trans-Poly(acetylene)



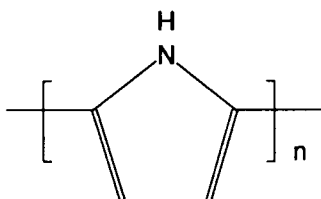
Poly(p-phenylene)



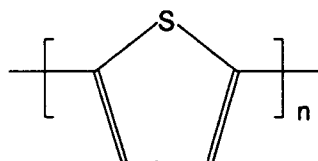
Poly(aniline)



Poly(p-phenylenevinylene)



Poly(pyrrole)



Poly(thiophene)

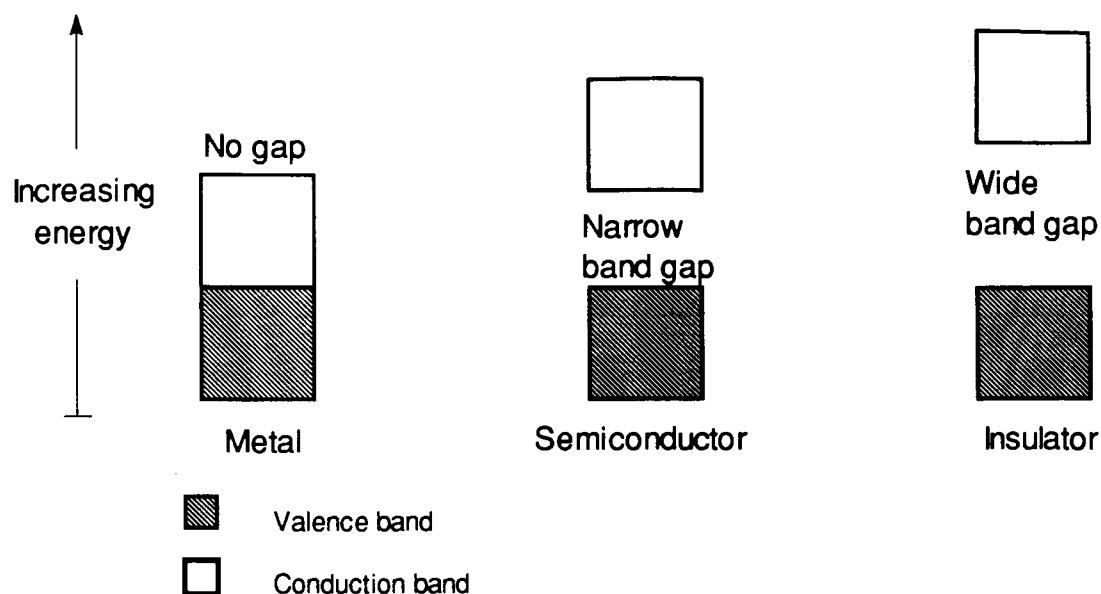
**Figure 1. Structure of common conducting polymers.**



Since most organic polymers do not have a high concentration of intrinsic charge carriers, appropriate charge carriers must be provided. This can be accomplished by a doping process which is a partial oxidation or a partial reduction of the polymer chain with appropriate chemical agents, "dopants". Thus, in order to exhibit high conductivity, organic polymers must possess both charge carriers and a  $\pi$ -electron system that will allow them to be mobile.<sup>4</sup>

The exact electronic and physical changes associated with doping are still a matter of debate, but some important aspects of the mechanisms are known.<sup>5</sup> Electricity flows by the movement of electrons and these electrons have to be free to move around. In solids that have extended networks of atomic bonds, the electrons move between discrete energy states called bands. These bands have to be partially filled since empty or full bands cannot carry electronic charge. Metals conduct electricity because they have partially filled energy bands. Insulators and semiconductor materials possess completely full and completely empty bands. The highest occupied band is called the valence band and the lowest empty band is the conduction band. The energy difference between these two bands is the energy gap. In insulator materials the energy gap is large, and in semiconductor materials the energy gap is much smaller. See figure 2.<sup>6</sup>

Conjugated unsaturated polymers present both insulator and semiconductor electronic profiles. Their valence band is full, their conduction band is empty and the bands are separated by a defined energy gap. Doping changes this profile by removing electrons from the valence band (oxidation) or by adding electrons to the conduction band (reduction), to create new energy bands which lie in between the conduction band and the valence band.<sup>7</sup> (The conduction mechanism will be discussed extensively in 3.3 Conductivity, 3.3.1 Theoretical considerations).



**Figure 2. Band structure.**

In the past 15 years conducting polymers have been the subject of numerous studies, generating entirely new scientific concepts as well as potential technological applications in rechargeable batteries,<sup>8</sup> electrochromic devices,<sup>9</sup> etc. Conducting polymers have attracted the interest of many researchers in fields as diverse as chemistry, solid state physics, and material science. However, additional work is necessary to fully understand the relationship between the chemical structure of the polymer's repeating unit and its electrical properties.

## **1.2 Poly(thiophene) and its derivatives**

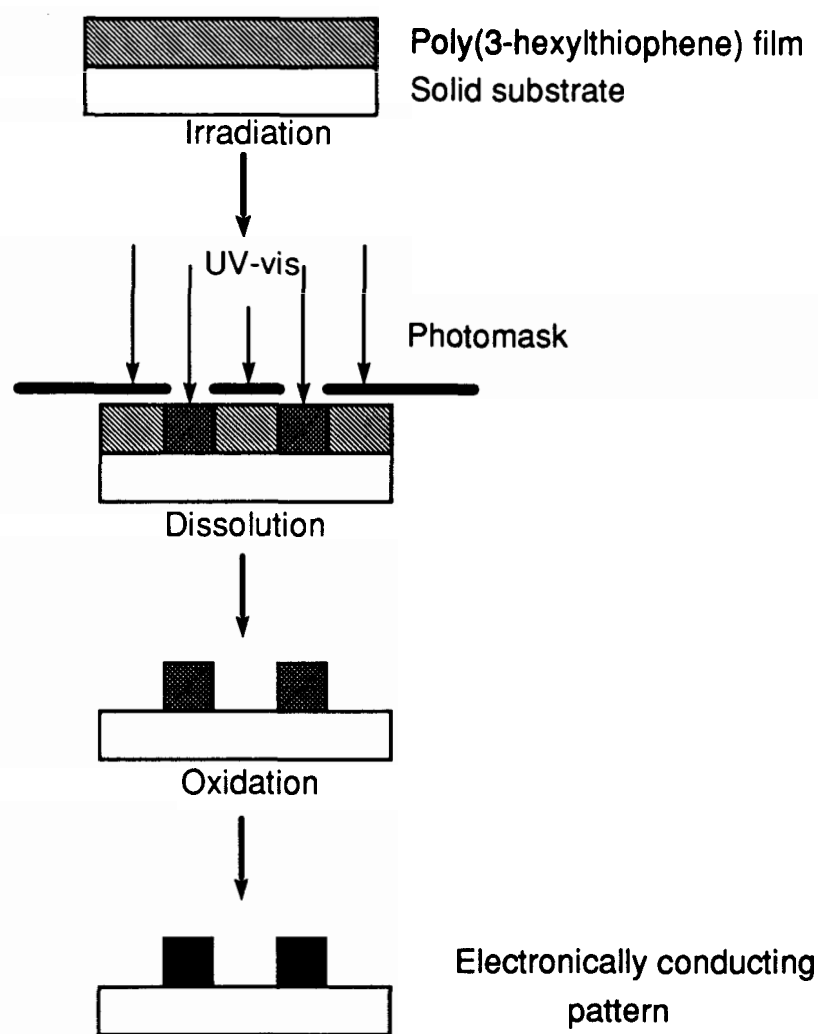
The work described in this thesis is focused on poly(thiophene) and its derivatives. These polymers were the first conducting polymers that were

chemically and electrochemically stable in air and moisture in both doped and undoped states, in contrast to most other organic conducting polymers.<sup>10</sup> Due to their rigid  $\pi$ -conjugated backbone and strong interchain interaction, all unsubstituted organic conducting polymers are insoluble and infusible.<sup>11</sup> These characteristics constitute a major obstacle in their study and development.

A significant advance in the field of conducting polymers was the synthesis of polymers that were soluble in common organic solvents. The first of these "soluble" polymers were the poly(3-alkylthiophenes) which were obtained by substitution of a long alkyl chain in the  $\beta$ -position of the thiophene ring.<sup>12</sup> It was known that incorporation of the side groups on conjugated polymer chains increases their processability, but it was also expected that substitution of long chains in the polymer backbone would seriously affect conductivity by modifying the planarity of the backbone, and thus interfere with the electron transport between polymer chains. The conductivities of long chain substituted poly(thiophenes) were lower than that of poly(thiophene), but the loss in conductivity was not dramatic and it was well compensated by the acquired solubility.<sup>13</sup>

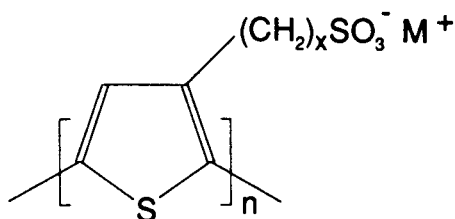
An example of poly(3-alkylthiophenes) is poly(3-hexylthiophene). This polymer presents high electrical conductivity together with solubility in organic solvents. When a film of poly(3-hexylthiophene) is irradiated with UV-Vis light, it undergoes crosslinking and becomes insoluble in organic solvents. These characteristics make poly(3-hexylthiophene) an interesting photoresist material for photolithography applications.<sup>14</sup> Films of the polymer can be spin cast onto solid substrates and irradiated through a photomask as is shown in figure 3. After UV-vis irradiation, unexposed polymer is soluble in organic solvent, leaving the insoluble polymer. The result is the negative image of the photomask.

Afterwards, the insoluble part is chemically oxidized resulting in an electronically conducting pattern. In conventional photolithography, the electronic properties exhibited by the polymeric photoresist are not relevant because it usually plays no role in device operation. In contrast, a soluble  $\pi$ -conjugated polymer, acts as both the photoresist and the precursor to an electronically conducting pattern.



**Figure 3. Conducting polymers for photolithographic application.**

The present work, describes the synthesis and properties of a series of water soluble poly(thiophenes), poly(3-(alkylsulfonate)thiophenes).<sup>15</sup> (see figure 4). The presence of a sulfonate group on the alkyl substituent makes this type of polymer water soluble and, at the same time, the electrical properties are similar to those reported for poly(3-hexylthiophene).



$x = 3, 6 \text{ and } 8$

$M = Na^+, H^+$

**Figure 4. Structure of poly(3-(alkylsulfonate)thiophenes).**

It was found that water soluble polymers can be cast onto solid substrates, oxidized and irradiated through a photomask to form a relief image. The unexposed part of the polymer is dissolved by aqueous solutions. The water soluble polymers are ideal candidates for photoimaging of conducting organic networks since the disadvantages, such as toxicity, cost, etc., of using organic solvents would be avoided. In this study photoimaging of these polymers was investigated. Polymers containing different alkylsulfonate chain lengths were synthesized. The change in length of the alkylsulfonate substituent does not affect the photochemistry of the polymers to a large extent, but is believed to affect their solubility. Further studies can be conducted to determine image contrast by controlling the rate of polymer dissolution during pattern development.

## 2 SYNTHESIS

### 2.1 Introduction

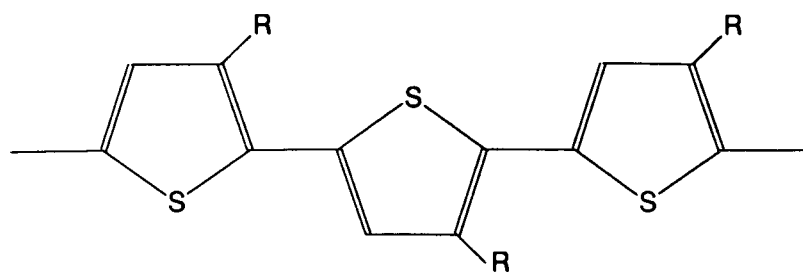
Poly(thiophene) and its derivatives are essentially prepared by two main routes: chemical<sup>16</sup> and electrochemical.<sup>17</sup> A chemically synthesized polymer is produced in its undoped state. This polymer can then be doped chemically or electrochemically to reach its conducting state. In contrast, an electrochemically generated polymer is directly obtained in its conducting state and, subsequently, can be reduced chemically or electrochemically to its semiconducting state.

The first report of poly(thiophene) prepared by electropolymerization was the anodic oxidation of bithiophene in 1980,<sup>18</sup> and it was not until two years later that Tourillon<sup>19</sup> electrosynthesized thiophene. Since then, extensive studies have been performed to find the optimum electrosynthetic conditions. In carrying out electrochemical polymerization, there are a number of experimental variables that have to be controlled.<sup>20</sup> These variables include solvent, concentration of reagents, temperature, nature and shape of the electrodes, and applied electrical conditions. The use of electrochemical techniques produces poly(thiophene) and its derivatives in the form of a film by coupling thiophene rings mainly at the 2- and 5- positions of the thiophene monomers by means of anodic oxidation. Electrochemically synthesized poly(thiophenes) are usually amorphous, containing a significant concentration of the units linked through the  $\alpha$ - $\beta$  position and therefore reducing the  $\pi$ -conjugation. Chemical synthesis is the more versatile route for the preparation of oligomers and polymers of homogeneous structure.<sup>21</sup>

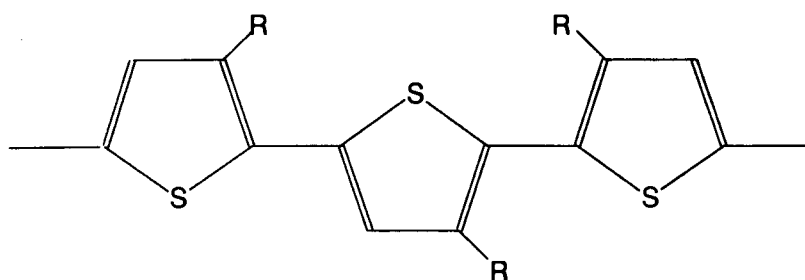
The main methods employed for the chemical preparation of poly(thiophenes) are polycondensation of di-Grignard and di-halogenated thiophenes using transition metal complexes as catalysts,<sup>22</sup> and oxidative coupling of bis-lithiated thiophenes<sup>23</sup> and thiophene monomers.<sup>24</sup>

Processing of poly(thiophene) is impossible since this polymer is insoluble and infusible. Chemists have learned how to solubilize poly(thiophenes) in aqueous and organic solvent, while maintaining their electrical properties, by attaching an alkyl or alkylsulfonate chain on the conjugated backbone, e.g., poly(3-alkylthiophenes) and poly(3-(alkylsulfonate)thiophenes). These poly(thiophene) derivatives can be melted, processed, cast from solution, etc., and their optical<sup>25</sup> and electrical<sup>26</sup> properties readily studied.

