Self-organising amphiphilic oligothiophene block co-polymers

Andreas Felix Michael Kilbinger

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SELF-ORGANISING AMPHIPHILIC OLIGOTHIOPHENE BLOCK CO-POLYMERS

Andreas Felix Michael Kilbinger

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July 1999

Abstract

SELF-ORGANISING AMPHIPHILIC OLIGOTHIOPHENE BLOCK CO-POLYMERS

Andreas F. M. Kilbinger Ph D Thesis July 1999

A new route to oligothiophene-PEO-block-co-polymers has been developed, in which well-defined α-oligothiophene blocks (from bithiophene to sexithiophene) alternate with poly(ethylene oxide) blocks. These materials show high solubility in common organic solvents. Sexithiophene derivatives with short PEO chains attached at the α-positions have been synthesised as model systems for the above sexithiophene polymer. PEO side-chains as short as pentaethylene glycol had a good solubilising effect on the otherwise insoluble sexithiophene. All compounds prepared exhibited surface activity, as shown by monolayer experiments on a Langmuir trough. Sexithiophene model compounds with short PEO side-chains could be compressed to form a two-dimensional condensed phase. X-ray diffraction of melt cast films of the oligothiophene polymers showed that a minimum oligothiophene block-length of five thiophenes (pentathiophene) was necessary to fully disturb PEO crystallisation. The sexithiophene polymer formed regions of crystalline/aggregated sexithiophene in the bulk. UV/Vis and fluorescence studies in solution indicated that the oligothiophene segments were molecularly dissolved in good solvents like chloroform. Aggregation of the oligothiophenes occurred in THF/water mixtures, which was consistent with observed shifts of the UV absorption maxima towards the blue and quenching of the fluorescence. An oligothiophene length of four thiophenes (quaterthiophene) was necessary to observe this aggregation phenomenon. A sexithiophene derivative with chiral pentaethylene glycol side chains showed a large circular dichroism effect in aqueous solution and no effect in chloroform solution, indicating the formation of a chiral superstructure upon aggregation.

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I would like to thank my supervisor *Professor W. James Feast.* The work described in this thesis would not have been possible without his great help, supervision and moral support. I would also like to thank *Professor Randal W. Richards* for many helpful discussions and also for allowing me to carry out physical measurements in his laboratories.

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I would like to thank all my former and present colleagues at the IRC in Polymer Science in Durham for providing an excellent working environment.

Finally I would like to thank my parents, as without their permanent help and support I would not have been able to master the last eight years of my studies.

Memorandum

The work reported in this thesis has been carried out at the Durham site of the Interdisciplinary Research Centre in Polymer Science and Technology between October 1996 and July 1999. This work has not been submitted for any other degree either in Durham or elsewhere and is the original work of the author except where acknowledged by means of appropriate reference.

Statement of Copyright

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Abbreviations

bithiophene	2,2'-bithiophene
DCM	dichloromethane
DIBAH	di-isobutyl aluminium hydride
DMF	dimethyl formamide
dppp	1,3-bis(diphenylphosphino)-propane
EI	electron impact
GPC	gel permeation chromatography
LD	laser desorption
MALDI	matrix assisted laser desorption ionisation
MS	mass spectroscopy/ mass spectrum
NMP	1-methyl-2-pyrrolidinone
NMR	nuclear magnetic resonance
PDI	poly dispersity index
pentathiophene	2,2':5',2'':5'',2''':5''',2''''-pentathiophene
quaterthiophene	2,2':5',2'':5'',2'''-quaterthiophene
r.t.	room temperature
sexithiophene	2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene
terthiophene	2,2':5',2''-terthiophene
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	tetramethyl ethylenediamine
TOF	time of flight

Contents

1 Introduction

1.1 Conducting Polymers

Most organic polymers show no electric conductivity and many of them are especially useful as insulators for cables and electric wiring. What these insulating polymers have in common is a large band-gap between the valence band and the conduction band (see Figure 1.1.1).

Polymers which have a conjugated π-electron backbone have a much smaller band-gap and exhibit properties like low ionisation potentials and high electron affinities. They can therefore be oxidised and reduced more easily than conventional polymers. Pure poly-conjugated polymers, however, are usually not conducting but they can be converted into almost metal-like conductors by treatment with an oxidising or reducing agent. After 1977, when Shirakawa *et al.*[1] showed that treatment with iodine increased the conductivity of polyacetylene by 10^{10} S cm^{-1}, similar effects were discovered for a wide range of conjugated polymers.

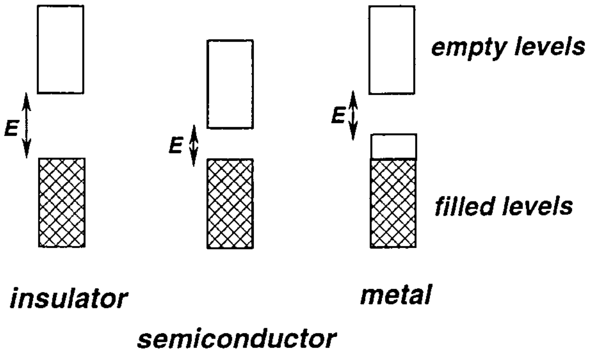


Figure 1.1.1 Differences in band-gap energy (E) between an insulator, a semiconductor and a metal. If energy is necessary to elevate electrons into the conductivity band (empty levels) the material is an insulator or semiconductor, depending on how large the band-gap is. No band-gap exists when the valence band is only partially filled or valence band and conducting band overlap.

Although the idea of having a poly-conjugated organic polymer that could replace metals is fascinating, more realistic applications for these materials, i.e. their use as semiconductors in their undoped states, were soon investigated.

The prototype of all poly-conjugated polymers is poly(acetylene) (PA) (Figure 1.1.2 a). Early syntheses of PA gave intractable, ill-defined materials which could not be fully characterised. In 1980 Edwards and Feast[2,3] introduced a new synthetic approach, in which a soluble and hence characterisable precursor polymer was prepared via ring opening metathesis polymerisation. Once processed, this polymer could be converted into PA by a thermal elimination reaction. Although well-defined, its low stability in air limited potential applications. Soon other air-stable π-conjugated polymers were developed, like poly(thiophene) or poly(phenylene vinylene) (see Figure 1.1.2 b and c).

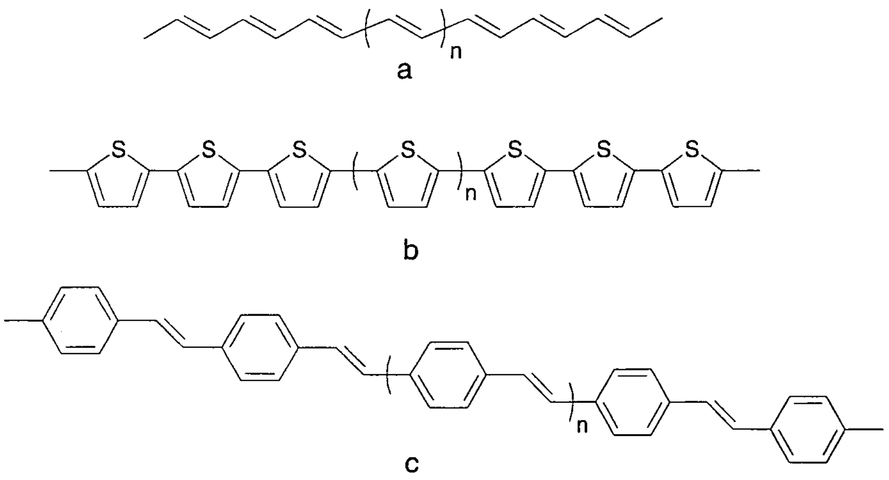


Figure 1.1.2 ***a****, All-trans poly(acetylene),* ***b****, poly(thiophene),* ***c****, all-trans-poly(phenylene vinylene).*

To improve the processability of these otherwise insoluble materials, a variety of solubilising substituents were introduced. Attaching flexible chains to the 3-positions of the thiophene residues in poly(thiophene) produces soluble material. Due to the relatively easy synthetic access to well-defined materials, poly(3-alkylthiophene)s (Figure 1.1.3) have been studied intensively.

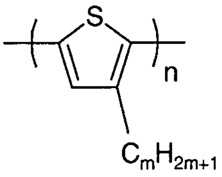


Figure 1.1.3 Poly(3-alkylthiophene)

A variety of substituents has been attached to poly(phenylene vinylene)s. Synthesis of well-defined poly(arylene vinylene)s with defined cis-trans content and various substituents attached to the double bond and/or the aromatic unit has been achieved by Daik.[4]

1.2 From Polymers to Oligomers

Various electronic device structures have been used to study the physics of the above mentioned π-conjugated polymers. Among these device structures is the Field Effect Transistor (FET), which has been envisioned as the key component for the development of displays in portable computers,[5,6] pagers and memory elements in transaction cards and identification tags.[7] The first generation of conjugated polymers studied in this way had poor structural definition and were largely amorphous. They had a large distribution of conjugation lengths and also conjugation defects due to sp3 carbon atoms. Progress demanded the synthesis of better defined materials.

The original strategy was to increase the chain length of the π-conjugated polymers in order to increase charge carrier mobility. This strategy failed and was replaced by the opposite, i.e. synthesis of well-defined oligomers. Interchain hopping is the limiting step in charge carrier mobility. However, using well-defined π-conjugated oligomers, highly ordered materials were obtained, in which interchain hopping was facilitated compared to their amorphous polymer analogues.

Among the series of thiophene oligomers, the hexamer, sexithiophene, was found to be the most promising material for use in organic transistors.[8]

Higher oligothiophenes (> quaterthiophene) cannot be processed easily because of their low solubility and high melting points. Solubilising substituents have been attached to the oligothiophene units in both the α- and the β-positions (Figure 1.2.1).

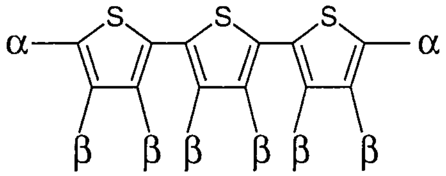


Figure 1.2.1 Terthiophene. A very simple model distinguishes only α and β sites for attaching substituents.

Highly soluble sexithiophene derivatives with β-side chains have been prepared,[9-13] but it was suggested that substitution anywhere other than at the 4- or 5-carbons of the terminal rings leads to distortions of conformation and decreased π-overlap (Figure 1.2.2).[14]

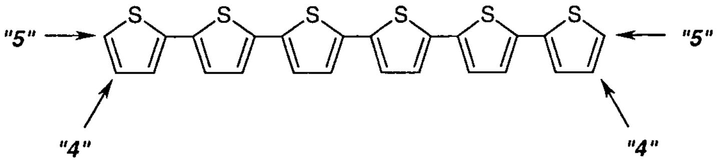


Figure 1.2.2 The only positions in sexithiophene where substitution does not lead to distortion of the all-planar conformation, according to Katz.[14]

Garnier *et al.*[15] compared the X-ray diffraction pattern observed for α,ω-dihexyl-sexithiophene (where the ω-position is equivalent to the α-position) and β,β'-dihexyl sexithiophene (mixture of β',β''''-dihexyl-sexithiophene isomers). Whereas in the former case a distribution of sharp X-ray intensities was observed, no clear structural organisation could be deduced from the β,β'-disubstituted sample. It is reasonable to assume that the increased solubility of the β-substituted derivative originates from its reduced ability to crystallise.

1.3 α-Di-Substituted Sexithiophene Derivatives and their Processability

Syntheses of various α-*side chain* substituted sexithiophene derivatives (= α,ω-disubstituted) have been reported in the literature.[15-18] Some of the materials described are shown in Figure 1.3.1 - Figure 1.3.4.

Figure 1.3.1 α,ω-Dihexyl-sexithiophene (α,ω-DH6T) synthesised by Garnier et al.[15]

One of the first examples of a sexithiophene derivative, substituted only at the two α-positions, was the α,ω-dihexyl-sexithiophene (α,ω-DH6T) (see Figure 1.3.1). To the surprise of the authors the material showed an extremely low solubility of ca. 1g l^{-1} in solvents like DCM or chloroform. The melting point of α,ω-DH6T was even 10°C higher than that of unsubstituted sexithiophene (290°C). The interpretation of this result was that hydrophobic-lipophilic interactions between the alkyl chains enhanced the cohesive forces between the sexithiophene units. X-ray diffraction experiments performed on thin evaporated films of α,ω-DH6T revealed a very high degree of order. From these results the authors proposed that "molecular engineering of conjugated oligomers by alkyl substitution (is) an elegant and powerful way for creating self-assembly properties...".[15]

α,ω-DH6T and a similar compound, di-hexylthio-sexithiophene (DHT-α-6T) (see Figure 1.3.2), were prepared by Katz *et al.*[18]

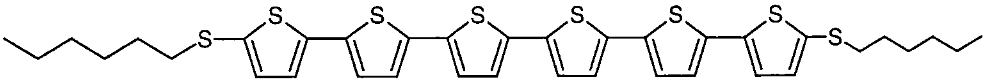


Figure 1.3.2 Di-hexylthio-sexithiophene (DHT-α-6T) synthesised by Katz et al.[18]

Unsurprisingly, DHT-α-6T showed an equally low solubility as α,ω-DH6T.

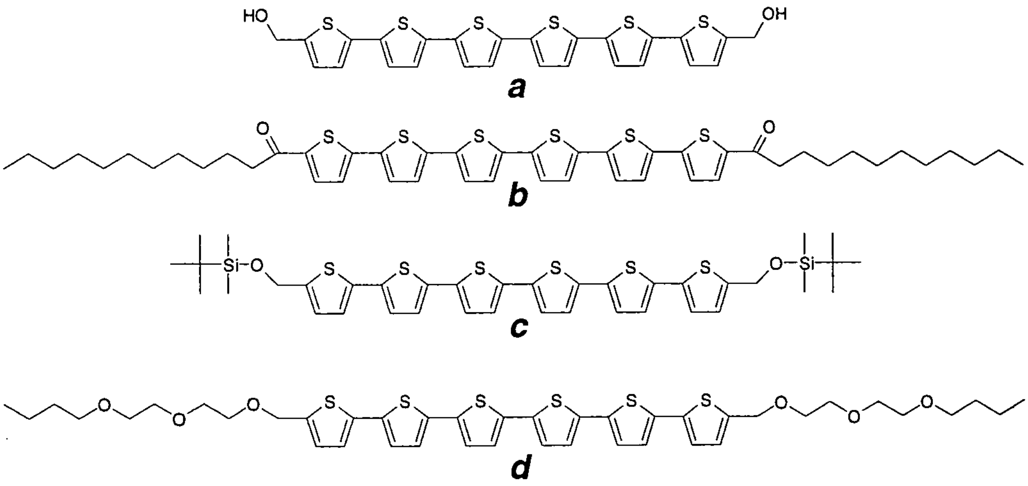


Figure 1.3.3 α,ω-Di-substituted sexithiophene derivatives synthesised by Wei et al.[16] ***a****, bis(hydroxymethyl)-sexithiophene,* ***b****, bis(n-dodecanoyl)-sexithiophene,* ***c****, bis((tert-butyldimethylsiloxy)methyl)-sexithiophene,* ***d****, bis((n-butoxyethoxy)ethoxymethyl)-sexithiophene.*

In 1996 Wei *et al.*[16] reported the synthesis of the series of α,ω-disubstituted sexithiophene derivatives shown in Figure 1.3.3. Quantitative solubility data for all the compounds is shown in Table 1.3.1.

compound	**solubility (g l^{-1})**	**solvent**
a	< 4 10^{-3}	THF
b	< 4 10^{-3}	THF
c	0.1	THF
c	0.1	chloroform
d	0.08	THF
d	1.8	chloroform

Table 1.3.1 Solubilities of the compounds shown in Figure 1.3.3 as reported by Wei et al.[16]

The solubility of derivatives **a, b** and **c** is very low. Compound **d** has the highest solubility in the series, much higher than that of compound **b**. This is a remarkable observation, as the length of both side-chains is very similar. However, the important structural difference is the presence of ether linkages in the case of compound **d**. The effect of oxygen atoms in the solubilising side chain was also described by Katz *et al.*[17] The materials investigated by this group are shown in Figure 1.3.4.

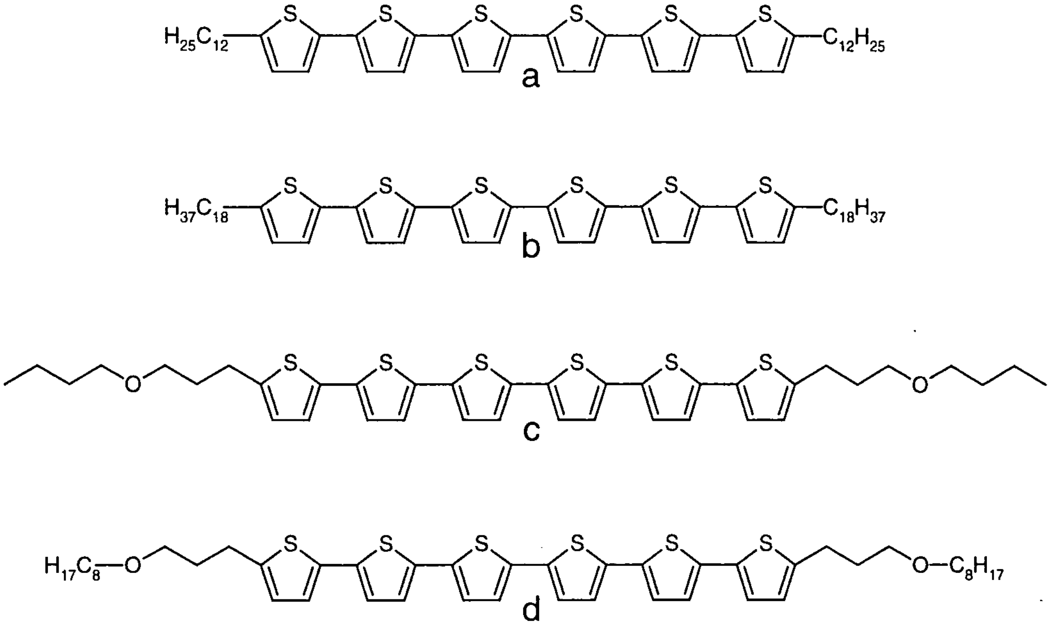


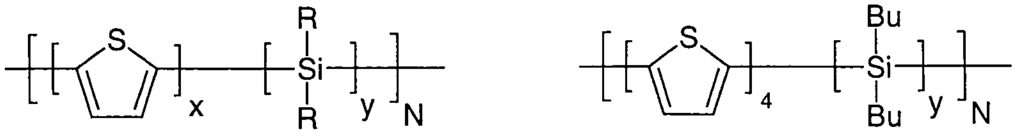
Figure 1.3.4 α,ω-Di-substituted sexithiophene derivatives synthesised by Katz et al.[17] ***a****, di-dodecyl-sexithiophene (DDα6T),* ***b****, di-octadecyl-sexithiophene (DOα6T),* ***c****, bis(3-butoxypropyl)-sexithiophene (C4OC3α6T),* ***d****, bis(3-octyloxypropyl)-sexithiophene (C8OC3α6T).*

Compound **c** was approximately twice as soluble as α,ω-DH6T in aromatic solvents. According to the authors, "the slight increase in rotational freedom of an internal ether group and the weak polar interaction with solvents are probably responsible for this solubility change". For sexithiophene derivatives with alkyl chains longer than hexyl, only a decrease in melting temperature was reported.

To the best of the author's knowledge, sexithiophene derivatives exhibiting higher solubilities than the ones reported here have not been described in the literature. Another way of attaching solubilising side chains to the α-positions only is to build an alternating block co-polymer from sexithiophene and a flexible spacer group. To date, no highly soluble α,ω-disubstituted sexithiophene derivative has been reported (see above). It is therefore not surprising that the alternating block co-polymers reported in the literature are build from oligothiophenes shorter than sexithiophene or carry β-substituents.

1.4 Alternating Oligothiophene Block co-Polymers

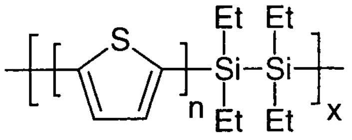
In Figure 1.4.1 - Figure 1.4.4 examples of alternating oligothiophene block co-polymers are shown in which the oligothiophene blocks are substituted in the α-positions only. For solubility reasons quaterthiophene is the longest oligothiophene block in most of the polymers shown. Synthesis of a pentathiophene block co-polymer has been reported by Ago *et al.*[19] but no data on the solubility of the material was given.



x=2, y=1,2 and R=Me
x=2, y=1,2 and R=Bu
x=3, y=1,2 and R=Me
x=3, y=1,2 and R=Bu

y=1,2

Figure 1.4.1 Alternating bi-, ter- and quaterthiophene block co-polymers, reported by Herrema et al.[20]



n=2-5

Figure 1.4.2 Alternating bi-, ter-, quater- and pentathiophene block co-polymers, reported by Ago et al.[19]

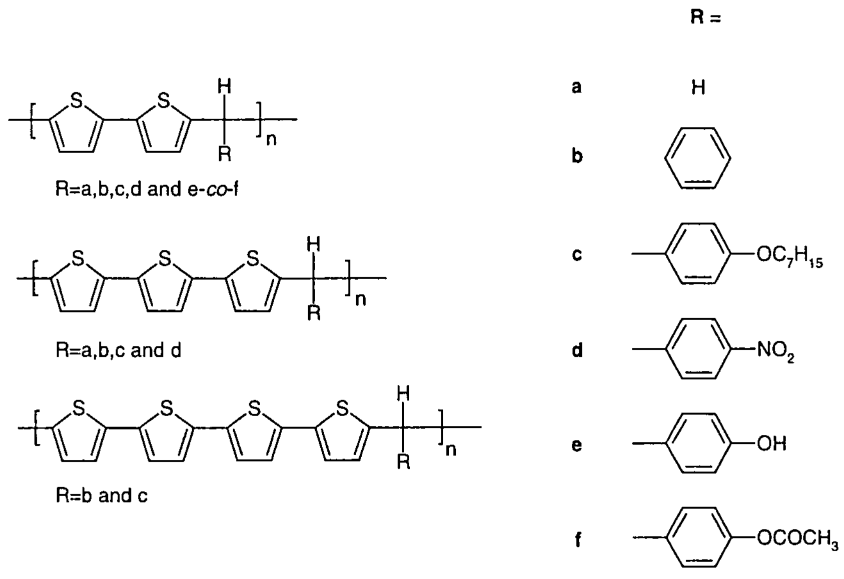


Figure 1.4.3 Alternating bi-, ter- and quaterthiophene block co-polymers, reported by Chen et al.[21]

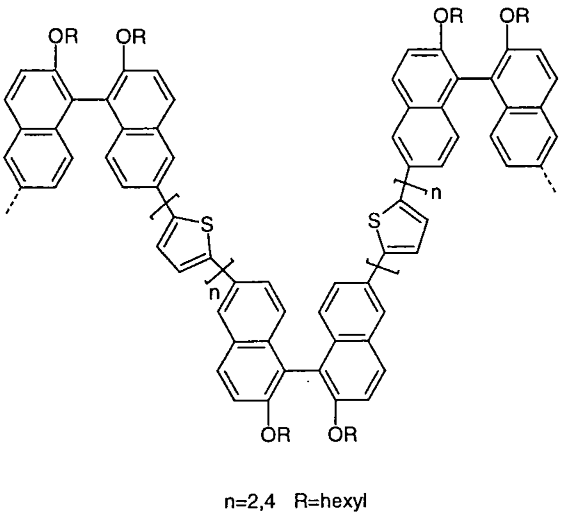


Figure 1.4.4 Alternating bi- and quaterthiophene block co-polymers, reported by Musick et al.[22]

The compounds prepared by Herrema *et al.*[20] (Figure 1.4.1) were found to be crystalline and of low solubility in the case of methyl substituted oligosilylene units. The polymers with butyl substituted oligosilylenes showed better solubility. Still, the quaterthiophene polymer precipitated during polymerisation, indicating that the solubilising groups could not compensate the low solubility of the quaterthiophene block.

Ago *et al.*[19] reported the synthesis of similar polymers with ethyl instead of butyl chains attached to a disilylene group (Figure 1.4.2). Synthesis of alternating block co-polymers incorporating bithiophene up to pentathiophene blocks were reported but unfortunately no data on molecular weight or solubility was provided.

In a study carried out by Chen *et al.*[21], polymers were prepared in which oligothiophenes ranging from bithiophene to quaterthiophene alternated with a substituted sp^3 carbon atom (Figure 1.4.3). The methylene bridged bi- and terthiophene polymers (R=a) were only partially soluble (< 1 wt%) in NMP and not at all in other solvents. Introduction of bulky substituents (R=b-f) increased solubility. The quaterthiophene polymers were not completely soluble(< 1 wt%) in THF, DMF, DMSO and NMP, suggesting, that the introduced bulky substituent could not prevent aggregation of the rigid quaterthiophene.

An example of a polymer in which bi- and quaterthiophene alternate with substituted binaphthyl groups was reported by Musick *et al.*[22] (Figure 1.4.4). No solubility data was given for either of the two polymers prepared but the molecular weight reported for the quaterthiophene polymer (Mn=5100, Mw=5500) was significantly lower than that of the bithiophene polymer (Mn=18100, Mw=30300), suggesting that aggregation of the quaterthiophene units prevented the formation of higher molecular weight material.

Figure 1.4.5 - Figure 1.4.10 show various oligothiophene block co-polymers in which the oligothiophene units carry substituents in the β-positions. These materials are generally very soluble in common organic solvents due to the decreased aggregation tendency of the β-substituted oligothiophenes. Quater-, penta-, sexi- and even octathiophene block co-polymers have been prepared.

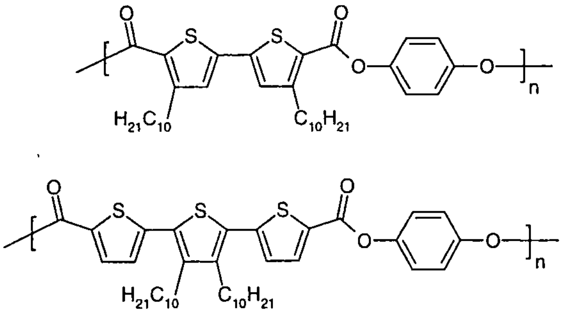


Figure 1.4.5 Alternating bi- and terthiophene block co-polymers, reported by Bellete et al.[23]

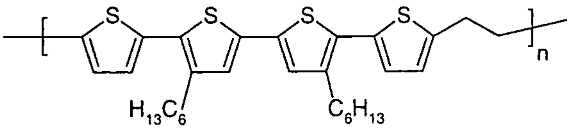


Figure 1.4.6 Alternating quaterthiophene block co-polymer, reported by Sato et al.[24]

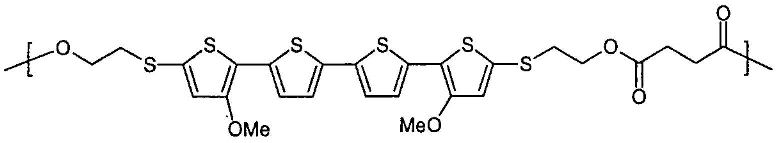


Figure 1.4.7 Alternating quaterthiophene block co-polymer, reported by Hong et al.[25]

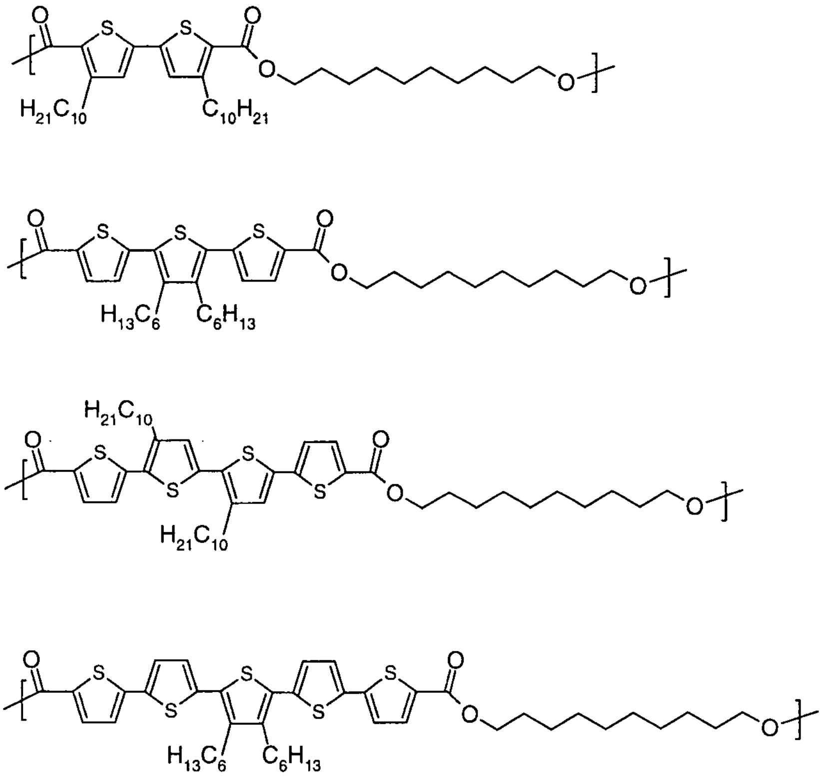


Figure 1.4.8 Alternating bi-, ter-, quater- and pentathiophene block co-polymers, reported by Donat-Bouillud et al.[26]

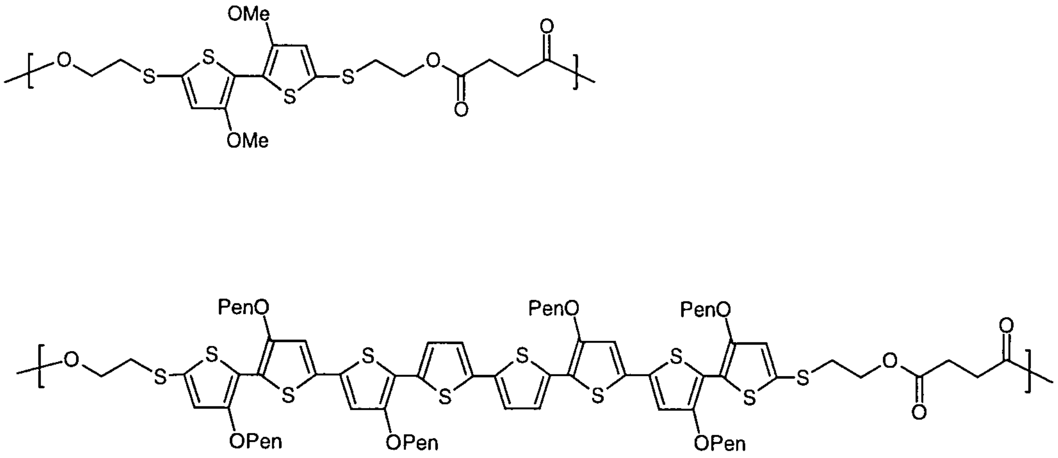
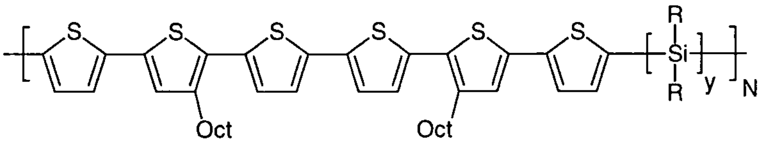


Figure 1.4.9 Alternating bi- and octathiophene block co-polymers, reported by Kunugi et al.[27]



y=1,2,4 abd 8 R=Me
y=1,2 R=Bu

Figure 1.4.10 Alternating sexithiophene block co-polymer, reported by Herrema et al.[20]

As the aim of the work reported in this thesis is the preparation of soluble alternating oligothiophene block co-polymers without β-substituents, the properties of the materials listed above will not be discussed further here.

1.5 Aim of this Work

The aim of this work is to synthesise AA- and BB-type monomers in which two α-functionalised terthiophene units (with either A- or B-functionalities) are linked via hydrophilic or hydrophobic flexible spacers (see Figure 1.5.1, top). Using aromatic cross-coupling of the α-functionalised terthiophenes as the polymer forming reaction gives sexithiophenes which are linked via hydrophobic and hydrophilic spacers in an alternating way (see Figure 1.5.1, bottom). Amphiphilic polymers of this kind were expected to be surface active (see Figure 1.5.2).

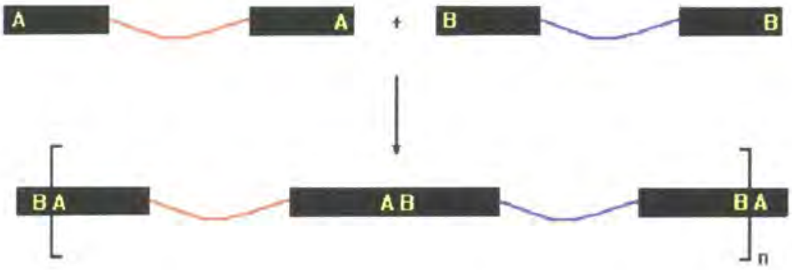


Figure 1.5.1 Schematic representation of the polymerisation of AA- and BB-type monomers via aromatic cross-coupling. The two aromatic endgroups are linked via a hydrophobic spacer in the AA-type monomer and a hydrophilic spacer in the BB-type monomer.

Oxygen atoms in the side chain attached at the α-position were known to enhance the solubility of the sexithiophene blocks (see above). Oligo or poly(ethylene glycol)s as the hydrophilic flexible spacer groups could be expected to provide very good solubility. Due to the amphiphilic character of this block co-polymer a dilute solution of the polymer, spread onto the aqueous sub-phase of a Langmuir trough is expected to assemble in the manner schematically shown in Figure 1.5.2. Compression of the monolayer should result in a highly oriented and densely packed array of sexithiophene rods, which should be the favoured orientation for interchain charge transport and thus high carrier mobility perpendicular to the sexithiophene rod axis.

The aim of this work was the synthesis and characterisation of soluble α,ω-disubstituted sexithiophene block co-polymers and a study of their processability into highly organised thin films.

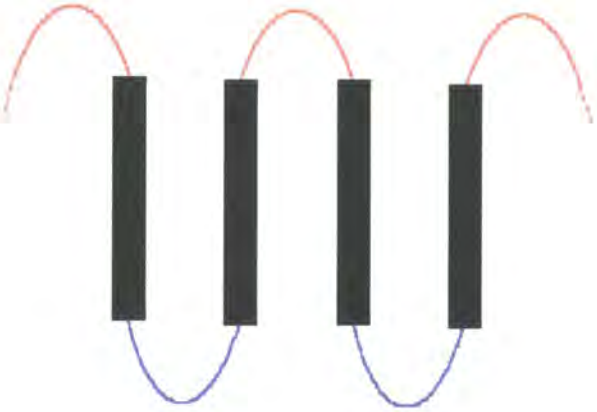


Figure 1.5.2 Spread on a water surface the alternating amphiphilic co-polymer self orientates on the water/air surface with the hydrophilic spacers pointing into the water- and the hydrophilic spacers into the air-phase. The sexithiophene units have to pack in a parallel manner which should increase π-overlap and thus charge carrier mobility.

1.6 References

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2 Attempted Syntheses of Sexithiophene Main-Chain Polymers Linked by Alternating Hydrophobic and Hydrophilic Spacer Sequences

2.1 Introduction

To synthesise a copolymer in which a sexithiophene block alternates with flexible spacer groups that are alternately hydrophilic and hydrophobic we retro-synthetically cut the target polymer into two monomer units (Figure 2.1.1). Both monomers consist of suitably functionalised terthiophene derivatives (here A and B) linked by either a hydrophilic or a hydrophobic flexible chain. Employing aromatic cross-coupling reactions these two types of monomer could be used to build up the sexithiophene block in the polymerisation step. This approach avoids the synthetic manipulation of oligothiophenes bigger than terthiophene which suffer from very poor solubility.

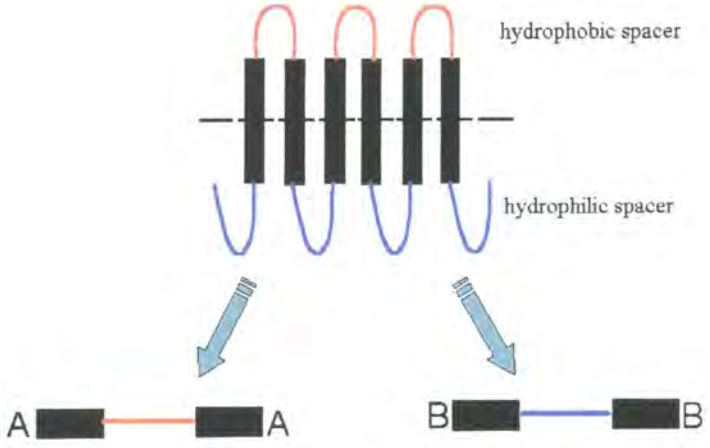


Figure 2.1.1 Target polymer with sexithiophene blocks (rectangles) alternating with hydrophobic and hydrophilic spacer groups. Cutting the sexithiophene groups (dashed line) produces the monomers (bottom of the picture).

The Suzuki- and the Stille cross-coupling reaction are examples of aromatic cross-coupling reactions which tolerate a large variety of functionalities. In this work both were investigated for their potential use in building up oligothiophene polymers.

2.2 Aromatic Cross-Coupling Reactions

Although only the Suzuki and Stille cross-coupling reactions were examined as tools for the synthesis of sexithiophene polymers, another type of cross-coupling reaction, the Kumada or Grignard coupling has been described as very useful for the synthesis of oligothiophenes. It was used here to prepare terthiophene and will therefore be described in this section as well.

The Stille cross-coupling reaction

The palladium catalysed cross-coupling reaction between organotin compounds and organic halides is generally referred to as the Stille cross-coupling reaction.[1] It is of great use to the organic chemist as it belongs to the relatively rare class of organic reactions that directly couples two carbon atoms to form a C-C bond (see also Suzuki coupling). The overall reaction is summarised in Figure 2.2.1. An organotin compound R'M (nucleophile) reacts with an organic halide RX (electrophile) to form a carbon-carbon bond R'-R and a tin halide MX under catalysis of a palladium complex M'.

$$R'M + RX \xrightarrow{M'} R'\text{-}R + MX$$

Figure 2.2.1 Stille cross-coupling reaction. R'M=organotin compound, RX=organo halide, M'=palladium catalyst

The nucleophiles can be alkyl-, vinyl-, alkenyl-, aryl-, allyl- or benzyl tin derivatives. The electrophiles are limited to those that do not carry a hydrogen on a β-sp^3-carbon atom; thus allyl-, benzyl-, vinyl- or aryl halides.

The generally accepted catalytic cycle is shown in Figure 2.2.2. The electrophile RX adds to the Pd^0 species in an oxidative addition, substituting two of the neutral ligands (here PPh$_3$). In a following transmetallation step the organotin compound transfers the organic residue R' to the square planar Pd^{II} complex, substituting the halide X.

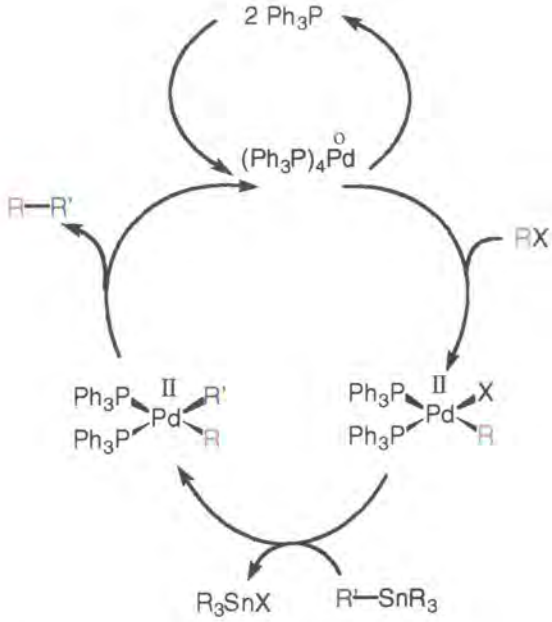


Figure 2.2.2 Catalytic cycle for the Stille cross-coupling reaction.

Transmetallation is the slowest and thus rate-determining step in this cycle. As β-elimination from the RX palladium adduct would proceed much faster than transmetallation, the reaction is restricted to the above mentioned electrophiles. Elimination of R-R' and addition of two neutral ligands brings the cycle back to its starting position. The reaction tolerates a variety of functional groups and various syntheses for organo tin derivatives have been developed.[1] The reaction has been employed to couple thiophene-tin derivatives in polyreactions. Two recent examples have been reported by Parakka *et al.*[2] and Zhang *et al.*[3] In both cases thiophenes are coupled in the α-positions and form polymers in the cross-coupling step.

The Suzuki cross-coupling reaction

The palladium catalysed cross-coupling reaction between boronic acids or esters and organic halides is generally referred to as the Suzuki cross-coupling reaction.[4] With this reaction it is possible to directly form a bond between two carbon centres. The net reaction is shown in Figure 2.2.3.

$$R'B(OR)_2 + OH^- + RX \xrightarrow{M'} R'\text{-}R + B(OR)_2OH + X^-$$

Figure 2.2.3 Suzuki cross-coupling reaction. R'B(OR)$_2$=boronic acid/ester, RX=organo halide, M'=palladium catalyst, B(OR)$_2$OH=boric acid/ester

R'B(OR)$_2$ represents a boronic acid or ester, RX an organic halide, M' a palladium catalyst and B(OR)$_2$OH boric acid or one of its esters. The catalytic cycle is summarised in Figure 2.2.4. In the first step an organic halide adds to the Pd^0-complex in an oxidative addition, replacing two of its neutral ligands. The boronic acid or ester is not reactive as such in the catalytic cycle but has to accept a base (usually OH$^-$) to show a high enough nucleophilicity to undergo a transmetallation reaction with the Pd-complex. In this transmetallation step the group R' is transferred to the Pd-centre, replacing the halide X. As in most of the Pd-catalysed reaction cycles the transmetallation step is very slow. Therefore the same restrictions apply to the electrophiles as in the case of the Stille cross-coupling reaction (see above).

