I have no special talents.
I am only passionately curious.
Albert Einstein

Table of contents

Chapter 1: Introduction

1. Polymers

Humanity can not imagine a world without polymers. As long as our planet exists, nature provided us with an enormous diversity of these materials, such as cotton, wood, and rubber. Not to forget, that all life forms are full of polymers (DNA, proteins,…). Although there is a great diversity of polymers, the definition is rather simple. The term polymer is derived from two Greek words *poly* and *meros*, which can be translated as “many parts”. A polymer is a macromolecule which exists of several repeating units connected via covalent bonds. For the first manmade synthetical polymer, we have to go back till the start of the 20th century. Baekeland experimented with mixtures of phenols and formaldehyde. Here a material originated which was resistant towards acids, organic liquids and heat. The material was called Bakelite and used successful in many applications, such ass telephone housings, bowling balls, and kitchenware. It has been assumed that Baekeland did not really know that he was making a polymer. In these days, polymer science was just an empirical field. Polymer “science” did really developed during the 1920’s and 1930’s with polymer studies and theories of people as Carothers, Staudinger and Flory. This was the start of the “plastic decades”. Different synthetic polymers as nylon, PET, polyethylene flooded the market and didn’t disappear ever since, because of their variety of properties and benefits. Last decennia even highly specialized polymers, such as Kevlar and Teflon are made, due to a strategic design.

1.1. Conducting polymers

In former years it seemed logical that polymers were insulators. They have been successfully used a lot as surrounding for electrical wires.

This vision had to be adapted in 1977. For years, Hideki Shirakawa attempted to make a high quality film of polyacetylene. In the same period Alan Heeger and MacDiarmid worked on inorganic polymers and were fascinated by the work of Shirakawa. A collaboration emerged from a casual contact. Polyacetylene shows poor electrical conductivity, but when the polyacetylene was “doped” with iodine the conductivity increases significantly,[1] this can be seen as the first truly conductive polymer.

Because of this discovery, Shirakawa, MacDiarmid and Heeger received the Nobel price in the year 2000.[2-5]

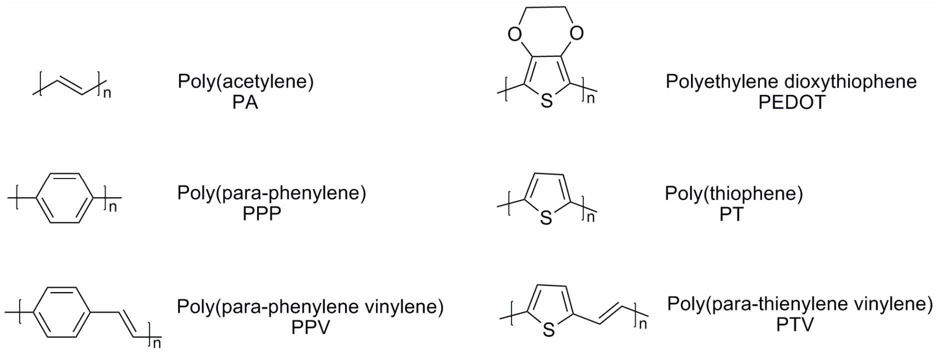


Figure 1. Some examples of conjugated polymers.

Ever since, the research field of conductive polymers or doped conjugated polymers increased rapidly. Numerous different polymers have been synthesized (figure 1) and tested. The conductive polymers gained specific attention because they can combine the advantages of metals and plastics. They have all the advantages of plastics: light weight, flexibility, great diversity of properties, possible to coat them on large surfaces… and they can conduct electricity. In the early 90’s, it was discovered that the pristine conjugated polymers showed semi-conductive properties. This opened a route towards a great variation of applications (figure 2). In this way, transistors can be made with the conjugated polymer as semiconductor layer, these transistors are used to build sensors, RFID tags,… Other important applications for conjugated materials are their use in OLEDs (Organic Light Emitting Diods) and OPVs (Organic PhotoVoltaic devices) (figure 3).

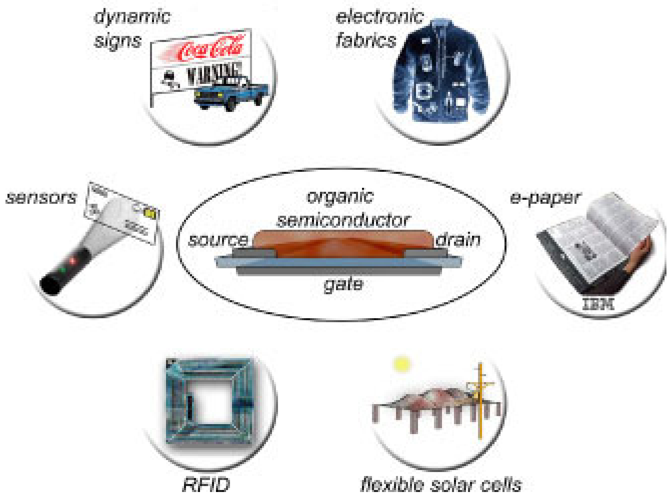


Figure 2. Applications of organic semiconductors.

Photo courtesy of United Solar Ovonic, LLC

Figure 3. OPV (left), OLED display (right).

1.2. Low band gap polymers

The band gap of a conjugated polymer is represented by the difference between its HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) level (figure 4). It can be determined from UV-Vis spectroscopy or estimated from Cyclic Voltammetry (electrochemical band gap). The term low band gap polymer can be applied for polymers with a band gap below 2.0 eV.

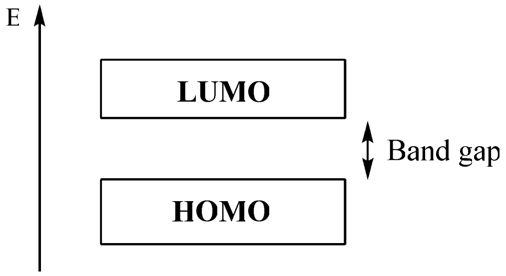


Figure 4. definition of the band gap.

For the use of conjugated polymers in solar cells, their absorption characteristics are rather important. Therefore a good overlap with the solar emission spectrum is crucial. In figure 5 the solar spectrum AM1.5 (the spectrum at the latitude of northern Europe and northern America) is presented. Here, three conjugated polymers are also displayed having different band gaps,[6] MEH-PPV (pink), P3HT (red) and a hypothetical low band gap polymer (green). From this figure it can be concluded that the low band gap polymer absorbs light in a much bigger and different area than the two other conjugated materials.

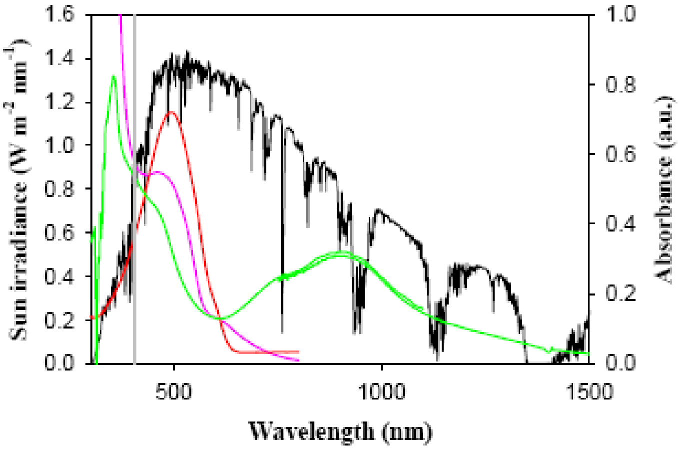


Figure 5. Solar spectrum and some absorption spectra from several polymers.