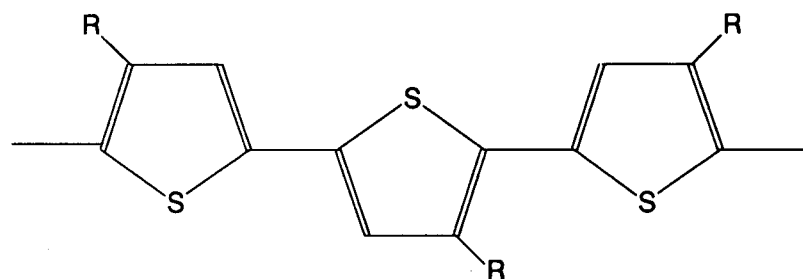
Poly(3-alkylthiophenes) have been synthesized both chemically<sup>27</sup> and electrochemically.<sup>28</sup> The synthetic routes used to polymerize 3-alkylthiophene monomers are similar to those used for thiophenes. These poly(thiophene) derivatives were first chemically synthesized by Elsenbaumer<sup>27a</sup> in 1986, through nickel-catalyzed coupling of the Grignard reagent derived from 3-alkyl-2,5-diiodothiophenes. It was observed that when the alkyl substituent group is equal or larger than butyl, these polymers are soluble in organic solvents such as tetrahydrofuran, dichloromethane, chloroform, toluene, and benzene. Oxidative coupling of 3-alkylthiophenes through the 2,5 positions of the thiophene ring results in structures with different degrees or regioregularity<sup>28</sup> (see figure 5). Homogeneous structures, containing exclusively head-to-tail coupling have recently been synthesized by chemical methods and have been shown to exhibit improved electrical properties.<sup>29</sup>



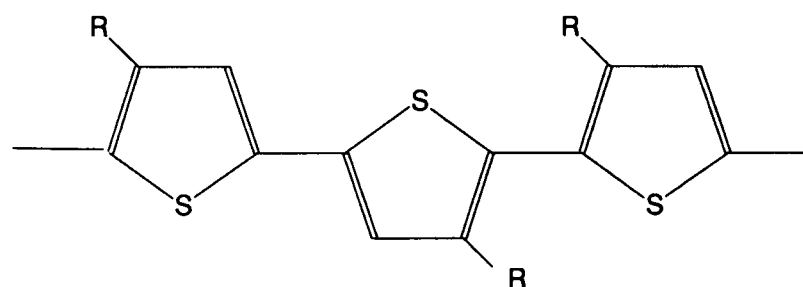
Head-to-tail, head-to-tail triad (HT-HT)



Head-to-tail, head-to-head triad (HT-HH)



Tail-to-tail, head-to-tail triad (TT-HT)



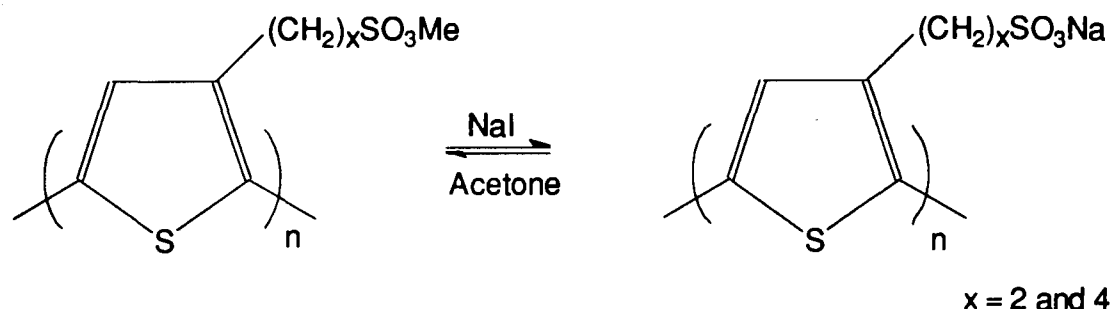
Tail-to-tail, head-to-head triad (TT-HH)

**Figure 5. Regioisomers of poly(3-alkylthiophenes).**



An addition to the class of soluble poly(thiophene) derivatives are the poly(3-(alkylsulfonate)thiophenes).<sup>15,30</sup> Other examples of water soluble conducting polymers include N-alkylsulfonate and 3-alkylsulfonate substituted poly(pyrroles),<sup>31</sup> and poly(anilines).<sup>32</sup>

The electrochemical synthesis of this class of polymer was first reported by Patil *et al.*<sup>15</sup> in 1987. Poly(3-(sodium ethylsulfonate)thiophene) and poly(3-(sodium butylsulfonate)thiophene) were obtained after treatment of the corresponding methyl sulfonylester with sodium iodide (see figure 6).<sup>30a</sup> These two polymers are soluble in water in their doped and undoped states.



**Figure 6. Synthesis of poly(3-(sodium alkylsulfonates)thiophenes).**

The synthesis of poly(3-(alkylsulfonate)thiophenes) introduced the concept of "self-doped" conducting polymers.<sup>33</sup> In these materials the charge injected into the  $\pi$ -electron system during oxidation is accompanied by proton (or  $\text{Na}^+$ , etc.) ejection. Since the anion is bound and cannot diffuse away from the polymer, it is always near a potentially charged site on the polymer and ready to serve as a counter ion. The result is a doped conducting polymer with the counter ion covalently bonded to the polymer. See figure 7.

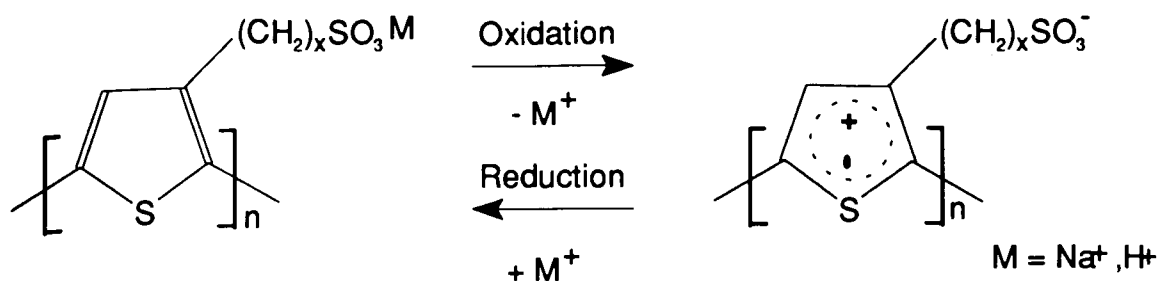


Figure 7. "Self doped" mechanism in conducting polymers.

## 2.2 Experimental and Discussion

Chemical synthesis of poly(3-(sodium propylsulfonate)thiophene) has been previously outlined,<sup>34</sup> however, the synthesis of polymers containing hexyl and octyl alkylsulfonate substituents has not been reported. In this thesis a detailed procedure for the synthesis of a series of poly(3-(sodium alkylsulfonates)thiophenes) (where alkyl = propyl, hexyl and octyl) is described. The polymers were prepared by chemical polymerization of sodium-*n*-(3-thienyl)alkanesulfonate monomers.

### 2.2.1 General conditions

Gas chromatographic analyses were performed on a Hewlett-Packard 5890 chromatograph. Electron impact (70 eV) mass spectra were obtained with a Hewlett-Packard 5985 G.C.-M.S. instrument; the peak of the ion of highest mass is reported. <sup>1</sup>H N.M.R. spectra were recorded on a Bruker AMX-400 (400 MHz.) spectrometer. Infrared spectra were recorded on a Bomem Michelson Model 120 FT-IR spectrometer.

Unless otherwise stated, all the reactions and manipulation of Grignard reagents were carried out under nitrogen atmosphere. Diethyl ether and ethanol were distilled under nitrogen over sodium and calcium sulfate respectively.

### 2.2.2 Synthesis of Poly(3-(sodium propylsulfonate)thiophene): ( Figure 8)

The general method proposed by Ikenoue<sup>34</sup> was followed. In this paper no detailed experimental conditions were given. Here the experimental conditions are fully described. Modifications to the procedure have been introduced to achieve better results.

#### *3-(3-Thienyl)propene: (2)*

14.7 ml ( $3.7 \times 10^{-2}$  mol) of 2.5 M n-butyllithium were added to a solution of 5.0 g ( $3.1 \times 10^{-2}$  mol) of 3-bromothiophene (1) (Aldrich Chemical) in 20 ml of dry ether at  $-75^{\circ}\text{C}$  over a period of 20 to 30 minutes. The reaction mixture was stirred two hours and checked by G.C. for the presence of 3-bromothiophene. When the reaction was complete, 2.7 ml ( $3.1 \times 10^{-2}$  mol) of allyl bromide was added, drop by drop, and the reaction mixture stirred for two hours at  $-75^{\circ}\text{C}$ . The reaction was quenched by pouring into a separatory funnel containing 5% HCl. Following three ether extractions, the combined organic layer was dried with  $\text{MgSO}_4$ . After evaporation of the solvent, a yellow oil was obtained which, upon passing through a silica gel (230-400 mesh) chromatographic column using hexane as eluent, gave a colorless oil (2) in 70% yield. N.M.R. ( $\text{CDCl}_3$ ,  $\delta$  rel. to TMS) 3.47 (2H, d,  $J_{2,3}$  6.7 Hz,  $\text{CH}_2\text{CH}=\text{CH}_2$ ) 5.13 (2H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{cis}}$  4.0 Hz,  $\text{CH}_2\text{CH}=\text{CHH}$ ) 5.18 (1H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{trans}}$  8.5 Hz,  $\text{CH}_2\text{CH}=\text{CHH}$ ) 6.07

(1H, m) 6.95 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{4,5}$  5.0 Hz,  $H_4$ ) 6.98 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{2,5}$  3.0 Hz,  $H_2$ ) 7.28 (1H, dd,  $J_{2,5}$  3.0 Hz,  $J_{4,5}$  5.0 Hz,  $H_5$ ). G.C.-M.S.  $m/e$  ( $M^+ \bullet 124$ ).

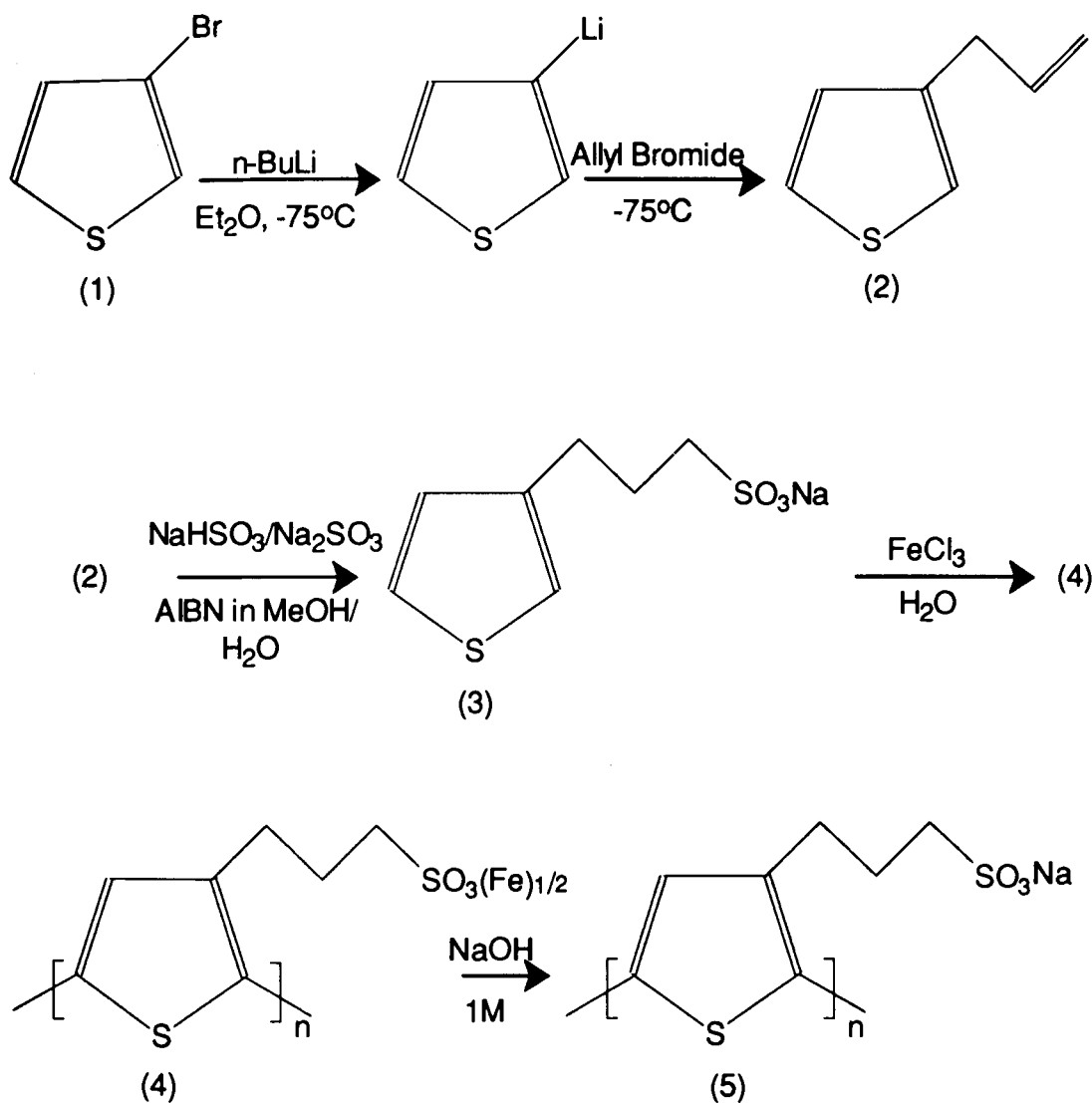


Figure 8. Synthesis of Poly(3-(sodium propylsulfonate)thiophene).

In the above reaction, it was observed that temperature control is important. 3-Bromothiophene (1) contains acidic hydrogens capable of undergoing halogen-metal interconversion.<sup>35</sup> The halogen is not situated at the most acidic position and, therefore, three reaction products can be obtained. When (1) was added to n-butyllithium at -75°C, halogen metal interconversion occurred and exclusively product (2) was obtained after alkylation. If the reaction mixture was allowed to be raised from -75°C to room temperature, there was a tendency for the initial product to transform to a mixture consisting of 2-thienyllithium and 3-bromo-2-thienyllithium.

*Sodium-3-(3-thienyl)propanesulfonate: (3)*

A solution of 1.872 g ( $1.8 \times 10^{-2}$  mol) of sodium bisulfite and 0.378 g ( $3.0 \times 10^{-3}$  mol) of sodium sulfite in 24 ml of water was added to a solution of 1.5 g ( $1.2 \times 10^{-2}$  mol) of (2) and 30 mg ( $1.8 \times 10^{-4}$  mol) of AIBN in 24 ml of methanol. The resulting mixture was stirred overnight at 80°C. The mixture was evaporated to dryness followed by washing with ether to remove the unreacted product (2) and organic products of AIBN thermal decomposition. The remaining solid was a mixture of the desired monomer (3) contaminated with excess sodium bisulfite and sodium sulfite. After extraction with dry ethanol, a white solid was obtained (3) in 50% yield. IR (KBr,  $\nu/\text{cm}^{-1}$ ) 3588m, 3520m, 3099w, 2975m, 2938m, 1631m, 1211s, 1156s, 1059s. N.M.R. ( $\text{D}_2\text{O}$ ,  $\delta$  rel. to TMS) 2.02 (2H, tt,  $J_{1,2}$  7.8 Hz,  $J_{2,3}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 2.74 (2H, t,  $J_{2,3}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 2.84 (2H, t,  $J_{1,2}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 7.02 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{4,5}$  5.0 Hz,  $\text{H}_4$ ) 7.13 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{2,5}$  3.0 Hz,  $\text{H}_2$ ) 7.35 (1H, dd,  $J_{2,5}$  3.0 Hz,  $J_{4,5}$  5.0 Hz,  $\text{H}_5$ ).