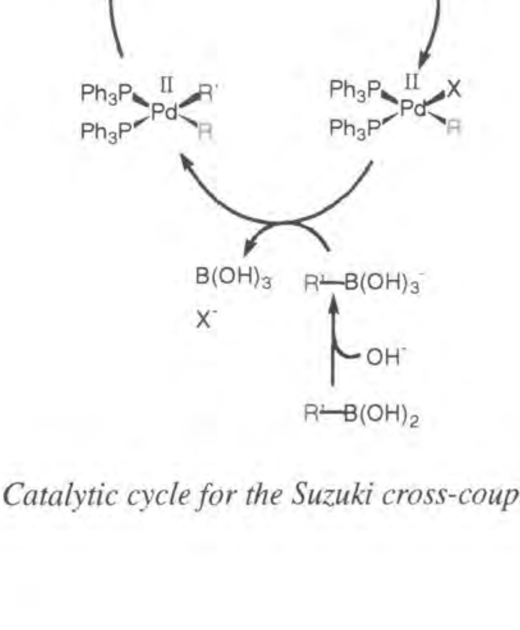


Figure 2.2.4 Catalytic cycle for the Suzuki cross-coupling reaction.

Elimination of the coupling product R-R' and reaction with two neutral ligands brings the cycle back to its starting position.

Although the Suzuki coupling is known to work for heteroaromatic rings like thiophene, reports of its use to synthesise oligothiophenes are rare.[5,6]

The Kumada cross-coupling reaction

The nickel catalysed reaction between a Grignard reagent and an aromatic halide is generally referred to as the Kumada cross-coupling reaction. The catalytic cycle is shown in Figure 2.2.5.

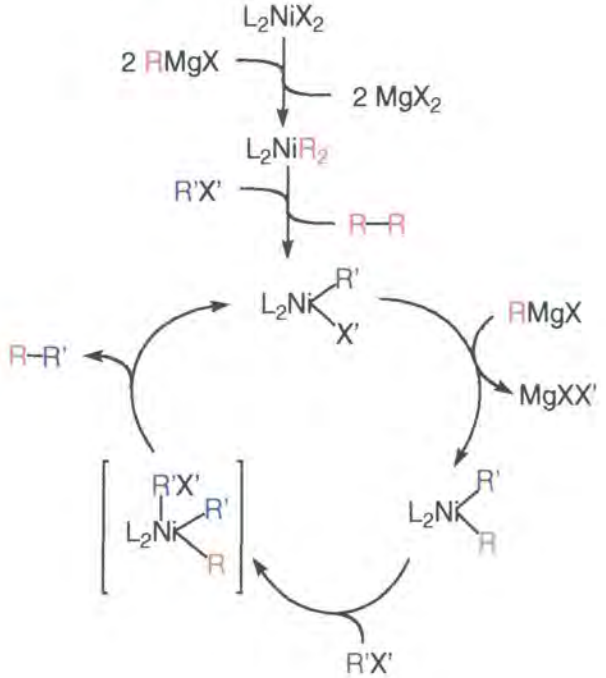


Figure 2.2.5 Catalytic cycle for the Kumada cross-coupling reaction.

A dihalo-diphosphine nickel complex L_2NiX_2 reacts with two equivalents of Grignard reagent to form the diorgano nickel complex L_2NiR_2. This then reacts with the electrophile R'X' to form the halo(organo)nickel complex L$_2$NiR'X', which is the species that takes part in the catalytic cycle. Transmetallation, i.e. transfer of a group R from the magnesium to the nickel substituting the halide X', gives a diorgano nickel complex L_2NiRR'. This reacts with the electrophile R'X', possibly via a pentacoordinate intermediate, to form the coupling product R-R' and the halo(organo)nickel complex $L_2NiR'X'$ from which the cycle started.

Various organic $C(sp^2)$-halides and numerous Grignard reagents can be used in the Kumada coupling reaction. Most remarkable is the fact that alkyl-Grignard reagents containing β-hydrogens give cross-coupling products in high yields without interference from β-elimination reactions forming transition metal hydrides and olefins. The alkylation of aromatic- or vinylic halides is therefore one of the most often employed reactions of the Kumada cross-coupling reaction.

Thiophene rings, though, cannot be alkylated via the Kumada procedure as alkyl-Grignard reagents exchange with the aromatic halides to form alkyl halides and aromatic Grignard reagents. It has proved to be very useful in the synthesis of oligothiophenes[7,8] and polythiophenes.[9]

2.3 Results and Discussion

2.3.1 Monomer syntheses

α-Terthiophene **1** was prepared via the Kumada cross-coupling reaction using thienyl magnesium bromide, 2,5-dibromo thiophene and a $Ni(dppp)Cl_2$ catalyst. α–Formylation to give **2** was achieved via the Vilsmeier reaction, α'-bromination with NBS gave **3** and reduction of the aldehyde to the primary alcohol **4** was accomplished following a synthesis described by Parakka *et al.*[10] (Figure 2.3.1). Reaction of the terthiophene aldehyde **3** with hexyl magnesium bromide in a Grignard reaction gave the racemic secondary alcohol **5**.

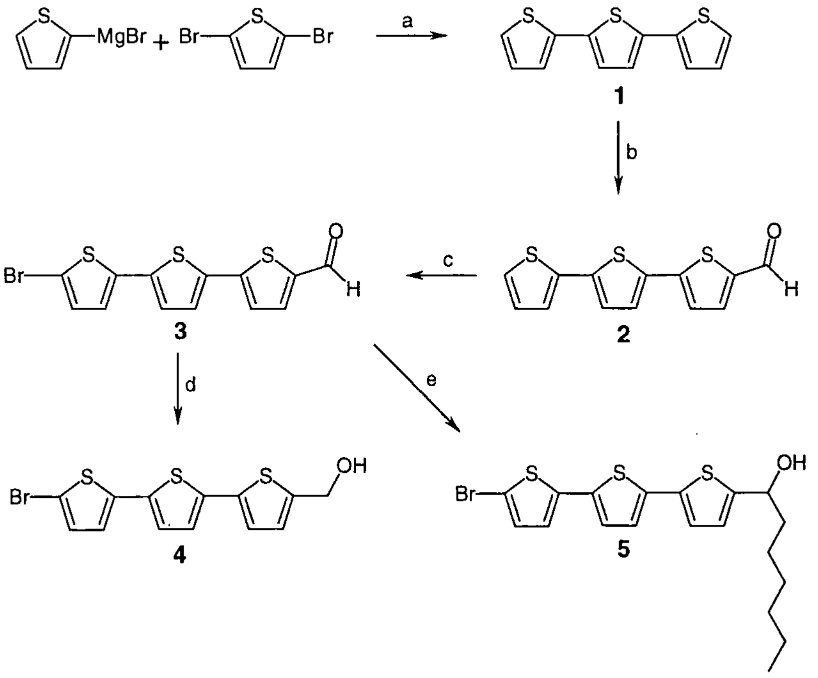


Figure 2.3.1 a) diethylether, Ni(dppp)Cl$_2$, b) 1.DCM, DMF, POCl$_3$ 2.NaOH$_{aq}$ c) DCM/AcOH (1:1), NBS d) THF, NaBH$_4$ e) diethylether, hexyl magnesium bromide

As outlined above two types of terthiophene monomer, one with a halogen- and one with an organometal (here tin or boron) functionality are necessary to build up the sexithiophene derivative in the cross-coupling step. The above terthiophene alcohols seemed good candidates to prepare one of the two monomers, as they provided an aromatic halide for later cross-coupling to an organometal centre and also an alcohol for connecting various types of flexible spacer groups.

Tetraethylene glycol was chosen as the hydrophilic spacer as it was commercially available and easily functionalised. To be able to prepare a monomer with the terthiophene alcohol **4** three tetraethylene glycol derivatives were synthesised (Figure 2.3.2). Tetraethylene glycol could easily be tosylated **6**[11] or brominated **7**[12] to introduce leaving groups that primary alcohols or other nucleophiles can readily replace. Oxidation of tetraethylene glycol to the di-acid **8** and subsequent conversion into the di-acid chloride **9**[13] produced another reactive spacer that could also be coupled via reactions with nucleophiles.

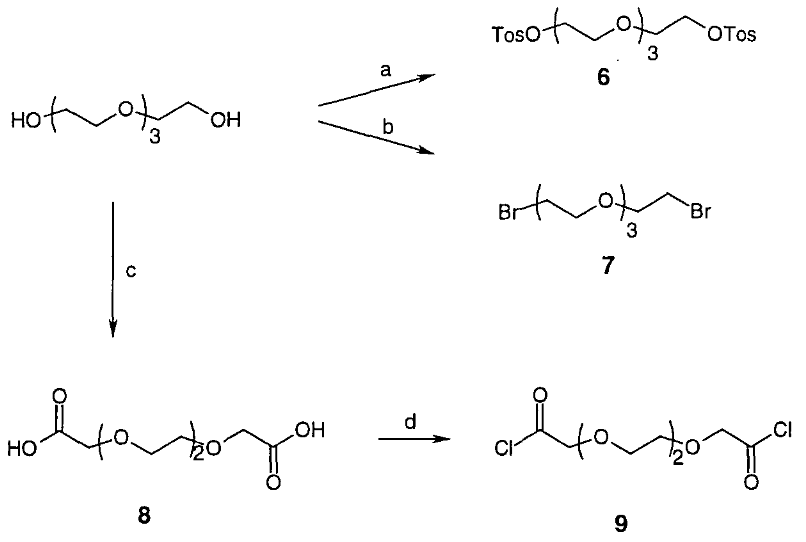


Figure 2.3.2 a) DCM, p-toluenesulfonic chloride, KOH b) diethylether, PBr_3 *c)* HNO_3 *d) toluene, oxalyl chloride, pyridine*

Using these flexible spacers three monomers could be prepared (Figure 2.3.3). Reaction of **4** with the tetraethylene glycol di-tosylate gave monomer **10** linked only by ether functionalities. It showed good solubility in a variety of organic solvents like chloroform, DCM and THF. Unfortunately the reaction was not reproducible despite enormous efforts to optimise the reaction conditions. Using the tetraethylene glycol di-bromide **7** did not give any better yields.

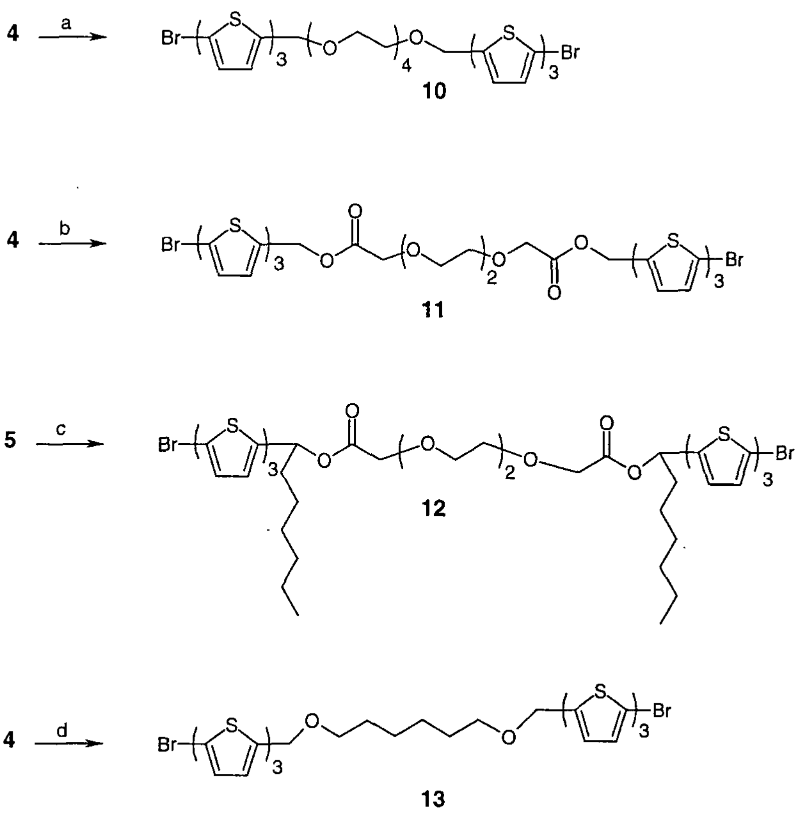
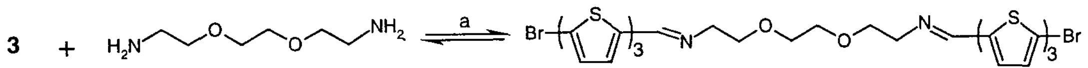


*Figure 2.3.3 a) THF, DMF, NaH, tetraethlene glycol di-p-toslate **6** b) monoglyme, pyridine, 2,5,8-trioxanonane-1,9-dicarbonyl chloride **9** c) toluene, pyridine, 2,5,8-trioxanonane-1,9-dicarbonyl chloride **9** d) DMF, NaH, 1,6-di-p-toluene sulfonyl hexane*

Reaction of **4** with the tetraethylene glycol di-acid chloride **9** gave a monomer **11** in good yields under reproducible conditions. Unfortunately the compound was not as soluble as the previously prepared ether linked species. As the only structural difference was the introduction of the ester group, its rigidity and/or polarity may be the reason for the lower solubility. To overcome the disadvantage of poor solubility while still exploiting the good yields, the terthiophene derivative **5** was coupled with the previously used di-acid chloride to give monomer **12** in good yield. Due to the introduction of flexible side chains its solubility was improved considerably compared to monomer **11**. The reaction of **4** with 1,6-hexanol-di-tosylate (**24**) was carried out to investigate the introduction of hydrophobic spacers to link the two terthiophene units. Purification of **13** turned out to be very difficult so that the material could not be fully characterised. Also, the solubility of the crude product was very low compared to that of the tetraethylene glycol linked monomers (**10**,**11**,**12**).

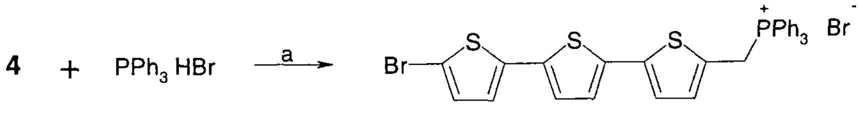
Finally the use of an imine bond to link the bromo-terthiophene-aldehyde **3** to a primary di-amine was investigated (Figure 2.3.4). The reaction gave the desired product, **14**, confirmed by ^{1}H-NMR spectroscopy. Unfortunately the solubility was again very low which made purification, full characterisation and eventual use impossible. Also, the imine bond was easily hydrolysed back to the primary amine and the aldehyde **3**.



14

Figure 2.3.4 A di-bromo monomer linked by imine groups. a) DCM, 1,8-diamino-3,6-dioxaoctane

Further routes to connect flexible spacers to the terthiophene derivatives already prepared were considered. The Wittig-reaction seemed a good candidate to link a flexible di-aldehyde to a terthiophene phosphonium salt (Figure 2.3.5).



15 **16**

Figure 2.3.5 Synthesis of the phosphonium salt. a)$CHCl_3$, PPh_3HBr

While benzyl alcohols can easily be brominated, the author's experience suggests that the analogue terthiophene alcohols can not. Bromination and also tosylation of the terthiophene alcohol **4** was tried under various conditions without success. The reaction of the terthiophene alcohol **4** with triphenyl phosphonium hydrobromide **15** (Figure 2.3.5) which probably proceeds via an intermediate bromination step seemed to give the desired product but it was not possible to separate it from impurities. Hence no complete characterisation was possible.

Linkage of the two terthiophene units via ester groups was the only successful route to di-bromo monomers established in this work. For cross-coupling, a second type of monomer would be needed either a di-boronic acid/ester or a di-(trialkyl)tin. These groups are most easily introduced via a metallation-nucleophilic substitution sequence. Although bromo-metal exchange is possible on terthiophene derivatives, esters or any other carbonyl groups can not be tolerated. Therefore we tried to introduce the reactive group necessary for cross-coupling before the introduction of the spacer, i.e. the ester.

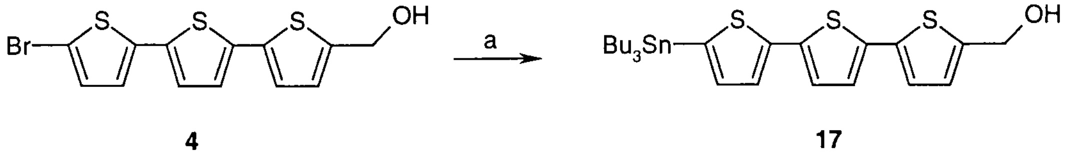


Figure 2.3.6 a)THF, LDA, tributyltin chloride

The bromo-terthiophene alcohol **4** was lithiated, with a first equivalent of LDA deprotonating the alcohol and a second replacing the bromine. The product was then reacted with tributyltin chloride. NMR spectroscopy of the crude product mixture indicated formation of the expected product **17** but separation from impurities was not achieved and hence no further characterisation was possible.

Much to our surprise terthiophene boronic acids have not been described in the literature and, despite enormous efforts, could not be prepared. Whereas the thiophene and bithiophene boronic acids are readily synthesised following literature routes, no formation of terthiophene boronic acid under similar reaction conditions was observed. Recently Effenberger *et al.*[6] reported that isolation of terthiophene boronic acid was not possible, however they reported that the dimethylester of terthiophene boronic acid could be coupled in situ.

As the syntheses of the organo-tin and organo-boron derivatives were unsuccessful, no cross-coupling with the above prepared di-bromide monomers could be carried out. Therefore we tried to homo-polymerise the di-bromo terthiophene monomer **12** following a synthetic procedure first described by Colon and Kelsey[14] (Figure 2.3.7).

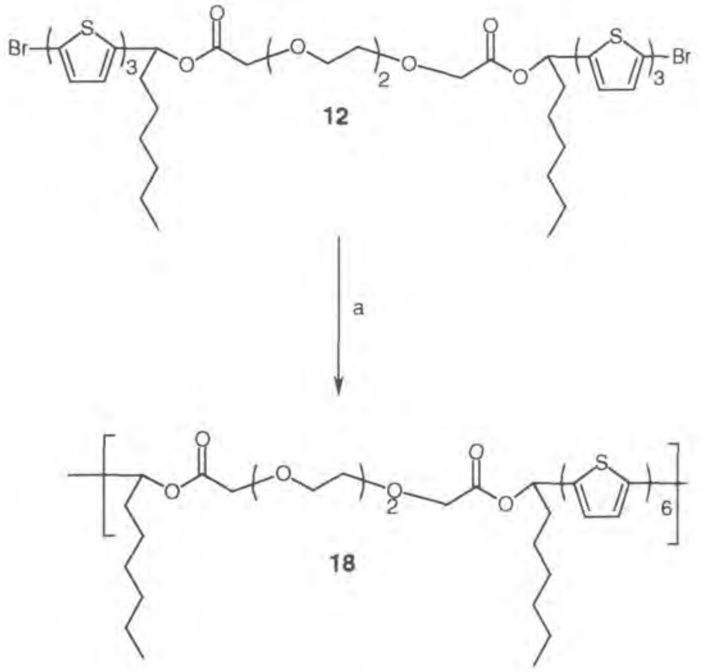


Figure 2.3.7 Homopolymerisation of the di-bromo monomer according to a procedure first described by Colon and Kelsey.[14] *a) DMF, Ni(COD)$_2$, 1,5-COD, PPh$_3$*

The dark red product of coupling **18** which precipitated from the reaction mixture was analysed by gpc and UV/Vis spectroscopy. Analysis of the ^{1}H-NMR spectrum was inconclusive. In the UV/Vis spectrum (Figure 2.3.8) of the coupling product (black trace) which is overlaid with the absorption spectrum of the monomer (red trace) one can clearly see two absorption peaks, one probably due to terthiophene endgroups at λ_{max}=375nm and one at λ_{max}=445nm probably due to absorption by the sexithiophene units formed.

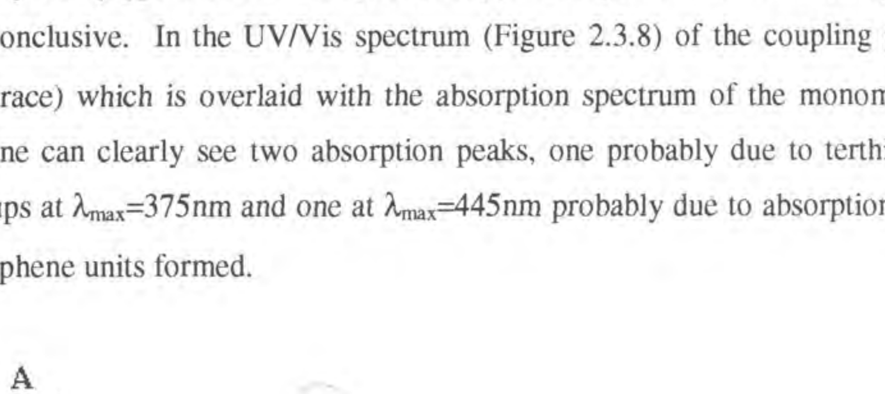


Figure 2.3.8 UV/Vis spectrum of the monomer ***12*** *(red) and the homo-coupling product* ***18*** *(black)*

The gpc analysis of the material suggested that at most dimerisation had taken place (Mn=1990 g mol^{-1}, Mw=2790 g mol^{-1}; MW(monomer)=1069.08 g mol^{-1}). These results together with the fact that the material precipitated from DMF during the reaction strongly demanded a different synthetic approach.

Two different synthetic routes were followed. Figure 2.3.9 outlines an investigation into the preparative value of the Stille cross-coupling reaction using di-halo monomers and di-tin oligothiophenes in a poly-condensation. To obtain this information quickly a simple synthesis was developed as shown in Figure 2.3.9. Only a quaterthiophene polymer was planned to be synthesised in this manner in order to minimise the preparative effort required for this preliminary investigation.

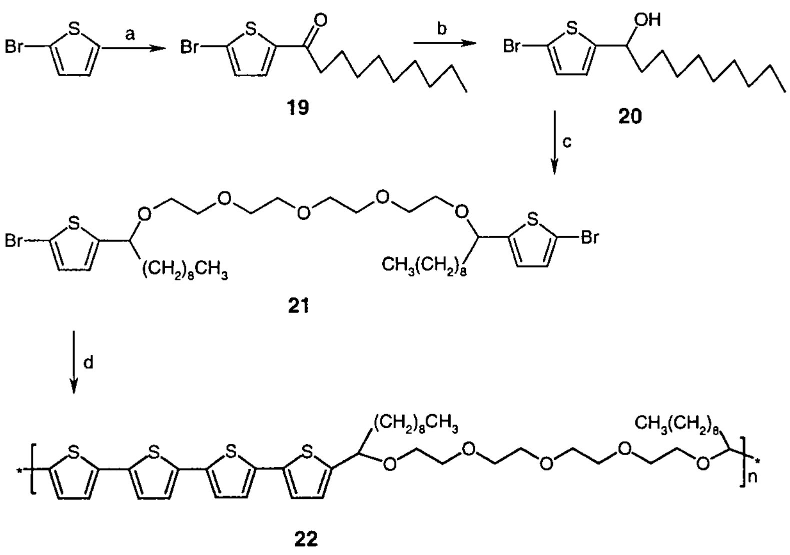


*Figure 2.3.9 a) CS_2, $AlCl_3$, decanoyl chloride b) ethanol, $NaBH_4$ c) THF, NaH, tetraethylene glycol di-p-tosylate **6** d) THF, 5,5'-bis(tributyltin)-2,2'-bithiophene **27**, $Pd(PPh_3)_2Cl_2$*

Starting from 2-bromothiophene the acylated derivative **19** was obtained easily by Friedel-Crafts chemistry. Subsequent reduction to the alcohol **20** and nucleophilic substitution of tetraethylene glycol di-tosylate **6** gave the di-bromo-thienyl monomer **21**. Stille cross-coupling of bis(tributylltin)bithiophene **27** and the above monomer, **21,** gave a red rubbery coupling product which was characterised by gpc (Mn=4600, Mw=7640, DP=6) and UV/Vis spectroscopy. Analysis of the ^{1}H-NMR spectrum of the soluble material was not conclusive with respect to structure assignment due to very broad peaks. Consequently we could not prove that the formation of a quaterthiophene unit had occurred. Nonetheless, an absorption band in the UV/Vis spectrum was observed (λ_{max}=435nm) which is in good agreement with that expected for a quaterthiophene derivative.

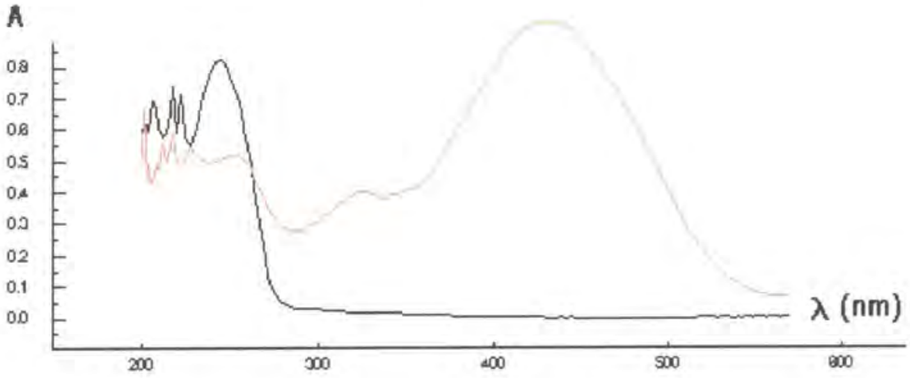


Figure 2.3.10 UV/Vis spectrum of the quaterthiophene polymer ***22*** *(red) and the monomer* ***21*** *(black).*

The second route pursued is summarised in Figure 2.3.11. Starting from 2-methyl thiophene, NBS bromination gave 2-bromomethyl-5-bromothiophene **23**. As described in the literature[15] this compound decomposes within days when kept at room temperature. Carbene formation by alpha elimination of hydrogen bromide is said to be responsible for this unusual instability. However, storage of the material in the solid state at –78°C resulted in no observed decomposition over a period of several days.

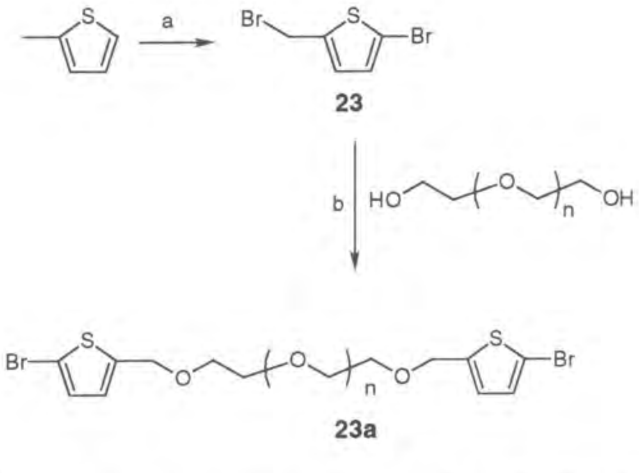


Figure 2.3.11 Strategy to prepare a reagent to end-cap PEO to form a di-bromo-thienyl macromonomer. a) benzene, NBS. Reaction b was carried out in THF with either NaH or NaOH but did not give the product shown.

An attempt to react the thienylic bromide **23** with commercial poly(ethylene glycol) (Mn=2000) to form the bis-end-capped di-bromo-macromonomer **23a** was made. The reaction of PEO with excess 2-bromomethyl-5-bromothiophene was carried out under various conditions but always with only small amounts of the desired polyether formed. This observation can be explained by the facilitated alpha elimination in the presence of base.

2.4 Conclusions

Various unsymmetrically substituted terthiophene derivatives have been prepared and coupled to flexible tetraethylene glycol derivatives to give di-halo monomers. These monomers vary greatly in their solubility depending on the exact nature of the linkage between terthiophene derivative and flexible tetraethylene glycol spacer. A di-halo monomer with a short hexyl spacer has also been prepared but suffers from poor solubility.

Homo-polymerisation of a soluble di-bromo-terthiophene monomer was tried but gave at most dimerisation.

Terthiophene monomers with organometal functionalities (carbon-boron or carbon-tin bonds) and spacer units turned out to be difficult to synthesise and purify. Consequently, no polymers with an alternating sequence of hydrophilic and hydrophobic spacers could be prepared by the routes examined here.

A model system, easy to synthesise, was developed to study whether the Stille cross-coupling reaction could successfully be employed in building up oligothiophene polymers. To achieve this, a tetraethylene glycol spacer was successfully end-capped with bromo-thiophene derivatives and cross-coupled with bis(tributyltin)bithiophene. The coupling product was polymeric according to gpc analysis. The UV/Vis absorption maximum was in the region expected for a quaterthiophene derivative. The Stille cross-coupling therefore provides a useful tool to prepare these types of polymers.

A synthetic strategy was developed in which poly(ethylene glycol) was end-capped by a bromo-thiophene derivative to give a hydrophilic macromonomer. Due to easy carbene formation of the end-capping reagent this approach was not successful.

Synthesis and successful end-capping of a different reagent will be described in chapter 3.

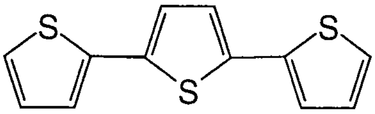
Thus, the approach outlined at the beginning of this chapter was shown to be unrealisable by the routes adopted. At this point the investigation was redirected to the synthesis of related, but more readily accessible, materials. This work is described in the next chapter.

2.5 *Experimental*

2.5.1 *General*

Melting points were obtained using an Electrothermal IA9200 series digital melting point apparatus. Elemental analysis data was recorded on an Exeter Analytical Elemental Analyser CE-440. Mass spectra were recorded on either a Micromass AutoSpec mass spectrometer or using a Hewlett Packard Series II gas chromatograph with a HP1 GC column, attached to a Fisons Trio 1000 mass spectrometer. NMR-spectra were recorded using either a Varian VXR400S (^{1}H at 399.95 MHz and ^{13}C at 100.58 MHz), a Varian Gemini (^{1}H at 200 MHz and ^{13}C at 50.2 MHz), a Varian Unity (^{1}H at 299.91 MHz and ^{13}C at 75.41 MHz) or a Varian Inova (^{1}H at 500 MHz and ^{13}C at 125 MHz). Chemical shifts are reported in parts per million with respect to the internal reference tetramethylsilane (TMS). Deuterated solvents were used as supplied (Goss). In cases where tin-hydrogen or tin-carbon couplings could be observed in the NMR-spectra, only the larger coupling constants to the isotope ^{119}Sn are reported. Calculated molecular weights are reported in g mol^{-1}. GPC analyses were performed using an ERC 7515A refractive index detector, three 5µm Polymer Laboratories gel columns (exclusion limits 100, 10^3, 10^5Å) and chloroform as eluent. Columns were calibrated using polystyrene standards (Polymer Labs). N-Butyllithium, 1,8-diamino-3,6-dioxaoctane and thiophene were purchased from Acros (Fisher Scientific), all other reagents were purchased from Aldrich Chemicals and used without further purification.

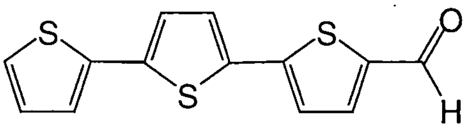
2.5.2 *2,2':5',2"-Terthiophene (1)*



A solution of 2-bromothiophene (20.8 g, 128 mmol) in dry diethylether (50 ml) was added dropwise to magnesium turnings (10 g, 411 mmol) in dry diethylether (50 ml). While adding the first drops of 2-bromothiophene the reaction mixture became cloudy and the diethylether started to reflux. After addition of the whole amount of 2-bromothiophene the dark brown reaction mixture was refluxed for 60 min. on a water bath. The mixture was cooled in an ice bath and the solution separated from excess magnesium by transferring to a second flask via a cannula.

A solution of 2,5-dibromothiophene (10.3 g, 43 mmol) and Ni(dppp)Cl_2 (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) (130 mg) in diethylether (50 ml) was transferred via a cannula into the 2-thienylmagnesium bromide solution. The reaction mixture was refluxed for 3 h, stirred at room temperature for 12 h, hydrolysed with water (200 ml), the ether phase was separated and the aqueous phase extracted with diethylether. The combined organic extracts were washed with water (3 x 50 ml), dried ($MgSO_4$) and then refluxed with a small amount of charcoal. After filtering, the solvent was evaporated and the crude solid re-crystalised from ethanol to give 2,2':5',2''-terthiophene, (5.12g, 48%) as yellow-greenish crystals, m.p. 97 °C (lit.[16] 92-93°C). Found C, 57.63; H, 3.18%; M(MS,EI) 248 (M^+). Calculated for $C_{12}H_8S_3$, C, 58.03; H, 3.25%; M 248.38. ^1H NMR (400MHz, $CDCl_3$) δ 7.03 (dd, J=5.2Hz, J=3.6Hz, 2H), 7.09 (s, 2H), 7.18 (dd, J=3.6Hz, J=0.8Hz, 2H), 7.23 (dd, J=5.2Hz, J=0.8Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.66, 124.27, 124.44, 127.85, 136.16, 137.09.

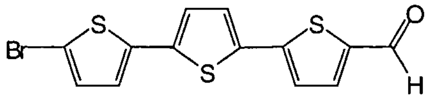
2.5.3 5-Formyl-2,2':5',2''-terthiophene (2) [10]



DMF (1.2 ml, 15 mmol) and dry dichloromethane (5 ml) were mixed at 0°C in an Erlenmeyer flask capped with a rubber seal. $POCl_3$ (1.4 ml, 15 mmol) was added dropwise with intermittent stirring. The mixture was removed from the ice bath and warmed to 40°C until a pale yellow solution was obtained. This solution was then added dropwise to a stirred solution of 2,2':5',2''-terthiophene (2.5 g, 10 mmol) in dichloromethane (15 ml) at 0°C. After standing for 12 h at r.t., the dichloromethane was evaporated and cold (10°C) aqueous NaOH (1 M) was added to the red solid. After heating on a water bath for 3 h the yellow solid was recovered by filtration and washed with water. Purification by flash chromatography on silica gel (Aldrich, 70-

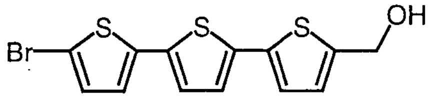
230 mesh) with hexane/dichloromethane (v:v=1:1) yielded 5-formyl-2,2':5',2''-terthiophene (2.6 g, 93 %) as orange crystals, m.p. 138 °C (lit.[10] 134°C). Found C, 56.42; H, 2.79%; M(MS,EI) 276 (M^+). Calculated for $C_{13}H_8OS_3$, C, 56.49; H, 2.92%; M 276.39. All ^{1}H-NMR signals appear twice due to s-cis/s-trans isomerism of the aldehyde group. The shift between the peaks is approximately $\Delta\delta$=0.002-0.003 ppm. Only one set of peaks is reported here. ^{1}H NMR (400MHz, $CDCl_3$) δ 6.97 (m, 1H), 7.04 (d, J=4.0Hz 1H), 7.15 (m, 2H), 7.19 (m, 2H), 7.59 (d, J=3.6Hz, 1H), 9.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.00, 124.47, 124.62, 125.37, 126.86, 128.05, 134.42, 136.38, 137.37, 139.13, 141.53, 146.78, 182.38 and 182.42 (carbonyl C due to s-cis/s-trans isomerism of the aldehyde group)

2.5.4 5-Bromo-5''-formyl-2,2':5',2''-terthiophene (3) [10]



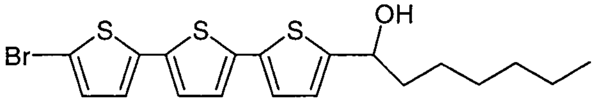
N-Bromosuccinimide (1.28g, 7.2 mmol) was added at r.t. to a stirred solution of 5-formyl-2,2':5',2''-terthiophene (2.0 g, 7.2 mmol) in a mixture of dichloromethane and glacial acetic acid (200 ml, v:v=1:1). After 24h the yellow precipitate was recovered by filtration, washed with water and dried under vacuum. The solid was dissolved in the minimum amount of boiling dichloromethane and hexane added until small crystals started to precipitate. The mixture was then cooled to -78°C and the crystalline product recovered by filtration after 1 h to give 5-bromo-5''-formyl-2,2':5',2''-terthiophene (2.23 g, 87 %) as orange crystals, m.p. 160 °C (lit.[10] 158°C). Found C, 44.05; H, 1.89%; M(MS,EI) 354 (M^+ [^{79}Br]), 356 (M^+ [^{81}Br]). Calculated for $C_{13}H_7BrOS_3$, C, 43.95; H, 1.99%; M 355.28. ^{1}H NMR (400MHz, $CDCl_3$) δ 6.94 (d, J=3.6Hz, 1H), 6.98 (d, J=3.6Hz, 1H), 7.04 (d, J=3.6Hz, 1H), 7.22 (m, 2H), 7.64 (d, J=4.0Hz, 1H), 9.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.19, 124.21, 124.51, 124.85, 126.77, 130.88, 135.10, 136.91, 137.94, 137.95, 142.07, 146.35, 182.12.

2.5.5 5-Bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (4) 10



5-Bromo-5''-formyl-2,2':5',2''-terthiophene (0.5 g, 1.4 mmol) was dissolved in dry THF (25 ml) and sodium borohydride (55 mg, 1.4 mmol) was added to the solution. After stirring the solution for 12 h at r.t. under nitrogen atmosphere a yellow solid precipitated. THF was evaporated and the yellow solid stirred with water for 2 h. After filtration and drying under vacuum the solid was dissolved in the minimum amount of boiling chloroform. Hexane was added until the beginning of crystallisation could be observed. The solid was recovered by filtration to give 5-bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (470 mg, 94 %) as orange crystals, m.p. 160 °C (lit.[10] 165°C). Found C, 44.06; H, 2.59%; M(MS,EI) 356 (M^+ [^{79}Br]), 358 (M^+ [^{81}Br]). Calculated for $C_{13}H_9BrOS_3$, C, 43.70; H, 2.54%; M 357.30. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.75 (broad, -OH), 4.81 (s, 2H, <u>CH</u>$_2$-OH), 7.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.21, 61.61, 111.20, 123.65, 123.84, 124.35, 124.65, 126.13, 130.72, 135.31, 136.79, 137.10, 143.63, 151.07.

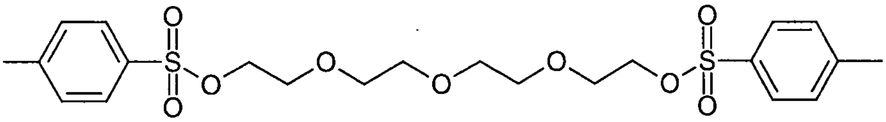
2.5.6 5-Bromo-5''-(1-hydroxyheptyl)-2,2':5',2''-terthiophene (5)



To a suspension of magnesium turnings (205 mg, 8.5 mmol) in diethyl ether (20 ml) was added 1,2-dibromoethane (0.1 ml) and the mixture heated with a hot air gun until a faint cloudiness indicative of Grignard formation could be observed. 1-Bromohexane (688 mg, 4.2 mmol) was added at once and the mixture refluxed for 1 h. After cooling 5-bromo-5''-formyl-2,2':5',2''-terthiophene (500 mg, 1.4 mmol) was added to the Grignard solution as a solid and the resulting orange solution refluxed for 1.5 h. The reaction mixture was poured into a saturated NH_4Cl solution, extracted with hexane/diethyl ether (1:1) and dried ($MgSO_4$). Evaporation of the solvent yielded *5-bromo-5''-(1-hydroxyheptyl)-2,2':5',2''-terthiophene* (3.1 g, 83%) as a pale yellow solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.88 (t, 3H), 1.2-1.5 (m, 8H), 1.86 (m, 2H), 2.00 (d, J=4.4Hz, 1H, -OH), 4.87 (m, 1H), 6.86 (d, J=4.4Hz, 1H), 6.89

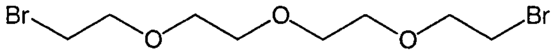
(d, J=4.0Hz, 1H), 6.96 (d, J=3.6Hz, 1H), 6.99-7.03 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.06, 22.58, 25.67, 29.04, 31.71, 39.17, 70.49, 110.99, 123.30, 123.68, 124.09, 124.49, 124.55, 130.66, 134.96, 135.90, 136.77, 138.56, 148.40.

2.5.7 Tetraethylene glycol di-p-toluene sulfonate (6) [11]



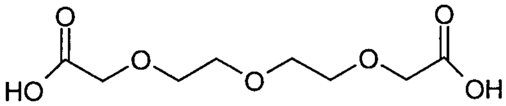
A 2-l three necked flask equipped with mechanical stirrer, thermometer, and nitrogen inlet was charged with tetraethylene glycol (35 g, 0.18 mol), p-toluenesulfonic chloride (70 g, 0.37 mol), and DCM (180 ml). The homogeneous mixture was cooled to 0°C with a CO_2/acetone bath. Freshly powdered KOH (80.8 g, 1.44 mol) was added in small amounts under vigorous stirring while maintaining the reaction temperature below 5°C. The mixture was stirred for 3 h at 0°C after which DCM (180 ml) and ice-water (220 ml) were added. The organic phase was separated, and the aqueous phase was extracted with DCM (2x 50 ml). The combined organic extracts were washed with water (40 ml), dried ($MgSO_4$), and concentrated under reduced pressure to give tetraethylene glycol di-p-toluene sulfonate (80.3 g, 94%) as a colourless viscous liquid. Spectral characterisation revealed that the product was pure enough to be used in further reaction steps without additional purification. As the recorded NMR data of the prepared tetraethylene glycol di-p-toluene sulfonate agreed with the data reported in the literature[11] and with the data we recorded from commercially available (Aldrich) tetraethylene glycol di-p-toluene sulfonate, no further analysis of the material was carried out. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.40 (s, 6H), 3.51 (s, 8H), 3.64 (m, 4H), 4.11 (m, 4H), 7.29 (d, J=8.5Hz, 4H), 7.73 (d, J=8.5Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.46, 68.45, 69.15, 70.32, 70.49, 127.74, 129.67, 132.71, 144.68.

2.5.8 *3,6,9-Trioxa undecane-1,11-dibromide (7)* [12]



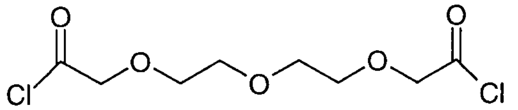
Tetraethylene glycol (10 g, 52 mmol) was dissolved in diethylether (100 ml) and the solution cooled to 0°C. Phosphorus tribromide (10 ml, 55 mmol) was added dropwise to the stirred solution via a syringe. The mixture was refluxed for 12 h then allowed to cool down and poured on ice (75 g). The phases were separated and the aqueous layer extracted with diethylether (100 ml). The combined organic extracts were washed with saturated sodium bicarbonate solution, dried ($MgSO_4$) and the solvent evaporated to give pure 3,6,9-trioxa undecane-1,11-dibromide (13g, 78%) in form of a pale yellow oil. Found C, 29.48; H, 4.97%. Calculated for $C_8H_{16}Br_2O_3$, C, 30.03; H, 5.04%. ^1H NMR (400MHz, $CDCl_3$) δ 3.40 (t, J=6.4Hz, 4H), 3.60 (s, 8H), 3.74 (t, J=6.4Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.33, 70.34, 70.46, 71.00.