When the graphic is converted from the sun irradiance towards the photon flux (figure 6), it can be understood that a polymer with an absorption maximum between 600 and 800 nm fits better with the solar spectrum, and therefore will gain better efficiencies in OPV devices.[7,8]

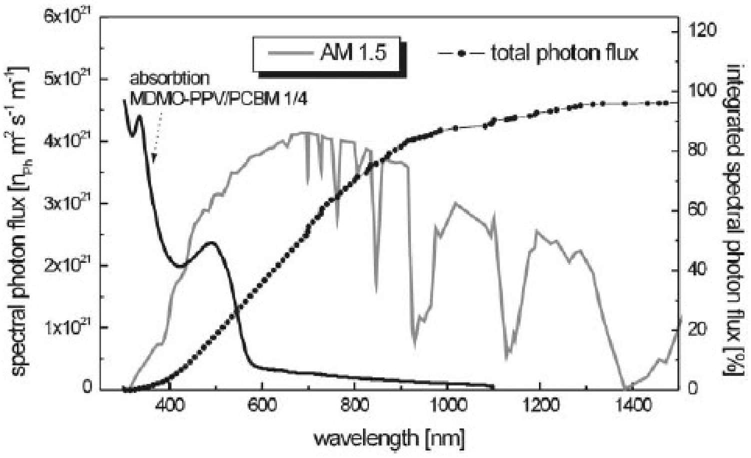


Figure 6. Solar spectrum defined as the spectral photon flux.

For this reason, a lot of research interest is focused on low band gap polymers. Numerous different derivatives have been made. Some examples are reported in Figure 7. The first well studied low band gap material was PITN (poly(isothianaphthene)). As well for the preparation method as for the synthesis of derivatives substantial work has been published.[9-12]. Depending on the side chain, band gap values of 0.9 till 1.22 eV have been reported. A second well studied low band gap group, are the fused poly(thienothiophene)s, here band gaps of 0.7 till 1.26 eV were noted.[13-15] Also, the well known polymer PEDOT (poly(ethylenedioxythiophene): Eg = 1.6 eV)[16] and the in this thesis synthesized PTV (poly(thienylene vinylene)) are considered to be low band gap materials. A summary of the different low band gap polymers can be found in review articles and books.[17-18]

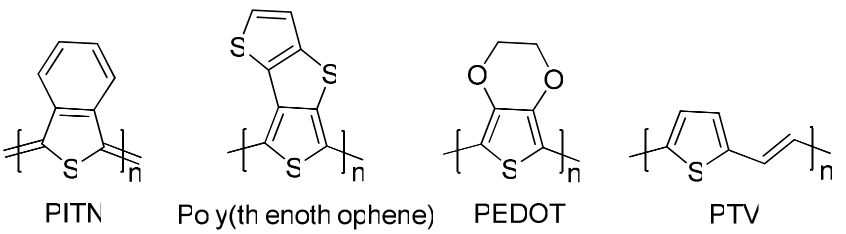


Figure 7. Some examples of low band gap polymers.

1.3. Band gap engineering

Synthetic chemists already adopted a lot of research work on the synthesis of various low band gap materials. Moreover, a lot of theoretical and experimental work has been devoted towards the characterization and analysis of the properties of these materials. In 1997, Roncali bundled all these studies and deduced some general “rules” for the control of the band gap of conjugated materials, so called “band gap engineering”.[19,20] According to Roncali five factors determine the band gap. The most important factor is the bond length alternation (E_{bla}). To understand this bond length alternation, we have to go back to the origin of the finite band gap in conjugated polymers. If, hypothetically, the electron delocalization would be complete, all C-C bonds would have the exact same lengths. Therefore, the material would act as a one-dimensional atomic system which can be compared with a metal. In “real” conjugated systems however, the Peierls distortion has to be kept in mind.[21] Peierls already predicted that an one-dimensional conjugated system would be unstable. In the conjugated systems dimerization, leading towards longer single and shorter double bounds, is in favor. A reduction of this bond length alternation will produce a decrease of the band gap.

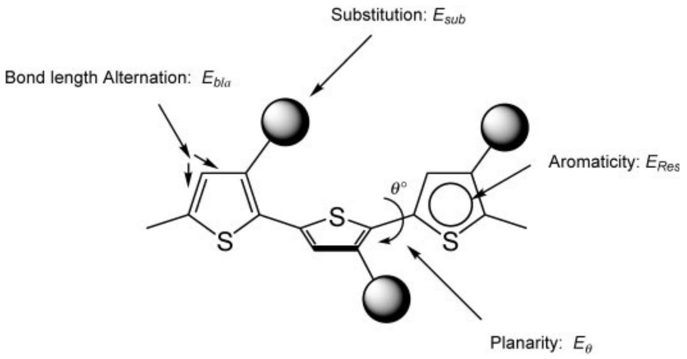


Figure 8. Factors influencing the band gap.

A second parameter which influences the band gap is called; the resonance effect (E_{res}). Conjugated structures can be described by two fundamental resonance forms, an aromatic and a quinoid form (figure 9). These resonance forms are not energetically equivalent. In most cases the aromatic form has the lowest energy. By consequence, it dominates the true structure and leads typically to a higher band gap. In general a structure where the quinoid resonance form would dominate, would lead to a rather lower band gap.

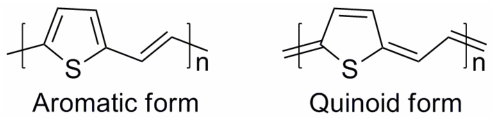


Figure 9. Aromatic and quinoid resonance forms of PTV.

Also the deviation from planarity, indicated by E_{θ}, has an influence on the band gap. The higher the deviation from coplanarity, the more E_g

will be increased. The last and most straightforward intramolecular parameter from a synthetical point of view, is the introduction of the substituents (E_{sub}).[22,23] Electron withdrawing substituents will lower both HOMO and LUMO levels, but the LUMO level will decrease more than the HOMO, so overall the band gap will be lowered. When introducing electron donating groups the HOMO level will be more increased than the LUMO, so overall the band gap will also be decreased. From the above, it is clear that the introduction of substituents has a major influence, not only on the band gap, but also on the position of the HOMO and LUMO levels.

The fifth factor relates to intermolecular interactions (E_{int}) of the polymer chains. So the organization of the individual molecules, which can be addressed by the morphology of the materials, can have an important impact on the value of the band gap.

2. Poly(thienylene vinylene)

In view of the previous paragraph, the advantages of poly(thienylene vinylene) can be explained. The introduction of an extra vinylene bond in comparison with polythiophenes will influence the band gap in multiple ways. First the resonance energy will be lowered, because of the extra vinylene bond between the aromatic rings. The π electrons will be better delocalized over the whole structure and therefore not concentrated anymore on the thiophene rings. Secondly, the vinylene bond acts as a spacer between the aromatic rings, so more molecular mobility is introduced. The molecule can adept its most energetically favored conformation. The more planar the structure, the smaller the band gap will be. Moreover, this can also have an influence on the intermolecular interactions of the polymer chains and therefore the morphology.

The main reason why PTV derivatives have gained a lot of interest is its natural small band gap of 1.7 eV or smaller, depending on the substituents.[17,24-27] Furthermore, it has been reported that PTV’s have a high charge carrier mobility in the same level as amorphous silicon.[28] Despite these advantages, limited research papers considering PTV’s have been published. This can be explained by the fact that the synthesis of PTV derivatives, and especially the monomers, is quite challenging because of the electron rich thiophene core. For the synthesis of PTV derivatives, two general pathways can be followed. Historically, the direct routes have been investigated first. In 1970 Kossmehl and coworkers synthesized plain PTV via a Wittig reaction.[29,30] Unfortunately the synthesized plain PTV is insoluble and therefore not a good candidate for device applications. To overcome this problem, two different solutions, to provide processibility were proposed. In a first strategy, the synthesis via condensation reactions or ring-opening metathesis polymerization will be followed but the monomers will be configured with side chains, which will improve the solubility of the final polymer.[31,32] The main drawback of this type of route are the obtained low molecular weights, which can have a negative influence on the formation of the thin films used in applications. To gain higher molecular weights a different strategy has also been tested: the precursor routes. The monomer is polymerized towards a soluble precursor polymer, which can be incorporated in a device. In a next step the precursor will be converted in situ, mostly thermal, in its insoluble conjugated state. In a latter stadium, the two solutions have been combined. Monomers with long flexible side chains have been synthesized and polymerized via a precursor route. So the polymer stays soluble, even in its conjugated form.