In the above reaction a buffer solution  $\text{HSO}_3^-/\text{SO}_3^{2-}$  was used to maintain an optimum pH (5-6) for the addition reaction. Autoxidation of bisulfite ions results in an increase in acidity (bisulfate is more acidic than bisulfite). This undesirable effect causes a change in the pH from optimum, slowing down the addition. This is avoided by buffering with sulfite ion.

*Poly(3-(sodium propylsulfonate)thiophene): (5)*

8.4 ml of an aqueous solution containing 0.85 g ( $3.7 \times 10^{-3}$  mol) of sodium-3-(3-thienyl)propanesulfonate (3) was added to a stirred solid of 2.4 g ( $1.48 \times 10^{-2}$  mol) of ferric chloride. The reaction mixture was stirred for 12 hours at room temperature. During the reaction solid ferric chloride was maintained in the reaction vessel. The resulting mixture was washed several times with water. The intermediate polymer (4) was insoluble in water. When treated with 1.0 M NaOH, it formed a soluble polymer that was recrystallized from methanol to yield 0.505 g (60%) of the desired orange-red polymer (5). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3466w, 2938w, 2866w, 2486w, 2362, 1653m, 1451s, 1182s, 1051m.

The polymerization process requires solid ferric chloride as an oxidant. The active polymerization sites are iron (III) ions at the crystal surface. The fact that ferric chloride is easily soluble in water explains the necessity for its excess. Soluble ferric chloride is inert.<sup>36</sup>

### 2.2.3 Synthesis of Poly(3-(sodium hexylsulfonate)thiophene): (Figure 9)

3-Alkylthiophene monomers are commonly synthesized from 3-bromothiophene and alkyl Grignard reagents using [1,3-bis(diphenyl

phosphino)propane]nickel (II) chloride as a catalyst with high yields.<sup>37</sup> In the synthesis of 6-(3-thienyl)hexene and 8-(3-thienyl)octene the route described for 3-alkylthiophenes was followed.

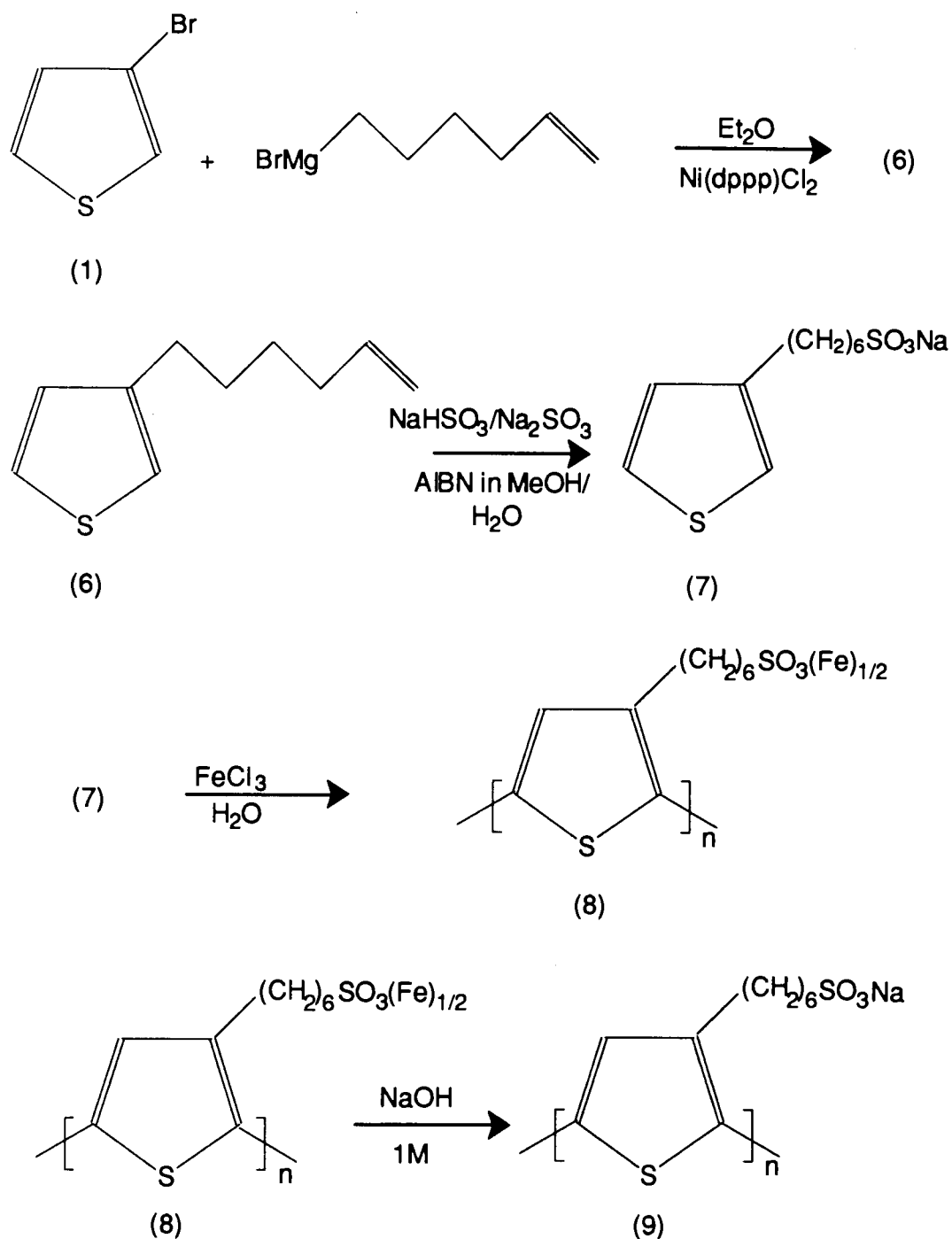
The nickel catalyst is effective for alkyl and simple aryl Grignard reagents but does not appear to work for allyl Grignard reagents.<sup>38</sup> In the synthesis of 3-(3-thienyl)propene, the use of n-BuLi is necessary to achieve the alkylation of 3-bromothiophene (see figure 8) since Ni(dppp)Cl<sub>2</sub> did not produce the desired product (2).

*1-Hexene-6-magnesium bromide:*

8.5 g ( $5.2 \times 10^{-2}$  mol) of 6-bromo-1-hexene was added to a stirred suspension of 1.5 g ( $6.2 \times 10^{-2}$  mol) of magnesium turnings in 80 ml of dry ether. To start the reaction, 0.5 g of 6-bromo-1-hexene was added to the magnesium suspension. The reaction flask was surrounded by a hot water bath that was removed when the reaction started. The remaining 6-bromo-1-hexene was added slowly at a rate that the reaction was under control, over a period of 1 hour. The reaction mixture was then refluxed for 1 hour and was allowed to cool down. The resultant solution, 0.65M of 1-hexene-6-magnesium bromide in ether (assuming 100% conversion) was transferred via canula.

*6-(3-Thienyl)hexene: (6)*

The title compound (6) was synthesized by coupling 9.75 g ( $5.2 \times 10^{-2}$  mol) of 1-hexene-6-magnesium bromide 0.65 M with 8.5 g ( $5.2 \times 10^{-2}$  mol) of 3-bromothiophene (1) (Aldrich reagent), using 90 mg ( $1.7 \times 10^{-4}$  mol) of [1,3-bis



**Figure 9. Synthesis of Poly(3-(sodium hexylsulfonate)thiophene).**

(diphenylphosphino)propane]nickel (II) chloride as a catalyst, in 50 ml of dry ether. The reaction was stirred overnight at 0°C and checked by G.C. for the



presence of 3-bromothiophene (1). The reaction was worked up by quenching the resulting mixture in a separatory funnel containing 5% HCl, followed by three ether extractions. The combined organic layer was dried with  $\text{MgSO}_4$  and evaporated to give a yellow oil. Chromatographic purification on silica gel (similar conditions used for product (2)) afforded a colorless oil (6) in 65-70% yield. N.M.R. ( $\text{CDCl}_3$ ,  $\delta$  rel. to TMS) 1.44 (2H, tt,  $J_{3,4}$  7.8 Hz,  $J_{4,5}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) 1.65 (2H, tt,  $J_{4,5}$  7.8 Hz,  $J_{5,6}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) 2.08 (2H, m) 2.6 (2H, t,  $J_{5,6}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) 4.98 (1H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{cis}}$  5.0 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHH}$ ) 5.01 (1H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{trans}}$  8.7 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHH}$ ) 5.80 (1H, m) 6.91 (1H, dd,  $J_{2,4}$  1.0 Hz,  $J_{2,5}$  3.0 Hz,  $\text{H}_2$ ) 6.95 (1H, dd,  $J_{2,4}$  1.0 Hz,  $J_{4,5}$  5.0 Hz,  $\text{H}_4$ ) 7.25 (1H, dd,  $J_{2,5}$  3.0 Hz,  $J_{4,5}$  5.0 Hz,  $\text{H}_5$ ). G.C.mass  $m/e$  ( $\text{M}^+$  166).

*Sodium-6-(3-thienyl)hexanesulfonate: (7)*

A mixture of 2.5 g ( $1.5 \times 10^{-2}$  mol) of the hexene (6), 38 mg ( $2.2 \times 10^{-4}$  mol) of AIBN, 2.34g ( $2.25 \times 10^{-2}$  mol) of sodium bisulfite, 0.4725 g ( $3.75 \times 10^{-3}$  mol) of sodium sulfite, and 30 ml of  $\text{H}_2\text{O}$  and 30 ml of methanol was heated at  $80^\circ\text{C}$  for 20 hours. The cooled reaction mixture was evaporated to dryness and extracted several times with ether. The remaining solid contained an excess of sodium salts. This mixture was recrystallized from dry ethanol to give monomer (7) with a 45-50% yield. IR (KBr,  $\nu/\text{cm}^{-1}$ ) 3522m, 3483m, 3112w, 2917m, 2862m, 1659m, 1194s, 1180s, 1056s. N.M.R. ( $\text{D}_2\text{O}$ ,  $\delta$  rel to TMS) 1.31 (2H, tt,  $J_{3,4}$  7.8 Hz,  $J_{4,5}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 1.40 (2H, tt,  $J_{2,3}$  7.8 Hz,  $J_{3,4}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 1.59 (2H, tt,  $J_{4,5}$  7.8 Hz,  $J_{5,6}$  7.8 Hz,

$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$  1.68 (2H, tt,  $J_{1,2}$  7.8 Hz,  $J_{2,3}$  7.8 Hz,  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$  2.61 (2H, t,  $J_{5,6}$  7.8 Hz,  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$  2.84 (2H, t,  $J_{1,2}$  7.8 Hz,  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$  7.02 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{4,5}$  5.2 Hz,  $H_4$ ) 7.06  
 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{2,5}$  3.5 Hz,  $H_2$ ) 7.35 (1H, dd,  $J_{2,5}$  3.5 Hz,  $J_{4,5}$  5.2 Hz,  $H_4$ ).

*Poly(3-(sodium hexylsulfonate)thiophene): (9)*

A polymerization reaction of 1 g ( $3.7 \times 10^{-3}$  mol) of monomer (7) as described for (3) afforded 55% yield of the desired red polymer (9). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3452w, 2934w, 2855w, 2494w, 2372w, 1653m, 1457s, 1186s, 1049m.

**2.2.4 Synthesis of Poly(3-(sodium octylsulfonate)thiophene): (Figure 10)**

*1-Octene-8-magnesium bromide:*

1-Octene-8-magnesium bromide was obtained by the method described for 1-hexene-6-magnesium bromide. 4.8 g ( $2.5 \times 10^{-2}$  mol) of 8-bromo-1-octene was added to 0.72 g ( $3.0 \times 10^{-2}$  mol) of magnesium in 40 ml of dry ether. The resulting solution 0.63M was transferred via canula.

*8-(3-Thienyl)octene: (10)*

The compound (10) was obtained by the method described for (6) using 4.1 g ( $2.5 \times 10^{-2}$  mol) of 3-bromothiophene, 5.4 g ( $2.5 \times 10^{-2}$  mol) of 1-octene-8-magnesium bromide 0.63M, and 45 mg ( $2.5 \times 10^{-4}$  mol) of [1,3-bis(diphenyl

phosphine)propane]nickel(II) chloride in 25 ml of ether. The crude product was obtained as a yellow oil that was purified by a chromatographic column (similar conditions used for product (2)), yielding 2.95 g (60%) of the pure compound (10). N.M.R. ( $\text{CDCl}_3$ ,  $\delta$  rel. to TMS) 1.35 (6H, m) 1.62 (2H, tt,  $J_{6,7}$  7.8 Hz,  $J_{7,8}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) 2.08 (2 H, m) 2.62 (2H, t,  $J_{7,8}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ) 4.95 (1H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{cis}}$  5.0 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHH}$ ) 5.08 (1H, dd,  $J_{1,1}$  1.0 Hz,  $J_{1,2\text{trans}}$  8.75 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHH}$ ) 5.82 (1H, m) 6.93 (1H, dd,  $J_{2,4}$  1.0 Hz,  $J_{2,5}$  3.0 Hz,  $\text{H}_2$ ) 6.96 (1H, dd,  $J_{2,4}$  1.0 Hz,  $J_{4,5}$  5.25 Hz,  $\text{H}_4$ ) 7.26 (1H, dd,  $J_{2,5}$  3.0 Hz,  $J_{4,5}$  5.25 Hz,  $\text{H}_5$ ). G.C.mass  $m/e$  ( $\text{M}^+$  194).

*Sodium-8-(3-thienyl)octanesulfonate: (11)*

A solution of 1.4 g ( $7.2 \times 10^{-3}$  mol) of 8-(3-thienyl)octene (10), 18 mg ( $1.1 \times 10^{-4}$  mol) of AIBN, 1.12 g ( $1.1 \times 10^{-2}$  mol) of sodium bisulfite, 0.2273 g ( $1.8 \times 10^{-3}$  mol) of sodium sulfite, in 14.5 ml of  $\text{H}_2\text{O}$ , and an equal volume of methanol was stirred using the same conditions described previously for (7). When the reaction was complete the product was worked up affording 1.2 g, (56% yield) of the monomer (11). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3527m, 3476m, 3104w, 2925m, 2855m, 1649m, 1194s, 1167s, 1060s. N.M.R. ( $\text{D}_2\text{O}$ ,  $\delta$  rel to TMS) 1.33 (8H, m) 1.58 (2H, tt,  $J_{6,7}$  7.8 Hz,  $J_{7,8}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 1.67 (2H, tt,  $J_{1,2}$  7.8 Hz,  $J_{2,3}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 2.61 (2H, t,  $J_{7,8}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 2.85 (2H, t,  $J_{1,2}$  7.8 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ) 7.01 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{4,5}$  5.25 Hz,  $\text{H}_4$ ) 7.06 (1H, dd,  $J_{2,4}$  1.5 Hz,  $J_{2,5}$  3.0 Hz,  $\text{H}_2$ ) 7.34 (1H, dd,  $J_{2,5}$  3.0 Hz,  $J_{4,5}$  5.25 Hz,  $\text{H}_5$ ).