2.5.9 *2,5,8-Trioxanonane-1,9-dicarboxylic acid (8)* [13]



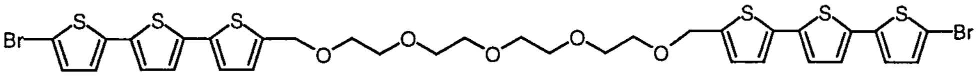
Tetraethylene glycol (20 g, 103 mmol) was added dropwise to nitric acid (69%, 70 ml) at 45 °C while stirring. After the NO_x-formation had stopped the brown-solution was heated at 40 °C for one hour, cooled to r.t. and stirred over night. Excess nitric acid was removed under reduced pressure and the remaining clear oil was dried under high vacuum until no NO_x vapours could be seen any more. The crude 2,5,8-trioxanonane-1,9-dicarboxylic acid (19 g, 83%) was used in the next reaction step without any further purification. The recorded NMR data for the prepared 2,5,8-trioxanonane-1,9-dicarboxylic acid agreed with the NMR data reported in the literature[13] and therefore no further analysis of the material was carried out. ^1H NMR (400MHz, $CDCl_3$) δ 3.71 (m, 8H), 4.17 (s, 4H), 11.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.95, 70.09, 70.63, 174.87.

2.5.10 2,5,8-Trioxanonane-1,9-dicarbonyl chloride (9) [13]



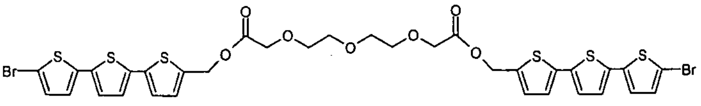
To a solution of 2,5,8-trioxa-1,9-dicarboxylic acid (5 g, 22.5 mmol) in toluene (35 ml) were added oxalylchloride (10 g, 78.8 mmol) and three drops of pyridine. The yellow solution was stirred at r.t. for 20 h and then filtered rapidly to remove pyridinium hydrochloride. The solvent was removed under vacuum to give 2,5,8-trioxanonane-1,9-dicarbonyl chloride (5.3 g, 90%) as a yellow liquid which was dried under high vacuum and used without further purification. The recorded NMR data for the prepared 2,5,8-trioxanonane-1,9-dicarbonyl chloride agreed with the NMR data reported in the literature[13] and therefore no further analysis of the material was carried out. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.57 (m, 4H), 3.67 (m, 4H), 4.42 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.31, 70.89, 76.25, 171.78.

2.5.11 Tetraethylene glycol di-(5'-bromo-2',2":5",2"'-terthiophene-5"'-ylmethyl) ether (10)



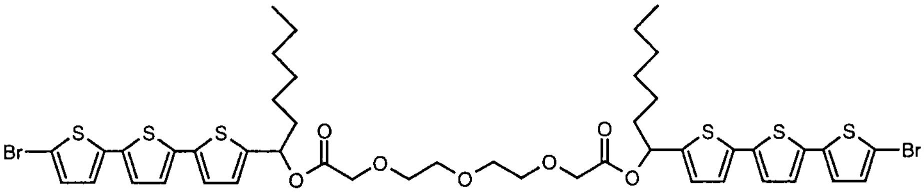
A solution of 5-bromo-5"-hydroxymethyl-2,2':5',2"-terthiophene (100 mg, 0.28 mmol) in THF (1 ml) was added to a stirred suspension of sodium hydride (100 mg, 4.2 mmol) in DMF (2 ml). After stirring at r.t. for 30 min. a solution of tetraethylene glycol di-p-toluene sulfonate (70.4 mg, 0.14 mmol) in THF (1 ml) was added to the yellow-brown suspension. After stirring at r.t. for 65.5 h the mixture was poured into methanol (50 ml) and the pale yellow precipitate was recovered by filtration and dried under high vacuum to give *tetraethylene glycol di-(5'-bromo-2',2":5",2"'-terthiophene-5"'-ylmethyl) ether* (55 mg, 45 %) as a pale yellow powder, m.p. 102-103°C (melt and decomposition). Found C, 46.73; H, 3.73%. $C_{34}H_{32}Br_2O_5S_6$ requires C, 46.79; H, 3.70%. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.67 (m, 16H, O-CH_2CH_2-O), 4.68 (s, 4H, Ar-CH_2-), 6.89 (m, 4H, arom.), 6.99 (m, 8H, arom.); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.73, 69.12, 70.59, 123.28, 123.67,124.16, 124.45, 124.52; 127.24, 130.64, 135.00, 136.64, 137.17, 138.51, 140.57.

2.5.12 2,5,8-Trioxanonane-1,9-di-carboxylic acid di-(5-bromo-5"-methylene-2,2':5',2"-terthiophene) ester (11)



5-Bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (975 mg, 2.73 mmol) was added to a mixture of monoglyme (90 ml) and pyridine (5 ml). Addition of 2,5,8-trioxanonane-1,9-dicarbonyl chloride (353 mg, 1.36 mmol) resulted in an instantaneous change of colour from brown to orange. After ca. 10-20 min. pyridinium hydrochloride started to precipitate. The reaction mixture was stirred for 2 h at r.t. before it was poured into hexane. The precipitate was recovered by filtration, washed with diethylether and dissolved in chloroform. The chloroform solution was washed with water, dried ($MgSO_4$) and the solvent evaporated to give *2,5,8-trioxanonane-1,9-di-carboxylic acid di-(5-bromo-5''-methylene-2,2':5',2''-terthiophene) ester* (1.8 g, 73%) as a pale yellow solid, m.p. 130-131°C. Found C, 45.21; H, 3.73%. $C_{34}H_{28}Br_2O_7S_6$ requires C, 45.34; H, 3.13%. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.70 (m, 8H), 4.18 (s, 4H), 5.28 (s, 4H), 6.89 (d, J=4.0Hz, 2H), 7.00 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.70, 68.50, 70.64, 70.94, 111.19, 123.34, 123.82, 124.55, 124.58, 129.50, 130.68, 135.47, 136.08, 136.46, 138.36, 138.57, 170.20.

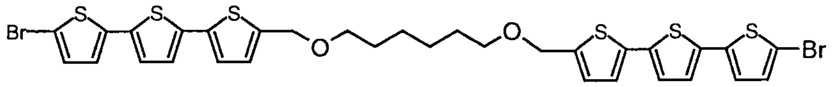
2.5.13 2,5,8-Trioxanonane-1,9-di-carboxylic acid di 5-bromo-5"-(1-heptyl)-2,2':5',2"-terthiophene) ester (12)



A solution of 5-bromo-5"-(1-hydroxyheptyl)-2,2':5',2"-terthiophene (1.1 g, 2.5 mmol), 2,5,8-trioxanonane-1,9-dicarbonyl chloride (322.8 mg, 1.25 mmol) and pyridine (0.13 ml) in toluene (18 ml) was stirred for 3 h with occasional heating with a hot air gun. The reaction mixture was poured into water and extracted with diethyl ether and dried ($MgSO_4$). Evaporation of the solvent gave a viscous oil, which was dissolved in dichloromethane and precipitated from hexane to give *2,5,8-*

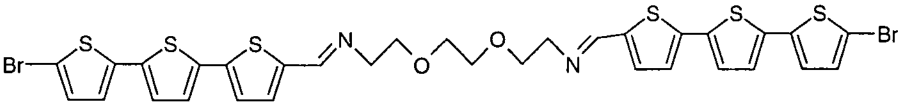
trioxanonane-1,9-di-carboxylic acid di 5-bromo-5"-(1-heptyl)-2,2':5',2"-terthiophene) ester (930 mg, 70%) as a pale yellow solid which was recovered by filtration, washed with hexane and dried under high vacuum. The product was used in the next reaction step without any further purification. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.87 (t, J=8.0Hz, 6H), 1.20-1.40 (m, 16H), 1.80-2.10 (m, 4H), 3.70 (m, 8H), 4.13 (m, 4H), 6.04 (t, J=8.0Hz, 2H), 6.90 (d, J=4.0Hz, 2H), 6.96-7.01 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.03, 22.53, 25.51, 28.80, 31.58, 35.99, 68.63, 70.57, 70.90, 71.79, 111.11, 123.19, 123.76, 124.37, 124.48, 124.55, 127.13, 130.68, 135.28, 136.34, 136.89, 138.45, 142.23, 169.79.

2.5.14 1,6-Di-(5-bromo-2,2':5',2"-terthiophene-5"-ylmethoxy) hexane (13)



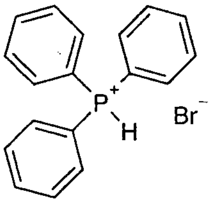
5-Bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (122 mg, 0.34 mmol) was dissolved in DMF (2 ml) and the solution added to a suspension of sodium hydride (16 mg, 0.68 mmol) in DMF (4 ml) to give a yellow-brown suspension. The mixture was stirred for 30 min. at r.t. before 1,6-di-p-toluene sulfonyl-hexane (73 mg, 0.17 mmol) was added as a solid. About 2 min. after that the suspension started to become more cloudy. After 4 h, water (50 ml) was added and the precipitate recovered by filtration and dried under vacuum. The crude material was then absorbed at the top of a short silica gel (Aldrich, 70-230 mesh) column and impurities were washed off with acetone and then methanol. An impure fraction of 1,6-di-(5'-bromo-2',2'':5'',2'''-terthiophene-5'''-ylmethoxy) hexane was collected by eluting with chloroform. Purification of the material was very difficult because of its low solubility. As no pure fraction of the material could be obtained no analysis other than ^{1}H NMR spectroscopy was carried out. The product was not used in any further reactions. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.40 (m, 4H, -CH_2-), 1.63 (m, 4H, -CH_2-), 3.50 (t, J=6.4Hz, 4H, -O-CH_2-), 4.61 (s, 4H, Ar-CH_2-), 6.86 (d, J=3.2Hz, 2H, arom.), 6.89 (d, J=3.6Hz, 2H, arom.), 6.96 (d, J=4.0Hz, 2H, arom.), 6.99 (d, J=3.6Hz, 2H, arom.), 7.00 (m, 4H, arom.).

2.5.15 N,N'-Bis(5-bromo-2,2':5',2''-terthiophene-5''-ylmethylene)-3,5-dioxaoctane-1,8-diamine (14)



To a solution of 1,8-diamino-3,6-dioxaoctane (208.6 mg, 1.4 mmol) in dichloromethane (40 ml) was added 5-bromo-5''-formyl-2,2':5',2''-terthiophene (1 g, 2.8 mmol) and dry activated molecular sieve 3A (11g). The suspension was refluxed for 5h. After 1.5 h a yellow solid started to precipitate from the orange solution. The molecular sieve was removed by filtration and washed with dichloromethane. The solvent was evaporated and the residue dried under high vacuum to give crude N,N'-bis(5-bromo-2,2':5',2''-terthiophene-5''-ylmethylene)-3,5-dioxaoctane-1,8-diamine as a yellow powder (1.05g, 90%). Purification of the material turned out to be difficult because of its low solubility. As no pure fraction of the material could be obtained no analysis other than ^{1}H NMR spectroscopy was carried out. The product was not used in any further reaction steps. ^{1}H NMR (200MHz, $CDCl_3$) δ 3.63 (s, 2H), 3.74 (s, 4H), 6.90 (d, J=4.0Hz, 1H), 6.98 (m, 2H), 7.08 (m, 2H), 7.15 (d, J=4.0Hz 1H), 8.30 (s, 1H).

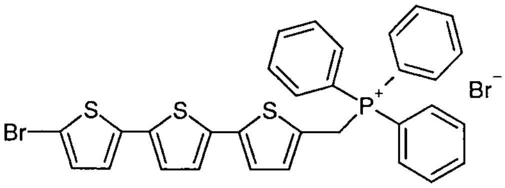
2.5.16 Triphenylphosphine hydrobromide (15) [17]



Triphenyl phosphine (10 g, 38.1 mmol) was added to aqueous HBr (48vol%, 27 ml). After stirring at 70 °C for 5 min., the solution was cooled and extracted with chloroform (3 x 12 ml). The combined organic extracts were dried ($MgSO_4$), and the solvent removed under reduced pressure. The residue was washed with warm ethylacetate (25 ml) to remove traces of triphenylphosphine, then dried under vacuum to give triphenylphosphine hydrobromide as a white solid (12 g, 91%), m.p. 202-203°C (lit.[17] 185-195°C). Found C, 62.70; H, 4.62%; M(MS,EI) 262 (M^+-HBr). Calculated for $C_{18}H_{16}PBr$, C, 62.99; H, 4.70%; M 872.79. ^{1}H NMR

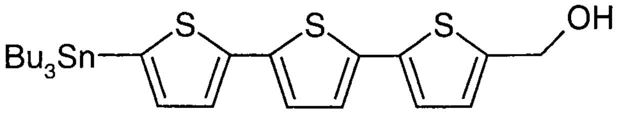
(400MHz, $CDCl_3$) δ 7.45-7.61 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.65 (J_{CP}=47.7 Hz), 133.09 (J_{CP}=413 Hz), 133.14 (J_{CP}=39.3 Hz), 134.26 (J_{CP}=10.5 Hz).

2.5.17 (5'-Bromo-2',2":5",2'"-terthiophene-5'"-ylmethyl)-triphenyl phosphonium bromide (16)



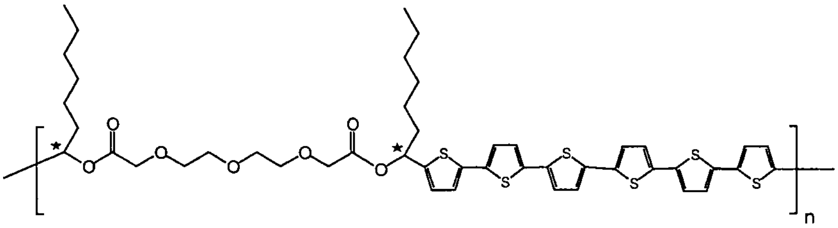
A solution of 5-bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (100 mg, 0.28 mmol) and triphenylphosphine hydrobromide (86.5 mg, 0.25 mmol) in chloroform (10 ml) was refluxed for 2 h and then poured into diethylether. The precipitate was recovered by filtration and dried under high vacuum to give crude *(5'-bromo-2',2'':5'',2'''-terthiophene-5'''-ylmethyl)-triphenyl phosphonium bromide* which could not be separated from impurities. As no pure fraction of the material could be obtained no analysis other than ^{1}H NMR spectroscopy was carried out. The product was not used in any further reaction steps. ^{1}H NMR (200MHz, $CDCl_3$) δ 5.87 (d, J_{HP}=13.6Hz, 2H), 6.74 (d, J=3.6Hz, 1H), 6.78 (m, 2H), 6.84 (d, J=4.0Hz, 1H), 6.88 (d, J=4.0Hz, 1H), 6.98 (m, 1H), 7.61 (m, 6H), 7.79 (m, 9H).

2.5.18 5-tributyl tin-5"-hydroxymethyl-2,2':5',2"-terthiophene (17)



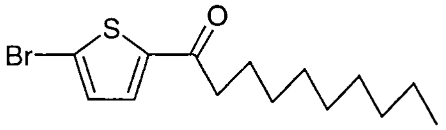
LDA (1.5 M, 10.1 ml, 15.2 mmol) was added slowly dropwise to a cooled (-78°C) suspension of 5-bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (840 mg, 3.0 mmol) in THF (16 ml). The mixture was left for 0.5 h with occasional stirring, followed by the dropwise addition of tributyl tin chloride (4.88 ml, 18.2 mmol) . The dry-ice bath was removed and the solution stired at r.t. for 1 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic solvent was washed with water several times, dried ($MgSO_4$) and evaporated to give crude *5-tributyl tin-5''-hydroxymethyl-2,2':5',2''-terthiophene* (686 mg, 40%) which could not be separated from impurities. As no pure fraction of the material could be obtained no analysis other than NMR spectroscopy was carried out. The product was not used in any further reaction steps. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.92 (t, J=7.4Hz, 9H, CH_3), 1.13 (m, 6H, CH_2), 1.37 (m, 6H, CH_2), 1.59 (m, 6H, CH_2), 2.00 (broad, 1H, -OH), 4.79 (d, J=5.2Hz, 2H), 6.90 (d, J=3.2Hz, 1H), 7.01 (d, J=3.2Hz, 1H), 7.05 (m, 3H), 7.29 (d, J=3.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.87 ($^1J_{CSn}$=710Hz), 13.65, 27.23 ($^2J_{CSn}$=114Hz), 28.92 ($^3J_{CSn}$=42Hz), 60.13, 123.06, 123.97, 124.30, 124.89, 126.21, 135.60, 136.16, 136.61, 137.06, 137.56, 142.32, 142.83.

2.5.19 Homopolymerisation of 2.5.13 (18)



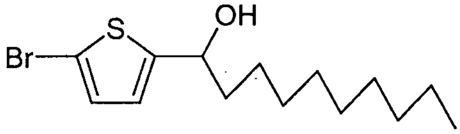
2,5,8-Trioxanonane-1,9-di-carboxylic acid di 5-bromo-5”-(1-heptyl)-2,2’:5’,2”-terthiophene) ester **2.5.13** (130 mg, 0.12 mmol), 1,5-cyclooctadiene (13 mg, 0.12 mmol), triphenyl phosphine (38.3 mg, 0.15 mmol) and bis(1,5-cyclooctadiene)nickel(0) (40 mg, 0.15 mmol) were dissolved in dry DMF (2 ml) and the reaction mixture stirred at 60°C for 16h. The clear reaction mixture was poured into a large amount of HCl-acidic methanol and stirred for 1/2 h. A red solid precipitated. The solid was recovered by filtration, washed with HCl/methanol mixture and dissolved in a small amount of DCM. The DCM solution was added dropwise to a large amount of stirred hexane. The precipitated red solid was recovered by filtration and dried under vacuum (45mg, 41%). Analysis of the coupling product by NMR-spectroscopy was not conclusive and the formation of sexithiophene could not be proved. The product was not fully analysed, as this synthetic route was not further investigated. Gpc ($CHCl_3$): Mn = 1990 g mol^{-1}, Mw = 2790 g mol^{-1}, PDI = 1.40, UV-abs.: λ_{max} = 375nm and 445nm.

2.5.20 2-Bromo-5-decanoyl thiophene (19)



Decanoyl chloride was added slowly dropwise (11.7 g, 12.73 mmol) to a cold (0 °C) suspension of 2-bromothiophene (10 g, 61.3 mmol) and $AlCl_3$ (9.8 g, 73.5 mmol) in carbon disulfide (50 ml). After addition the mixture was stirred for 2 h at r.t. before it was poured onto an ice/water mixture. The water phase was extracted with diethylether (2x 50ml), washed with small amounts of dilute HCl (2x) and water (1x) and dried ($MgSO_4$). Evaporation of the solvent and recrystallisation of the residue from ethanol gave *2-bromo-5-decanoyl thiophene* (13 g, 67%) as a green solid, m.p. 59-61°C. Found C, 53.08; H, 6.71%; M(MS,EI) 316 (M^+), 318 (M^+). $C_{14}H_{21}BrOS$ requires C, 53.00; H, 6.67%; M 357.30. ^1H NMR (300MHz, $CDCl_3$) δ 0.86 (t, J=7.2Hz, 3H), 1.25 (m, 12H), 1.70 (m, 2H), 2.79 (t, J=7.5Hz, 2H), 7.08 (d, J=3.9Hz, 1H), 7.41 (d, J=3.9Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 22.62, 24.64, 29.22, 29.25, 29.36, 29.38, 31.81, 38.71, 122.10, 131.00, 131.80, 146.00, 182.20.

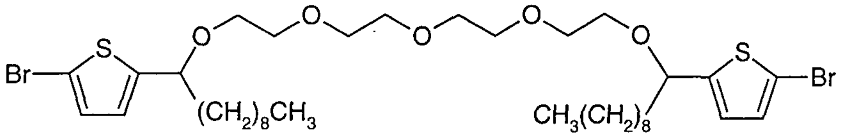
2.5.21 2-Bromo-5-(1-hydroxydecyl)-thiophene (20)



2-Bromo-5-decanoyl thiophene (1g, 3.15 mmol) was dissolved in ethanol (10 ml) and the suspension heated to 70 °C. Sodium borohydride (143 mg, 3.78 mmol) was added to the resulting solution and the mixture stirred for 3 h at 70 °C. TLC control on silica plates with THF/hexane mixture (v:v=1:2) was used to determine the end of the reaction. The reaction mixture was poured into water and extracted with diethyl ether. The combined ether extracts were washed with small amounts of water (3x), dried ($MgSO_4$) and the solvent evaporated to give *2-bromo-5-(1-hydroxydecyl)-thiophene* (780 mg, 77.5 %) as a yellow oil which was used directly in the next reaction step. ^1H NMR (300MHz, $CDCl_3$) δ 0.88 (t, J=6.0Hz, 3H), 1.26 (m, 14H), 1.75 (m, 2H), 2.76 (d, J=3.6Hz, 1H, -OH), 4.74 (m, 1H), 6.67 (d, J=3.6Hz, 1H), 6.87

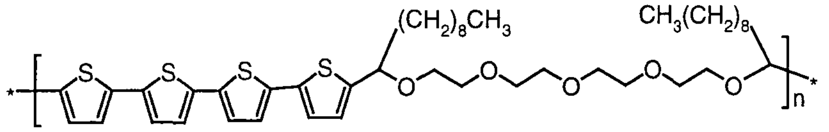
(d, J=3.6Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 22.63, 25.58, 29.25, 29.30, 29.47, 31.83, 38.97, 70.97, 70.41, 111.13, 123.82, 129.16, 150.56.

2.5.22 1,15-Di-nonyl-1,15-di-5-(2-bromothienyl)-2,5,8,11,14-pentaoxa penta-decane (21)



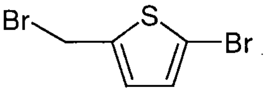
NaH (60 mg, 2.4 mmol) was added to a solution of 2-bromo-5-(1-hydroxydecyl)-thiophene (80 mg, 2.4 mmol) in THF (10 ml). The reaction mixture was stirred at r.t. for 1/2 h before tetraethylene glycol-di-p-tosylate (614 mg, 1.2 mmol) was added. After stirring at r.t. over night the mixture was poured into a large amount of aqueous KOH (1M) and extracted with diethylether (3x 30 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated. The oily residue was further purified by column chromatography on silica gel (Aldrich, 70-230 mesh) with THF/hexane mixture (v:v=1:2) to give *1,15-di-nonyl-1,15-di-5-(2-bromothienyl)-2,5,8,11,14-pentaoxa penta-decane* (750 mg, 78%) as a yellow oil. Found C, 54.43; H, 7.79%; M(MS,EI) 794 (M^+), 716 (M^+-Br), 636 (M^+-2Br). $C_{36}H_{60}Br_2O_5S_2$ requires C, 54.27; H, 7.59%; M 796.81. ^1H NMR (300MHz, $CDCl_3$) δ 0.83 (t, J=6.9Hz, 6H), 1.20 (m, 28H), 1.62 (m, 2H), 1.82 (m, 2H), 3.4-3.6 (m, 16H), 4.37 (t, J=6.9Hz, 2H), 6.63 (d, J=3.6Hz, 2H), 6.81 (d, J=3.6Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.91, 22.43, 25.41, 29.05, 29.11, 29.18, 29.26, 29.29, 31.62, 38.00, 67.69, 70.30, 70.37, 78.18, 111.22, 125.10, 128.72, 148.41.

2.5.23 Polymerisation of 2.5.22 (22)



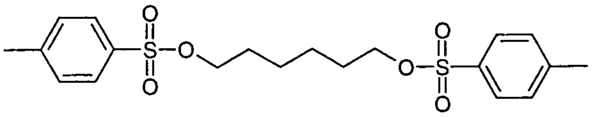
A solution of 5,5'-bis(tributyltin)-2,2'-bithiophene (934 mg, 1.3 mmol) and 1,15-di-nonyl-1,15-di-5-(2-bromothienyl)-2,5,8,11,14-pentaoxapentadecan (1g, 1.3 mmol) in THF (15 ml) was purged with nitrogen for 1/2 h. $Pd(PPh_3)_2Cl_2$ (44 mg, 0.06 mmol) was added and the reaction mixture refluxed for 12h. The reaction mixture was poured into dilute HCl, the resulting solid was recovered by filtration and washed with more dilute HCl then water before it was dried under vacuum (695mg, 61%). The obtained red solid was soluble in deuterated chloroform but ^{1}H-NMR analysis of the coupling product was not conclusive. It was not possible to prove the formation of a quaterthiophene derivative, therefore no NMR-data is reported here. Gpc ($CHCl_3$): Mn = 4600 g mol^{-1}, Mw = 7640 g mol^{-1}, PDI = 1.66, UV-abs.: λ_{max} = 435 nm.

2.5.24 2-Bromomethyl-5-bromothiophene (23) [15]



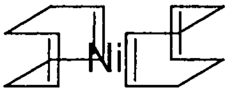
A solution of 2-methylthiophene (6.38g, 0.13 mol) and NBS (23.14g, 0.26 mol) in dry benzene (50 ml) was refluxed for 5 h. The solvent was removed under reduced pressure and the residue distilled under vacuum (2 mmHg, 85°C) to give 2-bromomethyl-5-bromothiophene (15g, 45%) as a clear liquid. The product was stored under nitrogen at -78°C as it decomposed within days at r.t. As the NMR data recorded for the product agreed with the one reported in the literature[15] no analysis other than NMR spectroscopy was carried out. ^{1}H NMR (300MHz, $CDCl_3$) δ 4.64 (s, 2H), 6.83 (d, J=3.6Hz, 1H), 6.89 (d, J=3.6Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.19, 113.75, 128.21, 129.73, 141.92.

2.5.25 1,6-Di-p-toluene sulfonyl-hexane (24)



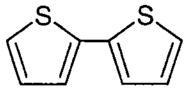
1,6-Dihydroxyhexane (5 g, 42.3 mmol) was dissolved in chloroform (40 ml) and p-toluene sulfonyl chloride (17.75 g, 93.1 mmol) and pyridine (7.4 g, 7.5 ml, 93,1 mmol) were added to the mixture. After stirring for 12 h at r.t. ice (75 g) and conc. HCl (26 ml) was added to the mixture. The phases were separated and the aqueous phase extracted with chloroform (250 ml). The combined organic extracts were washed with water several times, dried ($MgSO_4$) and the solvent evaporated. The resulting oil was stirred under high vacuum until it solidified. The solid was then suspended in dry diethylether and stirred vigorously for 1h. Filtration recovered 1,6-di-p-toluene sulfonyl-hexane (9.1 g, 49 %) as a white powder, m.p. 71°C (lit.[18] 70-71.5°C). Found C, 56.21; H, 6.18%; M(MS,EI) 426 (M^+). Calculated for $C_{20}H_{26}O_6S_2$, C, 56.32; H, 6.14 %; M 426.55. ^1H NMR (400MHz, $CDCl_3$) δ 1.24 (m, 4H, $-CH_2-$), 1.57 (m, 4H, $-CH_2-$), 2.43 (s, 6H, Ar-CH_3), 3,96 (t, J=6.4Hz, 4H, O-CH_2-), 7.33 (d, J=8.2Hz, 4H, arom.), 7.75 (d, J=8.2Hz, 4H, arom.); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.55, 24.68, 28.49, 70.21, 127.74, 129.78, 132.91, 144.72.

2.5.26 Bis(1,5-cyclooctadiene)nickel(0) (25) [19]



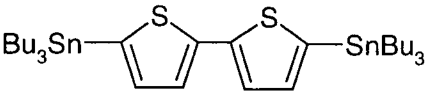
A Schlenk flask equipped with a stirrer bar and a dropping funnel was charged with bis(acetylacetonate)nickel(II) (4.67 g, 18.2 mmol) and briefly dried under vacuum with a heat gun. After cooling the solid was suspended in dry THF (25 ml) and treated with 1,5-cyclooctadiene (7.93 g, 72.3 mmol). The suspension was cooled to -78 °C and a 1.0 M solution of DIBAH (45.4 ml, 45.4 mmol) in THF was added over 1 h to give a dark brown solution which was then allowed to warm to 0 °C over a 1 h period. The solution was treated with dry diethylether to give a light brown precipitate, cooled to -78 °C and allowed to stand for 12 h to complete precipitation. The solid was filtered at -78 °C via a filter paper tipped cannula and the remaining solid washed with diethylether several times in the same manner until bis(1,5-cyclooctadiene)nickel(0) (2.9 g, 58%) was obtained as a light brown solid. The product was stored at -20 °C in a glove box. NMR spectra were recorded in sealed NMR tubes in benzene-d_6, dried over P_2O_5. Due to the sensitivity of the material no other analyses were performed. ^1H NMR (200MHz, benzene-d_6) δ 2.09 (broad, 8H), 4.32 (broad, 4H); ^{13}C NMR (50 MHz, benzene-d_6) δ 30.83, 89.65.

2.5.27 2,2'-Bithiophene (26)



Magnesium turnings (22 g, 192 mmol) were heated with a hot air gun under nitrogen flow and rapid stirring. After cooling, THF (300ml) was added to the magnesium and 2-bromothiophene (120 g, 0.74 mol) was added slowly via a dropping funnel. After complete addition the mixture was refluxed for 1h, cooled to r.t. and transferred into a dropping funnel thereby decanting the solution from excess magnesium. 2-Bromothiophene (100 g, 0.61 mol) was dissolved in THF (300 ml), the catalyst Ni(dppp)Cl_2 (1.5 g, 3.6 mmol) suspended in the THF mixture and the Grignard reagent added slowly via a dropping funnel. During addition of the Grignard reagent the reaction mixture had to be cooled (r.t.) with a water bath. After complete addition the mixture was stirred for another 5 h at 70°C and then at r.t. over night. A solid precipitated. Excess Grignard reagent was quenched with water and the remaining suspension extracted with diethylether. The combined organic extracts were washed with brine, dried ($MgSO_4$) and the solvent removed under vacuum. The remaining black oil was distilled under reduced pressure (1mmHg, 84°C) to give pure 2,2'-bithiophene (56.6 g, 46%) which crystallised in the receiver flask, m.p. 32-33°C (lit.[20] 34°C). Found C, 57.49; H, 3.54%; M(MS,EI) 166 (M^+). Calculated for $C_8H_6S_2$, C, 57.79; H, 3.64 %; M 166.27. ^1H NMR (300MHz, $CDCl_3$) δ 7.04 (dd, J=4.8Hz, J=3.6Hz, 2H), 7.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.71, 124.30, 127.72, 137.34.

2.5.28 5,5'-Bis(tributyltin)-2,2'-bithiophene (27)



N-Butyllithium (1.6 M, 9.8 ml, 15.6 mmol) was added to a solution of 2,2'-bithiophene (1.3 g, 7.8 mmol) in THF (50 ml) at r.t. A grey solid precipitated. After complete addition the suspension was stirred for another 10 min. at r.t. before tributyltin chloride (5.1 g, 15.6 mmol) was quickly added via a syringe. The reaction mixture was stirred over night at r.t. before the solvent was removed under reduced pressure. The oily residue was dissolved in a small amount of methanol and purified by column chromatography (neutral alumina) first with methanol then with DCM. Evaporation of the solvent of the DCM fraction gave the pure 5,5'-bis(tributyltin)-2,2'-bithiophene (2.8 g, 48%) in form of a pale yellow oil. Found C, 51.91; H, 7.86%; M(MS,EI) 742 (M^+), 744 (M^+), 746 (M^+). Calculated for $C_{32}H_{58}S_2Sn_2$, C, 51.64; H, 7.85 %; M 744.36. ^{1}H NMR (300MHz, $CDCl_3$) δ 0.90 (t, J=7.5Hz, 18H), 1.12 (t, J=8.3Hz, 12H), 1.38 (m, 12H), 1.60 (m, 12H), 7.07 (d, J_{HH}=3.6Hz, J_{HSn}=11Hz, 2H), 7.31 (d, J=3.6Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.86 ($^1J_{CSn}$=710Hz), 13.67, 27.27 ($^2J_{CSn}$=118Hz), 28.96 ($^3J_{CSn}$=42Hz), 124.66 (J_{CSn}=70Hz), 136.04 (J_{CSn}=44Hz), 137.35, 143.00.

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3 A General Synthetic Route to Alternating Oligothiophene-PEO-Block-co-Polymers

3.1 Introduction

The cross-coupling route

The results described in chapter 2 showed that the synthesis of a block-copolymer with an alternating sequence of hydrophilic and hydrophobic flexible spacer groups (shown in Figure 2.1.1) could not be achieved by the synthetic routes chosen. To simplify the target polymer synthesis, without giving up the original idea of preparing a processable amphiphilic polymer, we substituted the hydrophobic flexible chain with a hydrophilic one, now having only one type of flexible spacer in the molecule. A polymer of this type (Figure 3.1.1) would still be amphiphilic if the oligothiophene unit was chosen to be sufficiently large.

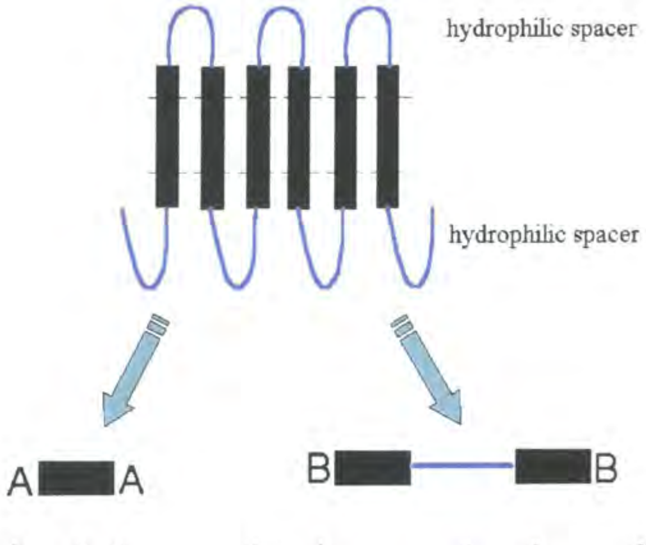


Figure 3.1.1 Second synthetic approach to the preparation of an amphiphilic block co-polymer in which all flexible chains are hydrophilic. Rectangles represent oligothiophene units (e.g. sexithiophene), the bent lines hydrophilic flexible spacer groups.

In Figure 3.1.1 the new synthetic approach is summarised. Instead of cutting the polymer retro-synthetically in the middle to give two oligothiophene terminated monomers (see Figure 2.1.1), it is now cut twice. The resulting monomers would be a short bifunctional oligothiophene derivative (here shown with functionality A), functionalised in a suitable manner to be cross coupled to the second monomer, a dihalogen terminated monomer (here shown with functionality B), which incorporates the flexible spacer group. Using a polymeric spacer like PEO would be advantageous to ensure good solubility of the polymer. Following the approach described in chapter 2 (Figure 2.3.11), it should be possible to react both hydroxyl end-groups of PEO with a suitable oligothiophene derivative to obtain a di-functional macromonomer. This could then be cross-coupled to the short bifunctional oligothiophene derivative (with functionality A) to build up the oligothiophene main chain polymer.

If the rectangles representing the oligothiophenes in the monomers in Figure 3.1.1 were all thiophene derivatives and A and B were to react in a polymerisation reaction, then a terthiophene polymer would be built up in the polymerisation process (T_1+ T_1+T_1 = T_3). If it was possible to synthesise thiophene and bithiophene derivatives for both types of monomers, i.e. the ones with A-functionalities as well as the ones with B-functionalities, then a series of oligothiophene main chain polymers would be easily accessible with oligothiophene blocks ranging in length from terthiophene to sexithiophene.

The precursor route

As an alternative to the route described above a second strategy, leading to the same polymers was developed. In the strategy described above the oligothiophene blocks had to be built up in the polymerisation step and, as blocks longer than quaterthiophene suffer from very poor solubility, this presents problems in making and manipulating functionalised reactive monomers. There is however a well-known route into five-membered heterocyclic aromatic rings using aliphatic 1,4-diketones and subsequently introducing the heteroatom to form the aromatic unit (Figure 3.1.2). In the case of thiophenes the heteroatom has been introduced by Lawesson's reagent, P_2S_5 or H_2S. This chemistry has been well established and is extensively used to prepare thiophene-, furan- and pyrrole derivatives.

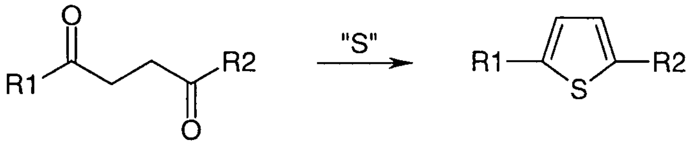


Figure 3.1.2 Preparing substituted thiophenes from 1,4-diketones

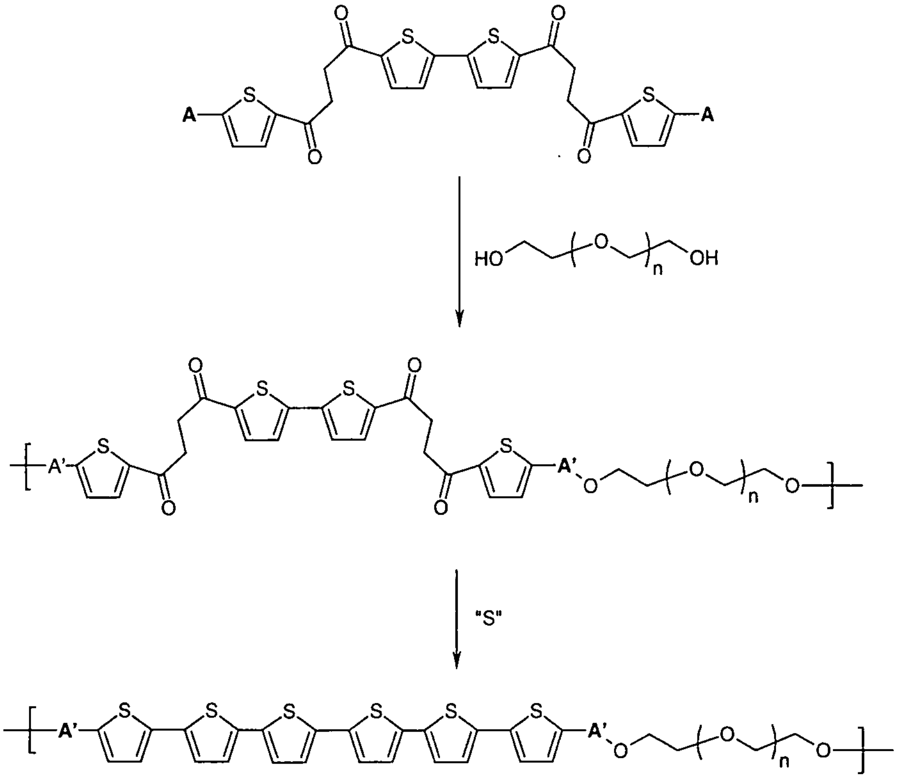


Figure 3.1.3 Scheme, describing a precursor route to oligothiophene main chain polymers.

A functionalised (here a reactive functionality A) sexithiophene precursor is shown in *Figure 3.1.3.* This should have a much higher degree of flexibility than the rigid sexithiophene and can be expected to be much more soluble. Such a sexithiophene precursor with suitable reactive functionalities could undergo step-growth polymerisation with, for example, PEO to give an alternating block-copolymer. In a second reaction the precursor has to be converted into sexithiophene to give the target block co-polymer.

The most used reaction to prepare aryl 1,4-diketones in this context is the Stetter reaction which will therefore be introduced here.

The Mechanism of the Stetter Reaction

The general mechanism of the Stetter reaction[1] is outlined in Figure 3.1.4. An aromatic aldehyde **A** reacts with a cyanide ion to form a cyanohydrin **B**. After proton transfer the more stable species **C** can act as carbon nucleophile and attack the α,β-unsaturated ketone **D** in a Michael addition.

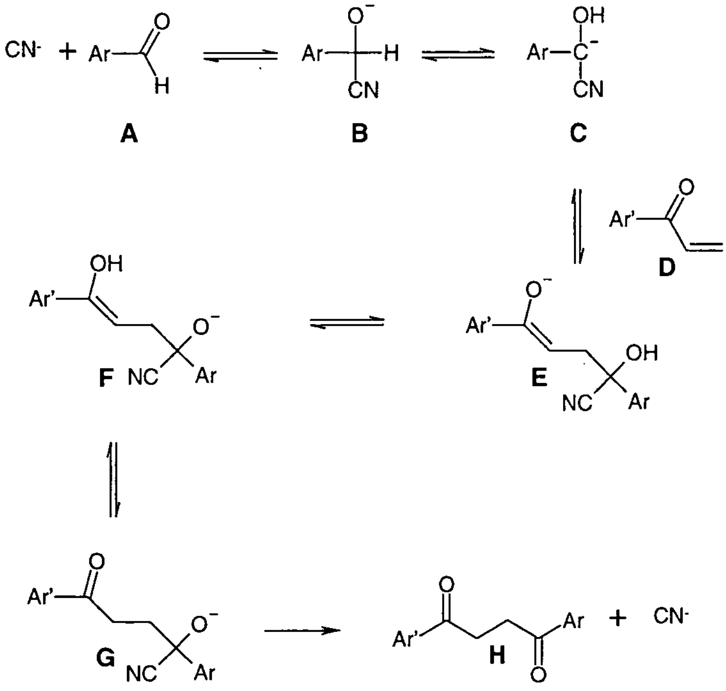


Figure 3.1.4 Mechanism of the Stetter reaction

After proton transfer (**E** to **F**) and tautomerisation of the enol **F** to the more stable keto-form **G** the cyanide ion is eliminated and the 1,4-diketone **H** formed. Species **C** can also attack unreacted **A** to give a benzoin condensation. However, all reaction steps apart from the one leading to the 1,4-diketone are reversible which eventually drives the reaction in the desired direction. Instead of the cyanide ion, ylides, prepared by deprotonation of thiazolium salts, have also been employed in the Stetter reaction but will not be discussed here.

Substituted oligomers of thiophene[2] as well as unsubstituted oligomers like terthiophene[3], quaterthiophene isomers[4] or pentathiophene[5] have been prepared via the Stetter reaction. The work reported in the literature prompted us to investigate the use of this approach for the preparation of sexithiophene precursors for poly-condensations.

3.2 Results and Discussion

To prepare a precursor compound for sexithiophene by the Stetter reaction one has to decide first which of the six thiophene rings to replace by 1,4-diketones. Substitution of rings 2 and 5 seems synthetically feasible. Two reaction pathways are possible which achieve this substitution pattern as outlined in Figure 3.2.1 (reaction path a and b).