2.1. Precursor routes

The study of the precursor routes for PTV derivatives started when Harper and West patented the Wessling route for PTV’s.[33] In this route, a bissulphonium salt has been polymerized under influence of a base and the conversion of the obtained precursor polymer to the conjugated form was performed thermally. Nevertheless, the research towards the PTV precursor route really started around 1987-1988, when Elsenbaumer and coworkers adapted this route.[34-36] As a monomer, they made use of a 5-bis(tetrahydrothiophenonium methyl) thiophene dichloride, which could be polymerized in water, and here high molecular weight precursor polymers were obtained. Unfortunately, the obtained precursors were not very stable and could lead to spontaneous conversion towards the conjugated PTV and consequently to gelation and cross linking. In the same time period, Saito et al. and Murase and coworkers both presented a PTV precursor polymer with methoxy leaving groups.[37-42] The main advantage of these materials was the good solubility of the precursors in different organic solvents, which is desired for the characterisation of the materials and their application in devices. Later on, this was further investigated by Eevers et al. and Xie and coworkers.[43-45] In 1989 Iwatsuki made a poly(2,5-thienylene-vinylene) film via a hydrogen transfer reaction from poly(2,5-thienylene-ethylene) (PTE) with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) as an oxidance. First, the PTE was synthesized and films were made via a vapor deposition technique. Later on, these films were converted in situ under the influence of DDQ. Although highly conjugated films with a high conductivity were formed, the need for vapor deposition of the films is of course a great disadvantage of this technique. In the same period (1989-1992) the properties of the PTV polymers have also been studied.[46-48] In 2001, Philips patented a thioether precursor route via 2,5-bisthioalkylmethylthiophenes.[49] This route has the main drawback that HCl is necessary to induce conversion towards the conjugated polymer, which is a serious problem for device applications. Around 2002, our research group also started the research for PTV derivatives. First, the synthesis via the sulphinyl precursor route have been studied.[50] A lot of problems occurred, the intermediary products of the monomer synthesis were very unstable, this due to the electron rich thiophene core. Therefore, these products degraded or solvent substitution couldn’t be avoided. Subsequently, the xanthate route has been investigated. Earlier this route has been successfully applied for PPV derivatives.[51-52] Finally, it was possible to synthesize stable monomers via this route.[53-54] Unfortunately, the resulted polymers were obtained in a very low yield and the polydispersity was very high (>15). Moreover, lower wavelengths have been obtained which can indicate that structural defects are incorporated in the polymer backbone. In 2003, the study of a new precursor route, using dithiocarbamate precursor polymers has been reported by our research group and Padmanaban and coworkers.[53,55] This route will be discussed in detail in the next paragraph.

2.2. Dithiocarbamate precursor route

The dithiocarbamate precursor route is presented in figure 10. This is the only route which makes it possible to prepare stable monomers from the electron rich thiophene structure and yield after conversion a well defined conjugated system.[60] In this route, a dithiocarbamate monomer will be polymerized under influence of a base towards a precursor polymer, which in a later stadium will be converted into its conjugated form.

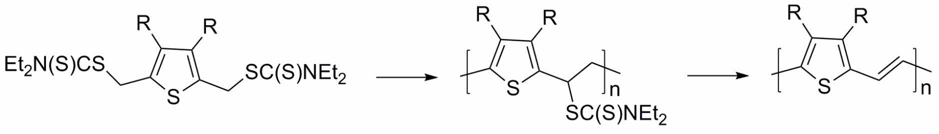


Figure 10. Dithiocarbamate precursor route.

The polymerization of the monomer is a very interesting reaction.[56-59] The dithiocarbamate monomer is actually a premonomer, which will be converted towards the real monomer due to the addition of a base. This base will abstract a proton and a 1,6-elimination will occur. This leads to the formation of a quinodimethane system, which represents the real monomer (figure 11).

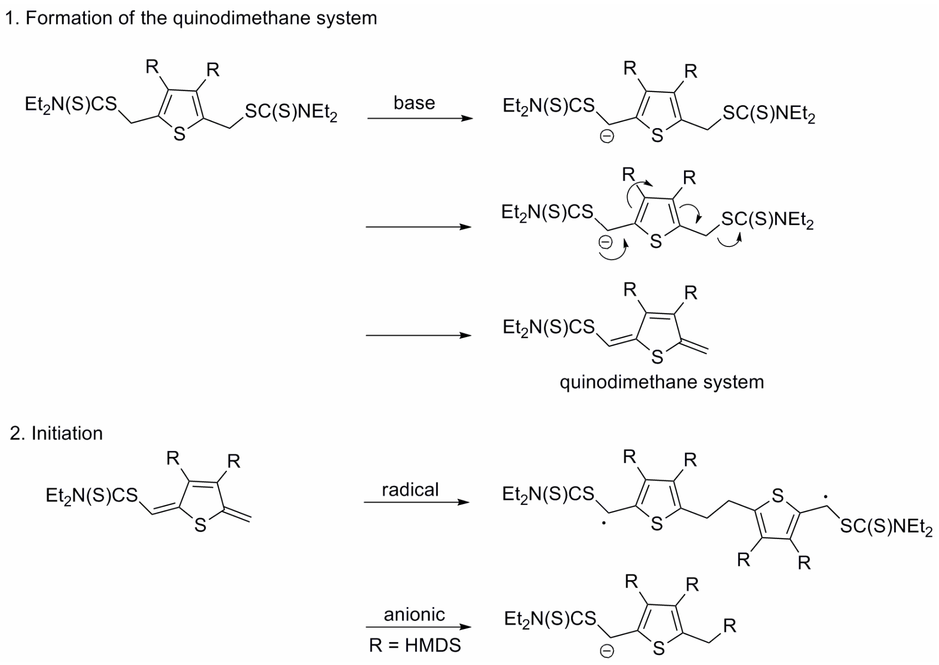


Figure 11. Initiation reactions for the dithiocarbamate route.

The actual initiation occurs when two of these quinodimethane systems combine and form a diradical from which the polymer chain can grow further via a radical chain polymerization. In some cases, the polymerization can also be initiated anionically. Here a nucleophile (HMDS or an impurity) will add to the quinodimethane system, from this initiating species the polymer chain can grow further via an anionic chain mechanism.

As a base, initially lithium diisopropylamide (LDA) has been used.[61,62] Here high molecular weight polymers could be formed for PTV derivatives without side chains. Unfortunately for the alkyl substituted PTV derivatives, a lot of side reactions appeared and only low molecular weight polymers could be formed (M_w < 14 000) in a low yield (< 5%). Side reactions (cleavage of the alkyl side chain, transfer of the isopropyl group) were also reported. In a later stage the LDA base has been replaced by lithium(trimethylsilyl)amide (LHMDS).[63,64] It has been expected that this, sterically more hindered base, would lead towards less side reactions. Due to this adaptation, also high molecular weight polymers for the substituted PTV derivatives could be formed without the appearance of side reactions. Unfortunately, all the polymerizations showed a bimodal character, which can be explained due to the competition between the radical and the anionic polymerization. Also, reproducibility of the polymerization was low. To overcome these problems, several bases have been tested. The optimization of the polymerization conditions will be discussed in chapter 2.

During the propagation step of the polymerization several structural defects can also appear (figure 12). Next to the normal addition, a head-to-head or tail-to-tail addition can appear as well. These last two additions can be seen as a structural defect and must be avoided. Here, it must be kept in mind that the head-to-head defects are partially related to the initiation step (radical mechanism). The amount of defects can be studied in detail by quantitative NMR measurements and will be reported in chapter 5.