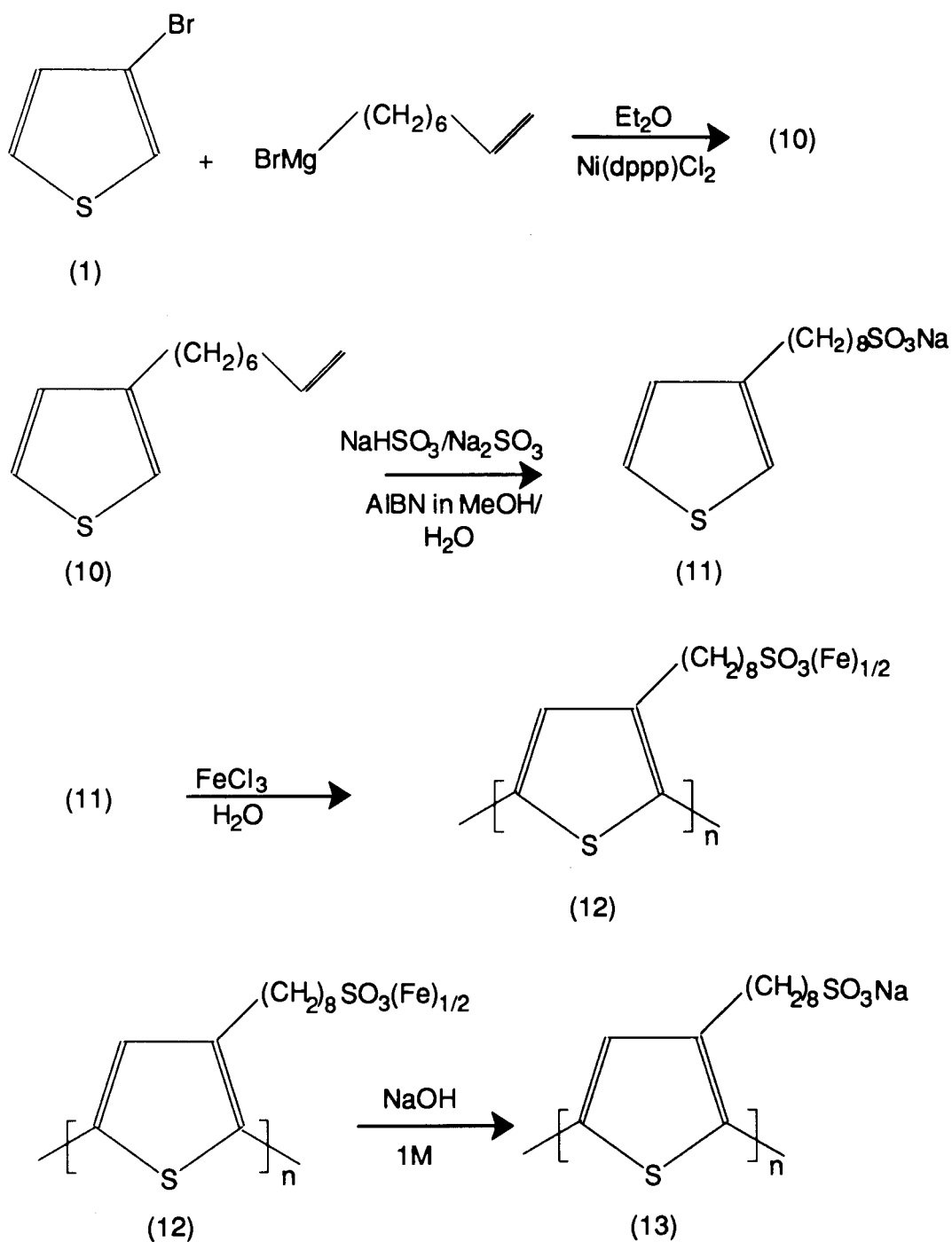


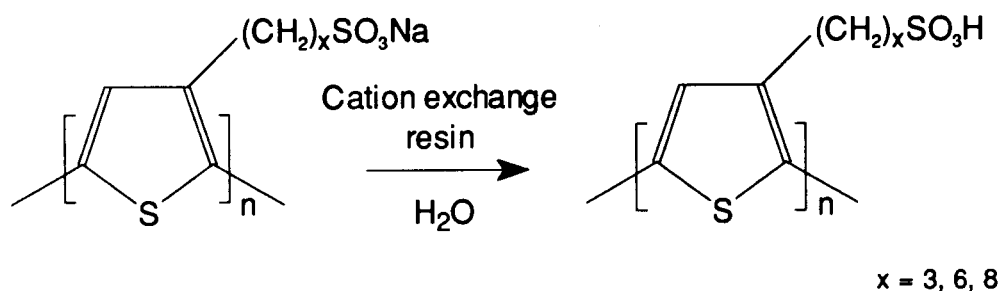
Figure 10. Synthesis of Poly(3-(sodium octylsulfonate)thiophene).

*Poly(3-(sodium octylsulfonate)thiophene): (13)*

A chemical polymerization of 500 mg ( $1.7 \times 10^{-3}$  mol) of monomer (11) with an excess of ferric chloride of 1.1 g ( $6.7 \times 10^{-3}$  mol) in 4 ml of water was performed following the same method as described for (3). This reaction yielded 280 mg (56%) of the polymer (13). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3445m, 2930m, 2861w, 2520w, 2382w, 1645m, 1458s, 1182s, 1051s.

### 2.2.5 Conversion of sodium salt to acid form of the polymers

All the synthesized polymers were soluble in  $\text{H}_2\text{O}$ . To convert the sodium salt of the polymers to the acid form, solutions of (5), (9) and (13), undoped state, were passed through a cation exchange resin column (AG 50W-X8, Bio Rad) using water as eluent (see figure 11).



**Figure 11. Ion exchange: Sodium salt to Acid form of the polymers.**

### 3. PROPERTIES OF THE SYNTHESIZED POLYMERS

#### 3.1 Molecular Weights

##### 3.1.1 Theoretical considerations

When polymers are prepared, a mixture of molecular sizes is usually obtained. The properties of a polymer sample depends on the average size of the molecules present. There are a number of ways in which such an average can be calculated, and different methods of averaging yield different results.

Methods based on counting the molecules in a given mass of material afford the number average molecular weight,  $M_n$ .<sup>39</sup> This is defined by the following expression:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (1)$$

$M_i$  is the molar mass of the molecular species  $i$ , and  $N_i$  is the number of molecules of  $i$  in the sample. Other methods measure quantities proportional to the mass of molecules. In this case, the mass average molecular weight,  $M_w$ ,<sup>39</sup> is obtained, and it is defined by the following expression:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (2)$$

Gel permeation chromatography (GPC) is used to determine the molecular mass of synthesized polymers. GPC is a size exclusion method for molecular weight measurements.<sup>40</sup> In this technique, a solution of the polymer is passed through a series of columns packed with a gel with defined pore size.

Low molecular weight fractions can penetrate the pores while high molecular weight fractions simply bypass the gel particles. High molecular weight species leave the column first, but the passage of low molecular weight components is retarded. A detector can be connected to the end of the column to measure the concentration of eluted materials by both differential refractive index and UV-vis absorption.

### 3.1.2 Experimental

The number average molecular weight of the synthesized polymers (5), (9) and (13) was measured by GPC using 250, 500, and 1000 Å ultrahydrogel columns at 25°C. Polymers were eluted with an aqueous solution of NaNO<sub>3</sub> 0.4 M and detected using a UV-vis spectrophotometer (Spectra Physics SP8400) and a differential refractometer (Waters R401). Polyethylene oxide of different molecular weights was used as a standard (see Table 1).

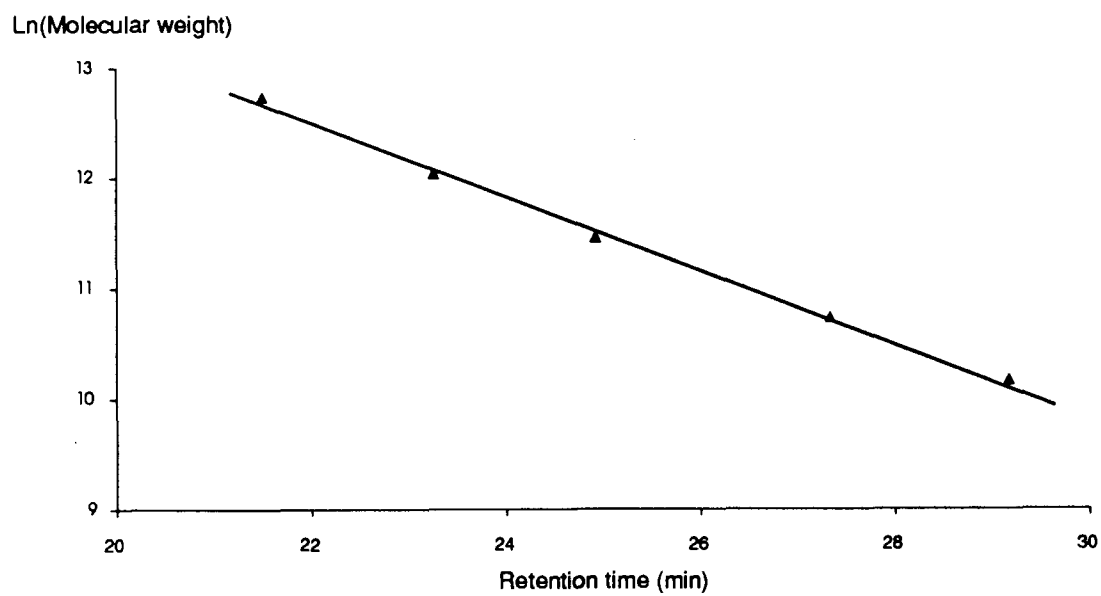
By plotting retention time vs. Ln (Molecular weight) of the standard (see figure 12), the following linear correlation was obtained:

$$y = 19.784 - 0.3311x \quad (3)$$

The number average molecular weight and polydispersity index of the water soluble polymers under investigation have been obtained by using polyethylene oxide as a standard (see Table 2). In order to determine true molecular weights, it is necessary to know the Mark-Houwink constants of the water soluble polymers.<sup>41</sup>

<b>Table 1. Polyethylene oxide standard.</b>	
Molecular weight of Polyethylene oxide $\times 10^{-4}$	Retention time (min) <sup>a</sup>
2.6	29.17
4.6	27.33
9.5	24.92
17.0	23.25
34.0	21.50

a: Peak retention time.



**Figure 12. Polyethylene oxide standard.**



<b>Table 2. Molecular weight of water soluble polymers.</b>			
Alkylsulfonate substituent	Number average Molecular weight	Polydispersity Index	Average degree of polymerization
Propyl (5)	3,100	1.3	13
Hexyl (9)	6,100	1.4	22
Octyl (13)	8,200	1.6	27

Even when the molecular weights determined by GPC are not the true molecular weights, the values are useful as an estimation.

### **3.2 Thermal analysis**

#### **3.2.1 Theoretical considerations**

Many synthetic polymers show a characteristic sequence of physical changes as they are heated. Many linear polymers are glasses at low temperatures, and as the temperature is increased the polymer changes from a glass to a rubber. The temperature at which a large change in properties is observed is known as the glass transition temperature ( $T_g$ ). This transition is second order. If the temperature is increased further the polymer changes successively from a rubber to a gum and possibly to a liquid state. These thermal transitions can be measured by thermoanalytical techniques.<sup>42</sup>

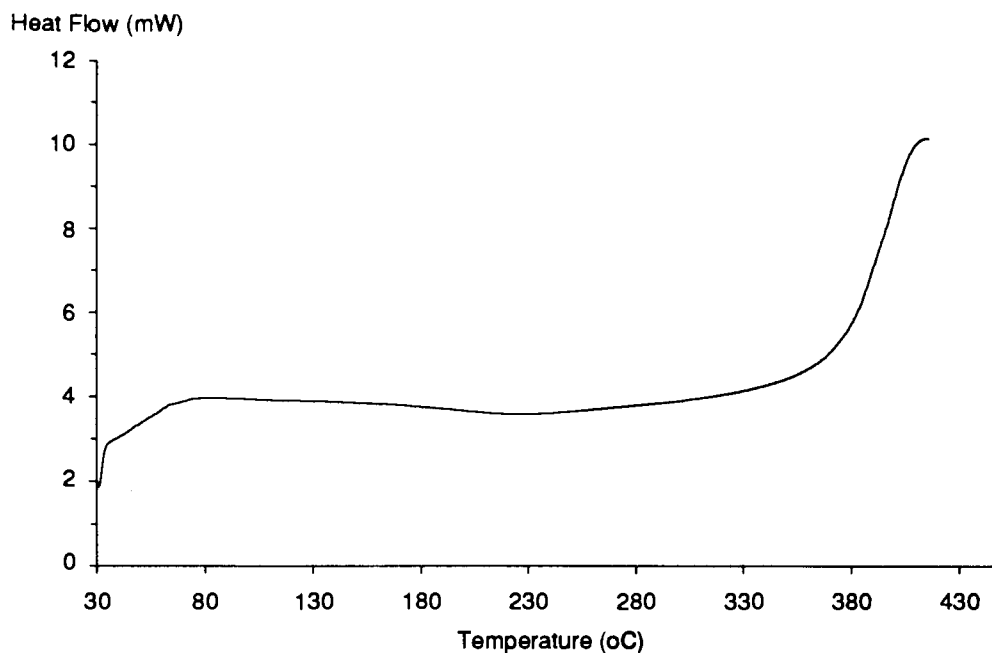
Thermoanalytical measurements have been commonly performed using calorimeters. Two important thermoanalytical methods are: differential thermoanalysis (DTA) and differential scanning calorimetry (DSC).

Differential scanning calorimetry is based on the comparison of a sample with an inert standard. This technique measures the difference in energy necessary to maintain the two samples at the same temperature as they are simultaneously heated at a constant rate. If any temperature difference appears between the sample and the reference, the instrument compensates by changing the heat flux, and the thermal energy difference per unit time is measured. The sample and the reference have two independent heating systems. Using DSC,  $T_g$ , melting, crystallization, and decomposition can be determined.

### **3.2.2 Experimental**

A differential scanning calorimeter (Perkin Elmer DSC7) was used to examine thermal characteristics in the temperature range 50 to 420 °C. A heating rate of 10.0 °C/min was used. A typical DSC response is shown in figure 13.