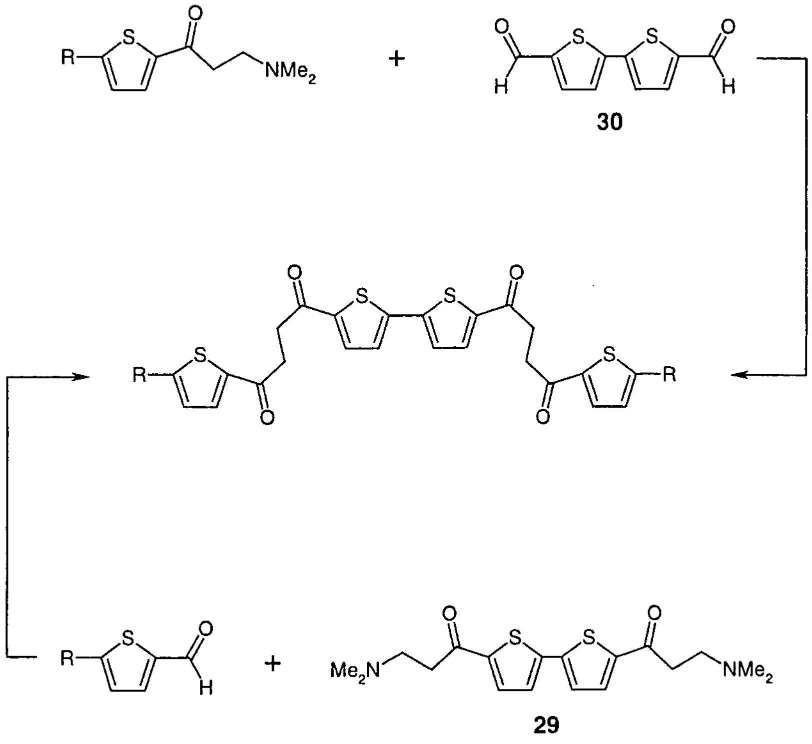


Figure 3.2.1 Two routes to a symmetric sexithiophene precursor in which thiophene rings 2 and 5 have been substituted by 1,4-diketones. Either a) a thiophene Mannich base reacts with bithiophene di-aldehyde or b) a bithiophene di-Mannich base reacts with a thiophene aldehyde to give the sexithiophene precursor.

Using the bithiophene di-aldehyde **30**, a substituted (in this case with group R) thiophene derivative has to be prepared as the Mannich base. If the bithiophene di-Mannich base **29** is employed in the reaction, the R-substituted thiophene aldehyde is required. The group R serves as a functionality to poly-condense the precursor with PEO in the next reaction step.

The two compounds that would form the inner rings of the precursor were prepared as shown in Figure 3.2.2 and Figure 3.2.3.

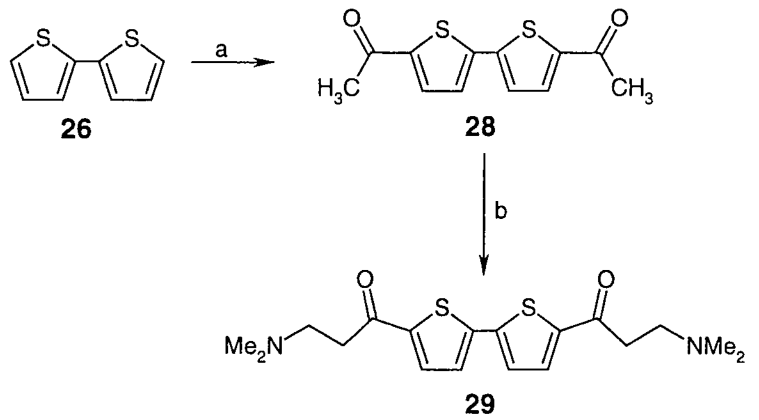


Figure 3.2.2 a) DCM, $AlCl_3$, acetyl chloride b) DMF, dimethylammonium hydrochloride, para formaldehyde, HCl

5,5’-Diacetyl-2,2’-bithiophene **28** was prepared by Friedel-Crafts acylation of 2,2’-bithiophene **26** with acetyl chloride (Figure 3.2.2). In a Mannich reaction this compound was extended by one carbon atom to form the Mannich base 5,5’-bis-(3-dimethylaminopropionyl)-2,2’-bithiophene **29**.

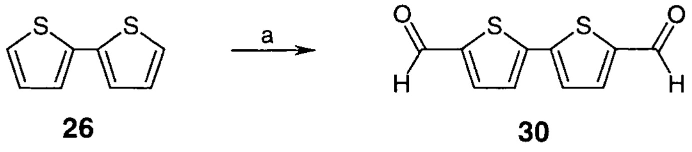


Figure 3.2.3 a) diethylether, 1.n-butyl lithium 2.DMF, 3.HCl

Di-lithiation of 2,2’-bithiophene **26** with n-butyl lithium, followed by addition of DMF and subsequent acidification gave 5,5’-di-formyl-2,2’-bithiophene **30** (Figure 3.2.3).

It has been reported that for an aldehyde to react in a Stetter-reaction with NaCN as catalyst, it must not be substituted with electron donating groups.[6] Electron withdrawing or neutral substituents on the other hand do not seem to affect the reaction. Bearing this in mind, an ester group was chosen as substituent R for the scheme shown in Figure 3.2.1. Being electron withdrawing and providing the possibility for conversion into an acid chloride, it seemed an appropriate substituent to use in this Stetter reaction. Synthesis of a methyl ester was easily accomplished and is outlined in Figure 3.2.4.

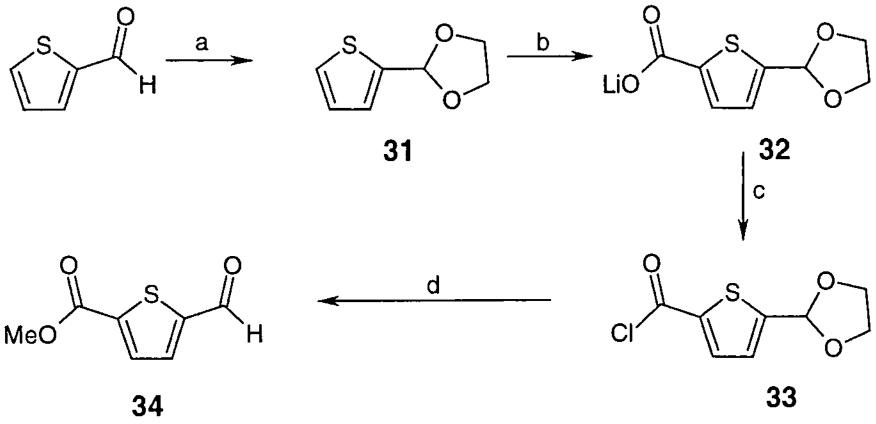


Figure 3.2.4 a)benzene, ethylene glycol, p-toluenesulfonic acid, Dean Stark conditions b) THF, n-butyl lithium, CO_2 c) toluene, $SOCl_2$ d) methanol, H_2SO_4 10%

2-Thiophene carboxaldehyde was protected as a 1,3-dioxolane **31**, then lithiated with n-butyl lithium and reacted with CO_2 to give the carboxylic acid lithium salt **32**. This was converted into an acid chloride **33** by reaction with $SOCl_2$. Interestingly, the cyclic acetal **32** was not converted back to the aldehyde in this step despite the acidic conditions. Esterification in methanol and acidic deprotection gave the desired 5-formyl-thiophene-2-carboxylic acid methyl ester **34**.

Attempts were made to react **34** with 5,5'-bis-(3-dimethylaminopropionyl)-2,2'-bithiophene **29** to form the 1,4-diketone but, despite several attempts, no evidence of reaction was observed by ^{1}H-NMR spectroscopy. It is possible that the ester group has a stabilising effect on the cyanohydrin anion, reducing its nucleophilicity. To break the conjugation between the ester group and the aromatic ring a derivative which would have a methylene group between the ester carbonyl group and the thiophene ring was prepared (Figure 3.2.5).

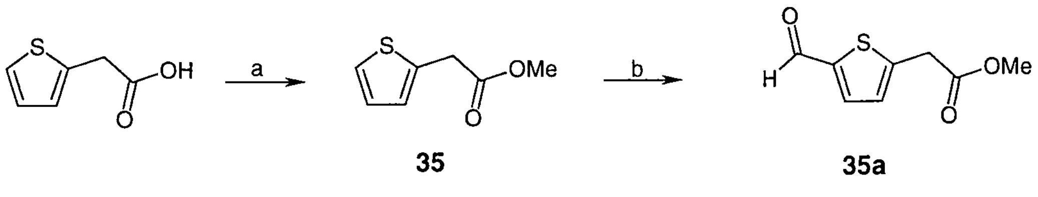


Figure 3.2.5 a) Methanol, H_2SO_4 b) All formylation attempts under Vilsmeier conditions failed.

Although conversion of the acid into the methyl ester **35** was achieved, formylation to give the aldehyde **35a** was not possible under Vilsmeier conditions ($POCl_3$, DMF) despite several attempts.

Commercially available 2-bromo-thiophene-5-carboxaldehyde was also used in an attempted Stetter reaction with 5,5'-bis-(3-dimethylaminopropionyl)-2,2'-bithiophene **29** but again without any observation of product formation (^{1}H-NMR). Figure 3.2.6 gives an overview over all reactions attempted in the pursuit of sexithiophene precursor monomers.

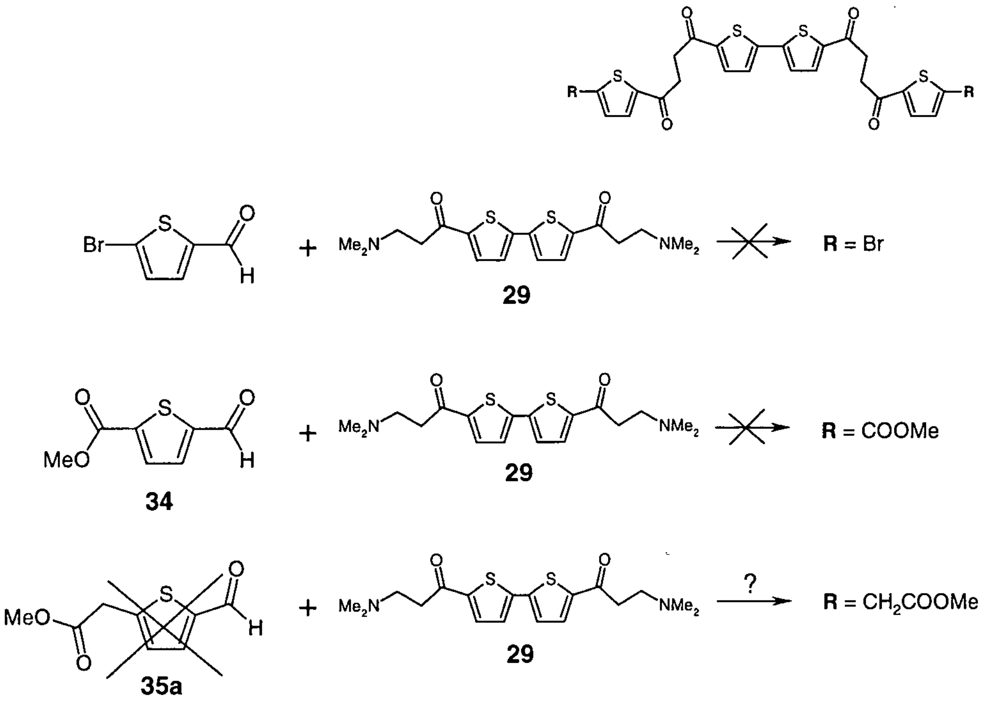


Figure 3.2.6 Overview. Top and middle: two attempted Stetter reactions where no formation of 1,4-diketones was observed. Bottom: The aldehyde compound could not be synthesised.

To investigate the reaction path *b* shown in Figure 3.2.1 two thiophene Mannich bases, **36** and **37,** were prepared (Figure 3.2.7).

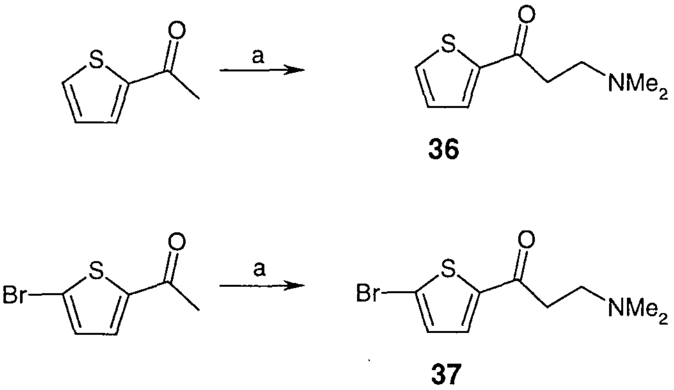


Figure 3.2.7 a) DMF, para formaldehyde, dimethylammonium hydrochloride, HCl

The successful syntheses of the Mannich bases were carried out under the same conditions as already described for compound **29** (Figure 3.2.2). Frustratingly, neither of the attempted syntheses of the sexithiophene precursor was successful as no 1,4-diketone formation could be observed by ^{1}H-NMR spectroscopy. Figure 3.2.8 summarises these two failed reactions.

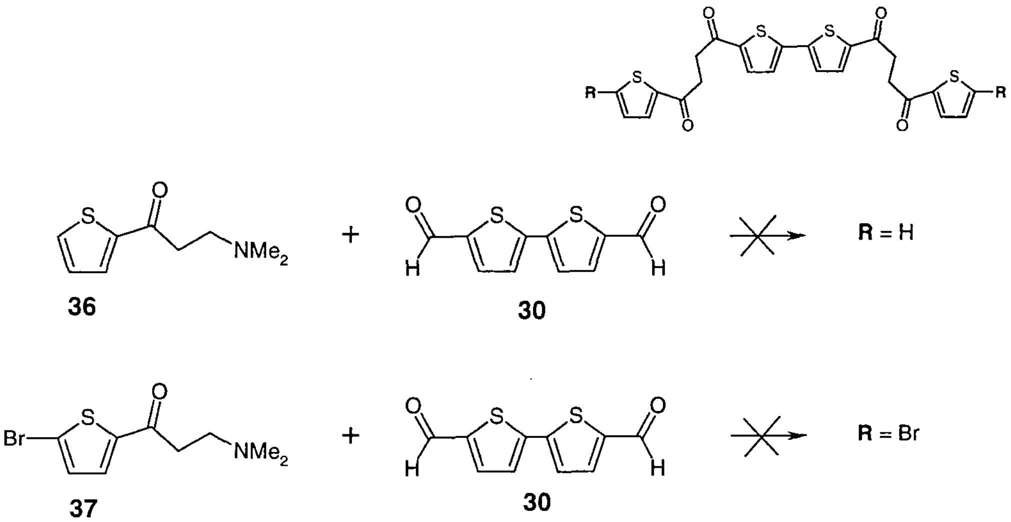


Figure 3.2.8 Two Stetter reaction attempts, where no formation of 1,4-diketones was observed.

Finally, a different approach to the synthesis of a sexithiophene precursor was examined (Figure 3.2.9). For an intial investigation the commercially available 2-bromothiophene was acylated with succinic anhydride to give the keto-acid **38**. An attempt was made to prepare and isolate the acid chloride **38a** but without success.

Attempts to prepare the acid chloride **38a** using oxalyl chloride, followed by in-situ Friedel-Crafts acylation did not give the target sexithiophene precursor.

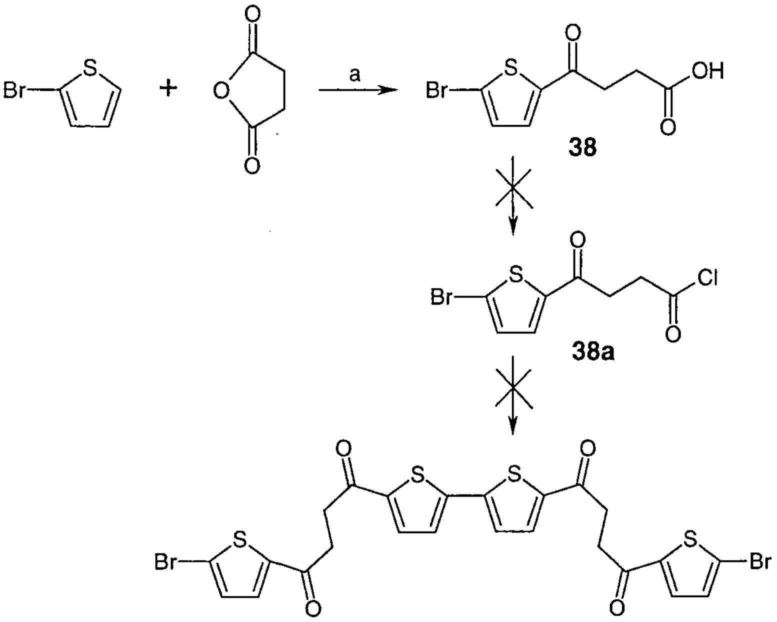


Figure 3.2.9 An attempt to prepare a sexithiophene precursor via a Friedel-Crafts acylation reaction. a) Nitrobenzene, $AlCl_3$

In conclusion, none of the Stetter reactions carried out gave the desired products. Several reactions were carried out in sealed NMR-tubes and were investigated spectroscopically . Very intense dark red colours were observed, probably indicating cyanohydrin formation, but the NMR-spectra did not provide any evidence for product formation. Although all 1,4-diketone syntheses described here were unsuccessful, the general idea, i.e. preparing sexithiophene precursors and polymerising them in a poly-condensation reaction, remains a potentially interesting synthetic approach. Once the synthesis of the precursor has been achieved, this route has the potential to give very high molecular weight and well defined sexithiophene main chain polymers. The Stetter reaction appeared to be a rather "non-general" synthetic procedure for the preparation of these types of precursors.

The other route, described in the introduction as the cross-coupling route, required the preparation of reagents that can react with the terminal hydroxyl groups of PEO to give difunctional macromonomers. In order to be able to polymerise these macromonomer to high molecular weights, the reaction with PEO termini must take place with very high conversion, i.e. all terminal hydroxyl groups of the PEO have to react. Low conversion in the end-capping reaction would result in incompletely functionalised macromonomers and premature termination of the step growth during polymerisation of the macromonomer. A suitable end-capping reagent was prepared and reacted with PEO (Mn=2000) as shown in Figure 3.2.10.

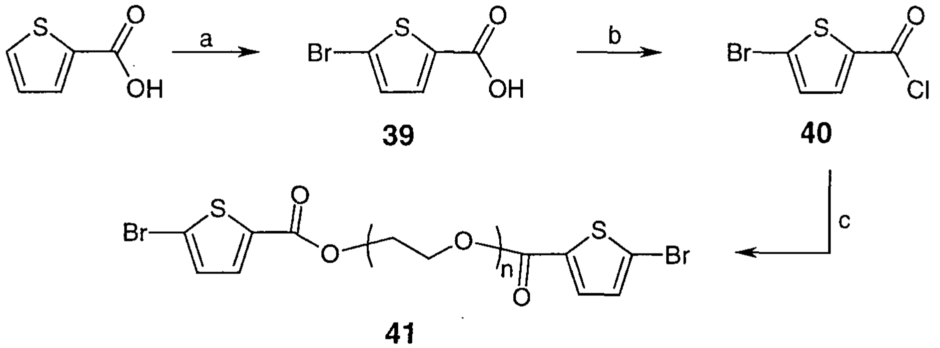


Figure 3.2.10 Successful synthesis of a bis-bromo-thiophene macromonomer. a) AcOH, Br_2, b) $SOCl_2$ c) toluene, pyridine, PEO (Mn=2000)

α-Bromination of 2-thiophene-carboxylic acid and subsequent reaction of the acid **39** with thionyl chloride gave the 2-bromo-thiophene-5-carbonyl chloride **40**. This compound was used as an end-capping reagent for PEO as it provided an aromatic bromide for later cross-coupling and an acid chloride functionality which can form esters with alcohols in a high conversion reaction. The macromonomer **41** was prepared in this way.

A second end-capping reagent, similar to the one described above but containing a bithiophene instead of a thiophene unit was prepared as outlined in Figure 3.2.11.

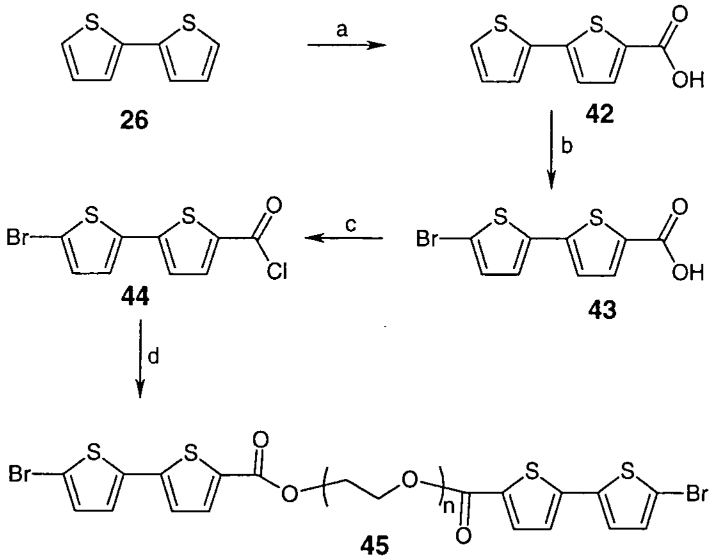
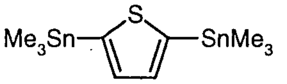


Figure 3.2.11 Successful synthesis of a bis-bromo-bithiophene macromonomer. a) THF, n-butyl lithium, CO_2 b) DMF, NBS c) $SOCl_2$ d) toluene, pyridine, PEO (Mn=2000)

Mono-lithiation of 2,2'-bithiophene **26** was achieved using n-butyl lithium at –78°C. Introduction of CO_2 gas into a solution of the anion gave 2,2'-bithiophene-5-carboxylic acid **42**. Bromination in the 5'-position was carried out using NBS at low temperatures. The 5-bromo-2,2'-bithiophene-5'carboxylic acid **43** obtained was converted into the acid chloride **44** using thionyl chloride. Reaction with PEO (Mn=2000) gave the macromonomer **45**.



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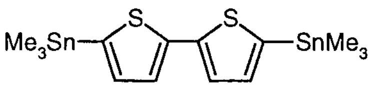


47

*Figure 3.2.12 top: 2,5-bis(trimethyltin)-thiophene **46**, bottom: 5,5'-bis(trimethyltin)-2,2'-bithiophene **47***

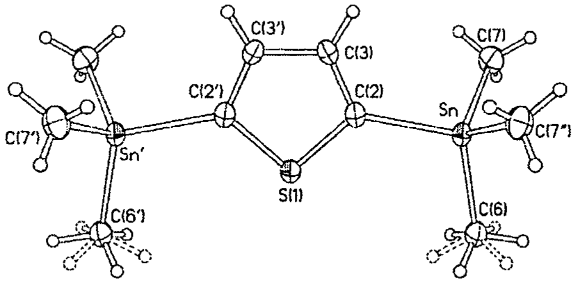


*Figure 3.2.13 Crystal structure of 2,5-bis(trimethyltin)-thiophene **46***

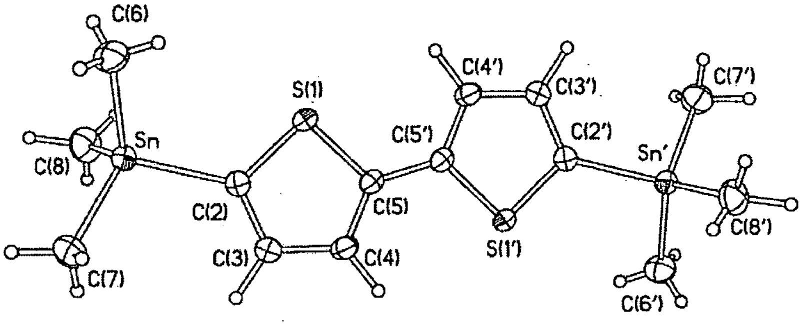


*Figure 3.2.14 Crystal structure of 5,5'-bis(trimethyltin)-2,2'-bithiophene **47***

2,5-Bis(trimethyltin)-thiophene **46** and 5,5'-bis(trimethyltin)-2,2'-bithiophene **47** were chosen as the monomers with organometal functionalities. They could easily be synthesised by di-lithiation and addition of bis(trimethyltin)chloride (see Experimental) and purified by recrystallisation (see Figure 3.2.13 and Figure 3.2.14). By polymerising the macromonomers **41** and **45** with either of the thiophene-tin derivatives **46** and **47** in a Stille cross-coupling reaction four different types of oligothiophene main chain polymers could be prepared (Figure 3.2.15).

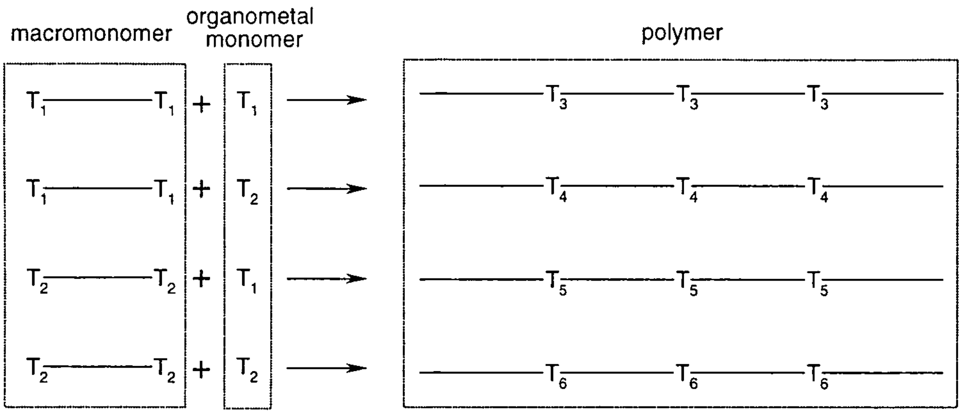


Figure 3.2.15 Four different combinations of monomers gave four different types of polymers. T_1=thiophene derivative, T_2=2,2'-bithiophene derivative

For polymerisation, the thiophene-tin derivative and the catalyst tetrakis(triphenyl phosphine) palladium(0) were dissolved in the macromonomer melt. This ensured the highest possible monomer concentration as is desirable for polycondensations. The approach was limited to polymers with oligothiophene blocks ranging from ter- to sexithiophene. An analogue bithiophene polymer was prepared via a different route, which is shown in Figure 3.2.16.

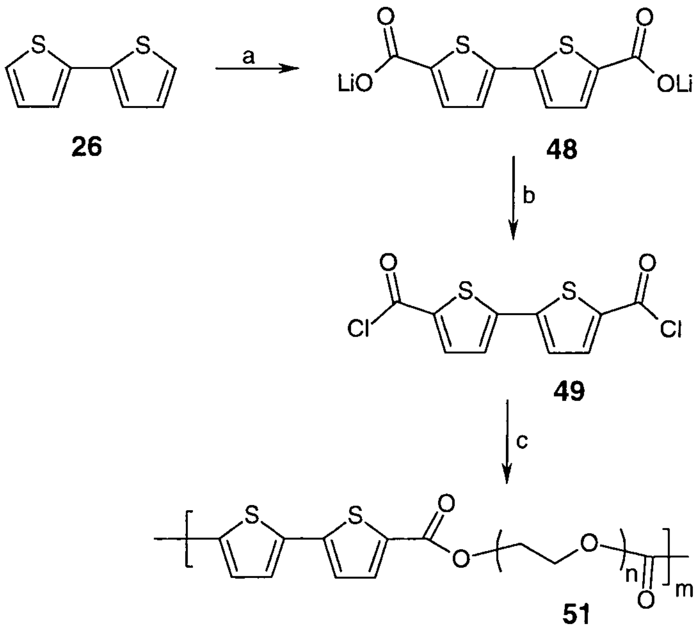
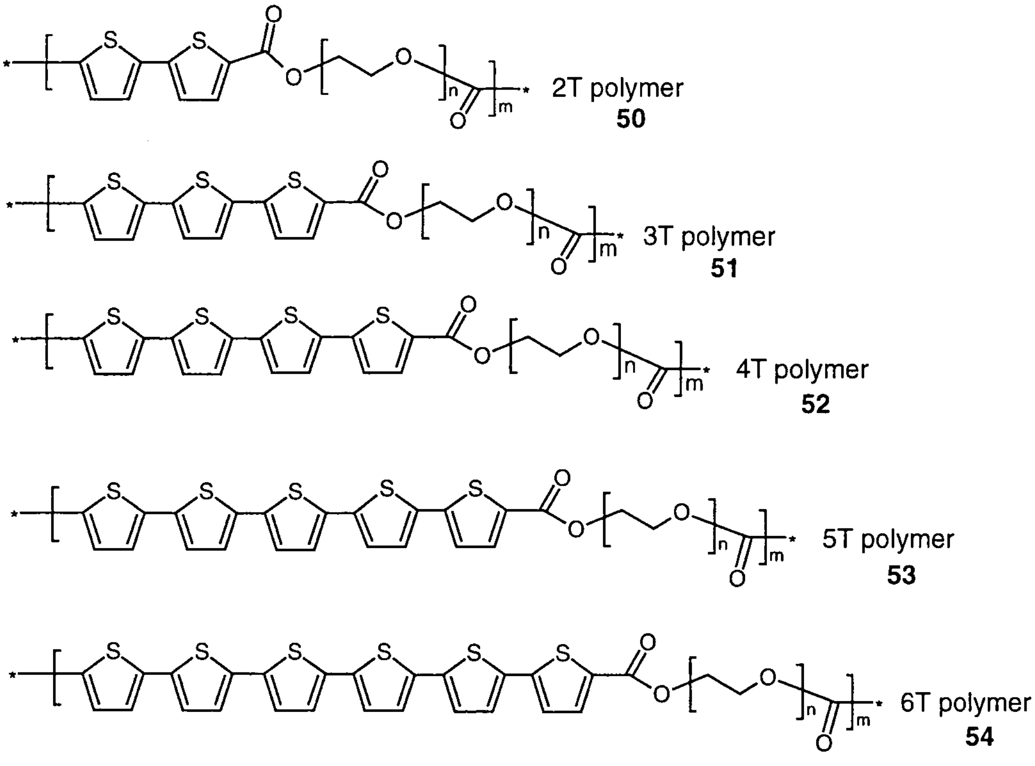


Figure 3.2.16 Synthesis of the bithiophene polymer. a) THF, n-butyl lithium, CO_2 b) $SOCl_2$ c) PEO (Mn=2000)

2,2'-Bithiophene **26** was di-lithiated in the α-positions and reacted with CO_2 gas to give the di-lithium carboxylate **48**. This was converted into a di-acid chloride **49** by reaction with thionyl chloride. Melt polymerisation with PEO (Mn=2000) gave the bithiophene polyester **50**.

The structures of all polymers prepared are shown in Figure 3.2.17.


2T polymer **50**

3T polymer **51**

4T polymer **52**

5T polymer **53**

6T polymer **54**

Figure 3.2.17 Structures of all polymers prepared.

All these polymers, except for the bithiophene polymer, were fractionated by dissolving the bulk sample in chloroform and slowly adding hexane until the onset of precipitation could be observed. Upon standing to allow equilibration a higher molecular weight fraction of the polymer phase separated from the rest of the solution in form of an oil. Both fractions were collected and analysed by gpc. The results of this procedure are recorded in Table 3.2.1.

	low molecular weight fraction		*high molecular weight fraction*	
compound	***Mn***	***Mw***	***Mn***	***Mw***
2T polymer **50**	13500	21100	-	-
3T polymer **51**	3710	9740	14360	21780
4T polymer **52**	11464	16600	14500	20700
5T polymer **53**	8150	10900	9300	16900
6T polymer **54**	12200	17400	13300	19000

Table 3.2.1 Molecular weights determined by gpc (for details see section 2.5.1, page 39) for the fractionated polymers.

All materials except for the bithiophene polymer are strongly coloured and highly fluorescent under UV light (Table 3.2.2).

compound	***colour***	***UV/Vis λ_{max}/nm (chloroform)***
2T polymer **50**	colourless	350
3T polymer **51**	yellow	391
4T polymer **52**	light orange	418
5T polymer **53**	dark orange	436
6T polymer **54**	red	450

Table 3.2.2 Colour and UV/Vis absorption maximum of all polymers.

All these polymers showed very good solubility in various organic solvents like chloroform, DCM, THF and aromatic solvents. Also, dilute solutions in THF or dioxane could be diluted with water without precipitation.

Pure PEO even of high molecular weight is a very brittle semi-crystalline material. Films made of PEO do not show any significant mechanical strength and break easily under mechanical stress. By contrast, the above polymers, although mainly consisting of PEO, exhibit quite a different behaviour. Films, prepared from the melt for X-ray diffraction analysis (see chapter 5) showed markedly different mechanical properties from those prepared from pure PEO. From the bithiophene polymer **50** to the sexithiophene polymer **54** a strong increase in mechanical strength can be observed. While the bithiophene polymer **50** exhibits a behaviour similar to pure PEO, the sexithiophene polymer **54** behaves like a cross-linked rubber. This behaviour can be explained by assuming aggregation of the oligothiophenes within the polymer. The aggregation strength is likely to be lower for shorter and higher for longer oligothiophenes leading to physically cross-linked polymers with the sexithiophene polymer **54** displaying the largest effect.

All polymers were analysed by NMR spectroscopy. The aromatic regions of the ^{1}H-NMR-spectra are shown in Figure 3.2.18. The spectra shown were recorded from chloroform solutions of the higher molecular weight fractions of the polymers. The coupling patterns of the symmetrically substituted oligothiophenes can easily be recognised. End-group analysis based on the NMR results could not be performed on any of the polymers as no signals were observed that could be assigned unambiguously to an unreacted macromonomer end-group.

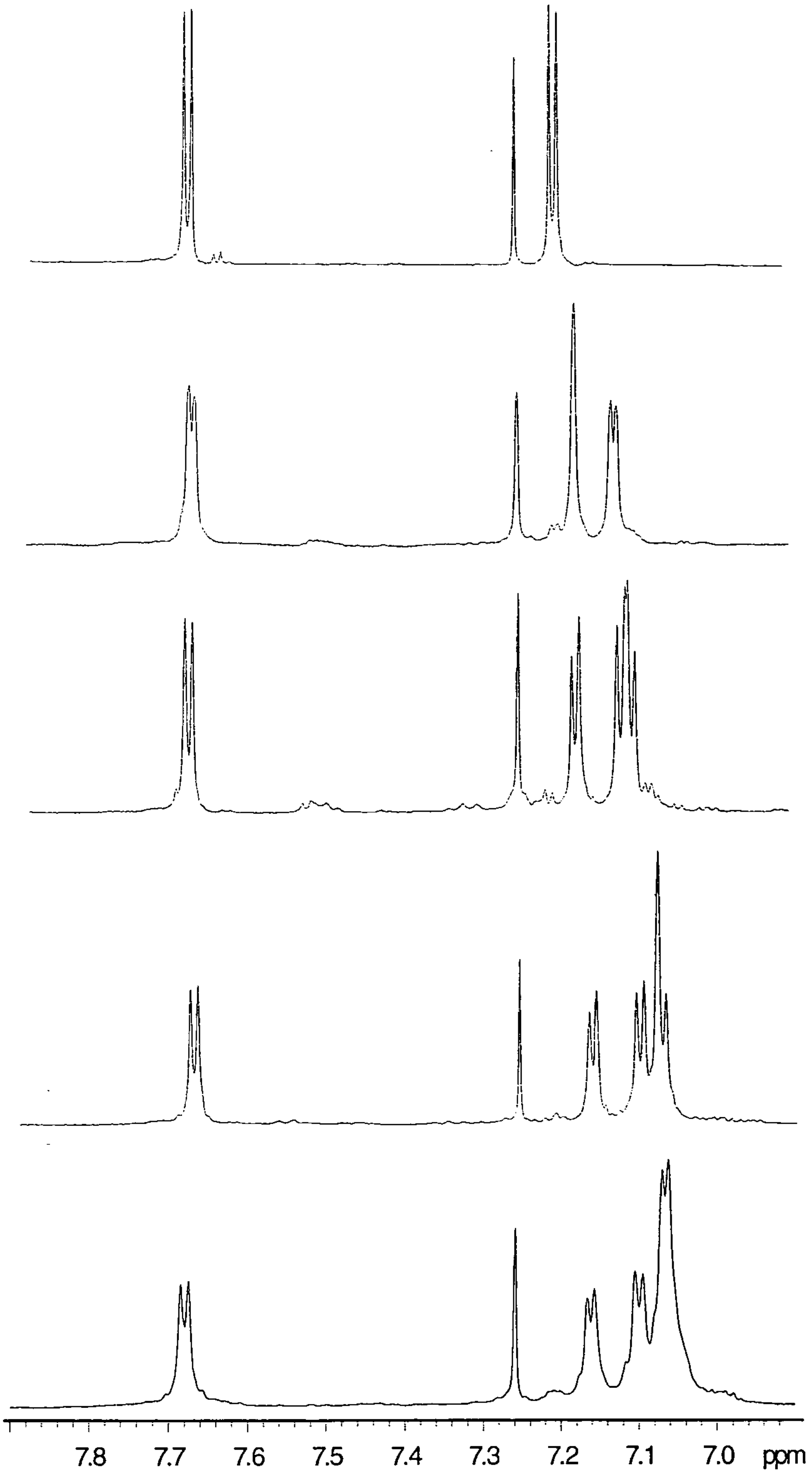
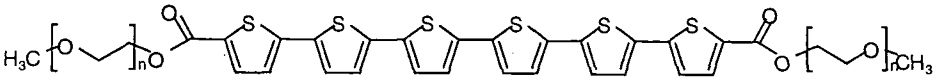


*Figure 3.2.18 ^{1}H-NMR spectra (300MHz, CDCl$_3$) of the aromatic region of all prepared polymers. From top to bottom: 2T polymer **50**, 3T polymer **51**, 4T polymer **52**, 5T polymer **53**, 6T polymer **54***

All of these polymers show excellent solubility in many organic solvents (see above). As unsubstituted α-oligothiophenes larger than the tetramer show low solubility in any organic solvent, the original idea of introducing PEO for solubilisation proved to be successful. To determine the PEO chain length dependence of the solubility two model compounds for the sexithiophene polymer were synthesised. End-capping two commercially available poly(ethylene oxide) mono methyl ethers of different molecular weights (M=350 and Mn=750) gave the corresponding esters **55** and **56** respectively (see Experimental section). The model compounds **57** and **58** (Figure 3.2.19) were prepared by Stille cross-coupling of the esters **55** and **56** with 5,5'-bis(trimethyltin)-2,2'-bithiophene **47**.



n = 8 **6T PEO 350 (57)**
n = 17 **6T PEO 750 (58)**

*Figure 3.2.19 Two model compounds **57** and **58** for the sexithiophene polymer 6T polymer **54***

Purification of these compounds was possible by chromatography on silica. Much to our surprise compound *6T PEO 750* **58** exhibits very good solubility in various polar and non-polar organic solvents (for example toluene and methanol) and also in water!

The compound was characterised by NMR-spectroscopy and LD-TOF mass spectroscopy (*Figure 3.2.20*).

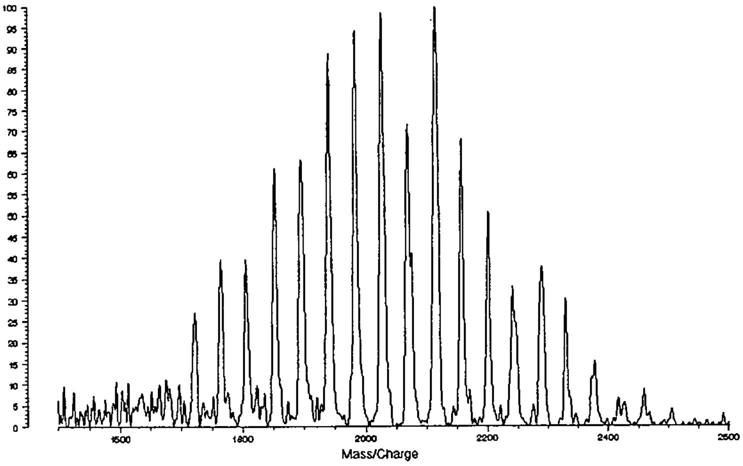
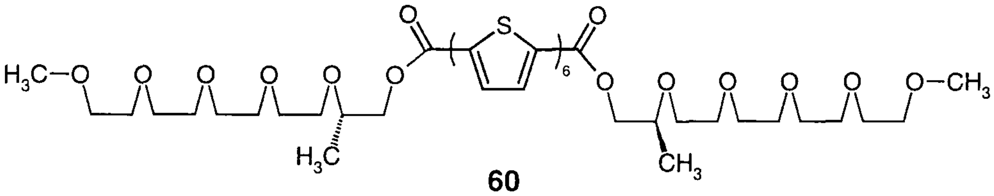


Figure 3.2.20 LD-TOF mass spectrum of ***6T PEO 750*** *(58)*

The analogous polymer *6T polymer* **54** with an even longer PEO chain length only dissolves in water when diluted from organic solutions like THF or dioxane. Model compound *6T PEO 350* **57** was also very soluble in polar and non-polar organic solvents but not soluble in water to the same extent as *6T PEO 750* **58**. Quantitative solubility measurements were not carried out due to the small amount of pure sample obtained after chromatography. Although the chain length was significantly reduced in either of the two model compounds, the solubility limit had not yet been reached. Encouraged by this promising result a collaboration with the group of E.W.Meijer in Eindhoven was initiated as they had previously been able to observe aggregation by chiroptical studies of polythiophenes substituted with short chiral methyl-substituted pentaethylene oxide chains. We were curious to investigate whether a pentaethylene oxide chain would still be long enough to ensure the solubility of sexithiophene. Also, we believed that, as previously observed for the oligothiophene polymers (esp. *6T polymer* **54**), aggregation occurred in these model systems as well. Once supplied with the chiral methyl-substituted pentaethylene oxide, (2*S*)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)propan-1-ol, end-capping with **44** produced the ester **59**. This could be cross coupled with **47** to give the substituted sexithiophene derivative **60** (Figure 3.2.21).



60

*Figure 3.2.21 A chiral sexithiophene derivative **60** synthesised for chiroptical studies.*

Purification by chromatography on silica was not possible for this compound but a very pure fraction could be obtained by chromatography on porous cross-linked polystyrene (BioRad, BioBeads SX-1). The compound gave a single peak on gpc analysis using a UV-detector (λ=254nm). MALDI-TOF mass spectroscopy showed the expected molecular ions formed by addition of a proton, a sodium and a potassium cation (Figure 3.2.22).