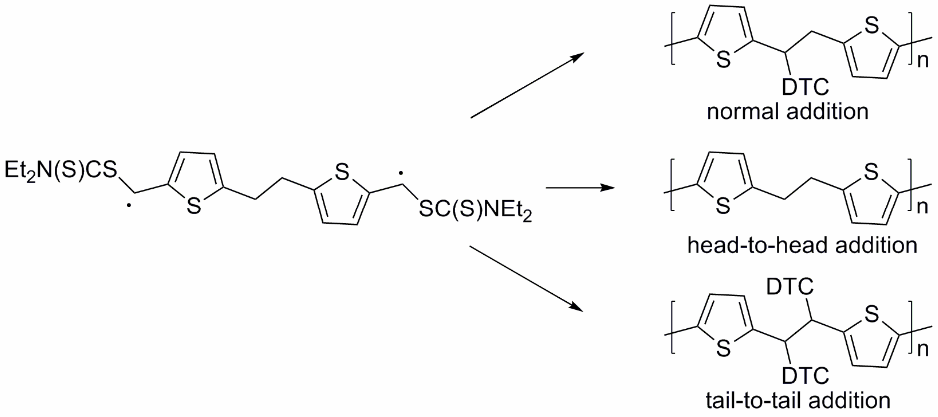


Figure 12. Structural defects in the polymer chain.

2.3. Conversion methods

In the last stage the precursor polymers have to be converted into their conjugated forms (figure 10). Initially, this has been done by a thermal elimination.[54,63,64] Typical temperatures of 180 °C are necessary to induce the elimination of the leaving group (figure 13), in this case a dithiocarbamate group. These high temperatures can already lead towards the degradation of the chromophore. Therefore, the conjugated backbone can be interrupted with defects and lower λ_{max} values will be obtained.

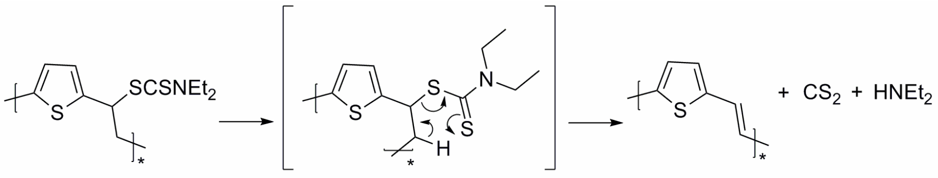


Figure 13. Thermal conversion.

In 2004, it has been discovered in a serendipitous way that dithiocarbamate groups are sensitive towards acids. Due to the addition of acids during the conversion reaction (figure 14), the used temperatures can be lowered to 70 °C or even to room temperature. This adaptation can prevent the degradation of the chromophores, and therefore qualitative better conjugated systems can be obtained.

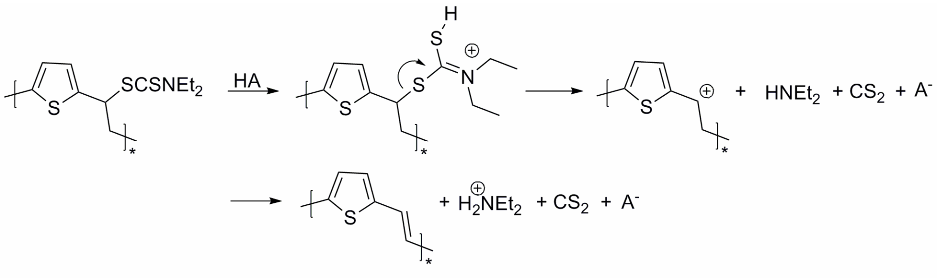


Figure 14. Acid induced conversion.

It has to be mentioned that the conjugated system did not always fully developed. This can be due to the presence of a competitive substitution reaction next to the elimination reaction. This very promising conversion reaction will be discussed in chapter 3. The mechanism of the conversion and the competition reaction will be explored in detail in chapter 4 (Figure 14).

3. Applications: Solar cells

3.1. Solar cells

Conjugated polymers are excellent candidates to be used as semiconducting materials in photovoltaics,[65] more specific in bulk heterojunction solar cells.[66-73] The general scheme of such a photovoltaic cell is described in figure 16. The photoactive layer of the cell is represented by a polymer-fullerene bulk heterojunction. This means that a blend of the conjugated polymer, which acts as a p-type electron donor material and a fullerene derivative (the n-type material) constitutes the active layer (figure 15). As fullerene derivative, (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) (figure 15) is commonly used.

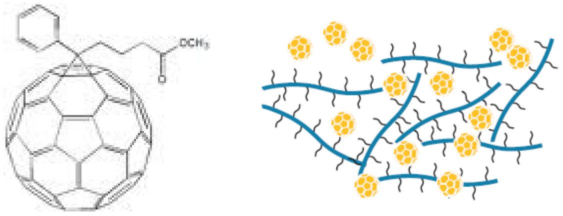


Figure 15. PCBM (left), blend of conjugated polymers & PCBM (right).

This photoactive layer is sandwiched between two electrodes. Usually a transporting layer, to improve contact, is introduced between the blend and the electrode. As cathode mostly metals, i.e. Ag, Au and often Al are used.[74] Here LiF is added as an electron transport layer to guarantee the charge transfer between the bulk heterojunction and the electrode.[75] As an anode a transparent electrode has to be used to allow the solar light to reach the photoactive layer, mostly ITO (Indium Tin Oxide) is utilized.[76] As anode buffer layer poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is applied, this material is known to be a good hole transporter.[77] To prevent the oxidation of the conjugated materials and electrodes, the device has to be "sealed" with a transparent protecting coating. This layer prevents contact of these materials with oxygen and moisture.

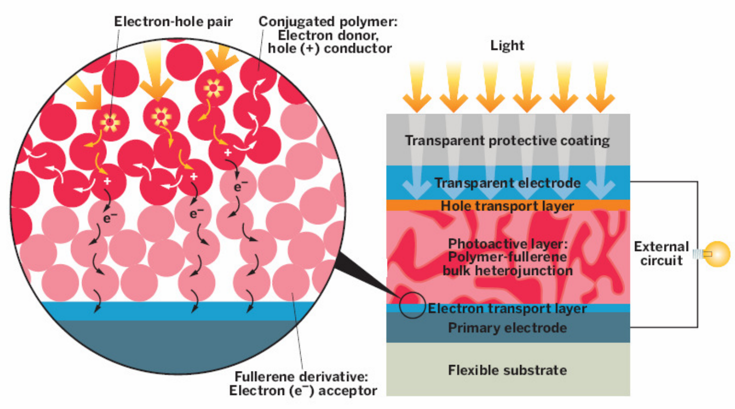


Figure 16. Schematic representation of a solar cell.

3.2. Photovoltaic principle

A photovoltaic cell can generate power by the conversion of solar energy into electrical energy. This has been referred to as "the photovoltaic principle".[78-80] During this process three stages will be passed (Figure 17). First, light will be absorbed by the conjugated polymer, which act as a p-type electron donor, and therefore an exciton will be formed. This means that an electron will be promoted from its highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO), while forming a hole in the HOMO (stage 1).

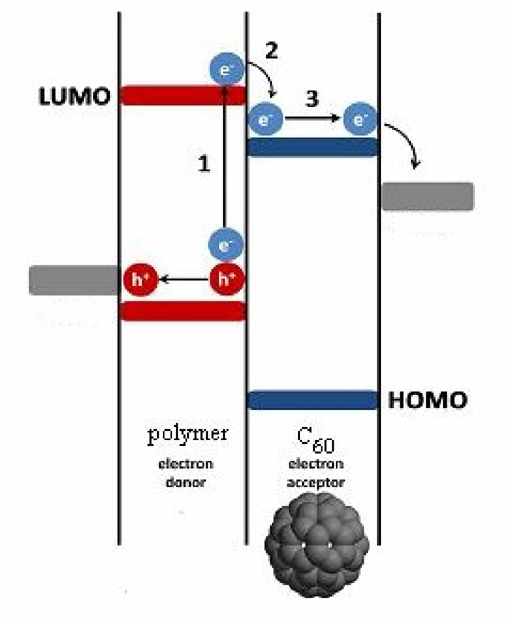


Figure 17. The photovoltaic principle.