For the polymers under investigation, (5), (9) and (13), the only change observed was their decomposition at temperatures higher than 400 °C. A second thermal cycle showed no transitions. This type of polymer possesses a defined crystalline structure due to the presence of formal charges in its side chain so that the polymer chains are well oriented. In consequence the only thermal transition observed is their decomposition.



**Figure 13. DSC response of poly(3-(sodium propylsulfonate)thiophene).**

### **3.3 CONDUCTIVITY**

#### **3.3.1 Theoretical considerations: Mechanism of conduction**

Initially, it was assumed that the conduction mechanism in conducting polymers was similar to that in inorganic semiconductors. It is important to remember that inorganic semiconductors contain atoms covalently bonded in three dimensions and charge mobility is high so that reasonable conductivities can be achieved at low doping levels.<sup>43</sup>

In organic polymers, each carbon atom in the chain possesses four electrons in its outer shell. Two of these electrons are used to form  $\sigma$  bonds that make up the polymer chain, the third electron is bound to a hydrogen atom, and the final electron occupies a  $p_z$  orbital that forms the  $\pi$  double bond. Organic

polymers can be considered as one dimensional conductors because they are only linked through bonds along the polymer, whereas the interactions between chains are weak.

Doping of organic polymers can be seen as a chemical modification since oxidizing or reducing agents have to be incorporated into the polymer, and charge transfer occurs with modifications of the chain geometry. These modifications affect the electronic structure by inducing localized electronic states in the gap between the valence and the conduction bands.

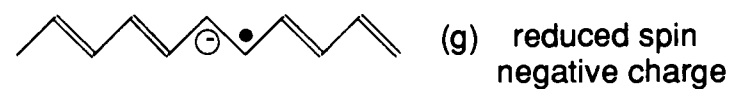
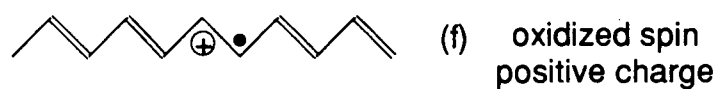
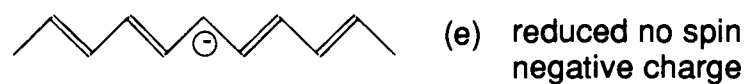
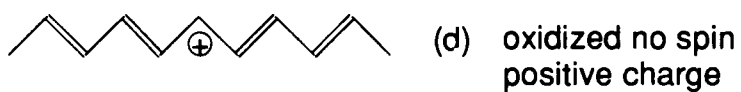
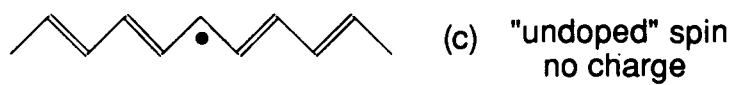
Poly(acetylene) has a degenerate ground state,<sup>44</sup> (figure 14 a, b). These two structures differ from one another by exchange of alternating single and double bonds (figure 14 c). This delocalized electron has spin but not effective charge. It is known as a soliton and can move along the polymer chain.

When the polymer is doped, positive or negative charged solitons are created in the polymer chain. Due to Peierls a distortion, the bond lengths will modify to accommodate the soliton, inducing new energy states mid-way in the band gap (figure 14 c, d, e). As the initial delocalized electrons are consumed, the oxidation or reduction process is forced to break  $\pi$  bonds and both spin and charge formation take place (figure 14 f, g). These spin-charge pairs are known as polarons. Two adjacent polarons can recombine to form a spinless soliton on the polymer chain.

The degenerate ground state of poly(acetylene) is a special case in conducting polymers. In poly(thiophenes) the resonance structures are not identical if they are superimposed<sup>45</sup> (figure 15).

In the quinonoid structure, the bond between rings has a stronger double bond character than in the aromatic structure. The quinonoid structure has a

higher total energy than the aromatic form. It is not possible, therefore, to have solitons in this system.



Band diagrams  
of solitons and polarons

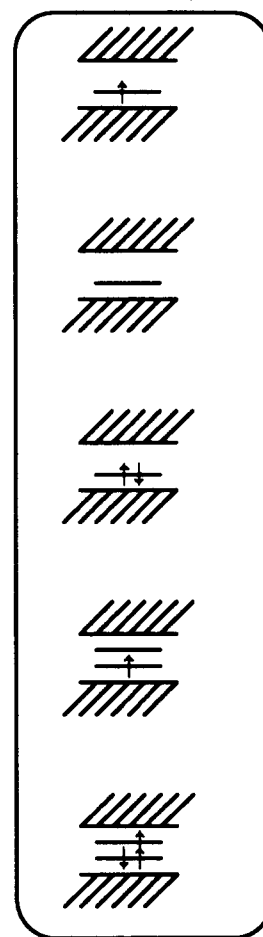
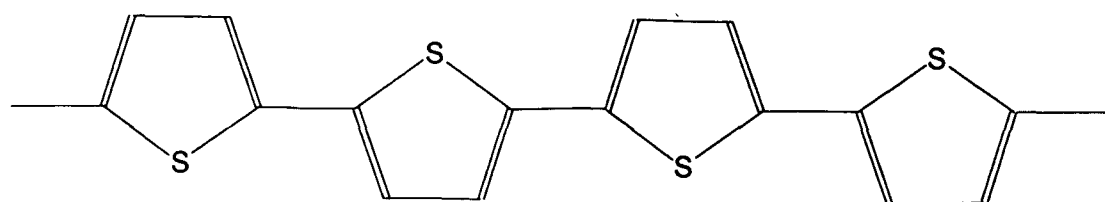
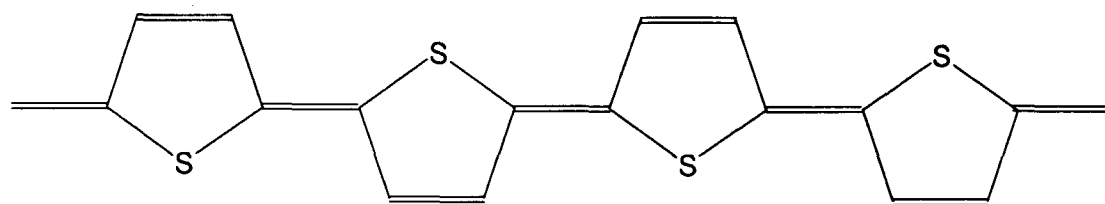


Figure 14. Structures of poly(acetylene).



Benzenoid structure



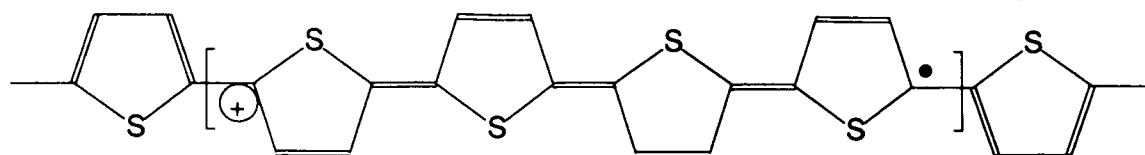
Quinonoid structure

**Figure 15. Resonance structures of poly(thiophenes).**

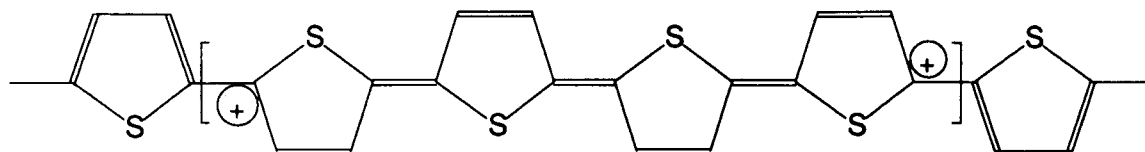
When the polymer is oxidized, it forms a radical cation (polaron) that resides in the middle of the chain rather than at the chain ends. The polaron can be delocalized over several units in the chain, and two new electronic states appear within the band gap. If the polymer is further oxidized, a bipolaron (dication) is formed. Bipolarons have no radical character.<sup>46</sup> See figure 16.

Bipolaron formation can be explained by two different mechanisms.<sup>47</sup> The first is that the polaron undergoes further oxidation, and the second is that two separated polarons disproportionate as shown in figure 17. The second mechanism has been widely accepted.

The electronic transitions observed in poly(thiophenes) are shown in figure 18. The monomer has a  $\pi$  to  $\pi^*$  transition observed in the UV region. The neutral polymer possesses two electronic bands, one filled and the other empty.

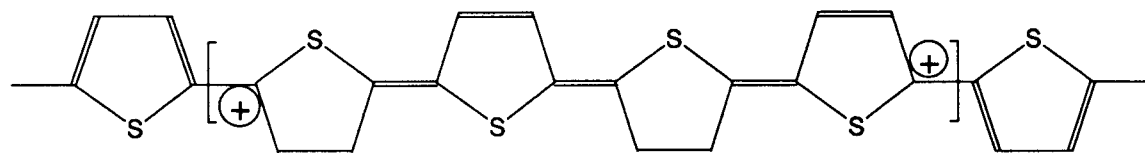
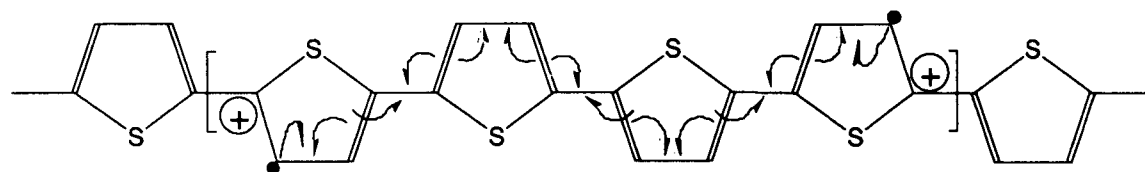


Polaron



Bipolaron

**Figure 16. Polaron and Bipolaron structures.**



Bipolaron

**Figure 17. Bipolaron formation.**

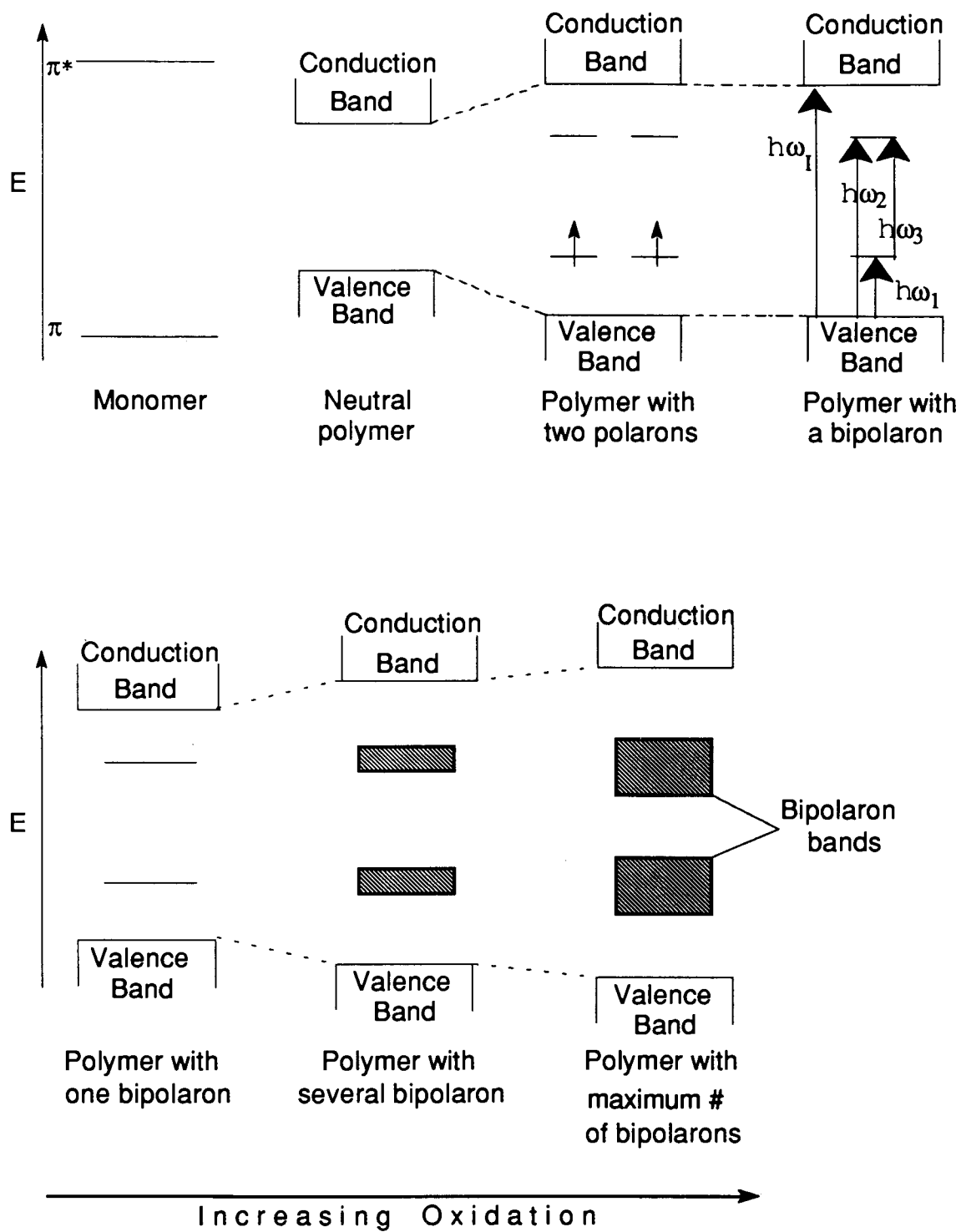


Figure 18. Electronic transitions in poly(thiophenes).



The lowest electronic transition observed for the neutral polymer is the band gap which is derived from the lowest  $\pi$  to  $\pi^*$  transition of the monomer. The band gap transition is observed in the visible region at approximately 450 nm. When the polymer is partially oxidized, new states between the band gap, with a spin 1/2 are formed. These new energy states are derived from orbitals near the upper edge of the valence band and the lower edge of the conduction band.

At low oxidation levels the  $h\nu_1$ ,  $h\nu_2$  and  $h\nu_3$  transitions are observed, but at higher levels the  $h\nu_3$  transition disappears; consistent with the formation of spinless bipolarons. As the doping level increases, the transitions become bands.

The electrical conductivity observed in poly(thiophenes) occurs via bipolaron movement along the chain, nevertheless, some interchain transfer must occur and bipolaron chain hopping also takes place. Although the bipolaron model has some weaknesses, it is still the best model to explain conduction in these systems.