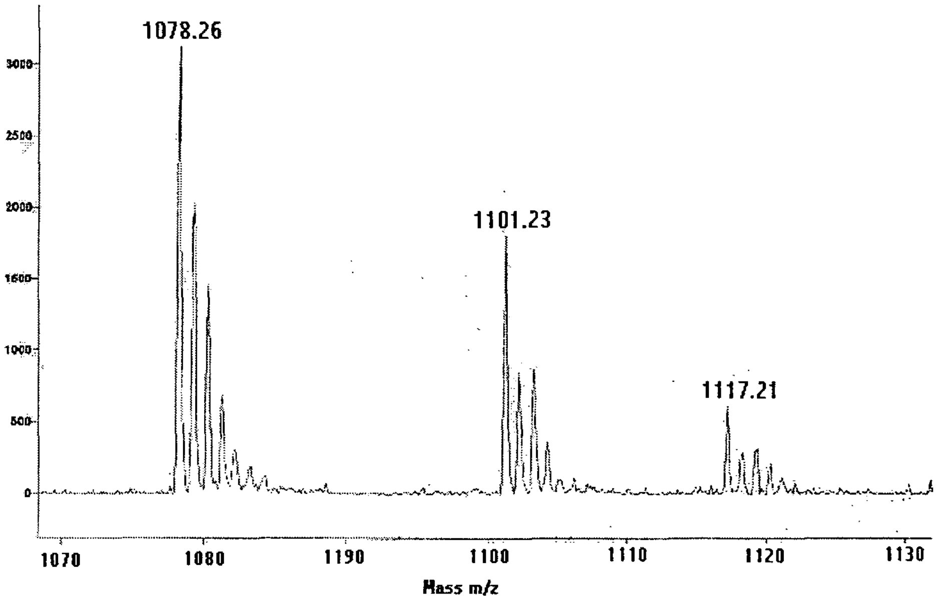


*Figure 3.2.22 MALDI-TOF mass-spectrum of 6T chiral **60** (α-hydroxy-4-hydroxy-cinnamic acid matrix). The mole peak and also the sodium and potassium ion adduct can be seen.*

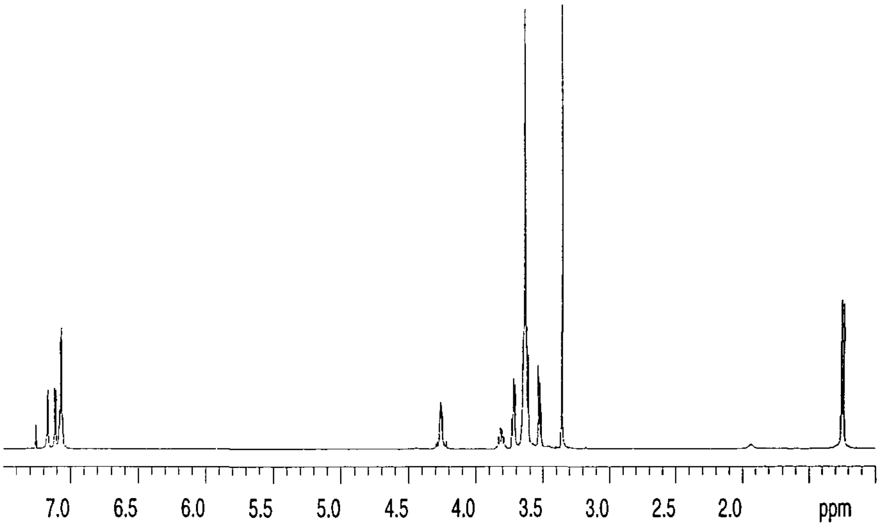


Figure 3.2.23 ^{1}*H-NMR of 6T chiral* ***60*** *(400MHz, CDCl$_3$)*

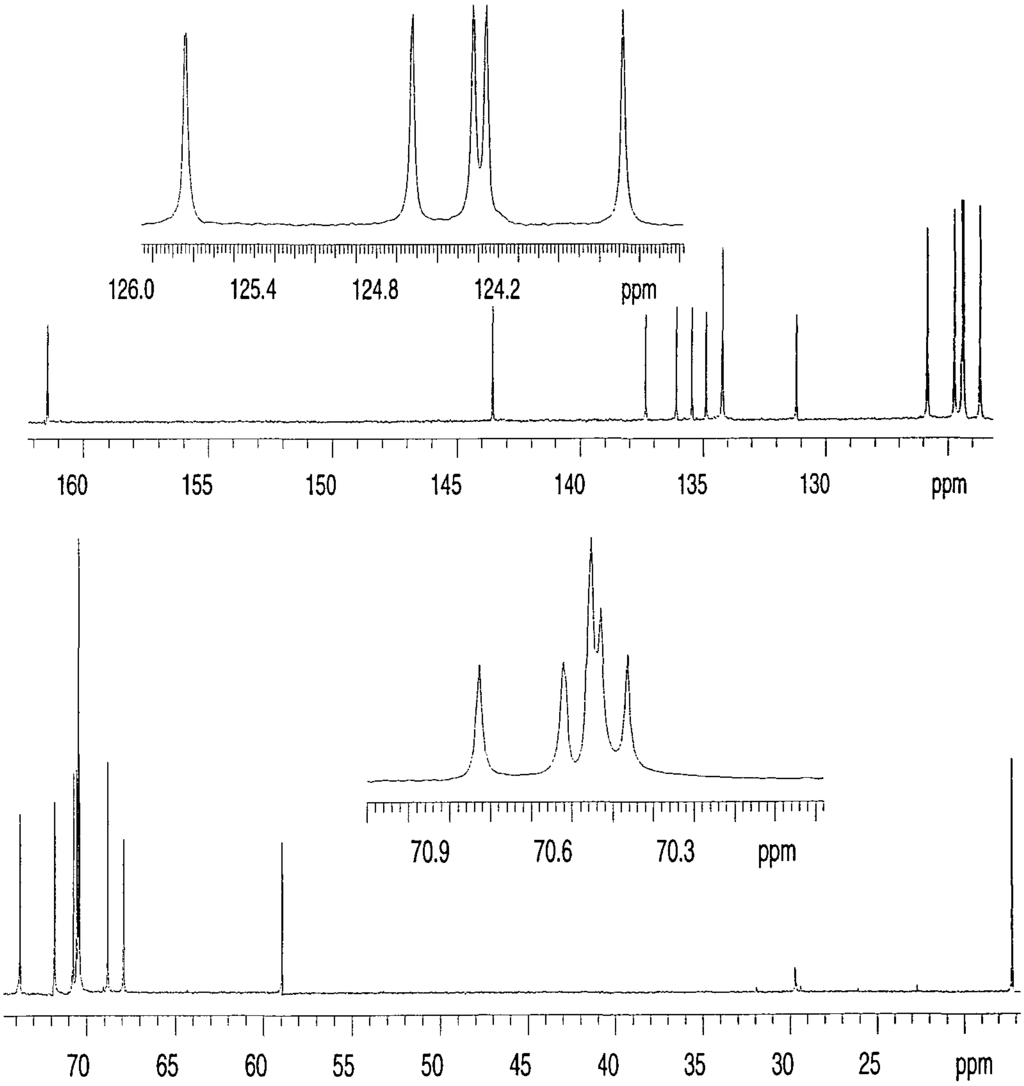


Figure 3.2.24 ^{13}*C-NMR of 6T chiral* ***60*** *(400MHz, CDCl$_3$)*

The compound was very soluble in chloroform or DCM. High resolution NMR spectra of the material are shown in Figure 3.2.23 and Figure 3.2.24.

Even dilution of a THF solution with water did not result in precipitation. Chiroptical measurements on this compound will be described in chapter 5.

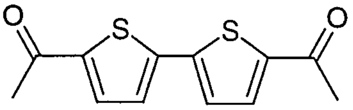
3.3 Conclusion

A synthetic procedure was developed with which it was possible to prepare alternating oligothiophene PEO block co-polymers with a PEO block length of 45 repeat units and an oligothiophene block length ranging from bithiophene to sexithiophene. These polymers showed very good processability, i.e. they were soluble in a variety of organic solvents at room temperature. To the best of our knowledge there are no other examples of exclusively α-substituted sexithiophenes or sexithiophene polymers in the literature that show as high solubility as the materials prepared here. Model compounds for the alternating sexithiophene-PEO block co-polymer have been prepared. In these, PEO mono methyl ethers of varying PEO lengths have been attached to the sexithiophene unit via the α-positions. It was shown that the chain length could be reduced significantly without loss of solubility.

A sexithiophene derivative with enantiomerically pure chiral methyl-pentaethylene oxide side chains was synthesised and fully characterised. Despite the short side-chains the solubility was very high in common organic solvents. Chiroptical studies of the aggregation behaviour of this compound will be discussed in chapter 5.

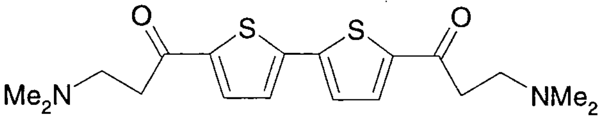
3.4 Experimental

3.4.1 5,5'-Diacetyl-2,2'-bithiophene (28)[7]



Aluminium trichloride (8.02g, 48 mmol) was added slowly in small portions to a solution of 2,2'-bithiophene (4g, 24 mmol) and acetyl chloride (4g, 50.9 mmol) in DCM (50 ml). An exothermic reaction occurred and the reaction mixture turned dark green. After complete addition the mixture was refluxed for 12h, washed with water (2x 20 ml) and dried ($MgSO_4$). Evaporation of the solvent gave 5,5'-di-acetyl-2,2'-bithiophene (3g, 50%) as a light brown solid, m.p. 231-233°C °C (lit.[8] 221-225°C). Found C, 56.02; H, 3.80%; M(MS,EI) 250 (M^+), 235 (M^+-CH_3). Calculated for $C_{12}H_{10}O_2S_2$, C, 57.57; H, 4.03 %; M 250.34. ^1H NMR (300MHz, $CDCl_3$) δ 2.56 (s, 6H), 7.28 (d, J=3.8Hz, 2H), 7.60 (d, J=3.8Hz, 2H). Due to low solubility no ^{13}C-NMR spectrum was recorded, despite the poor elemental analysis this material was pure enough for the next step.

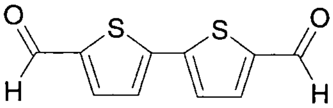
3.4.2 5,5'-Bis-(3-dimethylaminopropionyl)-2,2'-bithiophene (29)



HCl (conc., 0.3 ml) was added to a solution of 5,5'-diacetyl-2,2'-bithiophene (1.6g, 6.4 mmol), dimethylammonium hydrochloride (1.05g, 12.8 mmol) and paraformaldehyde (385 mg) in DMF (150 ml). The reaction mixture was heated to 90°C. After a few minutes a pale yellow solid started to precipitate. After stirring for 6h at 90°C the mixture was allowed to cool to r.t. The solid was recovered by filtration and washed with acetone to give pure 5,5'-bis-(3-dimethylaminopropionyl)-2,2'-bithiophene (970 mg, 40%). The free Mannich base was obtained by dissolving the salt in aqueous ammonia and extraction with DCM. The organic layer was washed with brine, dried ($MgSO_4$) and the solvent removed under reduced pressure.

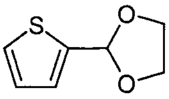
As the NMR spectra recorded for the material were in good agreement with those reported in the literature[7] no further analyses were carried out. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.25 (s, 12H), 2.72 (t, J=7.2Hz, 4H), 3.03 (t, J=6.9Hz, 4H), 7.26 (d, J=3.9Hz, 2H), 7.61 (d, J=3.9Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.33, 45.37, 54.42, 125.87, 132.51, 143.76, 143.92, 191.56.

3.4.3 5,5'-Di-formyl-2,2'-bithiophene (30)



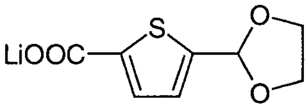
N-Butyllithium (1.6M, 24.2 ml, 38.7 mmol) was added dropwise to a cooled (-5°C) solution of 2,2'-bithiophene (3,22 g, 19.4 mmol) in diethylether (70 ml). After complete addition the solution was warmed to r.t. and refluxed for 1h. The mixture was cooled to -25°C before DMF (3.25 g, 44 mmol) was added quickly via a syringe. The mixture was stirred at -25°C for 1h, then allowed to warm to r.t. and stirred over night. The reaction mixture was poured into a mixture of HCl (conc., 150 ml) and ice-water (300 ml) and stirred for 1h. The precipitate was recovered by filtration, washed with aqueous $NaHCO_3$ and water, dried under vacuum and recrystallised from acetone to give 5,5'-di-formyl-2,2'-bithiophene (2 g, 23%) in form of a brown solid, m.p182-184°C (lit.[9] 185-195°C). Found C, 52.95; H, 2.59%; M(MS,EI) 222 (M^+). Calculated for $C_{18}H_{16}PBr$, C, 54.03; H, 2.72%; M 222.29. ^{1}H NMR (400MHz, DMSO-d_6) δ 7.67 (d, J=4.0Hz, 2H), 7.97 (d, J=4.0Hz, 2H), 9.92 (s, 2H). Due to low solubility no ^{13}C-NMR spectrum was recorded, despite the poor elemental analysis this material was used in the next step.

3.4.4 2-(Thiophene-2-yl)-1,3-dioxolane (31)



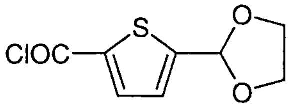
Thiophene carboxaldehyde (15.02g. 0.134 mol), toluenesulfonic acid mono hydrate (1.0g, 5 mmol) and ethylene glycol (8.3g, 0.134 mol) were dissolved in benzene (100 ml) and refluxed under Dean-Stark conditions over night. The reaction mixture was washed with aqueous Na_2CO_3 solution and extracted with diethylether. The organic layer was dried ($MgSO_4$) and shaken with a small amount of charcoal. The charcoal was removed by filtration and the solvent evaporated under reduced pressure to give 2-(thiophene-2-yl)-1,3-dioxolane (19.4 g, 93%) as a red-brown liquid which was used without further purification in the next reaction step. ^1H NMR (300MHz, $CDCl_3$) δ 3.9-4.2 (m, 4H), 6.12 (s, 1H), 7.00 (dd, J=3.4Hz, 1H), 7.19 (d, J=4.5Hz, 1H), 7.35 (d, J=4.5Hz, J=1.1Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.09, 100.11, 126.15, 126.24, 126.53, 141.58.

3.4.5 2-(Thiophene-5-lithium carboxylate-2-yl)-1,3-dioxolane (32)



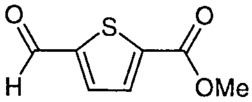
N-Butyllithium (1.6M, 34.1 ml, 54.5 mmol) was added dropwise to a solution of 2-(thiophene-2-yl)-1,3-dioxolane (8.46 g, 54.5 mmol) in THF (40 ml) at -60°C. After stirring the reaction mixture for 15 min. at -60°C CO_2 gas was introduced for 1.5h under vigorous stirring and cooling (-60°C). THF was removed under reduced pressure, the remaining solid stirred in hexane for 2d, recovered by filtration, washed with hexane and dried under vacuum to give 2-(thiophene-5-lithium carboxylate-2-yl)-1,3-dioxolane (11.1g, 98%) which was used directly in the next reaction step without further purification. No analysis of the material was carried out at this stage of the reaction sequence.

3.4.6 2-(Thiophene-5-carbonyl chloride-2-yl)-1,3-dioxolane (33)



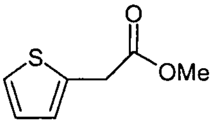
$SOCl_2$ (20 ml) was added slowly to a suspension of 2-(thiophene-5-lithium carboxylate-2-yl)-1,3-dioxolane (2g, 9.7 mmol) in toluene (10 ml). After refluxing the mixture for 2h $SOCl_2$ and toluene were removed under reduced pressure and the residue distilled under vacuum (109°C, 1mmHg) to give *2-(thiophene-5-carbonyl* *chloride-2-yl)-1,3-dioxolane* (1.1g, 52%) as a yellow oil which was directly used in the next reaction step. ^{1}H NMR (300MHz, $CDCl_3$) δ 4.00-4.10 (m, 4H), 6.09 (s, 1H), 7.18 (d, J=4.2Hz, 1H), 7.85 (d, J=4.2Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.36, 99.23, 126.71, 136.84, 137.70, 155.11, 159.67.

3.4.7 5-Formyl-thiophene-2-carboxylic acid methyl ester (34)



A solution of 2-(thiophene-5-carbonyl chloride-2-yl)-1,3-dioxolane (1.1 g, 5 mmol) and glacial acetic acid (1 ml) in dry methanol (10 ml) was stirred at r.t. for 20h. (A crude sample taken at this stage showed that the methyl ester and the di-methyl acetal had been formed.) The solvent was removed under vacuum and H_2SO_4 (10%w/w, 100 ml) added to the residue. The mixture was stirred at r.t. over night and extracted with diethylether (3x 50 ml). The combined organic extracts were washed with aqueous $NaHCO_3$, dried ($MgSO_4$) and the solvent removed under reduced pressure to give 5-formyl-thiophene-2-carboxylic acid methyl ester as a light brown solid (0.5 g, 58%), m.p. 83°C °C (lit[10] 88-89°C). Found C, 48.96; H, 3.54 %; M(MS,EI) 170 (M^+). Calculated for $C_7H_6O_3S$, C, 49.40; H, 3.55%; M 170.19. ^{1}H NMR (300MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.72 (d, J=3.9Hz, 1H), 7.81 (d, J=3.9Hz, 1H), 9.96 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.75, 133.31, 135.06, 140.85, 147.67, 161.87, 183.29.

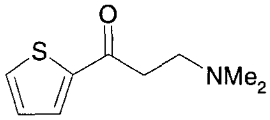
3.4.8 2-Thiophene acetic acid methyl ester (35)



A solution of thiophene acetic acid (10 g, 70.3 mmol) and H_2SO_4 (conc., 1.4 g, 14.1 mmol) in dry methanol (100 ml) was refluxed for 5h. The mixture was allowed to cool to r.t., then poured into aqueous NaOH and extracted with diethylether (3x 30 ml). The solvent was dried ($MgSO_4$) and removed under reduced pressure to give 2-

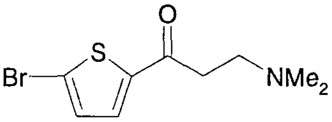
thiophene acetic acid methyl ester (8.8 g, 80%) as an oily liquid. As the NMR spectra recorded for the material were in good agreement with those reported in the literature[11] no further analyses were carried out. ^{1}H NMR (300MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.85 (s, 2H), 6.93-6.98 (m, 2H), 7.22 (dd, J=6.6Hz, J=4.8Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.08, 52.15, 124.94, 126.71, 126.74, 134.87, 170.79.

3.4.9 5-(3-Dimethylaminopropionyl)-thiophene (36)



HCl (conc., 80 drops) was added to a solution of 2-acetyl-thiophene (50 g, 0.4 mol), dimethylammonium hydrochloride (32.3 g, 0.4 mol) and paraformaldehyde (11.9 g, 0.4 mol) in DMF (250 ml). The reaction mixture was heated to 80°C. After a few minutes a solid started to precipitate. After 12h of stirring at 80°C the mixture was allowed to cool to r.t. The solid was recovered by filtration and washed with acetone to give 5-(3-dimethylaminopropionyl)-thiophene (64.4 g, 73%) m.p. 185°C (lit.[12] 179-180°C). Found C, 49.20; H, 6.41; N, 6.36%; M(MS,EI) 183 (M^+-HCl). Calculated for $C_9H_{14}ClNOS$, C, 49.20; H, 6.42; N, 6.37%; M 219.74. The free Mannich base was obtained by dissolving the salt in aqueous ammonia and extraction with DCM. The organic extracts were washed with brine, dried ($MgSO_4$) and the solvent removed under reduced pressure. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.04 (s, 6H), 2.52 (t, J=7.5Hz, 2H), 2.85 (t, J=7.5Hz, 2H), 6.89 (dd, J=4,8Hz, J=3.9Hz, 1H), 7.41 (dd, J=4.8Hz, J=1.2Hz, 1H), 7.51 (dd, J=3.9Hz, J=1.2Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.99, 44.85, 53.96, 127.59, 131.37, 133.11, 143.74, 191.24.

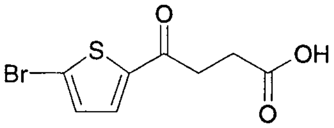
3.4.10 2-Bromo-5-(3-dimethylaminopropionyl)-thiophene (37)



HCl (conc., 10 drops) was added to a solution of 5-acetyl-2-bromo-thiophene (10 g, 49 mmol), dimethylammonium hydrochloride (4 g, 49 mmol) and paraformaldehyde

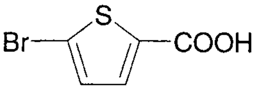
(1.47 g, 49 mmol) in DMF (34 ml). The reaction mixture was heated to 80°C. After a few minutes a solid started to precipitate. After 12h of stirring at 80°C the mixture was allowed to cool to r.t. The solid was recovered by filtration and washed with acetone to give pure *2-bromo-5-(3-dimethylaminopropionyl)-thiophene* (8.7 g, 59%), m.p. 186-187°C. Found C, 36.22; H, 4.40; N, 4.75%; M(MS,EI) 261 (M^+-HCl [^{79}Br]), 263 (M^+-HCl [^{81}Br]). $C_9H_{13}BrClNOS$ requires: C, 36.20; H, 4.39; N, 4.69%; M 298.63. The free Mannich base was obtained by dissolving the salt in aqueous ammonia and extraction with DCM. The organic extracts were washed with brine, dried ($MgSO_4$) and the solvent removed under reduced pressure. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.26 (s, 6H), 2.72 (t, 2H), 2.99 (t, 2H), 7.09 (d, 1H), 7.45 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.02, 45.42, 54.37, 122.68, 131.19, 131.91, 145.69, 190.89.

3.4.11 4-(5-Bromothiophene-2-yl)-4-oxo-butyric acid (38)



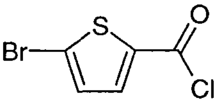
Succinic anhydride (6.14 g, 61.3 mmol) was dissolved in nitrobenzene (60 ml) and the solution cooled to 0°C. Powdered $AlCl_3$ (18 g, 134.9 mmol) was slowly dissolved in the reaction mixture followed by the dropwise addition of a solution of 2-bromothiophene (10 g, 61.3 mmol) in nitrobenzene (30 ml) over a period of 1/2h. The mixture was stirred for another 1/2h at 0°C and then at r.t. for 5h before it was poured into a HCl acidic ice/water mixture. The aqueous mixture was extracted with DCM (3x 50 ml) and the combined organic extracts extracted with strong aqueous base (NaOH). The aqueous phase was acidified and the white precipitate recovered by filtration, washed with water and dried under vacuum to give 4-(5-bromothiophene-2-yl)-4-oxo-butyric acid as a white solid (9.6 g, 59%), m.p. 140°C (lit.[13] 142°C). Found C, 36.47; H, 2.60%; M(MS,EI) 262 (M^+ [^{79}Br]), 264 (M^+ [^{81}Br]). Calculated for $C_8H_7BrO_3S$, C, 36.52; H, 2.68%; M 263.11. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.79 (t, J=6.3Hz, 2H), 3.17 (t, J=6.3Hz, 2H), 7.15 (d, J=4.2Hz, 1H), 7.49 (d, J=4.2Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.77, 33.02, 122.90, 131.25, 132.15, 144.78, 178.05, 189.62.

3.4.12 2-Bromo-5-thiophene-carboxylic acid (39) [14]



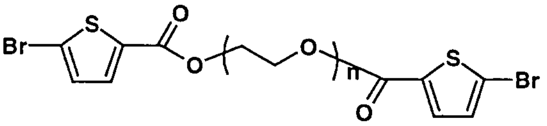
Bromine (187.3 g, 1.17 mol) was added to a solution of 2-thiophene carboxylic acid (100 g, 0.78 mol) in glacial acetic acid (500 ml) at r.t. and then heated to reflux for 2h. The solvent and residue bromine were removed under reduced pressure to give a light brown solid, which was recrystallised from water (4 l). A dark brown solid that crystallised very rapidly was removed by filtration and the filtrate cooled with ice. A white crystalline solid precipitated which was recovered by filtration, washed with cold water and dried under vacuum to give 2-bromo-5-thiophene-carboxylic acid (79.76 g, 49 %), m.p. 132°C (lit.[14] 135-136°C). Found C, 28.31; H, 1.31%; M(MS,EI) 206 (M^+ [^{79}Br]), 208 (M^+ [^{81}Br]). Calculated for $C_5H_3BrO_2S$, C, 29.01; H, 1.46%; M 207.05. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.11 (d, J=3.9Hz, 1H), 7.64 (d, J=3.9Hz, 1H), 11.4 (broad, COOH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.28, 131.34, 133.81, 135.34, 166.66.

3.4.13 2-Bromo-5-thiophene carbonyl chloride (40)[15]



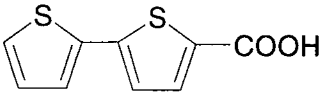
Thionyl chloride (150 ml) was added slowly to solid 2-bromo-5-thiophene carboxylic acid (50g0.24 mol) and the resulting suspension refluxed for 1h. The $SOCl_2$ was removed under reduced pressure and the residue distilled twice under vacuum (1mmHg, 60°C) to give pure 2-bromo-5-thiophene carbonyl chloride (50.23g, 92%), which crystallised in colourless needles in the receiver flask, m.p. 36-38°C (lit.[15] 41-42°C). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.18 (d, J=4.2Hz, 1H), 7.73 (d, J=4.2Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.55, 131.89, 138.00, 139.24, 158.46. Due to the rapid hydrolysis of the material no satisfying mass spectrum and elemental analysis data could be recorded of the compound.

3.4.14 Poly(ethylene glycol)-di-(2-bromo-5-thiophene carboxylate (41)



Poly(ethylene glycol) (M_n=2000, PDI=1.05, 50 g, 25 mmol) was melted in a round bottom single neck flask and the melt stirred under high vacuum for 1/2h. Toluene (100 ml) and pyridine (6g, 75 mmol) were added to the degassed polymer melt and the mixture stirred until a clear solution was obtained. A solution of 2-bromo-5-thiophene carbonyl chloride (18.1 g, 75 mmol) in toluene (50 ml) was added slowly to the polymer solution at r.t. After complete addition the mixture was stirred at r.t. for another 48h then filtered through Celite (Aldrich) and the clear solution precipitated into hexane. The crude polymer was recovered by filtration, dried under vacuum, re-dissolved in toluene and precipitated in hexane. The white waxy solid was recovered by filtration, washed with hexane and dried under high vacuum for 1d to give poly(ethylene glycol)-di-(2-bromo-5-thiophene carboxylate) (50 g, 84%). Gpc ($CHCl_3$): Mn = 4300 g mol^{-1}; Mw = 4500 g mol^{-1}; PDI = 1.05. ^{1}H NMR (300MHz, $CDCl_3$) δ 3.54 (m, 175H), 3.69 (m, 4H), 4.32 (m, 4H), 6.98 (d, J=3.9Hz, 2H), 7.46 (d, J=3.9Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.16, 68.64, 70.21, 70.28, 70.37, 119.93, 130.62, 133.51, 134.33, 160.56.

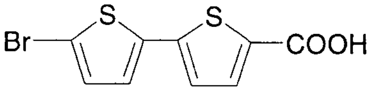
3.4.15 2,2'-Bithiophene-5-carboxylic acid (42)[16]



2,2'-Bithiophene (10 g, 60 mmol) was dissolved in THF (100 ml) cooled with a dry ice/acetone bath (-78°C) and stirred for 1/2h. N-Butyllithium (1.6M, 37.6 ml, 60 mmol) was added slowly dropwise to the cooled solution. After complete addition the mixture was stirred for an extra 1/2h at -78°C before CO_2 gas was introduced (1/2h) under vigorous stirring and cooling. The solvent was removed under reduced pressure, the residue dissolved in dilute aqueous NaOH, filtered and the filtrate acidified to precipitate a white solid. The solid was recovered by filtration, washed with cold water and dried under high vacuum to give 2,2'-bithiophene-5-carboxylic acid (11 g, 87%) which was used without further purification, m.p. >380°C. ^{1}H

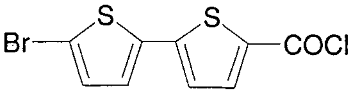
NMR (300MHz, DMSO-d_6) δ 7.12 (dd, J=5.1Hz, J=3.6Hz, 1H), 7.33 (d, J=3.9Hz, 1H), 7.47 (d, J=3.6Hz, 1H), 7.61 (d, J=5.1Hz, 1H), 7.65 (d, J=3.9Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 125.52, 126.85, 128.21, 129.63, 133.47, 135.23, 136.38, 143.85, 163.60. Data obtained by elemental analysis or mass spectrometry was not conclusive with the structure claimed here. The final product **44** in the reaction sequence could be analysed satisfactorily.

3.4.16 5-Bromo-2,2'-bithiophene-5'-carboxylic acid (43)



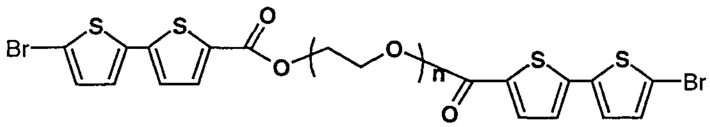
A solution of NBS (4.79 g, 26.9 mmol) in DMF (20 ml) was added slowly dropwise to a cooled (-10°C) solution of 2,2'-bithiophene-5-carboxylic acid (5.66 g, 26.9 mmol) in DMF (40 ml). After complete addition the mixture was stirred for another 1h at -10°C and then allowed to warm to r.t. The solution was stirred at r.t. for 12h before water (100 ml) was added to precipitate a white solid. The solid was recovered by filtration, washed with water and dried under high vacuum to give *5-bromo-2,2'-bithiophene-5'-carboxylic acid* (5 g, 64%) as a white powder which was used without further purification, m.p. >380°C. ^{1}H NMR (300MHz, DMSO-d_6) δ 7.22-7.36 (m, 3H), 7.64 (d, J=4.0Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 112.80, 125.79, 127.12, 132.57, 133.93, 134.82, 137.79, 142.03, 163.18. Data obtained by elemental analysis or mass spectrometry was not conclusive with the structure claimed here. The final product **44** in the reaction sequence could be analysed satisfactorily.

3.4.17 5-Bromo-2,2'-bithiophene-5'-carbonyl chloride (44)



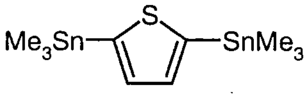
$SOCl_2$ (100 ml) was added slowly to 5-bromo-2,2'-bithiophene-5'-carboxylic acid (10 g, 34.6 mmol) and the resulting suspension refluxed for 1h until a clear yellow solution was obtained. The $SOCl_2$ was removed under reduced pressure and the residue recrystallised (3x) from hexane to give *5-bromo-2,2'-bithiophene-5'-carbonyl chloride* (6.6g, 62%) in form of yelllow crystals, m.p. 127.5°C. Found C, 34.91; H, 1.19%; M(MS,EI) 306 (M^+ [^{79}Br]), 308 (M^+ [^{81}Br]) . $C_9H_4BrClOS_2$ requires C, 35.14; H, 1.31%; M 307.62. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.05 (d, J=3.9Hz, 1H), 7.12 (d, J=3.9Hz, 1H), 7.15 (d, J=3.9Hz, 1H), 7.87 (d, J=3.9Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114,86, 124.48, 126.55, 131.28, 134.61, 136.69, 138.81, 148.20, 159.12.

3.4.18 Poly(ethylene glycol)-di-(5-bromo-2,2'-bithiophene-5'-carboxylate) (45)



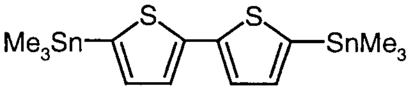
Poly(ethylene glycol) (M_n=2000,PDI=1.05, 10.8 g, 5.4 mmol) was heated (90°C) in a round bottom single neck flask and the melt stirred under high vacuum for 1/2h. Toluene (50 ml) and pyridine (1.3g, 16.3 mmol) were added to the degassed polymer melt and the mixture stirred until a clear solution was obtained. 5-Bromo-2,2'-bithiophene-5'-carbonyl chloride (5 g, 16.3 mmol) was added as a solid to the hot (90°C) polymer solution. After complete addition the mixture was stirred at 90°C for another 3h then at r.t for 3d. The mixture was filtered through Celite (Aldrich) and the clear solution precipitated into hexane. The crude polymer was recovered by filtration, dried under vacuum, re-dissolved in toluene and precipitated in hexane. The pale yellow waxy solid was recovered by filtration, washed with hexane and dried under high vacuum for 1d to give poly(ethylene glycol)-di-(5-bromo-2,2'-bithiophene-5'-carboxylate) (10 g, 73%). Gpc ($CHCl_3$): Mn = 4380 g mol^{-1}; Mw = 4660 g mol^{-1}; PDI = 1.06. ^{1}H NMR (300MHz, $CDCl_3$) δ 3.59 (m, 175H), 3.75 (m, 4H), 4.39 (m, 4H), 6.96 (m, 4H), 7.02 (d, J=3.9Hz, 2H), 7.64 (d, J=3.9Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.22, 68.89, 70.36, 70.42, 70.44, 70.52, 112.73, 123.91, 125.16, 130.80, 131.56, 134.17, 137.49, 142.81, 161.56.

3.4.19 2,5-Bis(trimethyltin)-thiophene (46)



N-Butyllithium (1.6M, 19.8 ml, 31.6 mmol) was added dropwise to a solution of thiophene (1.33 g, 15.8 mmol) and TMEDA (3.67 g, 31.6 mmol) in hexane (8 ml) at r.t. The mixture was refluxed for 1/2h then cooled to -60°C and a solution of trimethyltin chloride (6.29 g, 31.6 mmol) in THF (30 ml) added quickly. The mixture was stirred at -60°C for 10 min. before the dry ice/acetone bath was removed and the reaction mixture allowed to warm to r.t. The clear sloution was stirred at r.t. over night. The reaction mixture was poured into water and extracted with diethylether (2x 50 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude solid was recrystallised from ethanol to give 2,5-bis(trimethyltin)-thiophene (3.9 g, 60%) as light brown crystalls, m.p. 99.5°C (lit.[17] 100-101.6). Found C, 29.47; H, 4.93%; M(MS,EI) 408, 410, 412 (M^+, three most intense peaks of the isotope pattern). Calculated for $C_{10}H_{20}SSn_2$, C, 29.31; H, 4.92%; M 409.75. ^{1}H NMR (300MHz, $CDCl_3$) δ 0.39 (s, $^2J_{HSn}$=28.8Hz, 18H), 7.40 (s, $^3J_{HSn}$=13.2Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -8.18, 135.78 (J_{CSn}=102.0Hz), 142.99.

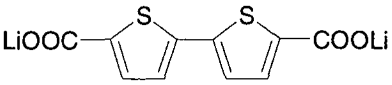
3.4.20 5,5'-Bis(trimethyltin)-2,2'-bithiophene (47)[18]



N-Butyllithium (1.6M, 37 ml, 60 mmol) was added dropwise to a solution of 2,2'-bithiophene (4.9g, 30 mmol) in THF (50 ml) at r.t. The resulting suspension was stirred at 50°C for 1/2h then cooled to -78°C and trimethyltin chloride (11.8g, 60 mmol) added quickly as a solid. The dry ice/acetone bath was removed, the reaction mixture allowed to warm to r.t. and then stirred for 1h at r.t., 1h at 60°C and over night at r.t. The THF was removed under reduced pressure and the residue recrystallised (2x) from ethanol to give pure 5,5'-bis(trimethyltin)-2,2'-bithiophene (12.5 g, 85%), m.p. 99.5°C (lit.[18] 95.5-96.5°C). Found C, 34.48; H, 4.51%;

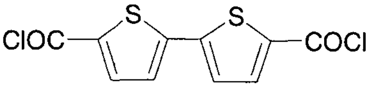
M(MS,EI) 490 (8.96%), 492 (9.05%), 494 (5.74%) (M^+, three most intense peaks of the isotope pattern). Calculated for $C_{14}H_{22}S_2Sn_2$, C, 34.19; H, 4.51%; M 491.88. ^{1}H NMR (300MHz, $CDCl_3$) δ 0.42 (s, $^2J_{HSn}$=27.9Hz, 18 H), 7.12 (d, $^3J_{HH}$=3.3Hz, $^3J_{HSn}$=16.5Hz, 2H), 7.31 (d, J=3.3Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -8.22, 124.80 (J_{CSn}=81.9Hz), 135.81 (J_{CSn}=56.4Hz), 135.97, 142.96.

3.4.21 2,2'-Bithiophene-5,5'-di-lithium carboxylate (48)



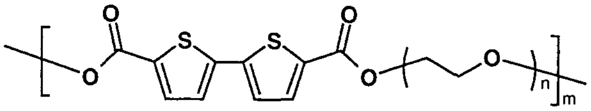
N-Butyllithium (1.6M, 12.5 ml, 20 mmol) was added slowly dropwise to a stirred solution of 2,2'-bithiophene (1.52 g, 9.1 mmol) in THF (30 ml). The mixture was heated to 50°C for 1/2h, cooled to r.t. and CO_2 gas introduced for 1/2h while stirring vigorously. After that the solvent was removed under reduced pressure and the residue stirred in hexane for 1h. The solid was recovered by filtration and washed with hexane to give 2,2'-bithiophene-5,5'-di-lithium carboxylate (0.8 g, 34%) which was used without further purification in the next reaction step. No analyses were performed at this stage of the reaction sequence.

3.4.22 2,2'-Bithiophene-5,5'-di-carbonyl chloride (49)



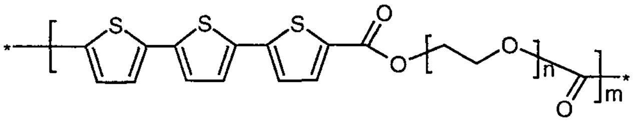
$SOCl_2$ (40 ml) was added slowly to 2,2'-bithiophene-5,5'-di-lithium carboxylate (2 g, 7.5 mmol) and the resulting suspension refluxed for 1h. The $SOCl_2$ was removed under reduced pressure and the residue recrystallised twice from $CHCl_3$/hexane mixture (v:v=4:1) to give pure *2,2'-bithiophene-5,5'-di-carbonyl chloride* (700 mg, 32%) in the form of orange needles, m.p. 172°C. Found C, 41.74; H, 1.50 %; M(MS,EI) 289.6 (M^+). $C_{10}H_4Cl_2O_2S_2$ requires C, 41.25; H, 1.38%; M 289.9. ^{1}H NMR (300MHz, $CDCl_3$) δ = 7.39 (broad, 2H), 7,93 (broad, 2H).

3.4.23 Poly[poly(ethylene glycol)-alt-(2,2'-bithiophene-5,5'-di-carboxylic acid)] (50)



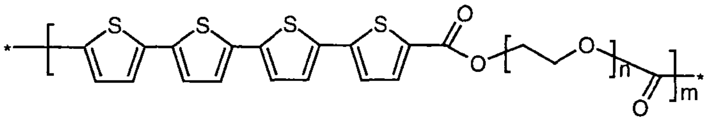
Poly(ethylene glycol) (3.67 g, 1.84 mmol) was melted and stirred under vacuum for 1/2h before toluene (10 ml) was added to give a clear solution. 2,2'-Bithiophene-5,5'-di-carbonyl chloride (535 mg, 1.84 mmol) and pyridine (0.2 ml) were added and the solution stirred at r.t. for 1/2h. All solvents were removed under reduced pressure and the melt stirred at 150°C under high vacuum for 5h. The viscous melt was dissolved in toluene, filtered through Celite (Aldrich) and precipitated into hexane to give poly[poly(ethylene glycol)-*alt*-(2,2'-bithiophene-5,5'-di-carboxylic acid)] (3.5 g) as a white powder. Gpc ($CHCl_3$): Mn = 13500 g mol^{-1}, Mw = 21100 g mol^{-1} PDI = 1.56. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.60 (m, 190H), 3.78 (m, 4H), 4.42 (m, 4H), 7.21 (d, J=4.0Hz, 2H), 7.69 (d, J=4.0Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.37, 68.93, 70.50 (broad), 125.24, 132.95, 134.25, 142.62, 161.53.

3.4.24 Poly[poly(ethylene glycol)-alt-(2,2':5',2''-terthiophene -5,5''-di-carboxylic acid)] (51)



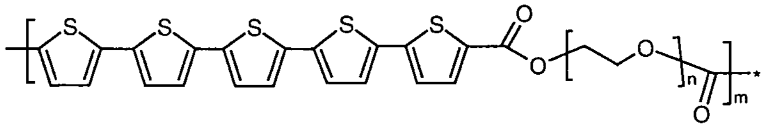
Poly(ethylene glycol)-di-(2-bromo-5-thiophene carboxylate) (10 g, 4.1 mmol) was heated to 100°C and the reaction flask purged with nitrogen for 1/2h while stirring the melt. 2,5-Bis(trimethyltin)-thiophene (1.69 g, 4.1 mmol) and $Pd(PPh_3)_4$ (237 mg, 0.2 mmol) were added to the melt and the mixture heated to 120°C for 42h. During the reaction a fraction of the 2,5-bis(trimethyltin)-thiophene sublimed. A crude ^{1}H-NMR sample was taken after 42h from which the amount of lost 2,5-bis(trimethyltin)-thiophene was determined. To account for this loss more 2,5-bis(trimethyltin)-thiophene (200 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.03 mmol) were added after 42h and the melt stirred at 120°C for another 12h. The melt was cooled to r.t., dissolved in toluene and precipitated into hexane. The yellow powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution which was precipitated into hexane. The oil was dissolved in more chloroform, precipitated into hexane and kept separately from the other fraction to give poly[poly(ethylene glycol)-*alt*-(2,2':5',2''-terthiophene -5,5''-di-carboxylic acid)] which had a higher average molecular weight than the crude product (determined by gpc). Analysis of the higher molecular weight fraction: Gpc ($CHCl_3$): Mn = 3710 g mol^{-1}, Mw = 9740 g mol^{-1} PDI = 2.62. ^{1}H NMR (500MHz, $CDCl_3$) δ 3.62 (m, 150H), 3.78 (m, 4H), 4.42 (m, 4H), 7.13 (d, J=3.5Hz, 2H), 7.19 (s, 2H), 7.68 (d, J=3.5Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.41, 68.10, 69.62 (broad), 123.31, 125.09, 130.91, 133.46, 135.66, 142.31, 160.79.