In a second stage, this electron has to be transferred from the donor material towards the LUMO of the acceptor. It is very important that a charge separated state is the most favorite pathway, and that the energy will not be lost via other processes like fluorescence, internal conversion, intersystem crossing or non-radiative decay. In a last stage (stage 3) the electron and the hole have to be collected at the electrodes. To achieve this, an electric field is necessary, which is provided by the asymmetrical work functions of the electrodes.

To characterize a solar cell typical I-V curves have been used (figure 18), so some important parameters have to be defined.

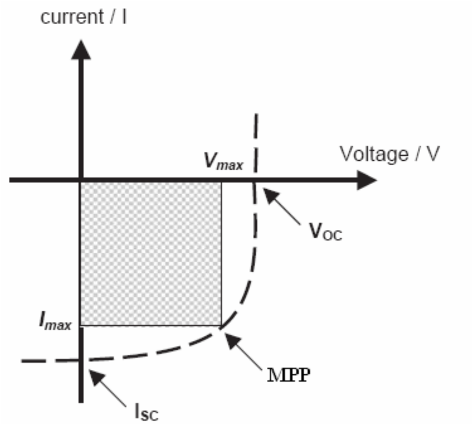


Figure 18. Schematical I-V curve for a solar cell.

- V_{oc} = Open-Circuit Voltage: The maximum possible voltage across a photovoltaic cell (in sunlight) when no current is flowing.
- I_{sc} = Short-Circuit Voltage: The maximum current that flows through a photovoltaic cell (in sunlight) when there is no external resistance, so it is the absolute maximum current that a device is able to produce.
- MPP = Maximum Power Point: The point on the I-V curve where the maximum power (P = I . V) is produced.
- FF = Fill Factor = a key parameter which describes the quality of the solar cell.

$$FF = \frac{V_{\max} . I_{\max}}{V_{oc} . I_{sc}}$$

- PCE = Power Conversion Efficiency: The amount of power a solar cell can produce relative to the power available in the incident solar radiation (P_{in}). Which is generally fixed at 100 W/cm².

$$PCE = \frac{I_{\max} . V_{\max}}{P_{in}}$$

3.3. How to improve the efficiency of solar cells

Over the last few years multiple attempts have been made to increase the efficiency of polymeric solar cells. For this purpose multiple “design rules” have been determined.[81-87] In this context three parameters are crucial. First, the V_{oc} of the polymer is of great importance. The V_{oc} is related to the energy difference of the HOMO level of the donor polymer and the LUMO level of the acceptor. Furthermore, it has been estimated that an energy difference of 0.3 eV of the LUMO levels of the donor polymer and acceptor would be optimal to maximize the V_{oc} and still acquire the exciton splitting and charge dissociation. So the V_{oc} can be raised by fixing the LUMO value of the donor polymer at the optimal level and lowering its HOMO value as low as possible. A second strategy to increase efficiency is to increase the value of the J_{sc}. Because this is correlated with the number of excitons created during solar illumination, it can be increased by tuning the absorbance spectra of the polymers. In this context, the use of low band gap materials to gain a better resemblance with the solar spectrum has already been discussed in figure 5 and 6. It should be emphasized that these first and second approaches are more or less contradictive. For the second approach the band gap should be as low as possible to resemble as much as possible the solar emission spectrum. For the first approach, in contrary, the band gap should be as high as possible to maximize the V_{oc}. So the challenge will be to find a certain optimum between these two rules. A third, and very important, parameter is the fill factor. This factor is mainly influenced by the physical interactions between the donor polymer and the acceptor material, and in the end also the quality of the interfaces at the electrodes. The former relates to the nano-morphology of the used blend. The proper morphology of the blends should promote charge separation and optimize the transport of charges. With these factors in mind, theoretical predictions have been done, to achieve the optimal materials for solar cells (figure 18). By fine tuning the band gap of the donor material and its LUMO level, the mythical power conversion efficiency of 10% should be possible to reach.

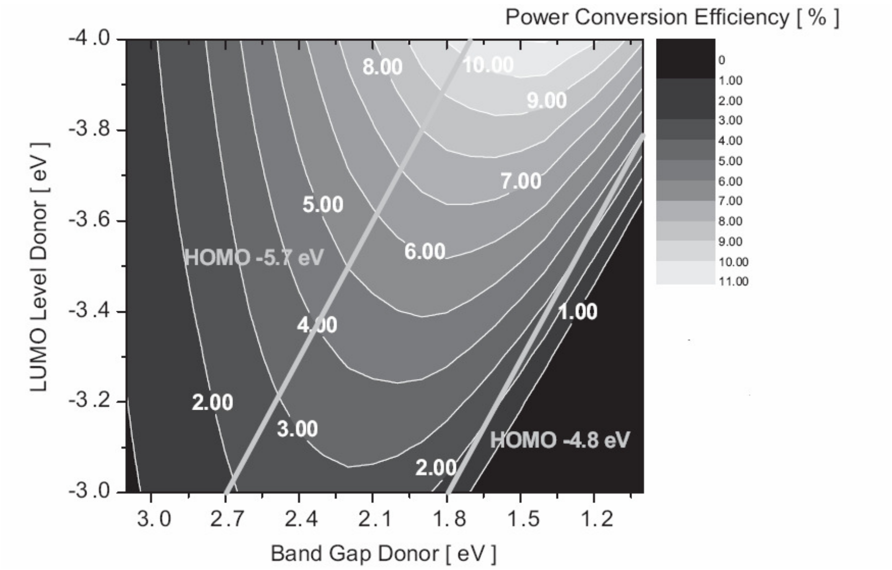


Figure 18. Contour plot showing the predicted energy conversion efficiencies in relation to the LUMO versus the band gap of the donor polymer.

4. Aim and outline

4.1. Aim

The research field of conjugated polymers is already explored for several years. Therefore, there is an interest for new low band gap materials. The aim of this thesis is the synthesis of some new low band gap PTV derivatives. They will be tested as semi conducting layer in transistors and solar cells, this to improve the performance of the devices. Secondly, and certainly equally important, the dithiocarbamate precursor route will be studied in detail. Finally, the different conversion methods of the precursor polymers will be investigated.

Chapters 2, 3, 4, 5, 6 and 7 are written as manuscripts for publications. Therefore all figures are numbered again in each chapter and formatting can differ from chapter to chapter, depending on the journals to which the chapter is to be submitted.

4.2. Outline

In **chapter 2**, two new conjugated polymers, i.e. poly(3-octyl-2,5-thienylene vinylene) (O-PTV) and poly(bis-octylphenyl-2,5-thienylene vinylene) (BOP-PTV), have been synthesized. Both polymers have been prepared via the dithiocarbamate (DTC) precursor route. The polymerization protocol of the monomer towards the precursor polymer has been optimized by the use of different bases. Processability has been guaranteed by the introduction of alkyl side chains. Finally the precursor polymers are converted towards conjugated polymers and their photovoltaic characteristics have been tested.

In **chapter 3**, an alternative for the thermal conversion of dithiocarbamate precursor polymers has been investigated, the acid induced conversion. This conversion technique has been tested on poly(thienylene vinylene) (PTV) and poly(phenylene vinylene) (PPV) derivatives. The advantage of this method is that the conversion temperature can be lowered and therefore degradation of the chromophore can by avoided. Moreover, a bathochromic shift has been established.

Chapter 4 explores the dithiocarbamate route via model compounds. It has been noticed that using the new acid induced conversion mechanism, described in chapter 3, the conjugated system did not always fully developed. This could be due to the presence of a competitive substitution reaction, next to the well known elimination reaction. To investigate the specific reaction mechanisms, multiple model compounds have been made and as well elimination as substitution reactions have been tested on them. The reaction kinetics and the influence of the substituents have been studied.

In a next stage the dithiocarbamate precursor route will be investigated via a ^{13}C-labeled O-PTV. In **chapter 5**, this precursor polymer has been studied by various NMR techniques, as quantitative ^{13}C NMR measurements, this to determine the structure of the polymer, its structural defects, and the end groups. Also, the conjugated polymer, converted thermally as well as acid induced, has been studied extensively via quantitative NMR techniques. Furthermore, multiple model compounds for the end groups and structural defects have been made, this to confirm the chemical shifts.