### 3.3.2 Experimental

Polymer films were cast onto glass slides under vacuum from their corresponding aqueous solution (10 mg/ml). Chemical doping was performed by immersing the neutral polymer film into a nitromethane solution of the oxidizing agent. After saturation the polymer film was washed with nitromethane to eliminate any excess of oxidizing agent. Electronic conductivity measurements were performed using the four probe technique.<sup>48</sup> Thicknesses of polymer films were estimated using conditions similar to those used for poly(3-hexylthiophene).<sup>49</sup>

### Sodium salts:

The undoped state of the polymer films gave conductivities  $< 10^{-6}$  S/cm. After doping with a solution of 0.1 M  $\text{FeCl}_3$  in nitromethane, the conductivities observed were in the order of  $10^{-4}$  -  $10^{-3}$  S/cm. When  $\text{AuCl}_3$  0.1 M in nitromethane was used as a doping agent, the conductivities increased to  $10^{-2}$  S/cm. The oxidized polymer films returned to their original neutral state within a couple of days upon exposure to the ambient atmosphere as indicated in the following table:

<b>Table 3. Conductivities of polymer films of the sodium salt.</b>				
Alkylsulfonate substituent	Conductivities* (S/cm)			
	t= 0 hours <sup>a</sup>		t= 48 hours	
	$\text{FeCl}_3$	$\text{AuCl}_3$	$\text{FeCl}_3$	$\text{AuCl}_3$
Propyl (5)	$3 \times 10^{-3}$	$2 \times 10^{-2}$	$5 \times 10^{-5}$	$8 \times 10^{-4}$
Hexyl (9)	$4 \times 10^{-4}$	$3 \times 10^{-3}$	$<10^{-6}$	$2 \times 10^{-5}$
Octyl (13)	$8 \times 10^{-3}$	$9 \times 10^{-2}$	$3 \times 10^{-5}$	$2 \times 10^{-4}$

\*: Films were kept in ambient atmosphere.

a: Conductivity measurement at t=0, were performed immediately after doping.

Polymer films remained water soluble after oxidation.

#### *Acid form:*

Films of "self-doped" polymers exhibited conductivities of  $10^{-2}$  S/cm. These polymers could be further doped using oxidizing agents. Table 4 summarizes conductivities observed before and after doping.

As observed for polymer films of the sodium salt, films of the acid form of the polymer were water soluble after doping.

### **3.3.3 Discussion**

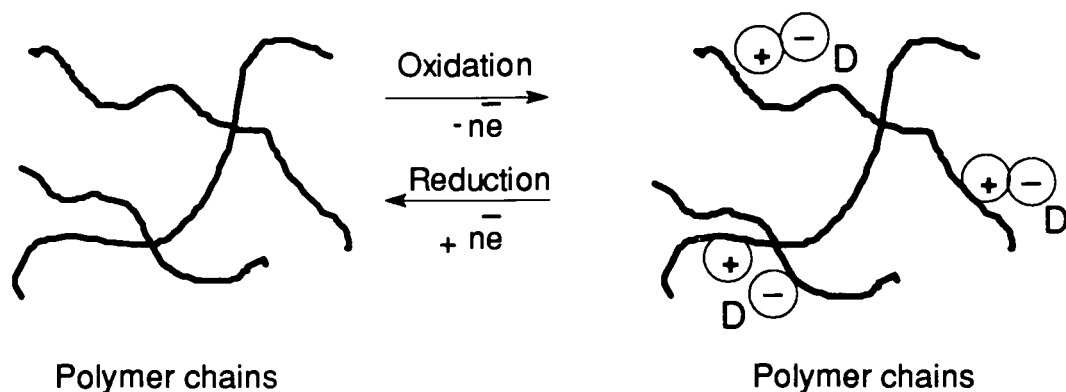
The doping process of "self-doped" polymers differs from other conjugated organic polymers. In poly(acetylenes), poly(thiophenes), poly(pyrroles), etc., doping follows a pathway where the injection of charges into the  $\pi$ -electron system requires that dopand agents have to diffuse into the polymer bulk because counter ions are necessary to maintain electroneutrality (see figure 19). In "self-doped" polymers, the counter ions ( $\text{SO}_3^-$ ) are covalently bonded to the polymer chain.

It is important to consider the nature of the cation that balances the counter ion in the neutral polymer. For example, polymer films in the acid form are extremely hygroscopic and the film surface is always coated with a layer of water. When the water is partially removed, the next best base to solvate the protons of the sulfonic acid is the polythiophene backbone, as shown in figure 20.<sup>30a</sup> The effect described above is not observed for the sodium salt. In consequence, the acid form of the polymers exhibits a higher conductivity than the sodium salt of the polymers in their neutral state.

Table 4. Conductivities of polymer films of the acid form.									
Alkylsulfonate substituent	Conductivities* (S/cm)								
	"self- doped"	t=0 hours <sup>a</sup>		t=24 hours		t=96 hours		t=336 hours	
		FeCl <sub>3</sub>	AuCl <sub>3</sub>	FeCl <sub>3</sub>	AuCl <sub>3</sub>	FeCl <sub>3</sub>	AuCl	FeCl <sub>3</sub>	AuCl <sub>3</sub>
Propyl	$6 \times 10^{-2}$	$4 \times 10^{-1}$	$1 \times 10^{-1}$	$1 \times 10^{-1}$	$2 \times 10^{-2}$	$1 \times 10^{-1}$	$1 \times 10^{-2}$	$8 \times 10^{-2}$	$5 \times 10^{-3}$
Hexyl	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$2 \times 10^{-3}$	$5 \times 10^{-4}$	$3 \times 10^{-4}$	$5 \times 10^{-4}$
Octyl	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$3 \times 10^{-3}$	$2 \times 10^{-3}$	$2 \times 10^{-4}$	$2 \times 10^{-3}$

\*: Films were kept in ambient atmosphere.

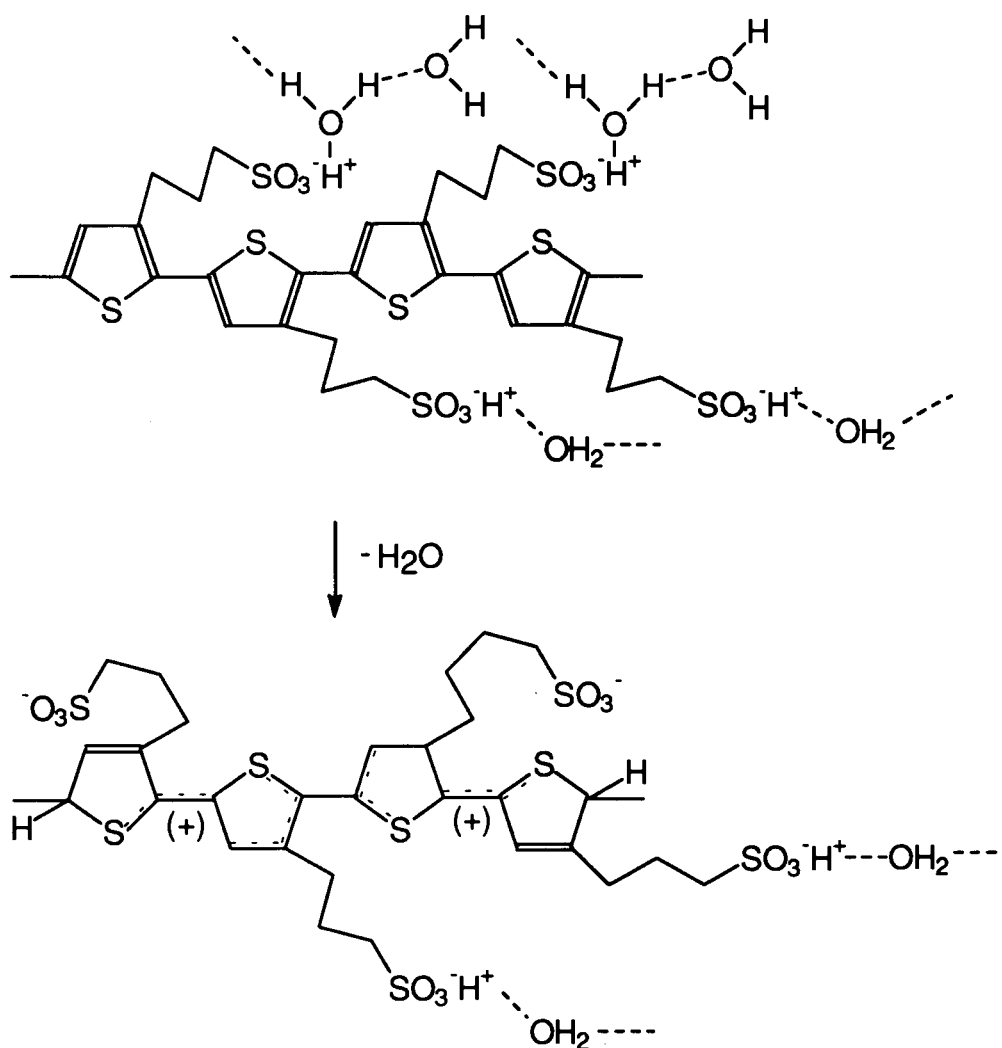
a: Conductivity measurement at t=0, were performed immediately after doping.



**Figure 19. The "doping" process.**

When conducting polymers are doped, they reach a certain conductivity maximum. At this point, the bipolaron states overlap and form two bands in the gap. There are a number of factors to consider, such as purity, regioregularity, etc., that affect the conduction mechanism in conducting polymers. It was seen, however, that the acid form of the polymers is in a doped state, and that conductivities can be increased with the use of extrinsic doping agents. Remarkably, these types of polymers provide stable electronically conductive materials with conductivities similar to semiconductor materials such as silicon or germanium.

Conductivity was not sensitive to the length of the alkylsulfonate side chain as has been reported for poly(3-alkylthiophenes),<sup>27d</sup> but, in general, when  $\text{AuCl}_3$  was used as a doping agent, higher conductivities were observed. This can be attributed to the greater oxidizing abilities of  $\text{AuCl}_3$  compared to  $\text{FeCl}_3$ .<sup>50</sup> The formation of bipolaron bands is more efficient in the presence of a strong oxidizing agent like  $\text{AuCl}_3$ .



**Figure 20. Acid form of polymers and "self-doping" mechanism.**

These preliminary conductivity measurements serve to characterize the synthesized polymers. Additional studies are required, however, to fully understand the conduction mechanism in "self-doped" polymers.

### 3.4 Electronic spectra

#### 3.4.1 Theoretical considerations

When a molecule absorbs radiation, its energy increases. The absorption of energy leads to the promotion of electrons, initially in the ground state, to an excited state of greater energy than the ground state. The energy difference between the electronic energy levels is given by:

$$\Delta E = h \nu \quad (4)$$

where  $h$  is Planck's constant, and  $\nu$  is the frequency of the radiation. The change in energy may be electronic, vibrational or rotational. Vibrational and rotational energy transitions usually give rise to infrared absorption spectra, but they can be observed as overtones accompanying UV-vis absorption.

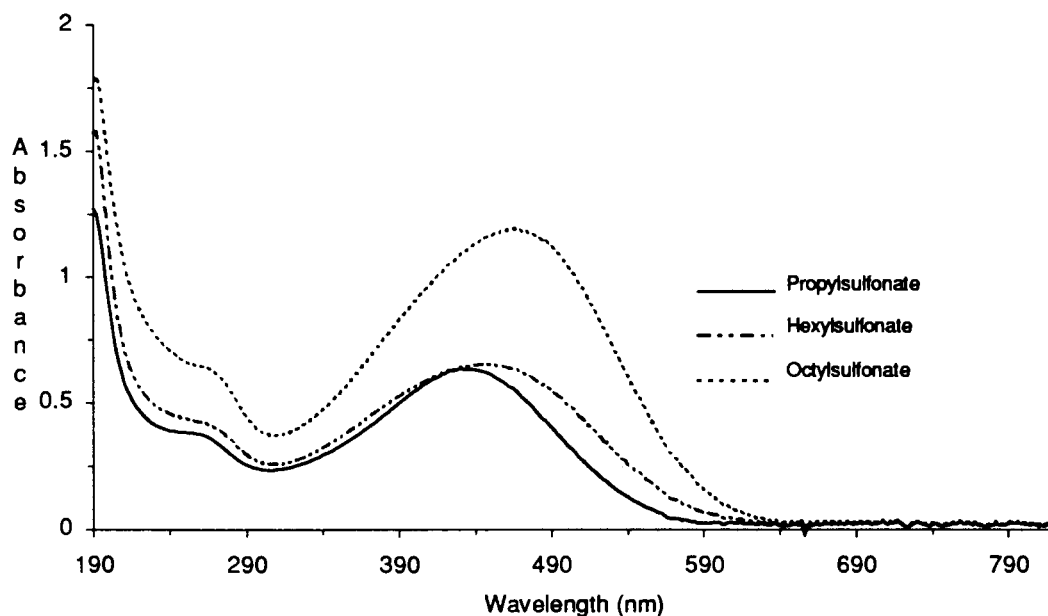
In general, neutral conducting polymers present a strong absorption band characteristic of the  $\pi$  to  $\pi^*$  transition. Upon doping, the energy gap decreases and the absorption peaks shift to higher wavelengths due to formation of solitons, polarons or bipolarons. (Figure 18).

#### 3.4.2 Results and Discussion

UV-vis spectra were recorded on a Perkin Elmer (Lambda 3A) spectrometer.

*Sodium form:*

The absorption spectra of polymers (5), (9) and (13) in solution are shown in figure 21. A change in the wavelength maximum as a function of the alkylsulfonate side chain was observed. Longer conjugation lengths are observed when the length of the side chain is increased. This observation suggests a rod-like conformation for longer alkylsulfonate substituents and a more helical conformation for shorter substituents, as has been reported for poly(3-alkylthiophenes).<sup>51</sup>

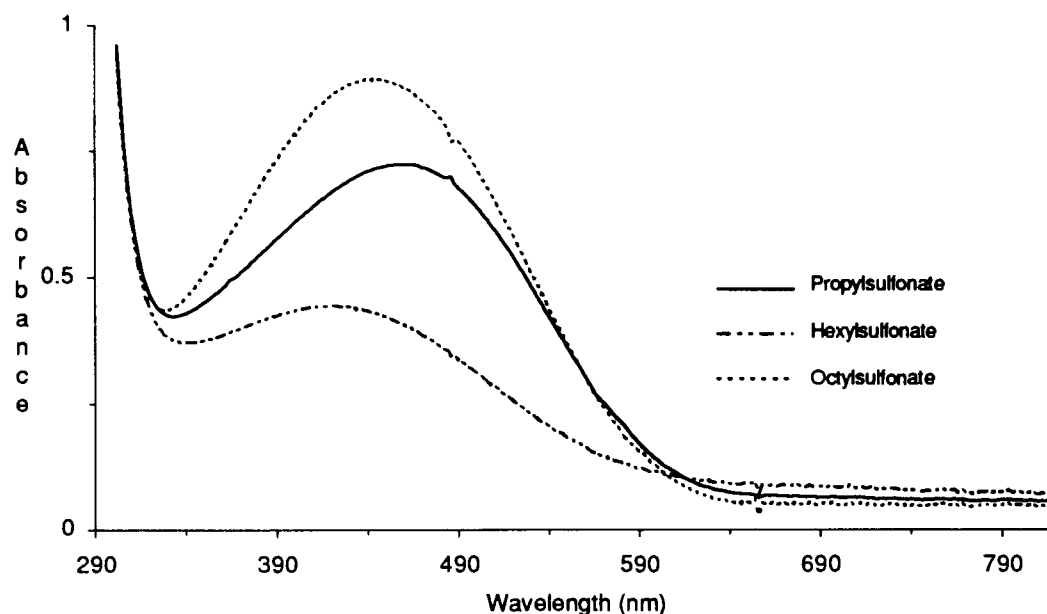


**Figure 21. Absorption spectra of polymers (5), (9) and (13) in solution.**

The absorption spectra of polymers (5), (9) and (13) in film are shown in figure 22. The spectra of figures 21 and 22 indicate a small spectral shift upon dissolution. This is in contrast to the results obtained for poly(3-



hexylthiophene)<sup>14a</sup> where a blue shift of approximately 60 nm. was found between the film and the solution spectra.