3.4.25 Poly[poly(ethylene glycol)-alt-*(2,2':5',2'':5'',2'''-quaterthiophene -5,5'''-di-carboxylic acid)] (52)*



Poly(ethylene glycol)-di-(2-bromo-5-thiophene carboxylate) (10 g, 4.1 mmol) was heated to 100°C and the reaction flask purged with nitrogen for 1/2h while stirring the melt. 5,5'-Bis(trimethyltin)-2,2'-bithiophen (2.02 g, 4.1 mmol) and $Pd(PPh_3)_4$ (237 mg, 0.2 mmol) were added to the melt and the mixture heated to 120°C for 22h. The melt was cooled to r.t., dissolved in toluene and precipitated into hexane. The orange powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution which was precipitated into hexane. The oil was dissolved in more chloroform, precipitated into hexane and kept separately from the other fraction to give poly[poly(ethylene glycol)-*alt*-(2,2':5',2'':5'',2'''-quaterthiophene -5,5'''-di-carboxylic acid)] which had a higher average molecular weight than the crude product (determined by gpc). Analysis of the higher molecular weight fraction: Gpc ($CHCl_3$): Mn = 14500 g mol^{-1}, Mw = 20700 g mol^{-1} PDI = 1.42. ^1H NMR (400MHz, $CDCl_3$) δ 3.66 (m, 184H), 3.79 (m, 4H), 4.43 (m, 4H), 7.12 (m, 4H), 7.18 (d, J=4.0Hz, 2H), 7.69 (d, J=4.0Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.28, 69.01, 70.52 (broad), 123.91, 124.90, 125.97, 131.46, 134.38, 135.45, 137.02, 143.53, 161.75.

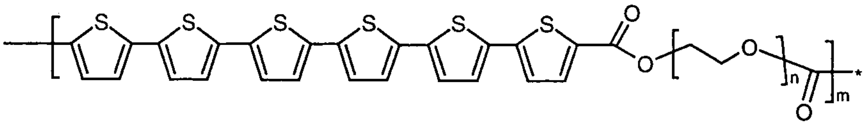
*3.4.26 Poly[poly(ethylene glycol)-*alt*-(2,2’:5’,2”:5",2'":5'",2""-pentathiophene -5,5""-di-carboxylic acid)] (53)*



Poly(ethylene glycol)-di-(5-bromo-2,2’-bithiophene-5’-carboxylate) (10 g, 3.83 mmol) was heated to 100°C and the reaction flask purged with nitrogen for 1/2h while stirring the melt. 2,5-Bis(trimethyltin)-thiophene (1.57 g, 3.83 mmol) and $Pd(PPh_3)_4$ (221 mg, 0.2 mmol) were added to the melt and the mixture heated to 120°C for 4d. During the reaction a fraction of the 2,5-bis(trimethyltin)-thiophene sublimed. A crude ^1H-NMR sample was taken after 4d from which the amount of lost 2,5-bis(trimethyltin)-thiophene was determined. To account for this loss more 2,5-bis(trimethyltin)-thiophene (1.2 g, 2.9 mmol) and $Pd(PPh_3)_4$ (270 mg, 0.03 mmol) were added after 4d and the melt stirred at 120°C for another 2d. The melt was cooled to r.t., dissolved in toluene and precipitated into hexane. The orange powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution that was precipitated into hexane. The oil was dissolved in more chloroform, precipitated into hexane and kept separately from the other fraction to give poly[poly(ethylene glycol)-*alt*-(2,2’:5’,2’’:5",2'":5'",2""-pentathiophene -5,5""-di-carboxylic acid)] which had a higher average molecular weight than the crude product (determined by gpc). Analysis of the higher molecular weight fraction: Gpc ($CHCl_3$): Mn = 9300 g mol^{-1}, Mw = 16900 g mol^{-1} PDI = 1.81. ^1H NMR (400MHz, $CDCl_3$) δ 3.64 (m, 186H), 3.67 (m, 4H), 4.42 (m, 4H), 7.08 (m, 4H), 7.39 (d, J=4.0Hz, 2H), 7.14 (d, J=3.6Hz, 2H), 7.63 (d, J=3.6Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.24, 68.98, 70.48

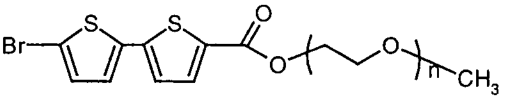
(broad), 123.77, 124.55, 124.82, 125.92, 131.29, 134.35, 135.08, 135.26, 137.26, 143.60, 161.72.

3.4.27 Poly[poly(ethylene glycol)-alt*-(2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene -5,5'''''-di-carboxylic acid)] (54)*



Poly(ethylene glycol)-di-(5-bromo-2,2'-bithiophene-5'-carboxylate) (12.65 g, 4.85 mmol) was heated to 100°C and the reaction flask purged with nitrogen for 1/2h while stirring the melt. 5,5'-Bis(trimethyltin)-2,2'-bithiophen (2.38 g, 4.85 mmol) and $Pd(PPh_3)_4$ (280 mg, 0.2 mmol) were added to the melt and the mixture heated to 120°C for 3h. After 3h the melt had become too viscous to be stirred any more. Toluene (7 ml) was added and the solution stirred for another 12h at 100°C. The solution was cooled to r.t., dissolved in more toluene and precipitated into hexane. The red powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution that was precipitated into hexane. The oil was dissolved in more chloroform, precipitated into hexane and kept separately from the other fraction to give poly[poly(ethylene glycol)-*alt*-(2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene -5,5'''''-di-carboxylic acid)] which had a higher average molecular weight than the crude product (determined by gpc). Analysis of the higher molecular weight fraction: Gpc ($CHCl_3$): Mn = 13300 g mol^{-1}, Mw = 19000 g mol^{-1} PDI = 1.42. ^1H NMR (400MHz, $CDCl_3$) δ 3.61 (m, 192H), 3.79 (m, 4H), 4.42 (m, 4H), 7.07 (m, 6H), 7.10 (d, J=4.0Hz, 2H), 7.16 (d, J=4.0Hz, 2H), 7.68 (d, J=3.6Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.25, 69.00, 70.41 (broad), 123.74, 124.45, 124.51, 124.81, 125.93, 131.24, 134.38, 134.97, 135.53, 136.15, 137.39, 143.67, 161.76.

3.4.28 Poly(ethylene glycol)-methyl ether-(5-bromo-2,2'-bithiophene-5'-carboxylate) (55,56)

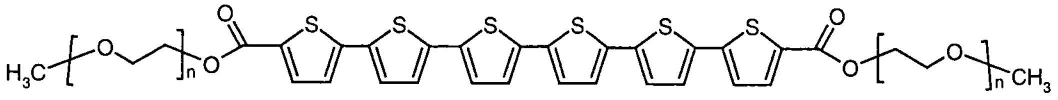


The synthesis with poly(ethylene glycol) methyl ether (M_n=750 g/mol) to give compound ***56*** *is described below. The same procedure was employed to react poly(ethylene glycol) methyl ether (M_n=350 g/mol)to give compound* ***55****.*

Poly(ethylene glycol) methyl ether (M_n=750 g/mol, 3.76 g, 5.0 mmol) was heated (90°C) in a round bottom single neck flask and the melt stirred under high vacuum for 1/2h. Toluene (20 ml) and pyridine (0.49, 6.2 mmol) were added to the degassed polymer melt and the mixture stirred until a clear solution was obtained. 5-Bromo-2,2'-bithiophene-5'-carbonyl chloride (1.85 g, 6.0 mmol) was added as a solid to the hot (80°C) polymer solution. After complete addition the mixture was stirred at 80°C for 1h then at r.t for 12h. The mixture was filtered through Celite (Aldrich) and the solvent evaporated. The crude red solid was dissolved in a small amount of chloroform and separated from impurities on a short silica gel (Aldrich, 70-230 mesh) filter-column with $CHCl_3$. The product was collected by flushing the column with acetone. The solvent was removed under reduced pressure to give poly(ethylene glycol)-methyl ether-(5-bromo-2,2'-bithiophene-5'-carboxylate) (3.1 g) as a yellow oil.

NMR shifts are identical for both compounds. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.17 (s, 3H), 3.30-3.50 (m, CH_2CH_2O), 3.61 (m, 2H), 4.24 (m, 2H), 6.83 (m, 2H), 6.90 (d, J=3.9Hz, 2H), 7.51 (d, J=3.9Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.70, 64.09, 68.76, 70.29, 71.60, 112.60, 123.79, 125.05, 130.70, 131.43, 134.06, 137.37, 142.66, 161.41.

*3.4.29 Poly(ethylene glycol)-***block***-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene-5,5'''''-di-carboxylic acid-***block***-poly(ethylene glycol) (57,58)*



The synthesis of a tri-block with poly(ethylene glycol) chains of Mn=750 g/mol (58) is described below. The same procedure was emloyed to prepare a tri-block with poly(ethylene glycol) chains of Mn=350 g/mol (57).

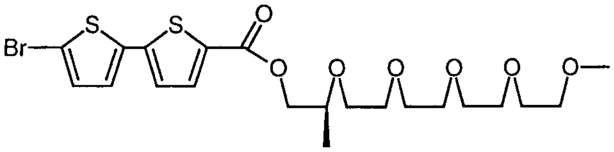
Poly(ethylene glycol)-methyl ether-(5-bromo-2,2'-bithiophene-5'-carboxylate) (3.12 g, 3.1 mmol) was stirred under vacuum for 1/2. 5,5'-Bis(trimethyltin)-2,2'-bithiophen (752 mg, 1.53 mmol) and $Pd(PPh_3)_4$ (177 mg, 0.1 mmol) were added to the oil and the mixture heated to 120°C for 12h. The crude reaction mixture was dissolved in acetone and precipitated into hexane. The dark red waxy solid was filtered and dried under high vacuum. Column chromatography on silica gel (Aldrich, 70-230 mesh) with methanol, to remove impurities, then THF, to collect the product, yielded poly(ethylene glycol)-*block*-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene-5,5'''''-di-carboxylic acid-*block*-poly(ethylene glycol) (440 mg) as a red waxy solid.

Compound 57, gpc ($CHCl_3$): Mn = 1900 g mol^{-1}; Mw = 2200 g mol^{-1}; PDI = 1.15

Compound 58, gpc ($CHCl_3$): Mn = 1700 g mol^{-1}; Mw = 2670 g mol^{-1}; PDI = 1.54

NMR shifts are identical for both compounds. ^{1}H NMR (300MHz, $CDCl_3$) δ = 3.34 (s, 6H), 3.50-3.70 (m, CH_2CH_2O), 3.78 (m, 4H), 4.41 (m, 4H), 7.04 (m, 6H), 7.08 (d, J=4.2Hz, 2H), 7.14 (d, J=3.9Hz, 2H), 7.67 (d, J=3.9Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 58.90, 64.24, 68.99, 70.43 (broad), 70.60, 71.79, 123.69, 124.40, 124.46, 124.76, 125.88, 131.23, 134.32, 134.94, 135.50, 136.12, 137.37, 143.63, 161.68.

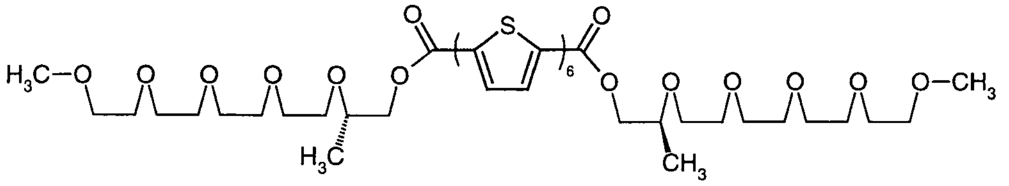
3.4.30 5-Bromo-2,2'-bithiophene-5'-carboxylic acid [(2S)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)propan-1-ol] ester (59)



(2*S*)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)propan-1-ol (2.03 g, 7.6 mmol, pyridine (1 ml, 12 mmol) and 5-bromo-2,2'-bithiophene-5'-carbonyl chloride

(2.58 g, 8.4 mmol) were dissolved in toluene (30 ml). After stirring for 3d at r.t. the mixture was filtered through Celite (Aldrich) and the solvent evaporated to give 5-bromo-2,2’-bithiophene-5’-carboxylic acid [(2S)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)propan-1-ol] ester (2.27g). NMR-spectroscopy revealed that unreacted alcohol was left in the reaction mixture. The amount of product in the reaction mixture was calculated to be 80%, therefore the yield 44.5%. Due to difficult separation of the unreacted alcohol from the formed ester, the crude reaction mixture was used without purification in the next reaction step. ^{1}H NMR (300MHz, $CDCl_3$) δ 1.19 (d, 3H), 3.31 (s, 3H), 3.48 (m, 2H), 3.57 (m, 12H), 3.65 (m, 2H), 3.76 (m, 1H), 4.20 (m, 2H), 6.95 (m, 2H), 7.05 (d, J=3.9Hz, 2H), 7.62 (d, J=3.9Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.94, 29.70, 58.81, 67.81, 68.70, 70.35, 70.38, 70.43, 70.60, 70.65, 71.70, 73.63, 112.74, 123.91, 125.14, 130.77, 131.55, 134.10, 137.47, 142.79, 161.41.

3.4.31 2,2’:5’,2”:5'',2''':5''',2'''':5'''',2'''''-Sexithiophene-5,5'''''-di-{carboxylic acid [(2S)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy) propan-1-ol] ester} (60)



5-Bromo-2,2’-bithiophene-5’-carboxylic acid [(2S)-2-(2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)propan-1-ol] ester (of 80% purity, 2.27g, 3.4 mmol) 5,5’-bis(trimethytin)-2,2’-bithiophene (830 mg, 1.7 mmol) and $Pd(PPh_3)_4$ (195mg, 0.17 mmol) were dissolved in dimethyl acetamide (6 ml) and the mixture degassed under high vacuum and flushed with nitrogen. After heating the reaction for 20h at 120°C the mixture was allowed to cool to r.t. Water (150ml) was added and the red suspension stirred for 1h. The water was decanted and the residue washed with more water and dried under vacuum. The remaining solid was suspended in acetone, stirred for 1h, recovered by filtration, washed with more acetone and then soxhlet extracted with chloroform for 24h. The solvent was removed from the orange solution obtained and the solid residue purified on a chromatography column (BioRad, BioBeads SX-1) with DCM to give spectroscopically pure

2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene-5,5'''''-di-{carboxylic acid [(2S)-2-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy) propan-1-ol] ester} (65mg, 3.5%) in form of a red solid. The low yield was probably due to the many purification steps which were necessary to produce a sample that could be used in chiroptical measurements. Found, MALDI TOF MS: 1078.26 (see Figure 3.2.22). $C_{50}H_{62}O_{14}S_6$ requires M 1079.43. ^{1}H NMR (300MHz, $CDCl_3$) δ 1.21 (d, 6H), 3.46 (s, 6H), 3.53 (m, 4H), 3.64 (m, 24H), 3.72 (m, 4H), 3.81 (m, 2H), 4.26 (m, 4H), 7.07 (m, 6H), 7.11 (d, J=4.0Hz, 4H), 7.17 (d, J=4.0Hz, 4H), 7.69 (d, J=4.0Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.26, 29.75, 59.01, 67.97, 68.89, 70.46, 70.53, 70.56, 70.62, 70.83, 71.88, 73.84, 123.69, 124.36, 124.43, 124.73, 125.84, 131.21, 134.23, 134.89, 135.47, 136.01, 137.35, 143.57, 161.46.

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4 Investigations of the Surface Activity of Amphiphilic Oligothiophene Block-co-Polymers

4.1 Introduction

Langmuir-Films[1,2]

At the interface between a liquid and a gas, the properties of the molecules on the surface of the liquid phase differ from those in the bulk phase. In the case of water, for example, the molecules in the bulk are surrounded by other water molecules and they interact via hydrogen bonding. The water molecules at the interface to another phase, be it a gas, a different liquid or solid, can interact with less water molecules for geometrical reasons and thermodynamic excess functions are used to describe their behaviour at the interface. One of these quantities is the surface tension γ, which is related to the partial derivative of the Gibbs free energy of the system with respect to the area A of the surface, i.e.

$$\gamma = (\delta G/\delta A)_{p,T,n}$$

Pure water has a surface tension $\gamma = 73$ mN/m (at 20°C), a much higher value than that of most other liquids.

When a solution of a suitable compound (the solvent has to be immiscible and less dense than water) is spread onto a water surface, the solution will very rapidly occupy the available surface area. When the solvent has evaporated, a thin, one molecule thick layer will remain on the water surface. There will be no interaction between molecules on the surface, if the mean distance between two of them is relatively large. This situation has been compared to a two-dimensional gaseous state. When the available surface area of this system is reduced, the molecules on the surface will start to interact in a repulsive manner. This interaction can be seen as the two-dimensional analogue to pressure and is usually called *surface pressure* (Π). The surface pressure is defined as

$$\Pi = \gamma - \gamma_0$$

where γ is the surface tension of the liquid in absence of the monolayer, γ_0 the surface tension in presence of the monolayer. If water at 20°C is used as the sub-phase, the surface pressure Π cannot exceed 73 mN/m.

Most molecules that exhibit surface activity consist of two parts, a hydrophilic and a hydrophobic part. In an ideal surface active molecule, the right balance between those two parts gives the compound a preferential orientation with respect to the interface but does not allow it to dissolve in the sub-phase. A classic example for such an amphiphilic molecule that can form monolayers on water is stearic acid (Figure 4.1.1).

Figure 4.1.1 Top: Stearic acid, bottom: representation of an amphiphilic molecule with hydrophilic head group (circle) and hydrophobic tail (straight line).

Here the long alkyl chain provides the hydrophobic and the carboxylic acid the hydrophilic part of the amphiphile. Spreading a dilute solution of this compound onto a water surface will result in a random distribution of molecules across the water surface with the polar head-group immersed in the water (Figure 4.1.2).

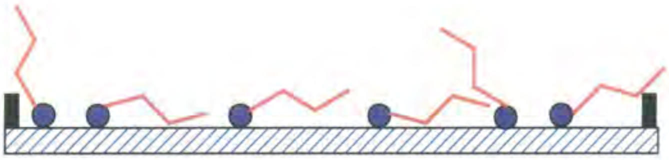

Figure 4.1.2 Expanded monolayer on water.

This state is also called the 'gaseous' phase. Upon reducing the available surface area, the stearic acid molecules start to interact (Figure 4.1.3). This 'liquid' state is also called the expanded monolayer phase.

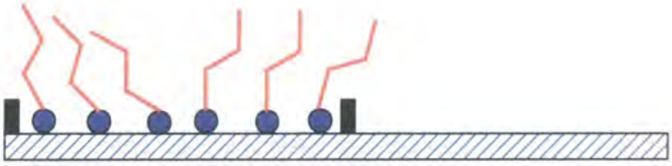

Figure 4.1.3 Partly compressed monolayer on water.

When reducing the surface area further, a condensed phase can appear (Figure 4.1.4) in which the molecules are highly oriented.

Figure 4.1.4 Closely packed monolayer on water.

The most important indicator of monolayer properties is a plot of surface pressure (Π) against area available per molecule (usually reported in $Å^2$). The surface pressure can be measured by a small rectangular piece of chromatography paper (Wilhelmy plate) that dips into the water surface and is attached to a balance which is used to monitor the force on the paper.

A schematic plot of surface pressure against molecular area is shown in Figure 4.1.5.

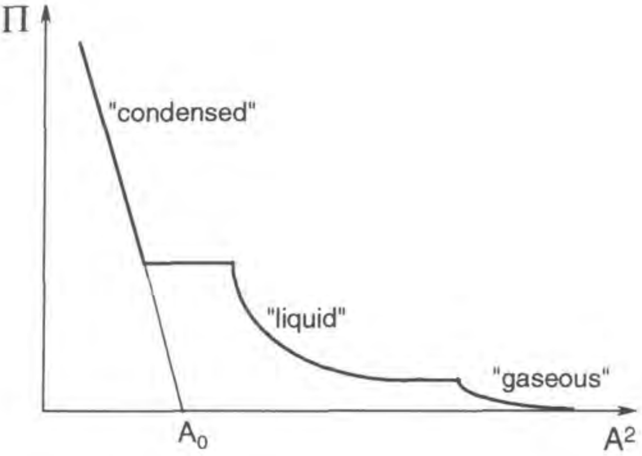

Figure 4.1.5 Schematic surface pressure/area isotherm.

The different two-dimensional aggregation states (see Figure 4.1.2 - Figure 4.1.4) can be detected by changes in surface pressure, as the area is reduced. Extrapolating the linear part of the isotherm representing the condensed phase to zero pressure (A_0 in Figure 4.1.5) will give an estimate for the molecular area occupied by the molecule in a closest packing under no external pressure. Once the condensed state is reached, further compression of the monolayer will eventually lead to collapse.

The case described above is idealised and for many materials no sharp phase transitions are observable at all.

Polymers can also be used in monolayer experiments when a sufficient number of hydrophilic groups are present. Although they show the same general behaviour as low molecular weight compounds, usually sharp phase transitions are not observed.

Langmuir-Blodgett Films

When a suitable substrate is slowly moved into the compressed monolayer, perpendicular to the sub-phase, the monolayer can transfer onto the substrate material. Transferred monolayers are called a Langmuir-Blodgett films and can be one or several layers in thickness depeding on the number of dipping-cycles. Care must be taken that the surface pressure remains constant during the monolayer transfer. This is done by constantly measuring the surface pressure and reducing the surface area until the required surface pressure is reached again. Most commonly, a substrate lowered into the sub-phase picks up the first monolayer on the upward movement. Once the first layer has been transfered, further layers will tansfer on the upward and downward movement. This type of deposition is called Y-type deposition. Transfer only on the upward movement (Z- deposition) or the downward movement (X-deposition) is also possible and depends on the substrate and the dipping conditions.

Langmuir-Films of Oligo- and Polythiophenes

Unsubstituted and derivatised oligothiophenes have been used to form Langmuir films. Nakahara *et al.*[3] reported the successful use of mono-α–substituted terthiophene derivatives in Langmuir experiments. On extrapolating the isotherms of the condensed state, values of 27-29 $Å^2$ per molecule were obtained. According to the authors, this suggests a "close packing with a nearly vertical terthiophene unit oriented towards the air as a hydrophobic group." α-Penta-, sexi- and septithiophene could be incorporated into monolayers but only in mixtures with arachidic acid. Here also, the results obtained suggested close packing of the rods with their long axes perpendicular to the water surface.

In a different study carried out by Liu *et al.*[4] a different α-substituted terthiophene derivative was synthesised and its surface pressure/area isotherm recorded. Extrapolation of the isotherm corresponding to the condensed phase gave a value of 13.5 Å^2 per molecule which in the authors' opinion agreed well with terthiophene molecules stacked perpendicular to the water surface. It has to be mentioned, though, that the area values obtained for closest packing of terthiophene derivatives perpendicular to the sub-phase surface , differ by a factor of two in the two studies.

Isz *et al.*[5] employed unsubstituted quater-, penta- and sexithiophenes, spread from very dilute chloroform solutions, to record surface pressure/area isotherms. After extrapolation of the isotherms to zero pressure the area value obtained for quaterthiophene varied from 5-10 Å^2 per molecule, suggesting the formation of multilayers. The values for penta- and sexithiophene were about 25 Å^2 per molecule, which in the authors' opinion, was in good agreement with theoretically predicted values for perpendicular stacking of the rods.

Polythiophenes with hydrophilic side chains have also been employed in Langmuir and Langmuir-Blodgett experiments. Bjornholm *et al.*[6] described the synthesis of various regioregular polythiophenes with ionic and non-ionic water soluble side-chain functionalities. These polymers form stable monolayers and collapse at surface areas of about 29Å^2 per repeat unit, which leads the authors to conclude that the rigid rods are closely π-stacked with the long axis of the rods parallel to the sub-phase surface. According to the authors, the value of 29Å^2 was in good agreement with that predicted for the repeat unit of the polymer. Other examples of monolayer forming polythiophenes have been reported[7,8] but will not be discussed here.

4.2 Results and Discussion

Chloroform solutions of approximately 1mg ml^{-1} of all compounds shown in Figure 4.2.1 were prepared and various amounts of these solutions spread onto a Langmuir trough with water as the sub-phase.

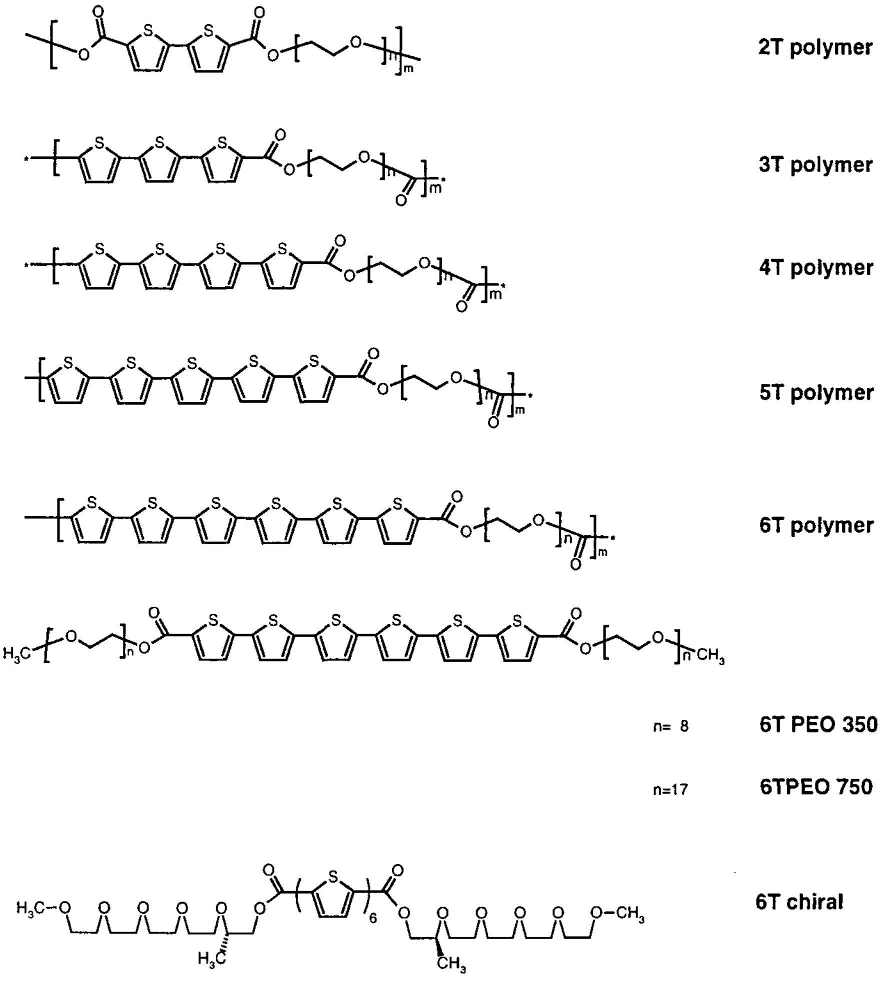

Figure 4.2.1 All materials of which surface pressure/area isotherms were recorded.

Surface pressure/surface concentration isotherms (Π–Γ-isotherms) were recorded and subsequently converted into surface pressure/area isotherms (Π–A-isotherms). Both isotherms are reported here, as phase transitions can sometimes be observed more easily in only one of the two. In the case of polymeric compounds (**2T polymer** – **6T polymer**) the number average molecular weight of the repeat unit was used to calculate *area per repeat unit* values (see Table 4.2.1). For compounds **6T PEO 350** and **6T PEO 750** average molecular weights of 1280 g mol^{-1} and 2080 g mol^{-1} were used in calculations. Compound **6T chiral** was monodisperse and its molecular weight was 1079 g mol^{-1}.

compound	number average molecular weight per repeat unit (g mol^{-1})
2T polymer	2252
3T polymer	2334
4T polymer	2416
5T polymer	2498
6T polymer	2580

Table 4.2.1. The molecular weight of the oligothiophene block was added to Mn=2000, the number average molecular weight of the PEO spacer, to give the number average molecular weights per repeat unit of the polymers investigated.

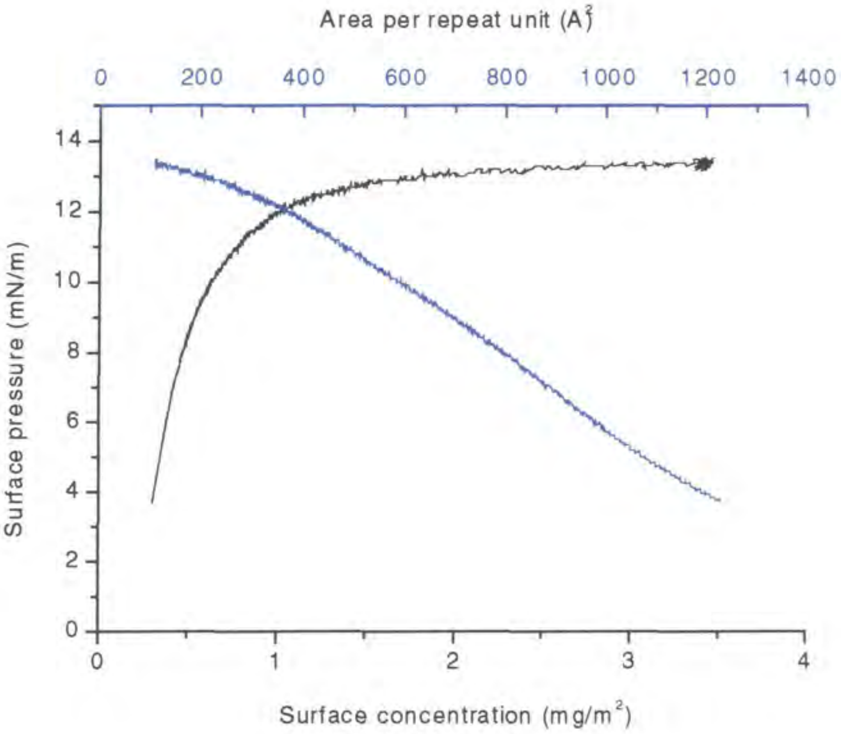

Figure 4.2.2 Surface pressure isotherm of ***2T polymer.*** *Black curve: surface pressure against surface concentration, blue curve: surface pressure against area per repeat unit.*

Figure 4.2.2 shows the surface pressure/area and surface pressure/surface concentration isotherms for **2T polymer**. The isotherms resemble those of pure poly(ethylene oxide) in shape. After a sharp rise in the Π–Γ-isotherm at low surface concentration, the curve levels out into a plateau area at a surface pressure value of about 13 mN/m.

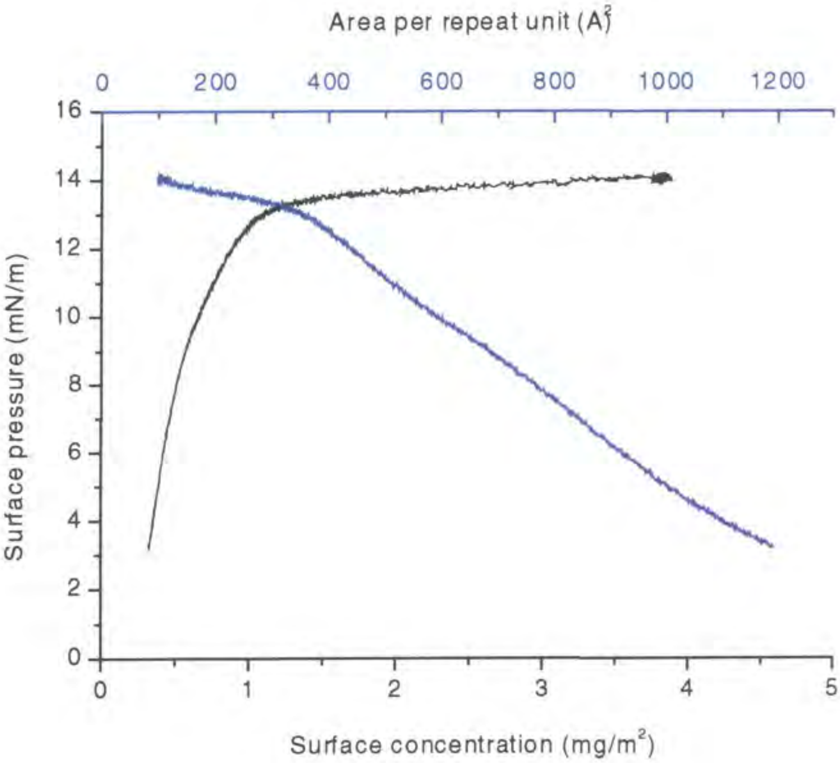

Figure 4.2.3 Surface pressure isotherm of ***3T polymer****. Black curve: surface pressure against surface concentration, blue curve: surface pressure against area per repeat unit.*

The recorded isotherms for **3T polymer** are shown in Figure 4.2.3. Although here, as well as in the case of **2T polymer**, the Π–Γ-isotherm reaches a plateau region for high surface concentration, a distinct phase transition at Π=13.1 mN/m (350 Å^2 per repeat unit) which was not present in the case of the bithiophene polymer, can be observed and must therefore be due to the presence of the higher oligothiophene homologue, terthiophene.

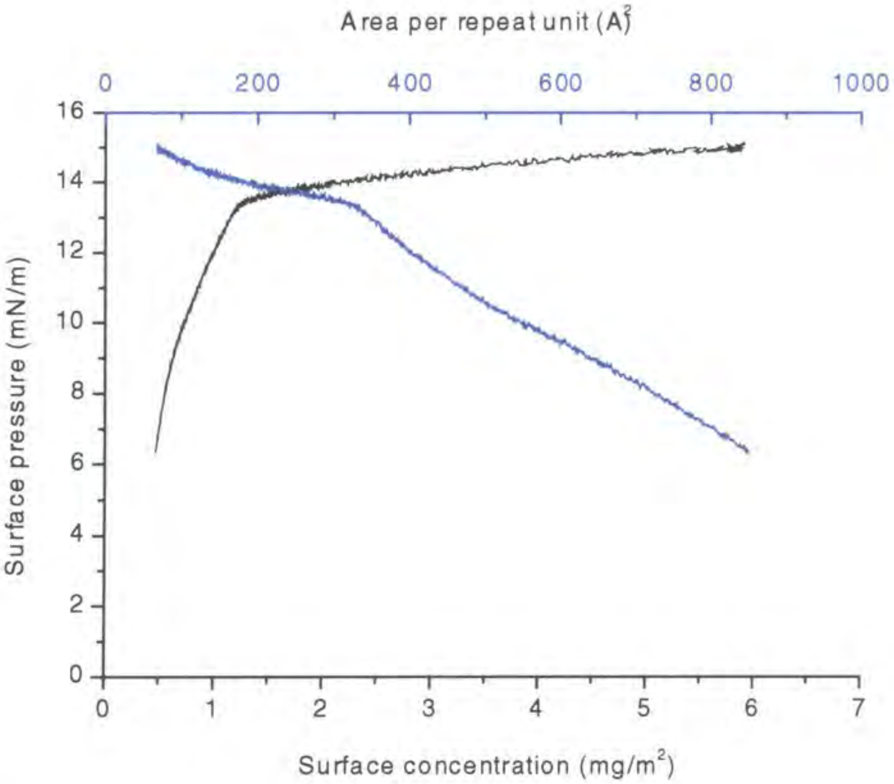

*Figure 4.2.4 Surface pressure isotherm of **4T polymer.** Black curve: surface pressure against surface concentration, blue curve: surface pressure against area per repeat unit.*

The Π–Γ-isotherm for **4T polymer** shown in Figure 4.2.4 shows an indistinct phase transition at Π=9.0mN/m (640Å^2 per repeat unit) before exhibiting an almost linear relationship between surface pressure and surface concentration. After a well-defined phase transition at Π=13.2mN/m (335 Å^2 per repeat unit) the curve enters into the plateau region as already observed in the cases of **2T polymer** and **3T polymer**.

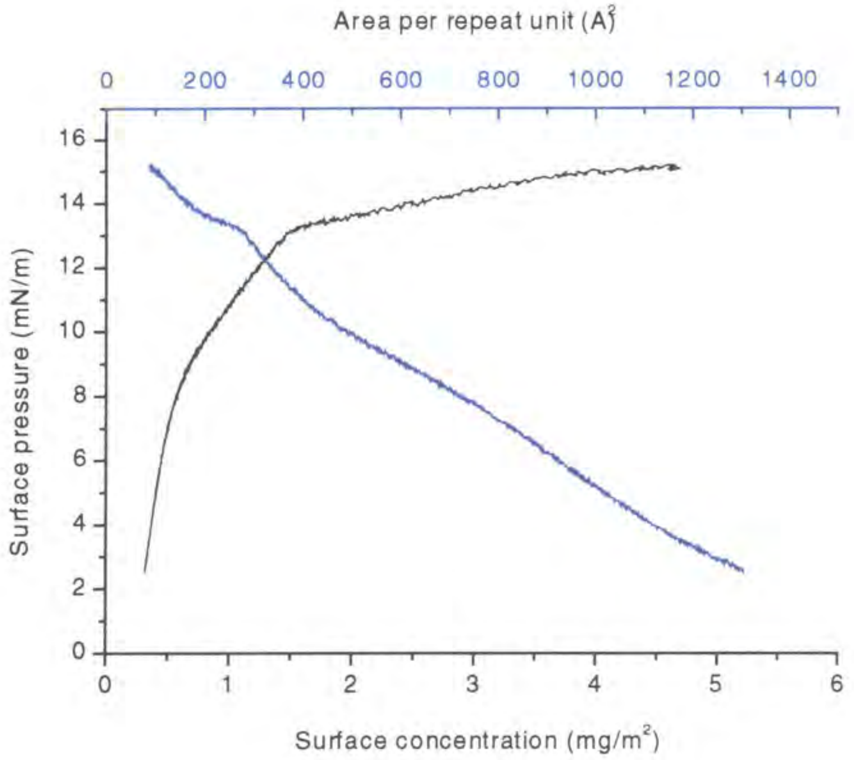

Figure 4.2.5 Surface pressure isotherm of ***5T polymer.*** *Black curve: surface pressure against surface concentration, blue curve: surface pressure against area per repeat unit.*

The features observed for **4T polymer** seem to be even more pronounced in the case of **5T polymer** (Figure 4.2.5). The phase transition at Π=8.5 mN/m (680Å^2 per repeat unit) is now quite distinct and is followed by a linear increase of surface pressure with surface concentration in the Π−Γ-isotherm that leads, after a sharp transition at Π=13.2mN/m (280Å^2 per repeat unit), to a region of slow surface pressure increase.

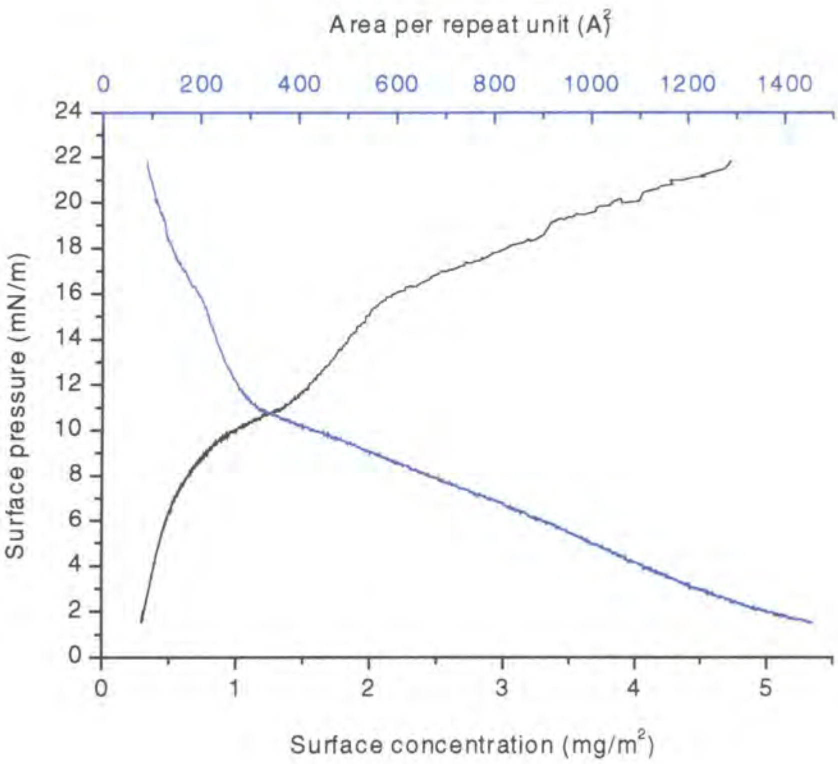

*Figure 4.2.6 Surface pressure isotherm of **6T polymer.** Black curve: surface pressure against surface concentration, blue curve: surface pressure against area per repeat unit.*

When comparing the surface pressure isotherms (Π–Γ and Π–A) for **6T polymer** (Figure 4.2.6) to those of the previously described polymers, one can immediately observe two new features. A phase transition at Π = 8.2 mN/m (641 Å^2 per repeat unit) is followed by a second transition at Π=11.4 mN/m (300 Å^2 per repeat unit) which then leads to a linear increase of surface pressure with surface concentration in the Π–Γ-isotherm, as previously observed. Also, the more defined transition at Π=15.9 mN/m (200Å^2 per repeat unit) is not followed by a plateau region but by a steady increase in surface pressure with increasing surface concentration or decreasing area per repeat unit.

To compare results, the Π–Γ- as well as the Π–A-isotherms of all polymers are plotted into two graphs (Figure 4.2.7 and Figure 4.2.8). The similar behaviour of polymers **2T polymer** – **5T polymer** can easily be seen in either of the two representations. **6T polymer** shows a distinctly different shape to the other oligothiophene main chain polymers.

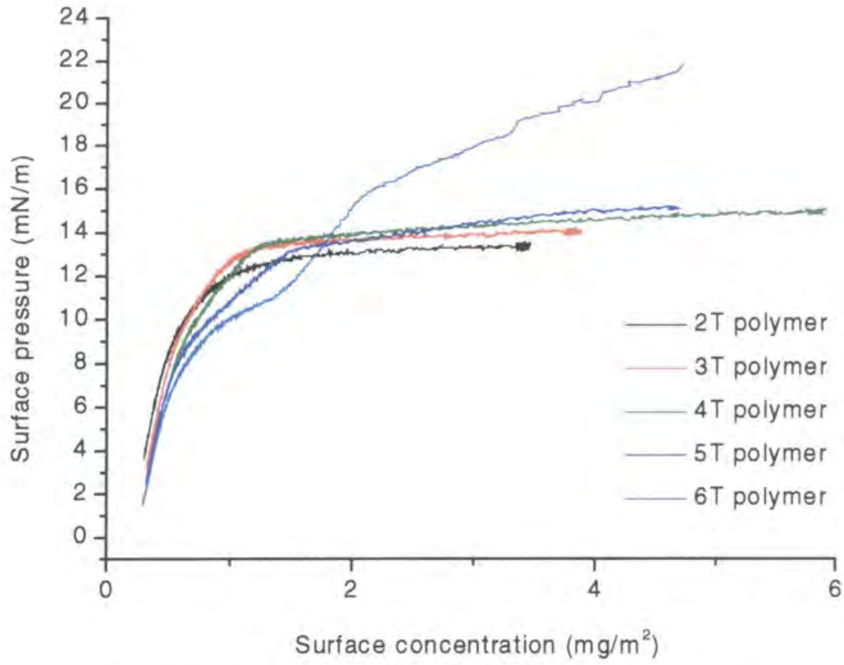

Figure 4.2.7 Surface pressure isotherms (surface pressure against surface concentration) of all polymers.