Not all model compounds for the defects, described in chapter 5, were synthetically available. So, in **chapter 6** the chemical shifts of the remaining model compounds will be calculated via theoretical calculations. The other model compounds will be used as a reference. Therefore, the structures of all the model compounds will be assigned by various NMR techniques.

In **chapter 7**, a much shorter and efficient synthetic pathway towards the dihexyl-PTV monomer has been designed. Furthermore, the polymerization of this, more steric hindered, monomer has been optimized. In a latter stage transistors are made from these materials.

The synthetic strategy for three new conjugated polymers has been designed in **chapter 8**. First, the synthesis of two polymers with electron withdrawing side chains will be tested, this to lower the HOMO and LUMO energy levels. Furthermore, the improvement of the polymer morphology has been tested via an alternative for the BOP-PTV.

5. References

[1] Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. C. S. Chem. Comm.* **1977**, 578–580.

[2] Heeger, A. J. *Rev. Mod. Phys.* **2001**, *73*, 681–700.

[3] Shirakawa, H. *Nobel lecture Chemistry 1996-2000*, World scientific Publishing Co., Singapore, **2003**.

[4] Macdiarmid, A. G. *Rev. Mod. Phys.* **2001**, *73*, 701–711.

[5] Shirakawa, H. *Rev. Mod. Phys.* **2001**, *73*, 713–718.

[6] Bundgaard, E. *PhD dissertation* **2007** Roskilde University centre.

[7] Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.

[8] Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *SPIE Newsroom* **2007**, 10.1117.

[9] Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382–3384.

[10] Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717–5723.

[11] van Asselt, R.; Hoogmartens, I.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aussems, M.; Aagaard, O.; Schellekens, R. *Synth. Met.* **1995**, *74*, 65–70.

[12] van Asselt, R.; Vanderzande, D.; Gelan, J.; Froehlin, P.E.; Aagaard, O. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 1553–1560.

[13] Inaoka, S.; Collard, D. M. *Synth. Met.* **1997**, *84*, 193–194.

[14] Inaoka, S; Collard, D. M. *J. Mater. Chem.* **1999**, *9*, 1719–1726.

[15] Arbizzani, C.; Catellani, M.; Mastragostino, M.; Cerroni, M. G. *J. Electroanal. Chem.* **1997**, *423*, 23–28.

[16] Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, 12, 481–494.

[17] Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; de Boer, B. *Polym. Rev.* **2008**, *48*, 531–582.

[18] Rasmussen, S. C.; Pomerantz, M. *Handbook of conducting polymers* **2007**, CRC Press, 12-1–12-42

[19] Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205.

[20] Roncali, J. *Macromol. Rapid Comm.* **2007**, *28*, 1761–1775.

[21] Peierls, R. E. *Quantum Theory of Solids* **1955**, Oxford University Press, London.

[22] Cutler, C. A.; Burrell, A. K.; Officer, D. L.; Too, C. O.; Wallace, G. G. *Synthetic Met.* **2002**, *128*, 35–42.

[23] Gustafsson-Carlberg J. C.; Inganäs, O.; Andersson, M. R.; Booth, C.; Azens, A.; Granqvist, C. G. *Electrochim. Acta* **1995**, *40*, 2233–2235.

[24] Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T.J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19–26.

[25] Gavrilenko, A. V.; Matos, T. D.; Bonner, C. E.; Sun, S-S.; Zhang, C.; Gavrilenko, V. I. *J. Phys. Chem.* **2008**, *112*, 7908–7912.

[26] Jeeva, S.; Lukoyanova, O.; Karas, A.; Dadvand, A.; Rosei, F.; Perepichka, D. F. *Adv. Funct. Mater.* **2010**, *20*, 1661–1669.

[27] Chen, X.; Elsenbaumer, R. L. *Synth. Met.* **2009**, *159*, 1464–1466.

[28] Fuchigami, H.; Tsumura, A.; Koezuka, H. *Appl. Phys. Lett.* **1993**, *63*, 1372–1374.

[29] Kossmehl, G.; Härtel, M.; Manecke, G. *Makromol. Chem.* **1970**, *131*, 15–36.

[30] Kossmehl, G.; Härtel, M.; Manecke, G. *Makromol. Chem.* **1970**,*131*, 37–54.

[31] Van De Wetering, K.; Brochon, C.; Nhov, C.; Hadziioannou, G. *Macromolecules* **2006**, *39*, 4289–4297.

[32] Horie, M.; Shen, I-W.; Tuladhar, S. M.; Leventis, H.; Haque, S. A.; Nelson, J.; Saunders, B. R.; Turner, M. L. *Polymer* **2010**, *51*, 1541–1547.

[33] Harper, K.; West, W. J. W. *Eur. Pat. Appl. No. 182548*, **1985**.

[34] Jen, K. Y.; Jow, R.; Eckhardt, H.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 49–53.

[35] Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309–311.

[36] Jen, K. Y.; Jow, R.; Shacklette, L. W.; Maxfield, M.; Eckhardt, H.; Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 69–77.

[37] Yamada, D.; Tokito, S.; H.; Tsutsui, T; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, *00*, 1448–1449.

[38] Tokito, S; Momii, T.; Murata, H; Tsutsui, T.; Saito, S. *Polymer* **1990**, *31*, 1137–1141.

[39] Tsutsui, T.; Murata, H.; Momii, T.; Yoshiura, K.; Tokito, S.; Saito, S. *Synth. Met.* **1991**, *41*, 327–330.

[40] Murata, H.; Tokito, S.; Tsutsui, T.; Saito, S. *Synth. Met.* **1990**, *36*, 95–102.

[41] Murase, I.; Ohnishi, T.; Noguchi, *T. Ger. Offen.* No. 3704411, **1987**.

[42] Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1987**, *28*, 229–231.

[43] Eevers, W.; De Wit, M.; Briers, J.; Geise, H. J.; Mertens, R.; Nagels, P.; Callaerts, R.; Herrebout, W.; Vanderveken, B. *Polymer* **1994**, *35*, 4573–4577.

[44] Eevers, W.; De Schrijver, D.; Dierick, T.; Peten, C.; Van Der Looy, J.; Geise, H. J. *Synth. Met.* **1992**, *51*, 329–338.

[45] Xie, H-Q.; Liu, C-M.; Guo, J-S. *Eur. Polym. J.* **1996**, *32*, 1131–1137.

[46] Onada, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Yoshino, K. *J. Chem. Phys.* **1991**, *95*, 8584–8591.

[47] Eckhardt, H.; Shacklette, L. W.; Jen, K-Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303–1315.

[48] Gelsen, O. M.; Bradley, D. D. C.; Murata, H.; Takada, N.; Tsutsui, T.; Saito, S. *J. Appl. Phys.* **1992**, *71*, 1064–1066.

[49] Ten Hoeve, W.; de Kok, M. M.; Huisman, B-H.; Herwig, P. T.; Van Breemen, A. J. J. M. *PCT Int. Appl. No. 1290059* **2001**.

[50] Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin solid films* **2004**, *451-452*, 472–579.

[51] Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376–378.

[52] Kesters, E.; Gillissen, S.; Motmans, F.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2002**, *35*, 7902–7910.

[53] Henckens, A. *PhD dissertation*, University of Hasselt, Diepenbeek, Belgium, October **2003**.

[54] Mitchell, W. J.; Pena, C.; Burn, P. L. *J. Mater. Chem.* **2002**, *12*, 200–205.

[55] Padmanaban, G.; Nagesh, K.; Ramakrishnan, S. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3929–3940.

[56] Wiesecke, J.; Rehahn, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 567–570.

[57] Schwalm, T.; Wieskcke, J.; Immel, S.; Rehahn, M. *Macromolecules* **2007**, *40*, 8842–8854.

[58] Hontis, L.; Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1999**, *40*, 6615–6617.