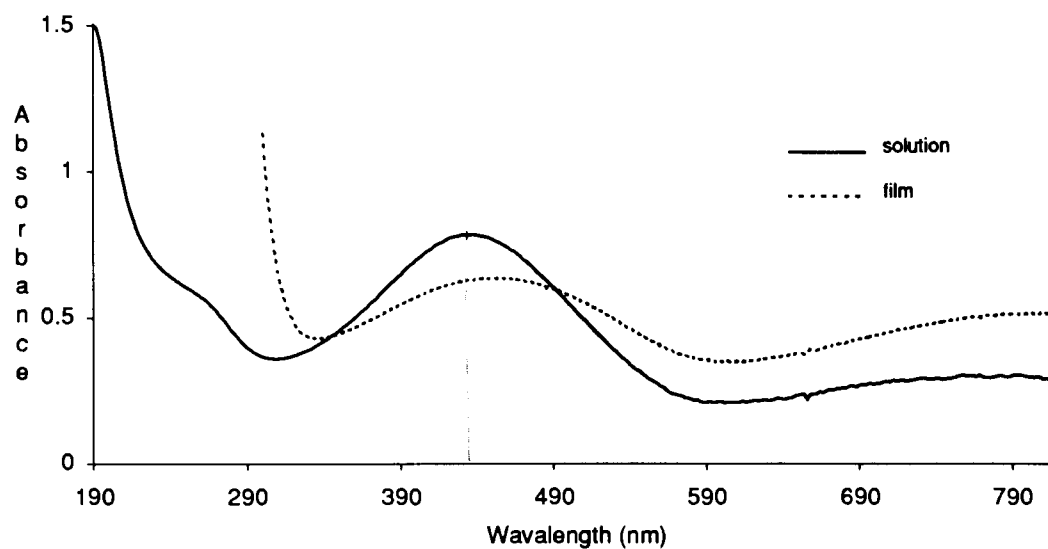
**Figure 22. Absorption spectra of polymers (5), (9) and (13) in film.**

The absorption spectra in film and in solution of poly(3-(sodium propylsulfonate)thiophene), (5), were similar to those reported by Patil<sup>33a</sup> and, therefore, independent of the molecular weights and the synthetic route utilized.

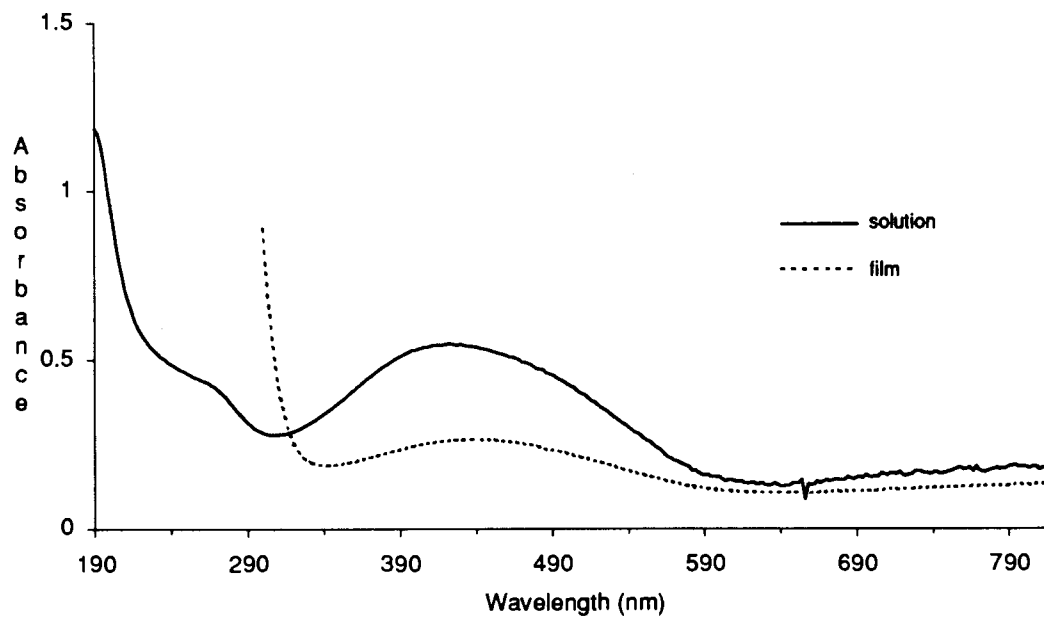
*Acid form:*

The absorption spectra of poly(3-(propylsulfonic acid)thiophene) in film and in solution are shown in figure 23. The acid form of the polymers exhibit a  $\pi$  to  $\pi^*$  transition at approximately 450 nm. In addition, other electronic transitions in the NIR (Near Infrared) region are observed at 800 nm. These are due to bipolaron bands, thus confirming the "self-doped" model.<sup>30a</sup>

The absorption spectra of poly(3-(hexylsulfonic acid)thiophene) in film and in solution are presented in figure 24.



**Figure 23.** Absorption spectra of poly(3-(propylsulfonic acid)thiophene).



**Figure 24.** Absorption spectra of Poly(3-(hexylsulfonic acid)thiophene).

Electronic spectra of the acid form of the polymers showed a red shift of their wavalength maxima when going from solution to the solid state. These polymers are "self-doped" and side chains interact with the polymer backbone as shown in figure 20. It appears that these polymers achieve a more efficient stacking in the solid state.

The experimental determination of electronic spectra gives insight about the extent of conjugation in conducting polymers. The existence of  $\pi$ -conjugation in these polymeric materials is implied by their red color. In conducting polymers, the extent of conjugation affects the energy of the  $\pi$  to  $\pi^*$  transition. The addition of the sulfonate group to the alkyl side chain does not affect significantly the electronic structure of the conjugated backbone.

### **3.5 Photochemical studies**

#### **3.5.1 Introduction**

The potential applications of the synthesized water soluble conducting polymers for photolithography make it necessary to investigate the chemical or physical changes that result from their interaction with UV-vis radiation.

It has been reported that poly(3-hexylthiophene) undergoes photochemical degradation upon UV-vis irradiation,<sup>14,52</sup> resulting in photobleaching, photochain scission and crosslinking where oxygen plays an important role. Photobleaching occurs in the presence of singlet oxygen that reacts with thienyl rings by a 1,4 Diels Alder addition. On th other hand, crosslinking follows a photo-oxidative free-radical pathway in which the poly(3-hexylthiophene) radicals produce a crosslinked polymer film.

### 3.5.2 Experimental

Photochemical studies were performed using an illumination source of 150-W mercury lamp (Illumination Industries Ltd.) focused to a 4 cm diameter. Irradiation light was passed through a water filter and a 300 nm cut-off filter to eliminate high energy radiation. Photochemical studies were performed in ambient air.

Polymer solutions were 10 mg/ml in concentration, and the solvent was H<sub>2</sub>O unless otherwise stated. The starting concentration was adjusted to give an optical density reading of 1.0 at maximum absorption wavelength. Polymer films were cast onto glass slides under vacuum from their corresponding aqueous solutions. Absorption spectra of the polymers, in solution and in film, were recorded during irradiation.

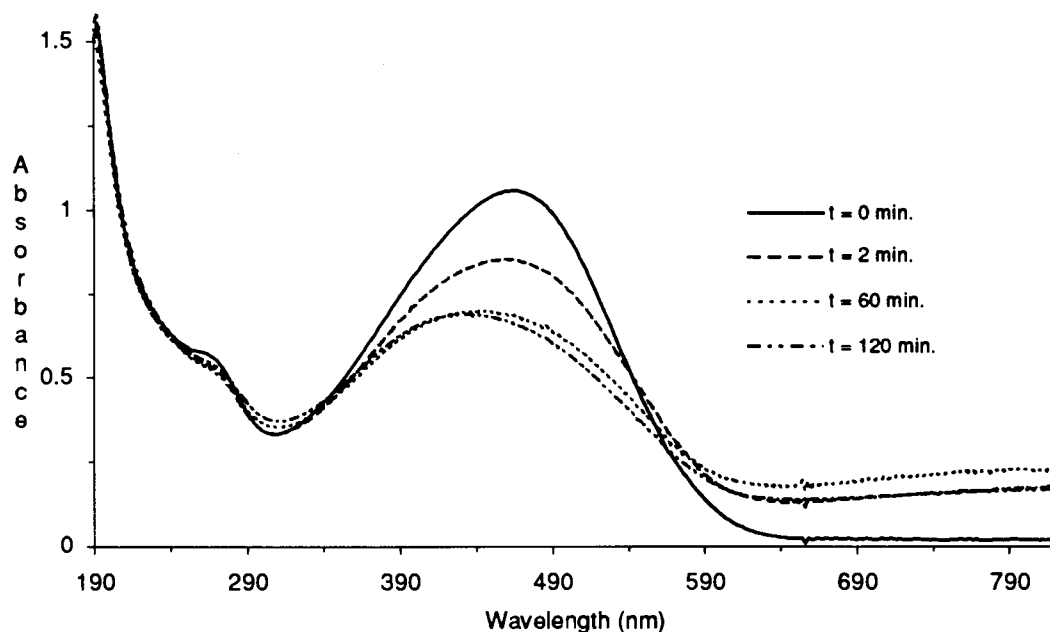
*Sodium salt:*

*Photolysis of polymer solutions:*

In contrast to poly(3-hexylthiophene), poly(3- (sodium alkylsulfonate)thiophenes) are relatively inert to UV-vis irradiation although these polymers exhibited some degree of photobleaching (see figure 25). An interesting characteristic of irradiation of poly(3-(sodium alkylsulfonate)thiophenes) was an initial increase of absorption intensity at 800 nm. This absorption intensity decreases with irradiation time.

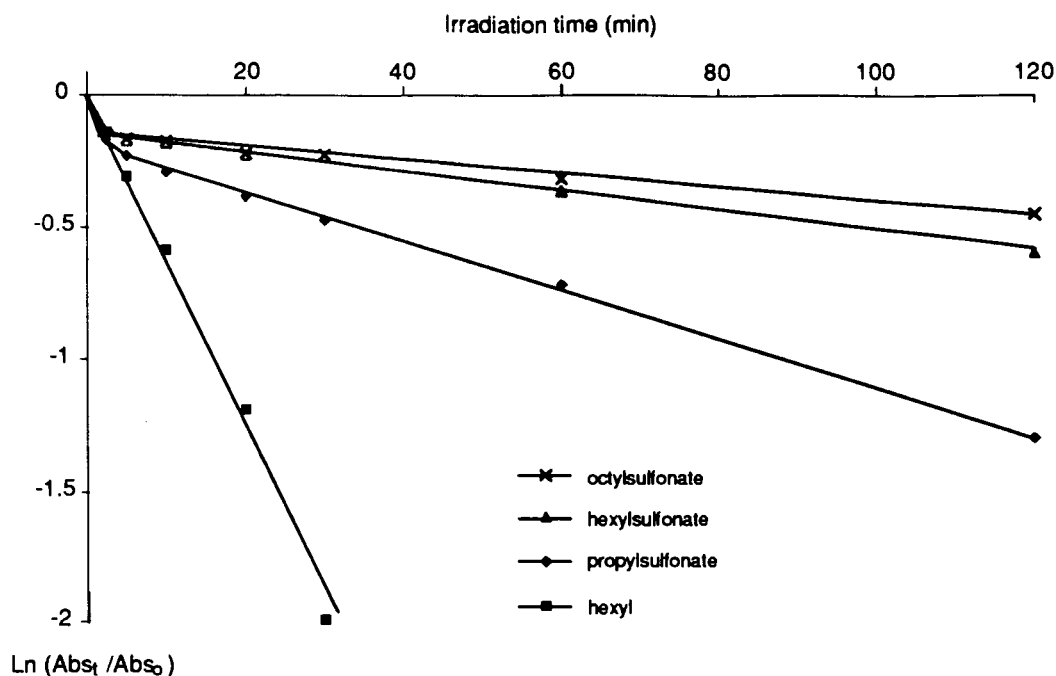
An estimation of photochemical degradation of polymer solutions is shown in figure 26. The photobleaching with time of polymer solutions increased in the

following order: octyl, hexyl and propyl. In this comparison, it is assumed that absorption spectra of polymer solutions have similar profiles (see figure 21).



**Figure 25. Photolysis of poly(3-(sodium octylsulfonate)thiophene) in solution.**

A solution of poly(3-hexylthiophene) in chloroform (similar conditions as poly(3-(sodium alkylsulfonate)thiophenes) was irradiated and its absorption intensity at  $\lambda$  maximum was monitored. In figure 26 the photobleaching of poly(3-hexylthiophene) is compared to the synthesized water soluble polymers.