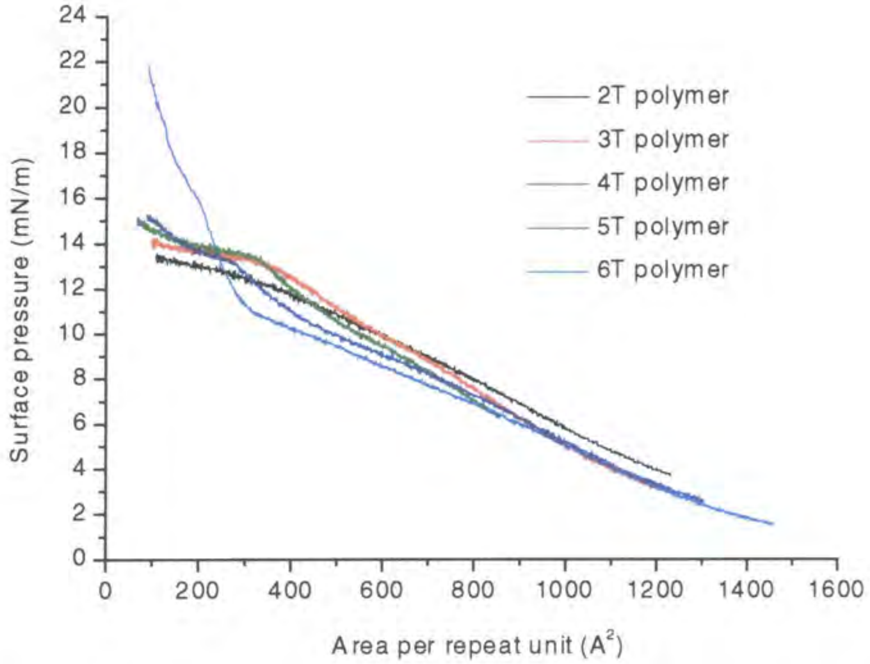

Figure 4.2.8 Surface pressure isotherms (surface pressure against area per repeat unit) of all polymers.

These results clearly indicate that the polymers prepared are surface active. However, if the poly(ethylene oxide) chains were completely immersed in the water sub-phase, with just the hydrophobic oligothiophenes occupying the water surface, a steeper rise in surface pressure would be expected for low areas per repeat unit. No region in any of the recorded isotherms resembles a condensed phase and therefore no zero-pressure-extrapolation of the isotherms to obtain meaningful areas per repeat unit were carried out. It is striking though, that the isotherms for all polymers (except for **2T polymer**) show a relatively sharp phase transition in the region of Π=11.4-13.2 mN/m (280-300Å^2 per repeat unit). These very high values for area per repeat unit could mean that poly(ethylene oxide) chains as well as oligothiophene rods cover the sub-phase surface and re-organise their structure at certain surface pressure values, giving rise to observable transitions in the recorded isotherms.

To investigate the effect of poly(ethylene oxide) chain length on the shape of the surface pressure isotherm, compounds **6T PEO 750**, **6T PEO 350** and **6T chiral** were also examined. Figure 4.2.9 shows Π–A-isotherms for **6T PEO 750** (blue curve) and **6T PEO 350** (black curve). Whereas the isotherm for **6T PEO 750** looks qualitatively similar to those of the oligothiophene polymers described before, the one for **6T PEO 350** is what one would expect for a classical low molecular weight amphiphile.

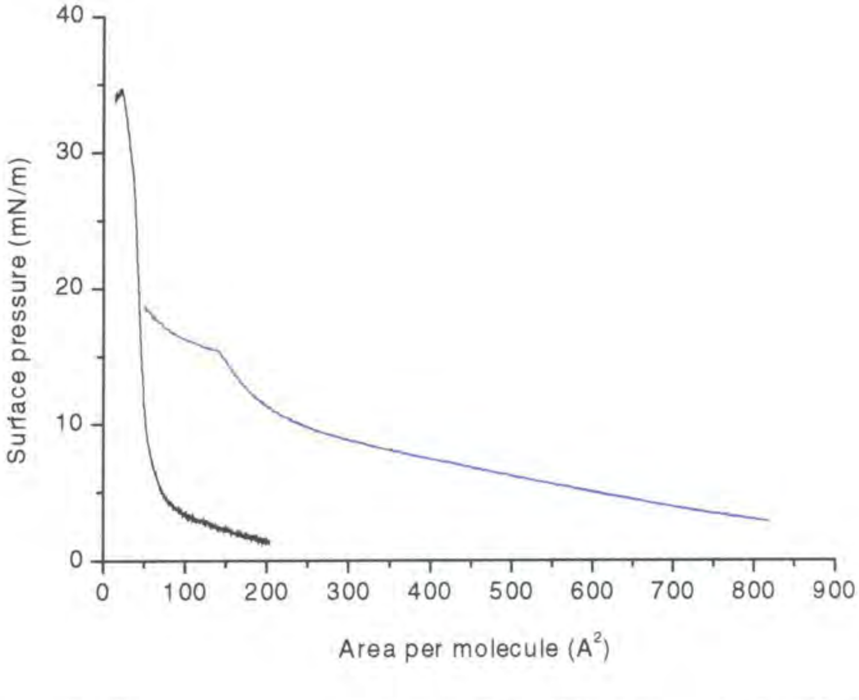

*Figure 4.2.9 Surface pressure isotherms of **6T 750** (blue) and **6T 350** (black).*

Both compounds were prepared with commercial poly(ethylene oxide) mono methyl ethers, which, due to the way they are synthesised, show a molecular weight distribution. In that respect these sexithiophene derivatives are no different to their polymeric analogue **6T polymer**. It has to be concluded, that it is merely the length of the poly(ethylene oxide) chains that determines the shape of the Π–A-isotherm. Extrapolating what can be regarded as the condensed region of the **6T PEO 350** isotherm to zero pressure gives a value of 56 Å^2 per molecule.

The Π–A-isotherm of **6T chiral**, a monodisperse compound, is shown in Figure 4.2.10. The shape of the isotherm is very similar to the one of **6T PEO 350**. Extrapolating the condensed region of this isotherm to zero pressure gives, again, a value of 56 Å^2 per molecule.

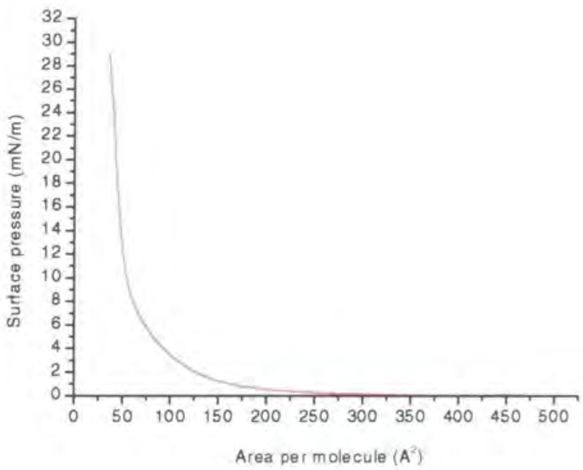

*Figure 4.2.10 Surface pressure isotherm of **6T chiral***

To interpret the obtained value of 56 Å^2 per molecule, models for the sexithiophene derivatives were calculated using molecular mechanics to optimise the geometry. Figure 4.2.11 shows the model for compound **6T chiral**, Figure 4.2.12 a side-on view of a section and Figure 4.2.13 a view along the long axis of a sexithiophene derivative. Figure 4.2.14 shows a section of a oligothiophene which was used to measure the distance across the oligothiophene ring, perpendicular to the long axis and in the ring plane.

*Figure 4.2.11 Molecular model for **6T chiral**. The distance from one terminal methyl group to the other (from left to right) is ca. 56.6Å.*

Figure 4.2.12 Molecular model for a sexithiophene derivative α,ω-di-substituted with two ethyl ester groups. The distance from one ether oxygen to the other is ca. 26 Å.

Figure 4.2.13 Molecular model for the same compound as shown in Figure 4.2.12 in a view along the long axis of the molecule. The distance across the molecule (left to right) is ca. 2.5 Å.

Figure 4.2.14 Molecular model of a section of an oligothiophene. The distance across (top to bottom) is ca. 6.9Å.

According to these rough estimates, an arrangement of oligothiophenes perpendicular to the sub-phase surface would require ca. 17 Å^2 per molecule. A "face on" arrangement, in which the rods lie with their long axes and the ring planes parallel to the sub-phase surface, would require ca. 180 Å^2 per molecule. If they were π-stacked with their long axes parallel to the sub-phase surface, ca. 65 Å^2 per molecule would be needed. This value is closest to the observed 56 Å^2 per molecule. As compounds **6T PEO 350** and **6T chiral** have a hydrophilic chain attached to both ends of their long axes, it is reasonable to assume that both chains are immersed in the sub-phase, leaving the rigid rod no other possible arrangement than to lie parallel on the surface. π-Stacking would be energetically favoured compared to a "face on" arrangement as described above.

Langmuir-Blodgett Films

Some preliminary experiments were carried out in which we tried to transfer compressed Langmuir films of the sexithiophene polymer **6T polymer** onto silicon wafers. These substrates were either used in their pristine (hydrophilic) forms or after treatment with hexamethyl disilazane to make their surface hydrophobic. The deposition of the films was very difficult. Although the films, which were transferred onto hydrophilic substrates, looked homogeneous when examined under a UV microscope, the transfer could not be monitored by recording changes of surface area and therefore no transfer ratio could be calculated. Transfer onto hydrophobic substrates resulted in very uneven films, as was observable with the naked eye and also UV microscopy. Transfer of material onto glass microscope slides resulted in films which looked homogeneous under a UV lamp. It did not seem to be possible to build up several layers of material, as the UV absorption of the film remained unchanged and very low. A dependence of UV absorption on the number of dipping cycles could not be observed.

4.3 Conclusions

It was shown that all materials prepared, the polymers as well as the sexithiophene model compounds, were surface active. Surface pressure/area isotherms were recorded for all materials. All polymeric compounds apart from the bithiophene main chain polymer showed distinct phase transitions in the region of $\Pi=11.4\text{-}13.2$ mN/m (280-300Å^2 per repeat unit). The shape of the isotherm of the sexithiophene main chain polymer was different to the shapes of the isotherms of the other polymers, which resembled each other. The phase changes could not be assigned to structural changes at a molecular level. Surface pressure/area isotherms, recorded for sexithiophene model compounds, revealed that the length of the PEO chains attached determined the behaviour of the compound on the sub-phase surface. Short chains did not seem to interact with the sexithiophene rods and isotherms that resembled those of classical low molecular weight amphiphiles could be recorded for these compounds. Longer poly(ethylene oxide) chains seemed to modify the overall behaviour of the compound when spread onto a water surface, with the shape of the isotherm resembling those of the polymeric materials. When extrapolating the isotherms to zero pressure, the molecular area obtained was 56 Å^2 for both compounds, **6T PEO 350** and **6T chiral**. Molecular models, based on molecular mechanic calculations, suggested that the sexithiophene rods were closely packed lying edgewise with their long axes oriented parallel to the surface, probably forming π-stacks. Preliminary attempts to transfer the sexithiophene main chain polymer **6T polymer** onto various substrates to build up Langmuir-Blodgett multilayers were unsuccessful.

4.4 Experimental

Surface pressure isotherms were recorded on a commercial LB trough (Nima TKB 2410A with a Nima pressure sensor, type PS4). Polymers and model compounds were dissolved in spectrograde chloroform (Aldrich) to give concentrations of approximately 1 mg ml^{-1}. The chloroform solutions were spread onto a de-ionised double distilled water surface at room temperature. The surface pressure isotherms were recorded at compression speeds of 20 cm^{2} min^{-1}.

4.5 References

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5 Aggregation of Oligothiophene Derivatives in the Solid State and in Solution

5.1 Introduction

The electronic and optical properties of π-conjugated oligomers and polymers are highly dependant on the conformation of the conjugated segment and the interaction between different polymer chains. It is known that π-conjugated polymers aggregate in poor solvents or upon cooling solutions in good solvents.[1-4] These aggregates exhibit properties which are similar to those observed in the solid state. For various β-substituted polythiophenes these phenomena have been extensively studied but very little data has been reported on the aggregation and stacking of α,ω-substituted oligothiophenes or α,ω-substituted oligothiophene main chain polymers. Information about the nature of the aggregation and orientation is of great interest, as it may provide information leading to development of an understanding of how changes at a molecular level can affect supramolecular organisation. For the use of α,ω-substituted oligothiophenes or oligothiophene main chain polymers in electronic devices, such as the FET, a high degree of order and orientation is necessary in order to obtain high charge carrier mobilities.

One way of getting information about supramolecular organisation requires that the aggregating species is placed in a chiral environment, for example by attaching enantiomerically pure chiral side chains. On aggregation, supermolecular chiral structures might be formed which can then be investigated by chiroptical measurements. For polythiophenes with enantiomerically pure chiral side chains in the β-positions aggregates with helical superstructures have been proposed. The proposal is based on the interpretation of the large circular dichroism (CD)-effects observed in the π–π* band of the materials in their aggregated forms. CD has been used extensively for the analysis of aggregation phenomena in biopolymers. It has been applied, for example, to the determination of conformational changes in proteins[5] and nucleic acids but has recently proved to be of great value in synthetic conjugated polymer chemistry especially in the detection and characterisation of chiral superstructures.[1,2,6-8]

Optical Activity and Circular Dichroism[9-13]

Circular dichroism (CD) is defined as the difference in molar absorption coefficients for left and right circularly polarised light:

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$$

A plot of $\Delta\varepsilon$ against wavelength is called a CD-spectrum and is only observable for optically active compounds in regions where they absorb light. Compounds that fulfill this requirement can be divided into the ones with inherently chiral chromophores (like hexahelicene, twisted biphenyls or twisted dienes) and those with symmetrical chromophores perturbed by a chiral environment (like the carbonyl groups in proteins). The requirement for optical activity is the absence of an alternating rotation-reflection axis in a compound. For a one-fold axis this represents the absence of a centre of inversion and for a two-fold axis the absence of a symmetry plane. This symmetry reqirement corresponds with that of a transition having electric and magnetic transition dipole moments with components in a common direction.

An electric dipole moment (μ) is the result of a linear displacement of charge whereas rotation of charge generates a magnetic dipole moment (m) perpendicular to the plane of rotation. A quantity that determines the sign of the CD and relating electric dipole moment (μ), magnetic dipole moment (m) and the angle (θ) between them, is the rotational strength R:

$$R = \mu \, m \cos \theta$$

It can be shown that the rotational strength equals zero for compounds not fulfilling the above symmetry requirements for optical activity (i.e. achiral compounds do not exhibit a CD effect). For angles θ between –90° and +90° the rotational strength will take positive values, for angles between 90° and 180° its value is negative. Parallel μ and m ($\theta = 0°$) will therefore result in a positive value of R, antiparallel μ and m ($\theta = 180°$) in a negative value of R.

Circular dichroism effects of inherently chiral chromophores like the twisted diene have been extensively studied[14-16] but are not relevant to this work and will not be discussed here. As mentioned earlier, achiral chromophores in a chiral environment also exhibit CD effects. In this context many empirical rules have been developed to obtain configurational information from CD spectra of various naturally occurring classes of optically active compounds. In these, the presence of the carbonyl n-π* transition makes CD investigations possible.

A third possibility to observe CD effects is provided by two or more chromophores arranged in a chiral array. Even if not directly in conjugation with each other, these chromophores can couple via a dipole-dipole interaction mechanism, when one is excited. This phenomenon has been studied for various model compounds and will be described here for the hypothetical case of a chiral array of sexithiophene molecules. In Figure 5.1.1, an α,ω-disubstituted sexithiophene derivative (top) as well as its quinoid excited state (bottom) is shown.

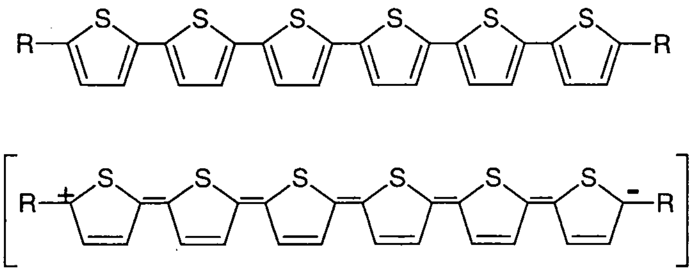


Figure 5.1.1 Top: α,ω-disubstituted sexithiophene. Bottom: simplified representation of the dipolar excited quinoid state of the α,ω-disubstituted sexithiophene.

In Figure 5.1.2 (1) two sexithiophene derivatives are shown in a chiral arrangement. The lighter one with the long axis pointing from the bottom left to the top right corner is behind and the darker one with the long axis from the top left to the bottom right corner in front of the paper plane. Moving from one of the two sexithiophenes to the other along an axis perpendicular to the paper plane one can see that they are arranged in a left handed or anticlockwise manner. They could represent a section of a helical arrangement of sexithiophenes.

If these two sexithiophenes were electronically excited to form the quinoid dipolar structures, two possible arrangements of charges across the two derivatives would be possible (Figure 5.1.2, 2 and 3). In representation **A** the ends of the excited quinoid sexithiophenes with like charges are relatively close together, giving rise to a net electric dipole moment pointing from the left to the right (Figure 5.1.2 4, μ_A)

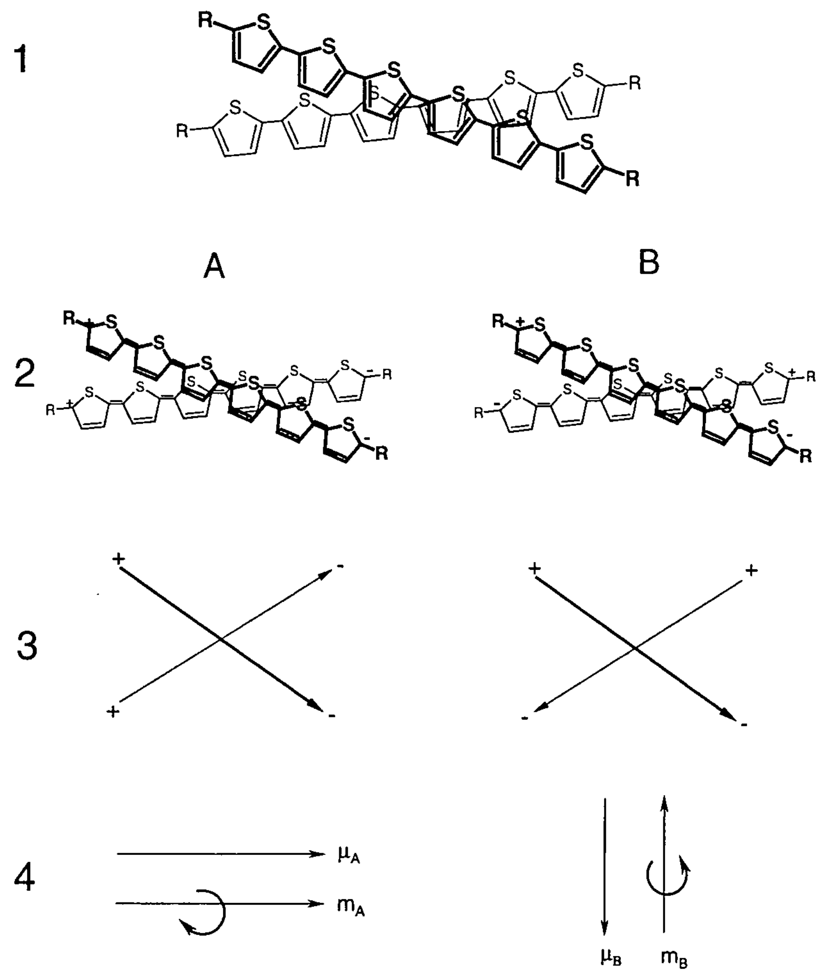


Figure 5.1.2 1: Two α,ω-disubstituted sexithiophenes stacked ontop of each other with an angle between the two long axes. 2: Two possible combinations of coupled dipoles, A and B. 3: Arrow representation of the two dipole coupled excited states A and B. 4: Electric dipole moments (μ) and magnetic dipole moments (m) for both dipole coupled excited states.

In representation **B** (Figure 5.1.2 2 and 3) like charges are arranged differently than in **A**, this time giving rise to a net electric dipole moment pointing downwards (Figure 5.1.2 4, μ_B). To recognise the direction of the magnetic dipole moments one can imagine the individual electric dipole moments as tangential forces on a hypothetical cylinder which has the net electric dipole moment as its rotation axis. This shows that in case **A** electric and magnetic dipole moments are parallel, whereas in case **B** they are antiparallel.

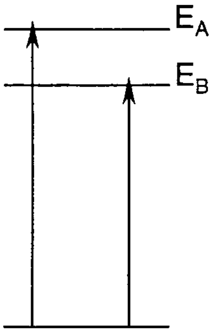


Figure 5.1.3 Energy diagram for the two possible coupled dipoles (see Figure 5.1.2)

The distribution of electrical charges in case **A** is energetically less favourable than in case **B**. The close proximity of charges of equal sign in case **A** leads to repulsion and therefore increase in energy whereas in **B** charges of different sign are very close together, resulting in an attractive interaction which is energy lowering.

The parallel orientation of μ_A and m_A gives rise to a positive rotational strength, R, the antiparallel orientation of μ_B and m_B results in a negative value of R. These considerations explain the observed peak (positive Cotton effect) at higher and a trough (negative Cotton effect) at lower energy in the CD spectrum with the curve going through zero near the absorption maximum of the chromophore.

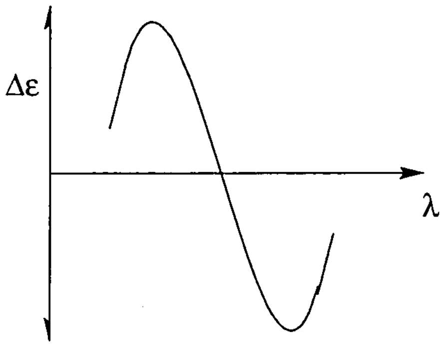


Figure 5.1.4 A bisignate CD-effect with a positive Cotton effect at higher and a negative Cotton effect at lower energy.

Such a curve is typical for coupled chromophores (also called exciton coupling), arranged in a left handed helical array (negative chirality) and the observed CD effects are usually quite intense. The splitting of the energy level into two states E_A and E_B when the chromophores are stacked in a near parallel manner is also referred to as *Davydov-splitting*.[11]

In a recent experimental and theoretical study Langeveld-Voss *et al.*[17] have shown, that for a chiral model compound in which two terthiophene units are sterically confined in a right handed manner with an angle of 67° between the long axes of the molecules, a bisignate Cotton-effect in the CD spectrum occurs. When the two stacked chromophores are arranged completely parallel to each other, exciton coupling theory predicts, that the transition (absorption and fluorescence) from the ground state to the lowest excited state and vice versa is formally forbidden (Figure 5.1.5). Both transitions become allowed as soon as a finite angle between the chromophores (as in the examples above) is present.

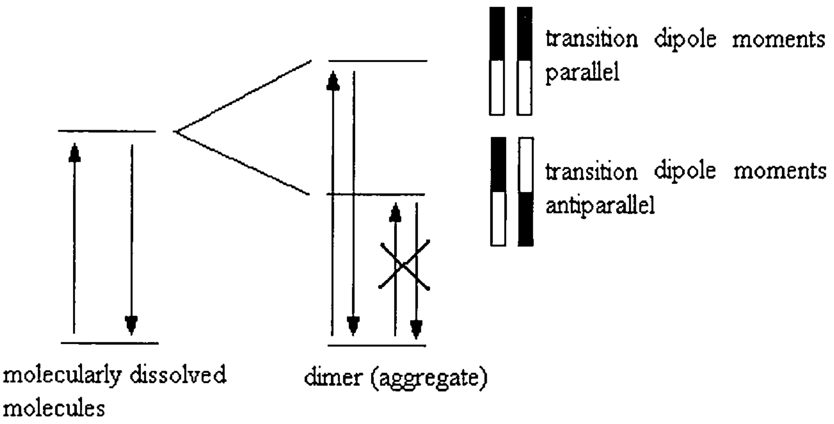


Figure 5.1.5 Davydov splitting. Left: Absorption and fluorescence of molecularly dissolved chromophores. Right: Interaction of the transition dipole moments of two aggregated chromophores leads to the splitting of the π–π absorption band.*

5.2 Spectroscopic Investigations of Oligothiophene Polymers and Model Compounds – Results and Discussion

The compounds investigated by spectroscopic (UV/Vis, fluorescence) methods are shown in Figure 5.2.1.

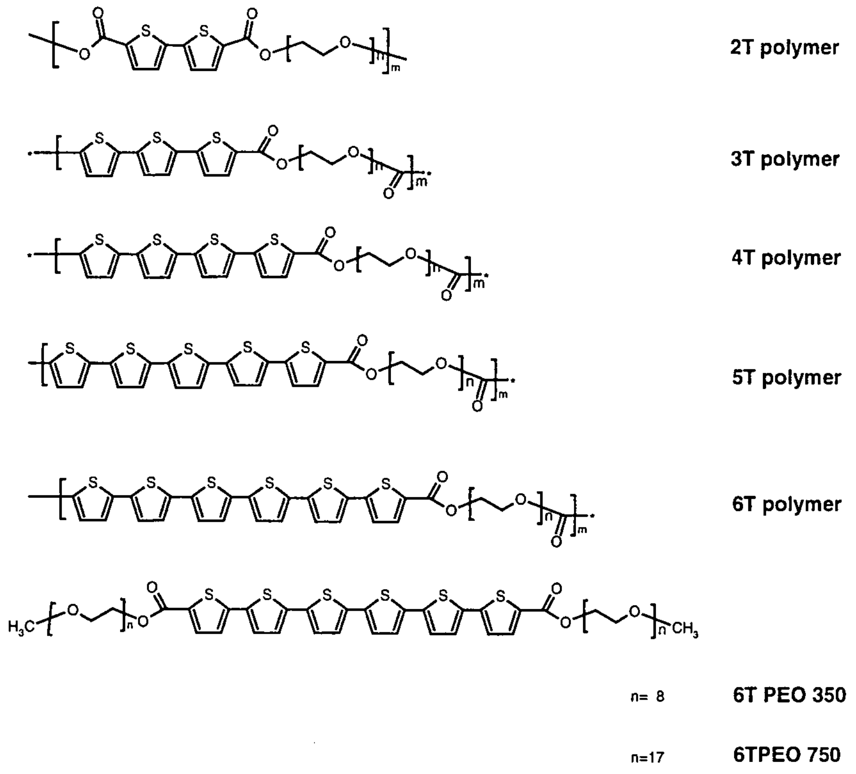


Figure 5.2.1 Compounds investigated by spectroscopic measurements.

Their synthesis and characterisation has been described in chapter 3. Solutions with a concentration of approximately 15 mg l^{-1} were prepared and the recorded spectra subsequently normalised to chromophore (oligothiophene) concentrations of 6.7 mol l^{-1} in order to be able to compare results. Optical spectra were recorded using a Perkin Elmer Lambda 900 spectrophotometer for UV-vis, a Jasco J-600 Spectropolarimeter for CD and a Perkin Elmer luminescence spectrometer for fluorescence. Low temperature spectra were recorded using an Oxford Optistat continuous flow cryostat. Spectra at different temperatures are not corrected for volume changes of the solvent. All polymers and sexithiophene derivatives were soluble in chloroform. Their UV/Vis- and fluorescence spectra recorded at room temperature are shown in Figure 5.2.2 and Figure 5.2.3. The absorption spectra show structureless bands as expected for molecularly dissolved chromophores. No vibronic fine structure could be observed. Due to increasing π-conjugation the absorption maximum shifts towards the red for the higher oligothiophenes. The fluorescence spectra show more fine structure than the absorption spectra. Each emission spectrum clearly shows three bands which have been identified as the vibronic replicas of the 0-0 transition.[18] The spectra recorded in water-THF mixtures (90%water, 10%THF) are in sharp contrast to those in chloroform.

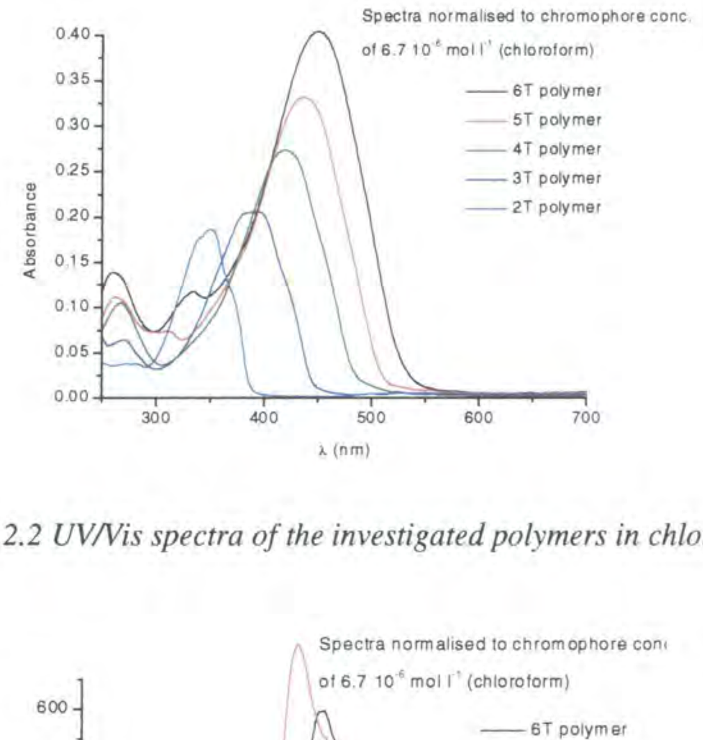


Figure 5.2.2 UV/Vis spectra of the investigated polymers in chloroform.

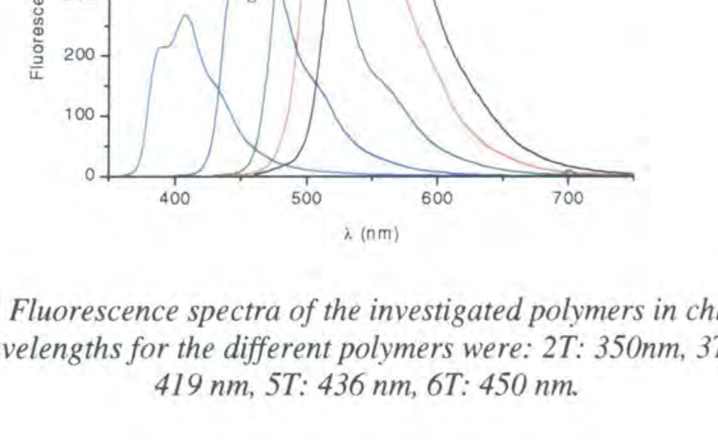


Figure 5.2.3 Fluorescence spectra of the investigated polymers in chloroform. The excitation wavelengths for the different polymers were: 2T: 350nm, 3T: 392 nm, 4T: 419 nm, 5T: 436 nm, 6T: 450 nm.

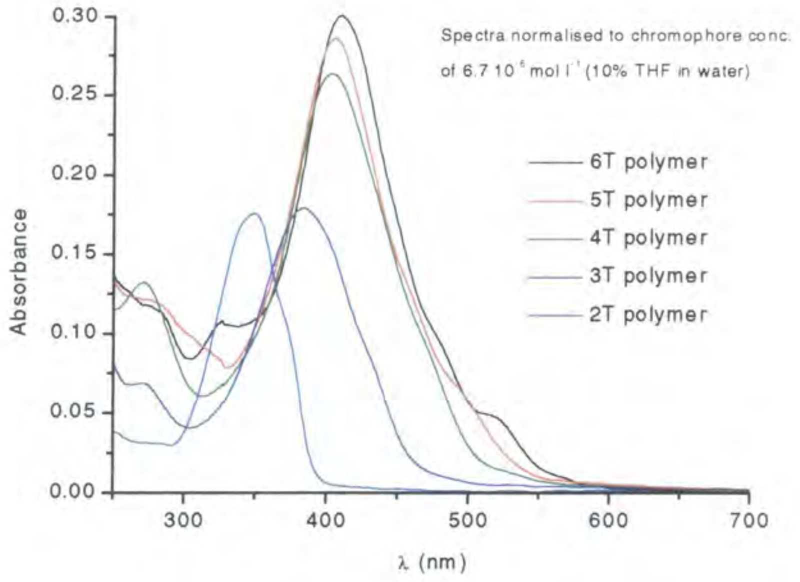


Figure 5.2.4 UV/Vis spectra of the investigated polymers in 90%water, 10%THF.

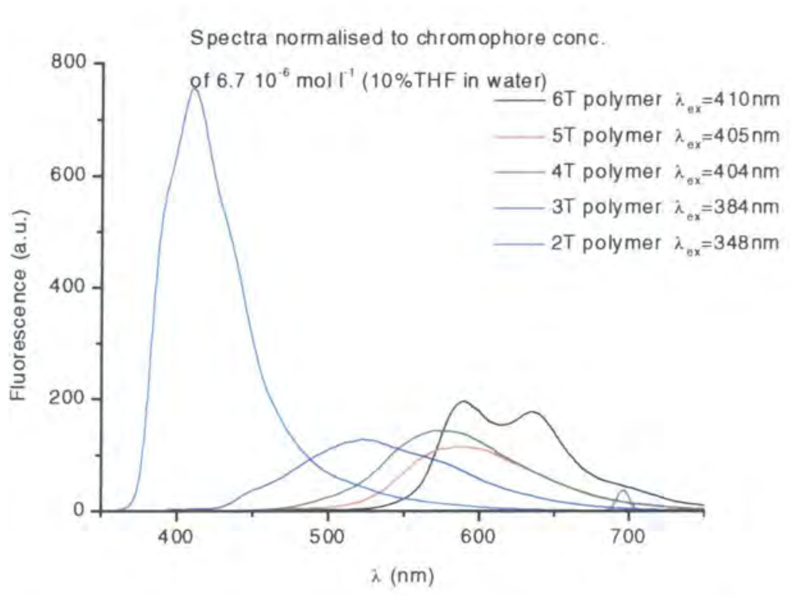


Figure 5.2.5 Fluorescence spectra of the investigated polymers in 90%water, 10%THF.

The role of the THF was merely to dissolve the polymers before injecting the solution into water, as they did not dissolve visibly when added to pure water as solids. Whereas the absorption peak maxima for **2T polymer** and **3T polymer** do not seem to have shifted at all, those for **4T polymer**, **5Tpolymer** and **6T polymer** have shifted significantly towards the blue, i.e. to higher energy (Figure 5.2.4). This can be explained by the above mentioned aggregation model, in which the oligothiophene rods aggregate in a parallel manner, leading to coupling of the transition dipole moments. In this case the transition to the lower Davydov component is dipole forbidden. The high energy transition is dipole allowed but of higher energy than observed for the molecularly dissolved oligothiophene. Small absorption peaks on the lower energy side of the main absorption band have been explained by Yassar *et al.* for the case of thin films of sexithiophene by assuming disordered domains are present.[18] In these disordered domains the excited state is not split into two exciton bands but both, ground and excited state, are shifted towards lower energies. The fluorescence spectra of the polymer solutions in water-THF mixtures are shown in Figure 5.2.5. The position of the emission band of **2T polymer** is unaltered but its intensity increased, which, together with the observations in the UV spectrum, suggests that this polymer is not aggregated even in aqueous solution. The author can offer no explanation for the increase of intensity. The emission spectrum of **3T polymer** is much broader than that recorded in chloroform, shifted towards the red but still showing a band at around 450nm where the main band for the freely dissolved polymer was observed. This could mean that at room temperature in aqueous solution aggregates, misaligned aggregates as well as molecularly dissolved terthiophene units are present. The first would not contribute to emission and the second give rise to emission at lower energy than observed for the molecularly dissolved terthiophene. For all other polymers the intensity of the bands is much lower than in the case of their chloroform solutions, indicating that the oligothiophenes are aggregated and do not contribute to the emission due to the dipole forbidden transition. The emission that occurs is at much lower energy than observed in the chloroform spectra, which can be explained by the above mentioned assumption of disordered domains.[18] From these results it can be concluded that the tendency to aggregate is higher for the longer oligothiophenes than for the shorter ones. To investigate the influence of incorporating the oligothiophene into a polymer compared to the situation where short PEO chains are connected to the α and ω position of the rod, the three sexithiophene derivatives **6T polymer**, **6T PEO 350** and **6T PEO 750** were examined spectroscopically . Solutions of these compounds were prepared in water, methanol and chloroform and the UV/Vis and fluorescence spectra recorded at room temperature. While the spectra in chloroform (Figure 5.2.6) for all three derivatives are essentially identical, in methanol (Figure 5.2.7) only the **6T polymer** seems to form aggregates exclusively, determined by the large blue shift in the absorption and reduced intensity in the emission spectrum.

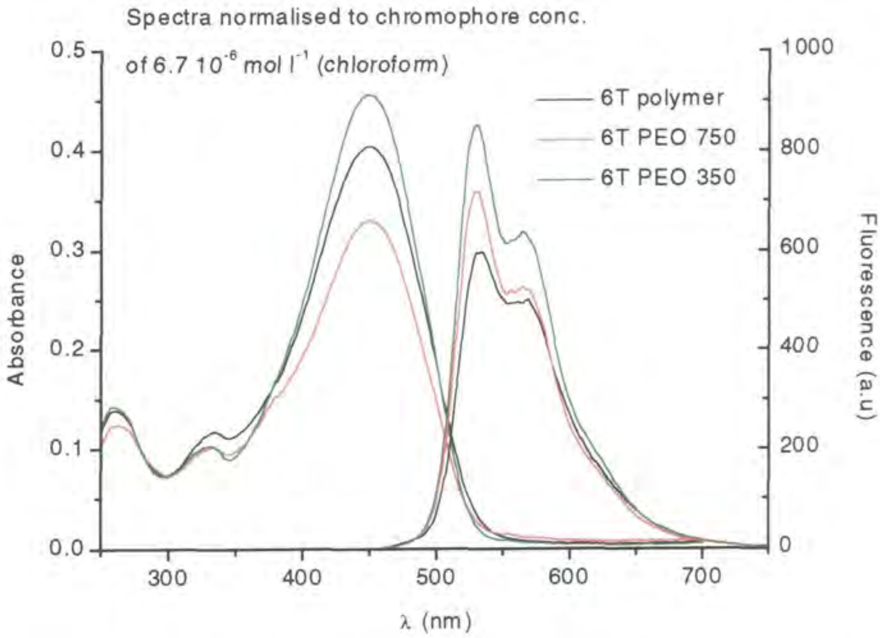


*Figure 5.2.6 UV/Vis and fluorescence spectrum of the sexithiophene derivatives **6T polymer** (λ_{ex}=450nm), **6T PEO 350** (λ_{ex}=450nm) and **6T PEO 750** (λ_{ex}=450nm) in chloroform solution.*

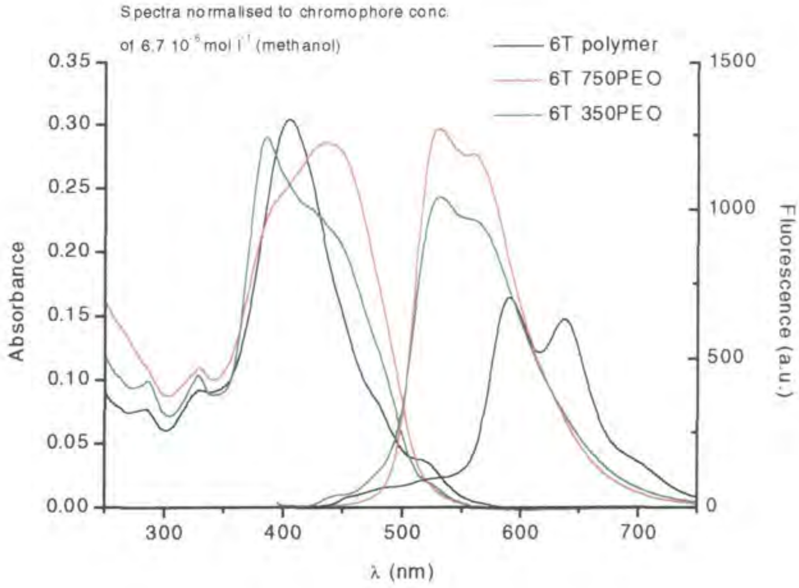


*Figure 5.2.7 UV/Vis and fluorescence spectrum of the sexithiophene derivatives **6T polymer** (λ_{ex}=400nm), **6T PEO 350** (λ_{ex}=385nm) and **6T PEO 750** (λ_{ex}=430nm) in methanol solution.*

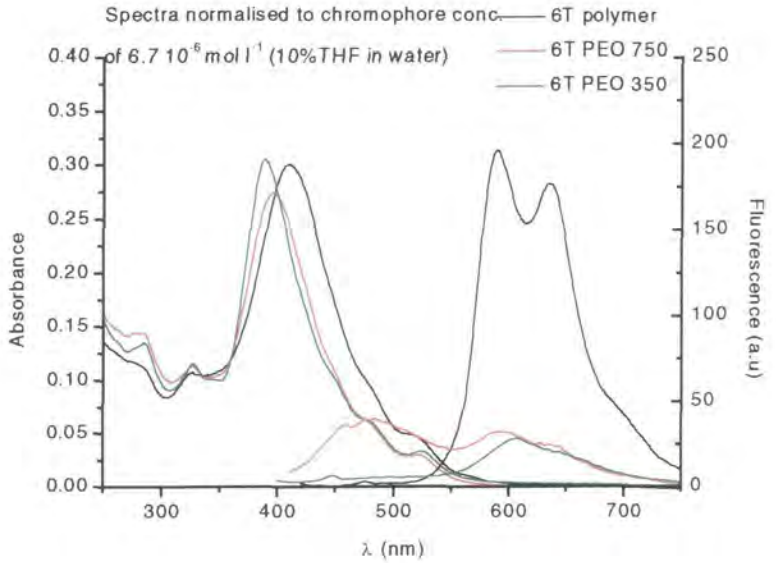


*Figure 5.2.8 UV/Vis and fluorescence spectrum of the sexithiophene derivatives **6T polymer** (λ_{ex}=410nm), **6T PEO 350** (λ_{ex}=389nm) and **6T PEO 750** (λ_{ex}=396nm) in aqueous solution*

6T PEO 750 as well as **6T PEO 350** show significant absorption bands at 450nm indicating individually dissolved sexithiophene rods. Also the fluorescence is far more intense and proves the presence of the non-aggregated form. Interestingly the compound with the longest PEO chain (**6T polymer**), which one would expect to be most soluble compared to the compounds with shorter PEO chains, aggregates most readily in methanol. This could be explained by the fact that in the polymer the sexithiophene rods cannot diffuse away from each other and therefore the probability of intramolecular aggregation is increased. In water (Figure 5.2.8) on the other hand all three compounds seem to form the aggregate as their UV/Vis spectra become very similar. The intensity observed in the fluorescence spectra is significantly decreased but different for the three compounds examined. Again, misalignment of the aggregates is probably responsible for the observed fluorescence.