[59] Adriaensens, P.; Van der Borght, M.; Hontis, L.; Issaris, A.; van Breemen, A.; de Kok M.; Vanderzande, D.; Gelan, J. *Polymer* **2000**, *41*, 7003–7009.

[60] Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J. *J. SPIE Proc*. **2004**, 52–59.

[61] Banishoeib, F.; Henckens, A.; Fourier, S.; Vanhooyland, G.; Breselge, M.; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, N. S. *Thin Solid Films* **2008**, *516*, 3978–3988.

[62] Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Eur. Phys. J.-Appl. Phys.* **2007**, *37*, 237–240.

[63] Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2006**, *90*, 2815–2828.

[64] Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

[65] De Boer, B.; Facchetti, A. *Polym. Rev.* **2008**, *48*, 423–431.

[66] Dennler, G.; Sariciftci, N. S. *P. IEEE* **2005**, *93*, 1429–1439.

[67] Sariciftci, N. S. *Mater Today* **2004**, 36–40.

[68] Mayer, A. C.; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D. *Mater Today* **2007**, 28–33.

[69] Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338.

[70] Jacoby, M. *Chem. Eng. News* **2010**, 12–16.

[71] Brabec, C. J.; Sariciftci, N. S.; Hummelen, J .C. *Adv. Funct. Mater.* **2001**, *11*, 15–26.

[72] Cai, W.; Gong, X.; Cao, Y. *Sol. Energ. Mat. Sol. C.* **2010**, *94*, 114–127.

[73] Po, R.; Maggini, M.; Camaioni, N. *J. Phys. Chem. C* **2010**, *114*, 695–706.

[74] Mihailetchi, V. D.; Blom, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849–6854.

[75] Brabec, C. J.; Shaheen, S. E.; Winder, C.; Sariciftci, N. S.; Denk, P. Appl. Phys. Lett. 2002, 80, 1288–1290.

[76] Fehse, K.; Olthof, S.; Walzer, K.; Leo, K.; Johnson, R. L.; Glowatzki, H.; Bröker, B.; Koch, N. *J. Appl. Phys.* **2007**, *102*, 073719-1–073719-5.

[77] Wakizaka, D.; Fushimi, T.; Ohkita, H.; Ito, S. *Polymer* **2004**, *45*, 8561–8565.

[78] Würfel, P. *Chimia* **2007**, *61*, 770–774.

[79] Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. Science 1992, 258, 1471–1476.

[80] Koster, L. J. A.; Smits, E. C. P.; Mihailetchi, V. D.; Blom, P. W. M. *Phys. Rev. B* **2005**, *72*, 085205-1–085205-9.

[81] Würthner, F.; Meerholz, K. Chem. Eur. J. 2010, 16, 9366–9373.

[82] Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297–302.

[83] Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *Appl. Phys. Lett.* **2006**, *88*, 093511-1–093511-3.

[84] Koster, L. J. A.; Mihailetchi, V. D.; Ramaker, R.; Blom, P. W. M. *Appl. Phys. Lett.* **2005**, *86*, 123509-1–123509-3.

[85] Zhou, H.; Yang, L.; Stoneking, S.; You, W. *Appl. Mater. Interf.* **2010**, *2*, 1377–1383.

[86] Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Adv. Mater. 2006, 18, 789–794.

[87] Servaites, J. D.; Ratner, M. A.; Marks, T. J. Appl. Phys. Lett. 2009, 95, 163302-1–163302-3.

Chapter 2: A deeper insight into the dithiocarbamate precursor route: Synthesis of soluble Poly(Thienylene Vinylene) derivatives for Photovoltaic Applications

The synthesis of, two new poly(thienylene vinylene) derivatives is described, i.e. poly(3-octyl-2,5-thienylene vinylene) (O-PTV) and poly(bis-octylphenyl-2,5-thienylene vinylene) (BOP-PTV). Both polymers have been prepared via the dithiocarbamate (DTC) precursor route. The polymerization protocol of the monomer towards the precursor polymer has been optimized by the use of different bases, leading to improved reproducibility of the polymerization step. Processability has been guaranteed by the introduction of alkyl side chains. Finally the precursor polymers were converted towards conjugated polymers and they were fully characterized by UV/VIS, IR, GPC and cyclic voltammetry. Bulk heterojunction solar cells with PCBM as acceptor showed promising power conversion efficiencies of 0.80 % for BOP-PTV and 0.92 % for O-PTV.

1. Introduction

There is a growing need for inexpensive renewable energy sources, polymer solar cells can come up to this demand. During the last decades the development of such photovoltaic cells has progressed rapidly.[1] An important limitation of the currently applied materials is the mismatch between the absorption spectrum of the polymers and the solar emission

---

* By H. Diliën, A. Palmaerts, M. Lenes, B. de Boer, P. Blom, T. J. Cleij, L. Lutsen, D. Vanderzande for Macromolecules, 2010, 43 (24), 10231–10240

spectrum AM1.5. The use of low band gap polymers (Eg < 1,8 eV) is a viable method to expand the absorption window of solar cells and therefore increase their efficiency.[2-5] From models it can be estimated that for a classical bulk heterojunction solar cell with a conjugated polymer as a donor in combination with PCBM as an acceptor, a band gap of 1.4 eV for the donor material would be optimal.[6,7] Since π-conjugated polymers allow endless manipulation of their chemical structure, tuning of the band gap of these materials is a research topic of ongoing interest. It is anticipated that this band gap engineering can give the polymer its desired electrical and optical properties. Earlier, it has already been proven that PTV's are interesting conjugated polymers because of their high mobility for charge carriers and low band gap of about 1.7 eV.[8-10]

The synthesis of PTV derivatives can be achieved by many pathways, all with their specific advantages and disadvantages. A first well studied method is the synthesis by condensation reactions, such as Horner-Wadsworth-Emmons coupling.[11] Using this route, only low molecular weights are obtained, which have a negative influence on the morphology of thin films made from these materials. A general method to synthesize poly(arylene vinylene)s and more specifically PTV derivatives, is based on precursor routes. In a precursor route, soluble precursor polymers are first synthesized, which in a next step are converted into their corresponding conjugated polymers. They contain typically a functional group in the main chain that is a precursor for a double bond.[12] Actually the Durham route represents the very first example of such precursor route.[13] Recently a quite new type of precursor route was introduced in which rather the solubilising side chains on the conjugated backbone are thermally cleaved. This converts the conjugated polymer into an insoluble material and may lead to a substantial stabilization of the nanomorphology of the active layer in bulk heterojunction solar cells.[14,15] A similar advantage can be achieved in principle for the many precursor routes that have been developed over the last decades towards for example PTV derivatives. These routes differ by their functional groups, their polymerization conditions and, more important, their specific benefits. However it is quite a challenge to tune conversion conditions such that in this way a controlled nanomorphology is produced. Consequently, in general and also in this work, preference is given to derivatives that yield a conjugated polymer which maintain solubilising side chains to guarantee easy processing also after conversion.