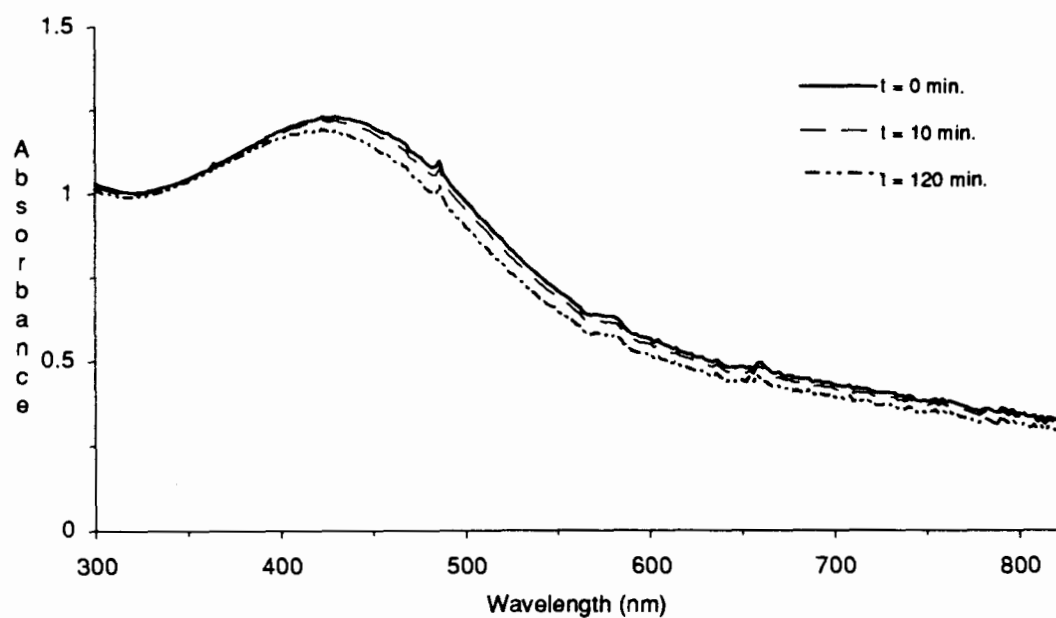


**Figure 26. Photolysis of poly(3-(sodium alkylsulfonate)thiophenes) and poly(3-hexylthiophene) in solution.**

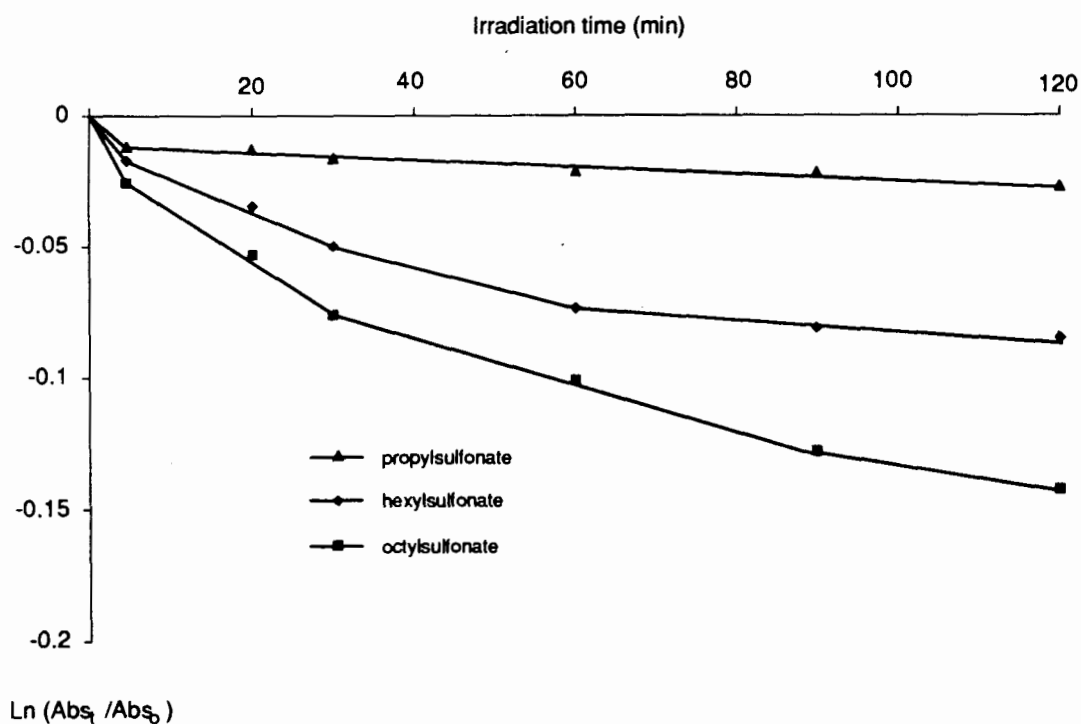
*Photolysis of polymer films:*

The photobleaching of polymer films was much slower compared to polymer solutions. Even when polymer films were exposed to irradiation for 2 hours, no significant change was observed (see figure 27). The photobleaching with time increased in the order propyl, hexyl, octyl. (see figure 28).

Polymer films remained water soluble after 2 hours of irradiation; no significant crosslinking occurred. In contrast, films of poly(3-hexylthiophene) turned totally insoluble after a short irradiation time.<sup>14a</sup>



**Figure 27.** Photolysis of poly(3-(sodium propylsulfonate)thiophene) in film.

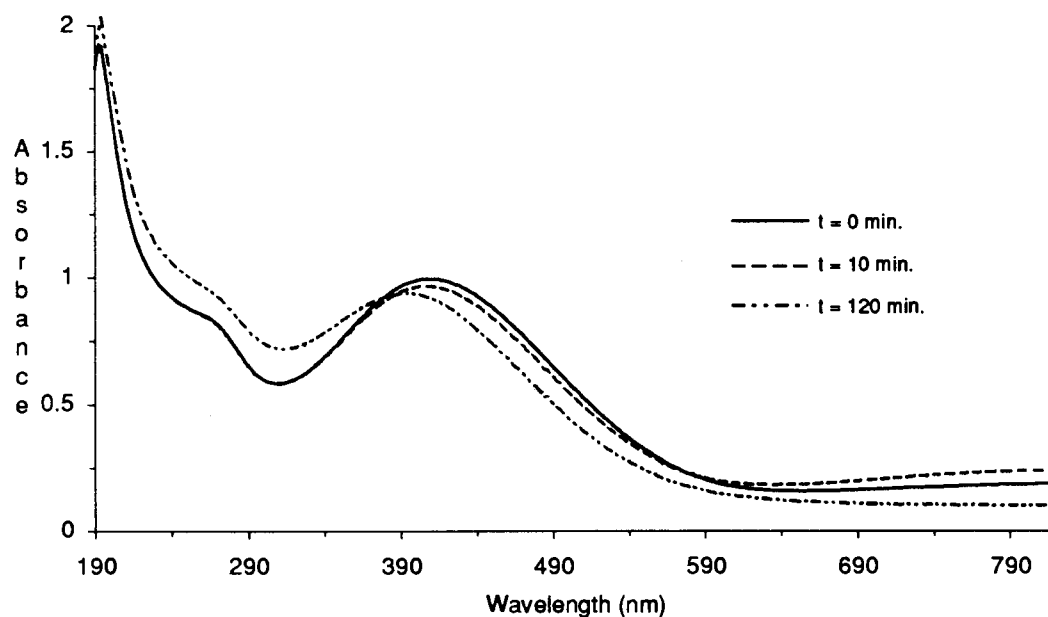


**Figure 28.** Photolysis of poly(3-(sodium alkylsulfonate)thiophenes) in films.

*Acid form:*

*Photolysis of polymer solutions:*

For polymer solutions of the acid form, the absorption intensity at 800 nm. increased after 2 min. of irradiation, reaching a maximum value after 10 min. After this time, absorption intensity decreased and the optical density at 800 nm. after 2 hours of exposure was lower than that initially observed. (see figure 29). The photochemical degradation process of polymer solutions of the acid form was slower compared to polymer solutions of sodium salts.

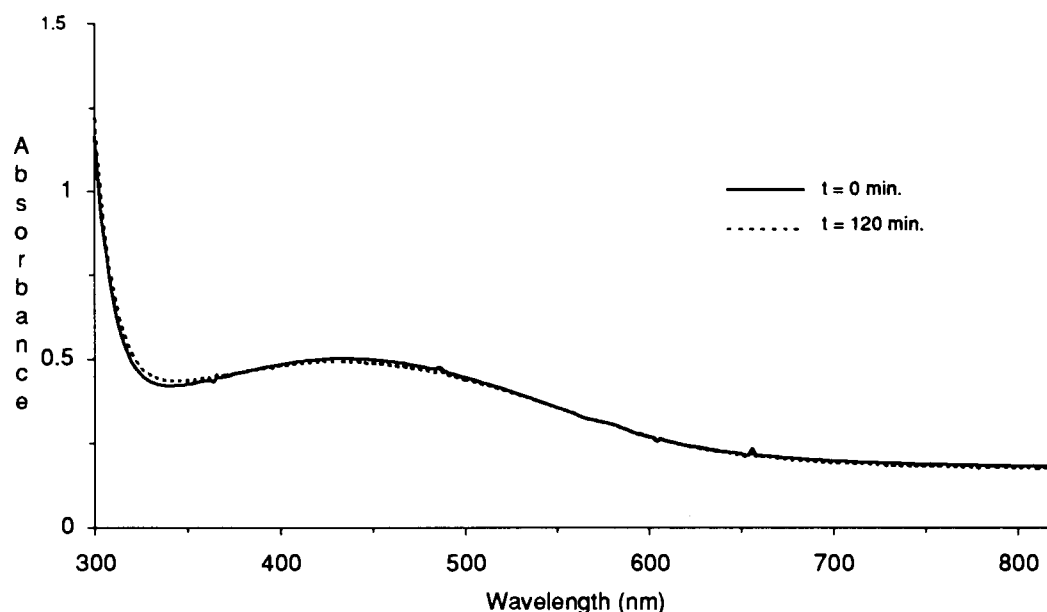


**Figure 29. Photolysis of poly(3-(hexylsulfonic acid)thiophene) in solution.**



### *Photolysis of polymer films:*

Polymer films of the acid form did not present a substantial change of their absorption spectra even when films were exposed to irradiation for 2 hours (see figure 30). As was observed for polymer films of sodium salts, polymer films in the acid form remained water soluble after irradiation indicating the absence of significant crosslinking.



**Figure 30. Photolysis of poly(3-hexylsulfonic acid)thiophene) in film.**

### **3.5.3 Discussion**

The photochemical studies performed on water soluble conducting polymers are qualitative, but can be viewed as a good starting point for testing the feasibility of using water soluble alkylsulfonate substituted poly(thiophenes) for photolithography applications. These preliminary observations give an

overview of the chemical changes resulting from the interaction of polymer solutions and polymer films with UV-vis irradiation.

*Polymers in solution:*

Polymer solutions displayed photobleaching and photochain scission upon exposure to UV-vis irradiation. These photochemical processes could not be quantified due to their low efficiency and to difficulties in determining absolute molecular weights. From figure 23, it is possible to estimate that photobleaching of poly(3-(sodium hexylsulfonate)thiophene) in aqueous solution is ten times more stable than photobleaching of poly(3-hexylthiophene) in chloroform.

In poly(3-hexylthiophene), photobleaching mechanism follow a pathway where singlet oxygen, generated when triplet oxygen is photosensitized by poly(thiophenes), reacts with thienyl rings and consequently breaks up the  $\pi$ -conjugated system.<sup>14,52</sup> If photodegradation of poly(3-(alkylsulfonate)thiophenes) proceeds in a similar fashion as poly(3-hexylthiophene), the rate of photobleaching is slower in aqueous solution because the life time of singlet oxygen is an order of magnitude shorter in aqueous solution (3  $\mu$ sec) than in chloroform (83  $\mu$ sec).<sup>53</sup>

When polymer solutions were irradiated, an increase in optical density at 800 nm was observed. This observation suggests that polymers are photochemically oxidized, generating polarons and bipolarons. At present there is insufficient evidence to postulate the electron accepting species. The proposed photo-oxidation would compete with photobleaching, and thus, explain the subsequent decrease of optical density upon further irradiation.

### *Polymers in film:*

In the solid state there is restricted rotation of the thienyl rings. As a result, polymer films have a lamellar-like structure, and are semi-crystalline. Photodegradation of films of polymers (5), (9) and (13) are slower compared to those of their corresponding solutions. Films of (5) were more inert to photochemistry than (9) and (13). This behavior is consistent with the fact that the interchain distance in polymers (9) and (13) is longer, causing oxygen to diffuse more easily than for shorter alkyl sulfonate side chains.

These preliminary studies have revealed that poly(3-(alkylsulfonate)thiophenes) are relatively stable to UV-vis irradiation. The photobleaching observed was less efficient in comparison to poly(3-hexylthiophene). The synthesized polymers are good candidates for photolithography applications since photodegradation would be considered a draw-back to photolithography.

### **3.6 Photoimaging**

Photochemical studies described earlier, have revealed that both the sodium salt and acid form of the synthesized polymers remained water soluble after UV-vis irradiation, thus precluding their use as photoresists. In contrast when poly(3-hexylthiophene) films are exposed to UV-vis irradiation they turned insoluble.<sup>14</sup> Chemical and spectroscopic analyses have determined that photo-insolubilization of poly(3-hexylthiophene) films occurs via a photo-oxidative mechanism.<sup>52c</sup> In this mechanism the presence of oxygen is required. In poly(3-(alkylsulfonate)thiophenes), photo-oxidation and consequent crosslinking does

not occur to an appreciable extent. With the aim of using poly(3-(alkylsulfonate)thiophenes) for direct photolithography applications, it was necessary to introduce a photoinitiator into the polymeric matrix prior to irradiation. In doing so, insoluble crosslinked polymer films were obtained after UV-vis irradiation.

In order to obtain a photoimage of poly(3-(alkylsulfonate)thiophenes), a polymer film of poly(3-(octylsulfonic acid)thiophene) was cast from its corresponding solution under vacuum. The film was subsequently oxidized with a solution of  $\text{FeCl}_3$  0.1M in nitromethane and dried. The doped polymer film was irradiated for 15 seconds (similar conditions as those in photochemical studies). After irradiation, the unexposed part of the polymer film remained soluble while the exposed part was insoluble when an aqueous solution of acetic acid (50%v/v) was used as a solvent developer. The negative image of the mask gave a conductivity  $< 10^{-6}$  S/cm. The polymeric image was chemically oxidized by immersing the substrate into a solution of 0.1 M of  $\text{FeCl}_3$  in nitromethane. The result is an electronically conducting pattern ( $10^{-1}$  S/cm). Figure 31 shows a photograph of the photoimage.

When the film of poly(3-(octylsulfonic acid)thiophene) was doped and irradiated, the formation of  $\text{Fe}^{2+}$  and a free radical could have taken place. If so, the free radical that was generated could attack the  $\alpha$ -carbon atom of the alkyl group, resulting in H-abstraction. The alkylsulfonate side chain radical can react with oxygen, leading to the formation of a crosslinked polymer as has been postulated for poly(3-hexylthiophene) films.<sup>52c</sup>



Resolution of image = 0.5mm.

**Figure 31. Photoimage of water soluble conducting poly(3-(octylsulfonic acid)thiophene).**

#### 4. CONCLUSION

Two new water soluble conducting polymers, poly(3-(sodium hexylsulfonate)thiophene) and poly(3-(sodium octylsulfonate)thiophene) have been synthesized and characterized. The synthetic procedure utilized is described in detail.

Poly(3-(sodium alkylsulfonate)thiophenes) can be converted to their corresponding acid form by ion-exchange chromatography. The acid form of the polymers is "self-doped".

Preliminary analysis and study of molecular weight, differential scanning calorimetry, electronic absorption spectra, photochemistry and solubility of the synthesized water soluble conducting polymers have been performed. These studies give an insight to the properties and potential applications of the synthesized polymers.

Electronic absorption spectra have confirmed the existence of a  $\pi$ -conjugated system in these polymers. Electronic spectra of the acid form of the polymers showed a broad band in the NIR region confirming the existence of the "self-doped" model.

Poly(3-(alkylsulfonate)thiophenes) were more stable to photochemical degradation than poly(3-hexylthiophene). Polymer solutions underwent photobleaching, as has been observed for solutions of poly(3-hexylthiophene). Polymer films did not crosslink upon UV-vis irradiation in contrast to films of poly(3-hexylthiophene).

To obtain crosslinked polymer films, a photoinitiator was introduced before irradiation.

The potential applications of water soluble conducting polymers have been demonstrated by obtaining a conducting photoimage of a film of poly(3-(octylsulfonic acid)thiophene).

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