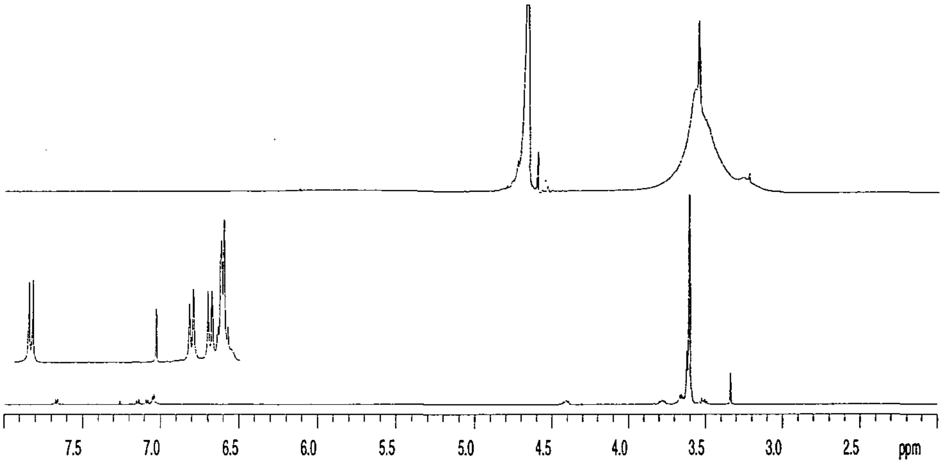


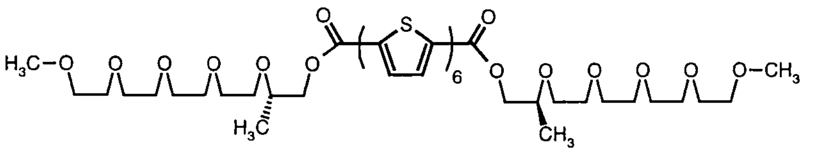
Figure 5.2.9 ^{1}H-NMR spectrum of 6T PEO 750 in D_2O (top) and chloroform (bottom)

Compound **6T PEO 750** showed very good solubility in a large variety of solvents. Its unusual solubility in water was exploited to observe the aggregation via ^{1}H-NMR spectroscopy in D_2O. Spectra (300 MHz) were recorded in $CDCl_3$ and D_2O (Figure 5.2.9). The fine structure in the aromatic region (δ=7.0 - 7.7 ppm) is well resolved in $CDCl_3$ indicating individually solvated molecules. In D_2O on the other hand, no sharp peaks can be observed in that region. Also the sharp peak occurring at δ=3.6

ppm in chloroform due to the PEG methylene hydrogens has broadened substantially in D_2O. Both observations fit well into a model where the sexithiophene rods aggregate, giving rise to very broad ^{1}H-NMR signals.

5.3 Chiroptical Studies of a Chiral Sexithiophene Derivative – Results and Discussion

Circular dichroism has been established as a valuable technique for investigating the structures of supramolecular architectures of chiral chromophores (see introduction). A chiral group was therefore introduced into a sexithiophene derivative (Figure 5.3.1).



6T chiral

Figure 5.3.1 A C_2-symmetrical chiral sexithiophene derivative synthesised for chiroptical studies.

6T chiral had a surprisingly high solubility in chloroform and dichloromethane. It was even soluble in water, although only at low concentrations. The UV/Vis spectrum shows clearly that in chloroform all molecules are individually solvated. As seen for the achiral sexithiophene analogues only a broad featureless band with an absorption maximum at λ_{max}=450nm is observed (Figure 5.3.2). The fluorescence spectrum shows the typical vibrational fine structure and the observed high intensity provides further evidence that the material is molecularly dissolved.

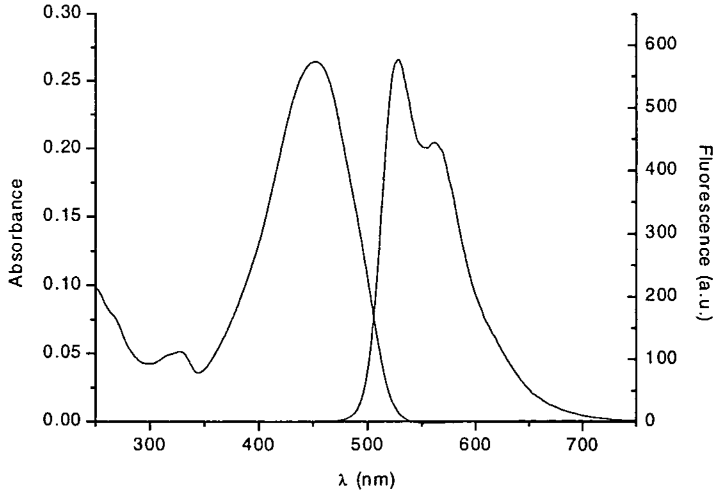


Figure 5.3.2 UV/Vis and fluorescence spectrum of ***6T chiral*** *(λ_{ex}=450nm) in chloroform.*

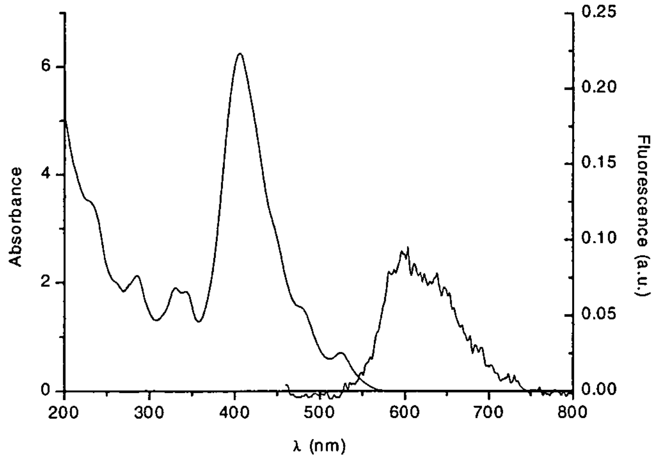


Figure 5.3.3 UV/Vis and fluorescence spectrum of ***6T chiral*** *(λ_{ex}=400nm) in water at r.t.*

The UV/Vis spectrum of **6T chiral** in water on the other hand is typical for aggregated sexithiophene derivatives (see above) with a blue shift of the main band of ca. $\Delta\lambda$=50nm to λ_{max}=400nm and smaller bands at longer wavelengths. The fluorescence intensity is reduced, consequent on the dipole forbidden transition (see above).

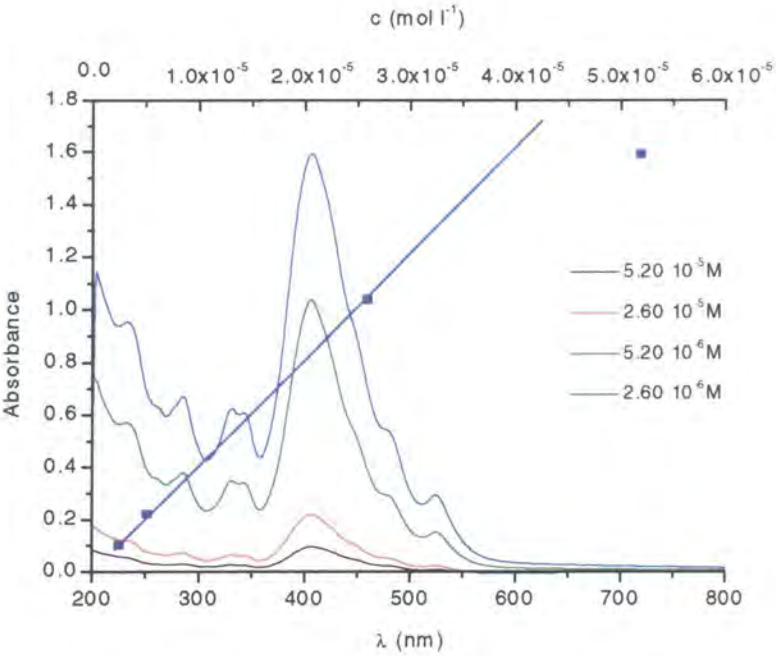


Figure 5.3.4 UV/Vis spectrum of a concentration series of ***6T chiral*** *at r.t. A linear concentration dependence of absorption (blue line) can be observed for low chromophore concentrations (black, red and green curve).*

The UV/Vis absorption spectrum was recorded at different concentrations in water as shown in Figure 5.3.4. For low concentrations (the three lowest traces in Figure 5.3.4) the Beer-Lambert law is followed, giving a linear relationship between the absorbance at λ_{max}=400nm and the concentration. It is remarkable that even at very low concentrations no non-aggregated species can be observed.

CD spectra were recorded (Figure 5.3.5) for aqueous solutions of **6T chiral** of different concentrations. Again, the magnitude of the effect was proportional to the concentration, indicating that aggregation occurred even at very low concentrations. A negative Cotton effect is observed exhibiting a trough at lower and a peak at higher energy (Figure 5.3.6) with the CD signal going through zero near the absorption maximum of the chromophore. This is a strong indication for exciton coupling due to aggregated sexithiophene rods forming a chiral superstructure with negative chirality (see example in Figure 5.1.2).

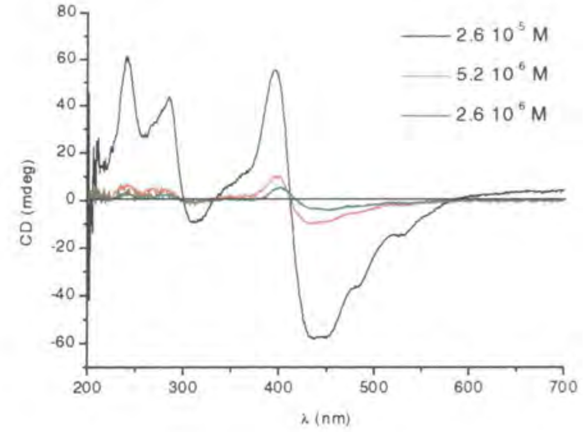


*Figure 5.3.5 CD spectrum for **6T chiral** in aqueous solution.*

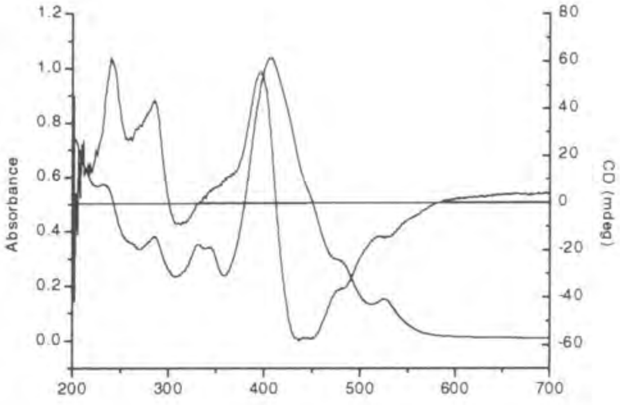


*Figure 5.3.6 UV/Vis and CD spectrum of **6T chiral** in water.*

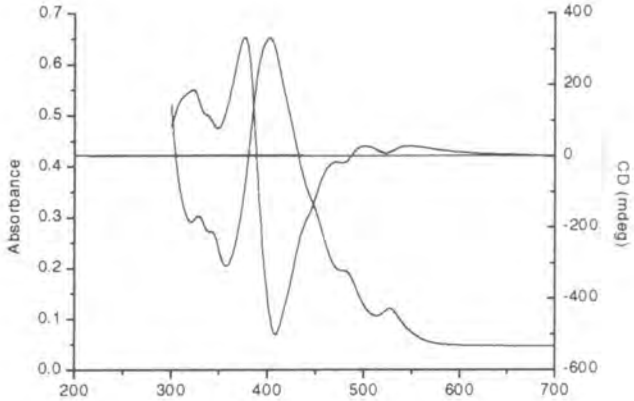


*Figure 5.3.7 UV/Vis and CD spectrum of a drop cast film of **6T chiral** from THF solution.*

Despite a relatively low absorption at the absorption maximum, a drop cast film of **6T chiral** (from THF solution) gave an even more intense CD-effect than the one measured in aqueous solution. The shape of both CD spectra was similar (Figure 5.3.7). This suggests that the chiral superstructure formed in the solid state might be of similar nature to the one formed in water.

The dissymmetry factor, a wavelength dependent measure of chirality, is defined as:

$$g_{abs} = 2\Delta\varepsilon/\varepsilon = 2\theta/(32980\ A)$$

Here θ is the ellipticity obtained from the CD experiments and A the absorption obtained from UV spectroscopy. For the solution in water (Figure 5.3.6) a maximum value of $g_{abs} = +3.48\ 10^{-3}$ was found at $\lambda = 391$ nm. For the solid state (Figure 5.3.7) a maximum value of $g_{abs} = +6.22\ 10^{-2}$ was found at $\lambda = 370$ nm. The Davydov splitting was estimated by calculating the difference in energy between the maxima of the positive and negative Cotton effects for both, the solution in water and the solid film. It was 0.29 eV in the former and 0.33 eV in the latter case.

The influence of temperature on aggregation was examined by heating an aqueous solution of **6T chiral** from 10°C to 80°C and recording the CD spectrum in 10°C intervals (Figure 5.3.8). As expected, the CD effect becomes more intense by lowering the temperature. From 10°C up to 40°C a steady decrease in the effect can be seen with every curve for each temperature changing sign at the same wavelength (λ=412nm). For temperatures higher than 40°C totally different CD spectra are detected. This could be explained by the cloud-point phenomenon, known for poly(ethylene glycol), which becomes less soluble in aqueous solution upon heating.

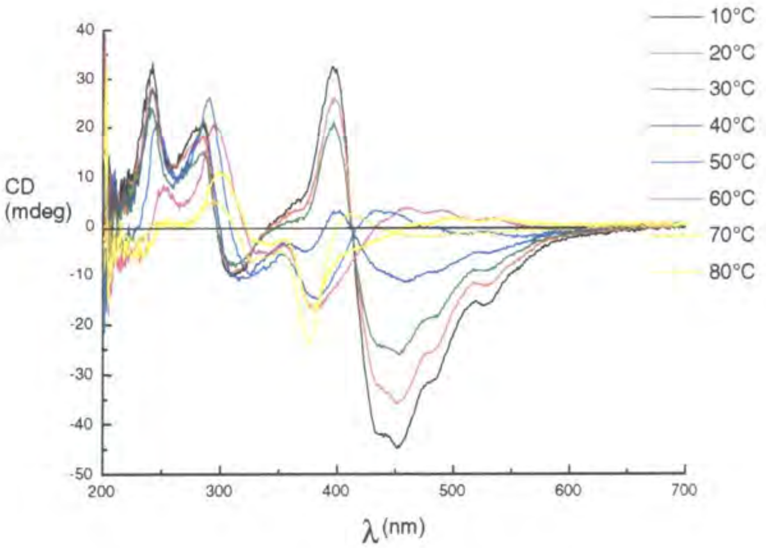


Figure 5.3.8 CD spectra of ***6T chiral*** *in water at different temperatures.*

After the heating run (80°C) a precipitated red solid could be seen at the bottom of the cuvette. The experiment was repeated in n-butanol in which the compound was soluble over a wider temperature range (from -10°C to 80°C). The solution was initially cooled to –10°C and then gradually warmed up to 80°C with time allowed for equilibration (10 min.) of the sample at each recorded temperature. Upon cooling, CD spectra were recorded at the same temperatures showing essentially the same traces that were recorded for the heating run. Both runs (*Figure 5.3.9*, *Figure 5.3.10*) show a very sharp transition temperature at 30°C at which the chiral superstructure seems to "de-aggregate" (see Figure 5.3.11 for a plot of CD intensity against temperature).

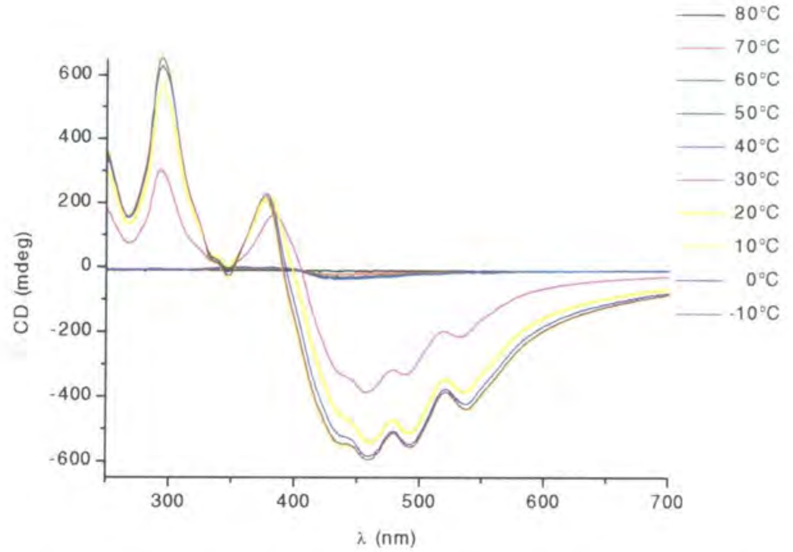


Figure 5.3.9 Temperature dependence of the CD effect upon heating ***6T chiral*** *in nBuOH.*

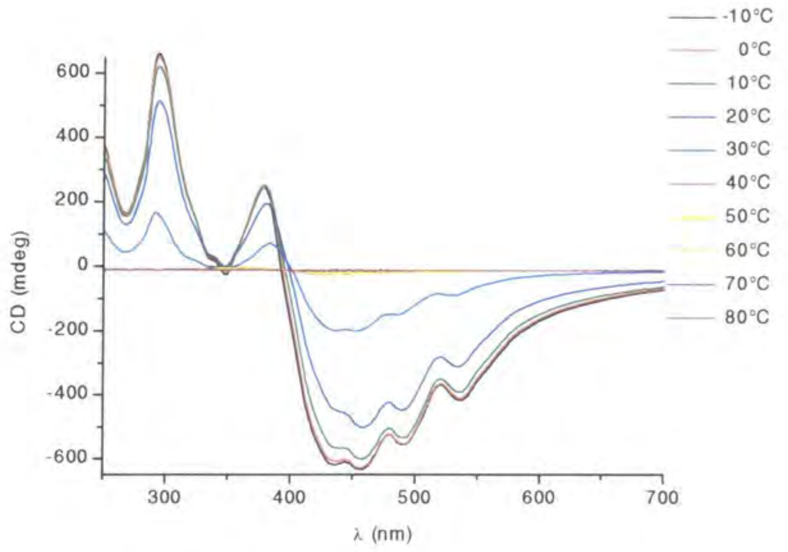


Figure 5.3.10 Temperature dependence of the CD effect upon cooling ***6T chiral*** *in nBuOH.*

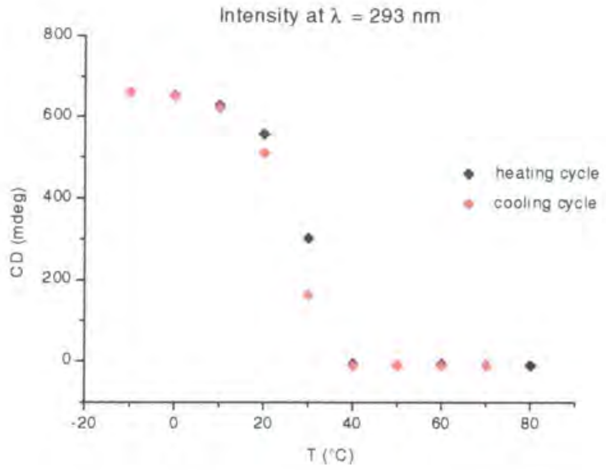


Figure 5.3.11 Intensity of the CD effect at λ=293nm for the heating and for the cooling cycle plotted against temperature.

This could be due to either of the following two cases. Under conditions where the chiral superstructure is observed the chiral centre on the penta ethylene glycol chain must necessarily have a preferential orientation on all chains. Upon heating, this preferred orientation might be destroyed due to increased conformational flexibility while the aggregate as such is still unaffected. On the other hand heating could "melt" the aggregate to produce molecularly dissolved chromophores and the chiral superstructure is destroyed in that way. To unambiguously distinguish between the two cases, fluorescence spectra were recorded of the same sample in n-butanol at temperatures varying from –10°C to 50°C, thus covering the range of interest. For excitation the wavelengths chosen was λ_{ex}=400nm (Figure 5.3.12).

If upon heating only the chiral side chains became more flexible, with the aggregate itself not undergoing any changes, the fluorescence should remain quenched until at some unknown higher temperature the aggregate would break up and an increase in fluorescence intensity could be observed. If destruction of the aggregates themselves was the reason for the loss of the chiral superstructure, then the fluorescence intensity against temperature should show the same transition temperature as the CD intensity against temperature.

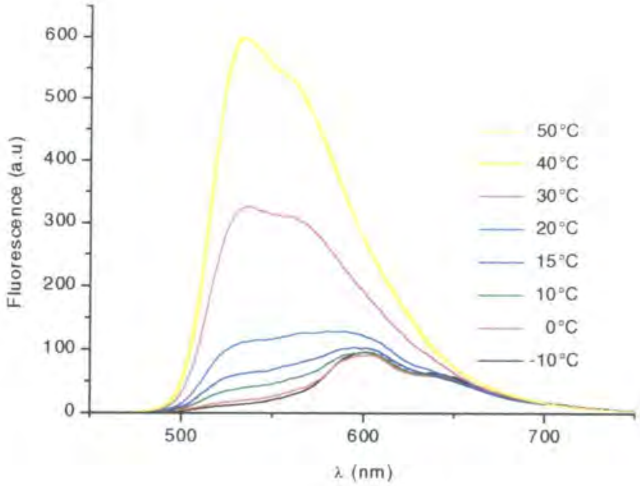


Figure 5.3.12 Temperature dependence of the fluorescence of 6T chiral in n-butanol (λ_{ex}=400nm).

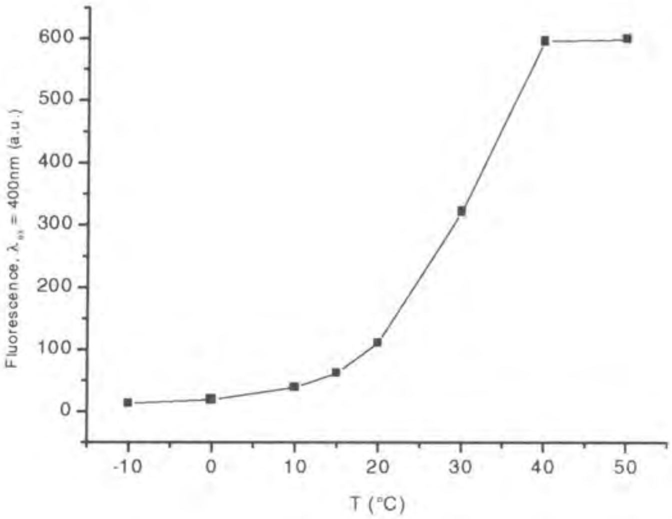


*Figure 5.3.13 Temperature dependence of fluorescence intensity of **6T chiral** in n-butanol. λ_{ex}=400nm. Observed at λ=533nm.*

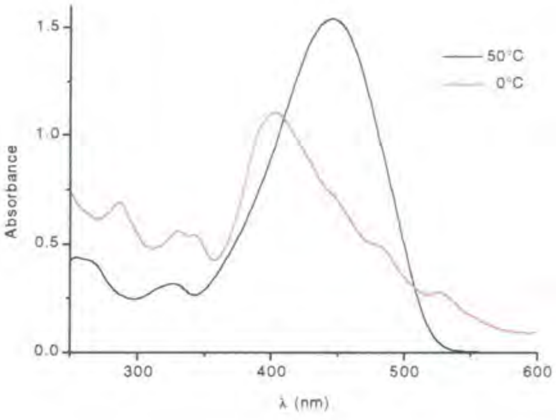


Figure 5.3.14 UV/Vis spectrum of ***6T chiral*** *in n-butanol at 0°C and 50°C.*

The intensity of fluorescence at λ=533nm was plotted against temperature (Figure 5.3.13). From Figure 5.3.12 it is immediately obvious that the fluorescence intensity increases with increasing temperature. From Figure 5.3.13 the same transition temperature (30°C) can be observed as was observed before from the plot of CD intensity against temperature (Figure 5.3.11). This unambiguously shows that it is the aggregate breaking up rather than the side chains becoming more flexible that leads to the loss of the chiral information of the superstructure.

5.4 X-Ray Diffraction of Oligothiophene Polymers – Results and Discussion

All oligothiophene polymers shown in Figure 5.2.1 were investigated by X-ray diffraction. Films of the polymers (ca. 3 cm^2) were cast from the melt, cut to size and placed in a sample holder. Poly(ethylene glycol), with the same chain length as was used to synthesise the polymers (DP≈45, M_n≈2000), was melted and the melt poured into the sample holder. The formation of spherulites could be seen. After complete solidification of the sample the X-ray diffraction pattern was recorded for comparison (Figure 5.4.1). X-Ray diffraction measurements were carried out using Cu K_α radiation. The spacings were calibrated by reference to those of a quartz single crystal. Figure 5.4.2-Figure 5.4.6 show the diffraction patterns recorded for all polymers.

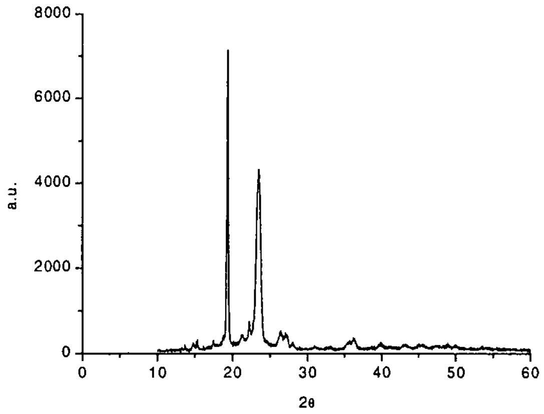


Figure 5.4.1 X-ray diffraction pattern of crystalline poly(ethylene glycol) (Mn=2000) sample.

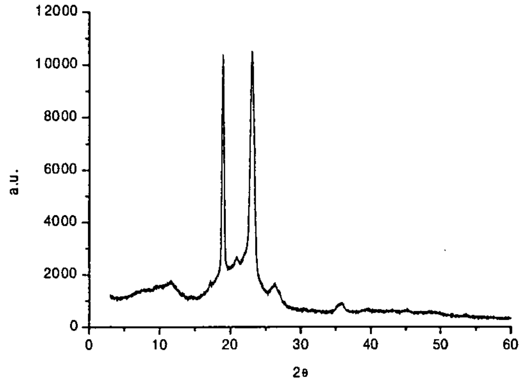


Figure 5.4.2 X-ray diffraction pattern of a melt cast film of ***2T polymer.***

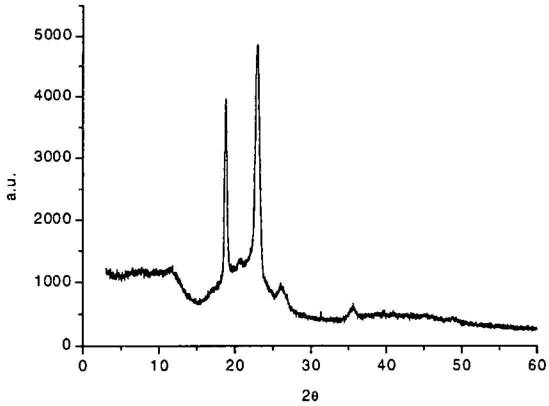


Figure 5.4.3 X-ray diffraction pattern of a melt cast film of ***3T polymer.***

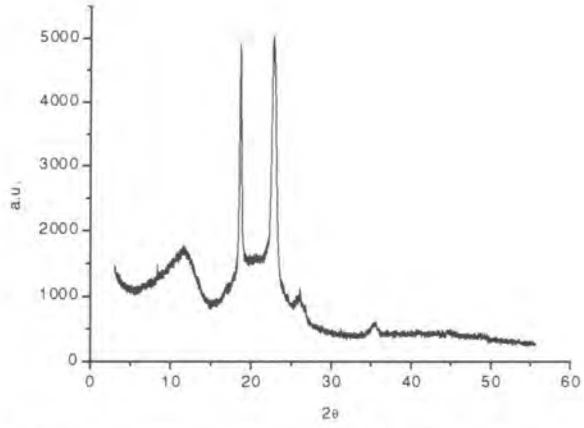


Figure 5.4.4 X-ray diffraction pattern of a melt cast film of ***4T polymer.***

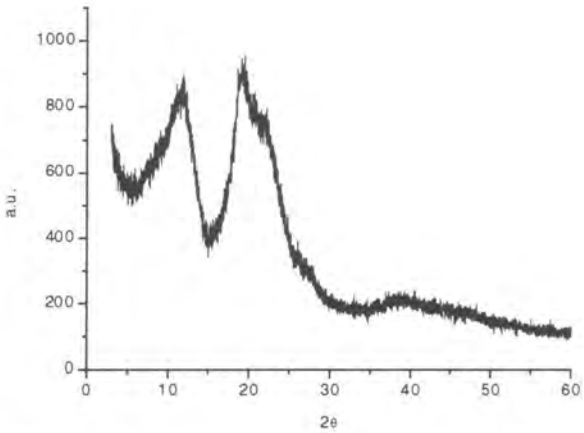


Figure 5.4.5 X-ray diffraction pattern of a melt cast film of ***5T polymer.***

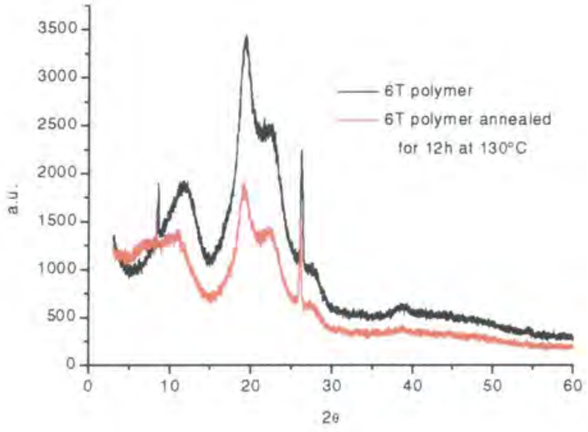


Figure 5.4.6 X-ray diffraction pattern of a melt cast film of ***6T polymer.***

The broad halo at around 2θ = 11°, which became visible when samples of lower intensity were recorded, was identified as arising from the amorphous plastic sample holder.

The structure of crystalline poly(ethylene oxide) has been extensively studied.[19-23] It is now believed that a PEO chain forms a distorted (7/2) helix.[24] Here, (7/2) means that the seven monomeric units turn twice per fibre period. Four of these helices form the unit cell. The dimensions are a=8.05Å, b=13.04Å, c=19.48Å (fibre axis) and β=125.4°. An idealised (7/2) helix, as was assumed in earlier studies, consists of a sequence of O-CH_2, CH_2-CH_2, CH_2-O bonds that are trans, gauche and trans, respectively. The distortion of the ideal helix has been attributed to intermolecular crystal-packing forces. In an early study[19], crystalline poly(ethylene oxide) samples of different molecular weights, ranging from 2400 to 100,000 g mol^{-1}, were shown to exhibit identical diffraction patterns. The Bragg-reflections we observed in the diffraction pattern of PEO of Mn=2000 (Figure 5.4.1) were in good agreement with those reported in the literature[19].

The most dominant feature of the diffraction pattern of PEO are the two very intense peaks at 2θ=19.36° and 2θ=23.46° and four less intense ones at 2θ= 26.4°, 27.1°, 35.4° and 36.2°. On incorporating bithiophene into the PEO polymer (**2T polymer**, Figure 5.4.2) the two intense signals can still be seen in the diffraction pattern, the four less intense ones have merged into two broad peaks. Also, a broad halo has emerged in the region between 2θ=15° and 2θ=19°. The features described here for the case of **2T polymer** are also exhibited in samples **3T polymer** (Figure 5.4.3) and **4T polymer** (Figure 5.4.4). For the samples **5T polymer** (Figure 5.4.5) and **6T polymer** (Figure 5.4.6), two very broad peaks in the positions where the intense peaks for pure PEO have been observed (see above), can be seen. The **6T polymer** diffraction pattern also shows a set of two very sharp peaks at 2θ=8.3° and 2θ=26.1°, which gained some intensity when the sample was annealed at 130°C for 12h. The two signals could be interpreted as a first and third order diffraction peak, corresponding to a spacing of d=10.2-10.6Å.

The appearance of a broad halo in the samples **2T polymer**, **3T polymer** and **4T polymer** suggests that the presence of oligothiophenes in the polymer disrupts the crystallinity of PEO in some places, with areas of amorphous next to those of crystalline PEO. The well-defined diffraction pattern arising from the crystalline parts of these samples is essentially identical to that of pure PEO. This indicates that the crystalline areas of the samples remain unaffected by the presence of oligothiophene.

For **5T polymer** and **6T polymer** no well defined diffraction pattern can be seen. Very broad peaks, roughly at the same position as those observed for pure PEO, indicate, that the crystallisation of the PEO throughout the sample has been frustrated by the presence of the oligothiophenes. There is no longer a clear separation between amorphous halo and well defined Bragg-peak, which shows that the previously observed amorphous and crystalline regions no longer co-exist. The appearance of two new diffraction peaks in the case of **6T polymer** could be due to sexithiophene units aggregating and thereby physically cross-linking the polymer sample. This would greatly disturb the crystallisation of the PEO and could also explain the observed rubber-like behaviour of the material, which was described earlier. The spacing of d=10.2-10.6Å, however, is too large to be explained by π-stacking of the rods. It is also unclear if the absence of further diffraction peaks is due to their weak intensity or whether only one spacing is present in the structure. All unsubstituted α-oligothiophenes pack according to a herringbone structure[25] whereas β-substituted polythiophenes pack parallel to one another with an interchain distance of about 3.8Å.[26] High[27] and a low temperature[28] crystal structures for sexithiophene have been reported. There, the distance between parallel sexithiophene rods (distance between equivalent atoms, not perpendicular to the long axis of the rod) is about 10Å, a value very similar to the spacing calculated from the **6T polymer** diffraction peaks. To explain a single spacing of d=10.2-10.6Å, one could speculate about a one-dimensional herringbone structure in which the distance between parallel rods equalled the value observed for *d* (Figure 5.4.7).

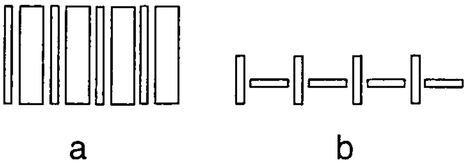


Figure 5.4.7 Schematic representation of a hypothetical one-dimensional herringbone structure, formed by rigid rods. ***a****, view from the top* ***b****, side-on view.*

5.5 Conclusions

UV/Vis and fluorescence spectroscopy showed that oligothiophene main chain polymers and sexithiophene model compounds are molecularly dissolved in chloroform solution. The bithiophene polymer, **2T polymer**, exhibits the same spectroscopic characteristics in THF-water mixtures as in chloroform, indicating complete solvation of the bithiophene unit. **3T polymer** appears to be a borderline case with some of the terthiophene rods aggregated, others solvated in THF-water mixture. All higher oligothiophene polymers showed strong aggregation phenomena in THF-water mixture, including splitting of the excited state into two exciton levels (Davydov splitting). A spectroscopic examination of methanol solutions of the three sexithiophene derivatives, **6T polymer, 6T PEO 750** and **6T PEO 350**, was carried out. **6T polymer** appeared to be completely aggregated, whereas the two sexithiophene models showed characteristic absorptions for both, the aggregated and the non-aggregated form. Compound **6T PEO 750**, which was surprisingly soluble in water, was dissolved in both, deuterated water and deuterated chloroform, and investigated by ^{1}H-NMR-spectroscopy. Good resolution of the aromatic signals in the latter and line broadening in the first solvent were observed, which provided further evidence for the postulated aggregation.

The chiral sexithiophene derivative **6T chiral** was investigated by UV/Vis, fluorescence and circular dichroism spectroscopy in various solvents. Strong aggregation phenomena in aqueous solution together with a large CD-effect could be observed, indicating the formation of chiral superstructures in water. A solution cast film showed an even more intense CD-effect, with a CD-spectrum similar to that observed in water. The intensity of the CD-effect and the intensity of the fluorescence was recorded as a function of the temperature in n-butanol solution. Loss of chiral information and increase in fluorescence intensity unambiguously showed that the aggregates broke up and became molecularly dissolved at ca. 30°C.

X-ray diffraction patterns were recorded for all oligothiophene polymers. An amorphous halo as well as the sharp PEO diffraction peaks could be seen for the bi-, ter- and quaterthiophene polymers, implying the presence of both, crystalline and amorphous regions in the polymer. For the pentathiophene as well as the sexithiophene polymer only very broad diffraction peaks could be observed. In the case of sexithiophene a set of two very sharp Bragg peaks was observed which were attributed to the formation of sexithiophene aggregates. They corresponded to a spacing of ca. 10.2-10.6Å, a value too large for π-stacking of the sexithiophene rods. A one-dimensional herringbone structure was proposed but could not be proved unambiguously on the basis of the analytical results obtained. The exact structure of both aggregates, in solution and in the bulk, remains yet to be determined.

5.6 References

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6 Overall Conclusion and Proposal for Future Work

6.1 Conclusions

A route has been developed, which allows the synthesis of alternating oligothiophene-poly(ethylene oxide) block co-polymers. Commercially available poly(ethylene glycol) blocks with a narrow molecular weight distribution were used in the synthesis. The oligothiophene blocks were built up during the polymerisation process via aromatic cross-coupling reactions. With the synthesis described here, the oligothiophene block length can easily be varied from the dimer, bithiophene, to the hexamer, sexithiophene. Although all polymers prepared had the same poly(ethylene oxide) chain length, model compounds with two poly(ethylene oxide) mono methyl ether chains of varying lengths, attached to a sexithiophene block, were prepared, using the same methodology. A monodisperse sexithiophene derivative, in which sexithiophene is linked to two chiral pentaethylene oxide derivatives, was also synthesised. To the best of the authors' knowledge, none of the oligothiophene derivatives synthesised here have been described previously. All of the materials show good processablility, i.e. they dissolve in common organic solvents and can be melted. Free standing films could be prepared of all of the polymeric materials. The sexithiophene main chain polymer as well as the sexithiophene model compounds are the first examples of sexithiophene derivatives that are only α,ω-disubstituted and still show high solubility in organic solvents. Although not determined quantitatively, the solubility was high enough to record high quality ^{13}C-NMR spectra of all sexithiophene derivatives.

Dilute solutions of all compounds were spread at the air-water interface of a Langmuir trough. Although all materials showed surface activity, condensed phase formation could only be assumed in the case of sexithiophene model compounds with short PEO chains. The results obtained, suggested that the PEO chain length determined the behaviour of the material when spread onto a water surface.

The alternating block co-polymers with quater-, penta- and sexithiophene units show strong aggregational behaviour in solvent mixtures of good and non-solvents as determined by UV/Vis, fluorescence and NMR-spectroscopy. In the case of the chiral sexithiophene derivative, the results obtained by circular dichroism spectroscopy suggested that the compound aggregated, forming a chiral superstructure, when dissolved in mixtures of good solvents and non-solvents.

Observation of Bragg-reflections in the X-ray diffraction patterns recorded from melt cast films of the oligothiophene polymers suggested, that at least in the case of the -sexithiophene polymer, aggregation took place in the bulk.

The mechanical properties of melt cast films were different from those of pure poly(ethylene oxide). Melt cast films of the sexithiophene polymer showed a flexible, rubber-like behaviour. These results also supported the assumption that aggregation occurred in the materials in the bulk form, with the oligothiophene aggregates acting as physical cross-linkers within the material. The detailed structure of the aggregates in solution and in the bulk has not yet been determined.

The work described here has made a new class of potentially electroactive materials accessible. High solubility and processability of oligothiophene derivatives without the need of β-substituents could be shown and has opened a wide area for future research.

6.2 Future Work

In the eyes of the author, various aspects of this work deserve further investigations.

One aim should be the fabrication of electroactive devices. Sexithiophene derivatives linked to short PEO chains, whether polymeric or of low molecular weight, seem to be very interesting materials for further Langmuir-Blodgett experiments. Exhibiting a region which resembles that of a condensed phase in the surface pressure/area isotherm, potentially very densely packed Langmuir-Blodgett films could be prepared from such monolayers. A high degree of order in the semiconducting material is one of the prerequisites for high charge carrier mobilities in organic field effect transistors. Short PEO-chain substituted sexithiophenes seem good candidates to be further examined by the Langmuir-Blodgett technique.

Self-organisation and formation of chiral superstructures under certain conditions in solution could be seen in the case of the chiral sexithiophene derivative. In a further study, both, a chiral sexithiophene derivative and its achiral analogue could be synthesised. Solutions of the aggregated forms could be obtained by dissolving the compounds in solvent/non-solvent mixtures. By examining solutions in these mixed solvents by circular dichroism spectroscopy, information about the stability and/or exchange of the two compounds could be obtained. Further studies could investigate the structural organisation of chiral sexithiophene polymers in solution and in the bulk.

To unambiguously prove the structure of the sexithiophene derivatives in the bulk, larger amounts of monodisperse material has to be prepared in order to be able to characterise it by X-ray diffraction techniques. In this work only the cross-coupling route has been successfully employed to prepare these materials. Oxidative coupling of terthiophene derivatives, which are easily synthesised, might provide an easier route to larger amounts of di-*flexible spacer*-substituted sexithiophene derivatives.