The first precursor route toward PTV was based on the Wessling route and has been patented by Harper and West[16], also Elsenbaumer et al. explored this route.[17,18] Unfortunately unstable precursor polymers, which spontaneous eliminate towards insoluble PTV, were obtained. Later on, the Wessling route has been modified by both Saito[19-21] and co-workers and Murase.[22] Their merit consists of an adaptation of the leaving group in the precursor polymer. The sulphonium group has been replaced by a methoxy leaving group. Due to this modification a precursor polymer which is soluble in organic solvents has been created. A second studied pathway is the sulphinyl precursor route.[23] This pathway has been investigated in our research group, but the monomer synthesis seemed to be very problematic as a result of the instability of the intermediary products towards the monomer. In the search towards stable monomers also the xanthate route has been studied, as well in our research group[24] as by Burn et al..[25] Notwithstanding the fact that stable monomers can be formed and moreover that these monomers can be polymerized and converted towards PTV-derivatives, this route had still some drawbacks. First, the polymerizations have a rather low yield and secondly the obtained polydispersities are high (PD > 15). At last the, in this study discussed, dithiocarbamate route can be used.[26] This procedure has been chosen as the precursor route of preference to make PTV's, since it is the only route which enables to prepare stable monomers from the electron rich thiophene structure. The polymerization of the monomers starts with a base induced elimination leading to the formation of a *p*-quinodimethane system which is the actual monomer. For this elimination, a relative strong and sterically hindered base has to be used. In the past lithium diisopropylamide (LDA) and lithium bis(trimethylsilyl)amide (LHMDS) have been used for this purpose.[27] The use of LDA suffers from a lot of side reactions (cleavage of the alkyl side chain, transfer of the isopropyl group) and the polymerization of 3-alkyl substituted PTV's affords low molecular weight polymers (M_w < 14.000) in low yields (5%).[28] To avoid these side reactions, LHMDS has been used as a base, to achieve greater selectivity. Previous results showed that polymerization using LHMDS, leads to high molecular weights but with a limited reproducibility.[29]

To gain more insight in the polymerizations of these monomers a number of different bases have now been evaluated. Besides LHMDS also the sodium and potassium equivalent of LHMDS (NaHMDS and KHMDS), have been analyzed. The, less sterically hindered, Na*t*BuO has been used as well. The change of base leads to more reproducible results while the precursor polymer still reaches high molecular weights.

After optimization, two new conjugated polymers have been synthesized; poly(3-octyl-2,5-thienylene vinylene) (O-PTV) and poly[3,4-bis-(octylphenyl)-2,5-thienylene vinylene] (BOP-PTV). Octyl side chains have been chosen because in the past, it was observed that butyl and hexyl side chains were insufficient to guarantee solubility. The polymers were characterized by means of UV-Vis, IR and cyclic voltammetry and they were tested on their photovoltaic properties in bulk heterojunction solar cells with PCBM as acceptor.

2. Experimental section

2.1. General

All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone.

2.2. Techniques

^{1}H NMR spectra were taken on a Varian Inova 300 spectrometer. For all synthesized substances spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm (relatively to TMS) was used as reference. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by Size Exclusion Chromatography (SEC). Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10 μm, 30 cm, Polymer Labs) and a relative index (RI) detector (Shodex). GC/MS analyses were carried out on TSQ – 70 and Voyager mass – spectrometers (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB. Melting points (uncorrected) were measured with a digital melting point apparatus – Electrothermal IA 9000 series. Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). Ultraviolet visible spectroscopy (UV-Vis) was performed on a VARIAN CARY 500 UV-Vis-NIR spectrophotometer. Thin film electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 Potentiostat/Galvanostat using a conventional three-electrode cell under N_2 atmosphere (electrolyte: 0.1 M $TBAPF_6$ in anhydrous CH_3CN). For the measurements, an Ag/$AgNO_3$ reference electrode (0.01 M $AgNO_3$ and 0.1 M $TBAPF_6$ in CH_3CN), a platinum counter electrode and an Indium-Tin Oxide (ITO) coated glass substrate working electrode were used. For the measurements, the polymers were deposited by spin coating directly onto the ITO substrates. Cyclic voltammograms were recorded at 50 mV/s. All potentials were referenced using a known standard, ferrocene/ferrocinium, which in CH_3CN solution is estimated to have an oxidation potential of -4.98 eV *vs.* vacuum.

2.3. Synthesis of O-PTV

2.3.1. Monomer synthesis

*3-Octyl-2,5-di-bromo-thiophene (**1c**)*

To a solution of 3-octylthiophene (**1b**) (65 g, 333 mmol) in DMF (200 mL) a solution of N-bromosuccinimide (130 g, 733 mmol) in DMF (200 mL) was added slowly at 0 °C via a dropping funnel. The mixture was stirred for 72 h in darkness. The reaction mixture was poured onto a solution of NaOH (300 mL, 2.5 M) and stirred at 0 °C. The mixture was extracted with diethyl ether and the combined organic layers were washed with NaOH (2.5 M) and brine. The organic layers were dried over $MgSO_4$, the solvent was evaporated and product **1c** was obtained as yellow oil (yield 86 %, 101g).

^1H NMR ($CDCl_3$): 6.77 (s, 1H), 2.50 (t, J = 7.78, 2H), 1.56-1.46 (m, 2H), 1.28-1.23 (m, 10H), 0.86 (t, J = 1.23, 3H); ^{13}C NMR ($CDCl_3$): 143.0, 130.9, 110.3, 107.9, 31.8, 29.6, 29.5, 29.3, 29.2, 29.1, 22.7, 14.1; MS (EI, m/e): 352, 354, 356 (M^+)

*3-Octyl-2,5-thiophenedicarboxaldehyde (**1d**)*

In a three-necked round bottom flask a solution of 2,5-dibromo-3-octylthiophene (**1c**) (35 g, 99 mmol) in THF (100 mL) was stirred under nitrogen atmosphere at -78 °C. A solution of *n*-butyl lithium (135 mL, 215 mmol of a 1.6 M solution in hexane) was slowly added with a cannula, the mixture was stirred for 30 minutes and afterwards 1-formylpiperidine (24.6 g, 217 mmol), freshly distilled, was slowly added. The resulting mixture was stirred for 12 hours at room temperature. HCl (2M) was added to quench the excess of *n*-BuLi followed by extraction with chloroform. The organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. The obtained compound was purified by column chromatography on silica gel with $CHCl_3$/hexane (1/1) as a solvent. The dialdehyde **1d** was obtained as an orange oil (yield 71 %, 18 g).

^{1}H NMR ($CDCl_3$): 10.12 (s, 1H), 9.95 (s, 1H), 7.62 (s, 1H), 2.97 (t, J = 7.88, 2H), 1.73-1.63 (m, 2H), 1.31-1.23 (m, 10H), 0.86 (t, J = 7.08, 3H); ^{13}C NMR ($CDCl_3$): 183.4, 183.0, 152.0, 147.8, 143.3, 137.1, 31.8, 31.2, 31.2, 29.2, 29.2, 28.5, 22.6, 14.1; MS (EI, m/e): 252 (M^+)

*2,5-Bis(hydroxymethyl)-3-octyl-thiophene (**1e**)*

In a three-necked round bottom flask a mixture of $LiAlH_4$ (3.8 g, 15 mmol) in dry THF (50 mL) was made under argon atmosphere. This slurry was cooled to 0 °C and a solution of aldehyde **1d** (1.1 g, 0.03 mol) in THF (50 mL) was slowly added with a dropping funnel. When the addition was complete the slurry was heated at reflux temperature for 5 hours. Sequently, the mixture was placed in an ice bath and quenched very careful with water and an aqueous 15% NaOH solution. The solution was extracted with diethyl ether, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The diol was obtained as a yellow oil in a yield of 73% (5.6g).

^{1}H NMR ($CDCl_3$): 6.76 (s, 1H), 4.73 (s, 2H), 4.70 (s, 2H), 2.52 (t, J = 8.08, 2H), 1.57-1.47 (m, 2H), 1.28-1.22 (m, 10H), 0.85 (t, J = 6.88, 3H); ^{13}C NMR ($CDCl_3$): 142.3, 140.3, 136.8, 127.7, 60.2, 57.8, 31.9, 31.0, 30.9, 29.4, 29.3, 28.3, 22.6, 14.1; MS (EI, m/e): 256 (M^+)

*2,5-Bis(chloromethyl)-3-octyl-thiophene (**1f**)*

To a cooled (0 °C), stirred solution of diol **1e** (4.67 g, 18.2 mmol) in THF (30 mL) was added a solution of $SOCl_2$ (5.41 g, 45.5 mmol) in THF (40 mL). The temperature of the reaction mixture was allowed to increase to room temperature under continuous stirring for 1 hour. Then, the mixture was cooled down again at 0 °C and a saturated sodium bicarbonate solution was added drop wise until neutral. The mixture was extracted with diethyl ether, dried over $MgSO_4$ and filtered. The solvent was evaporated and the highly reactive dichloride **1f** was obtained as an orange oil. Because of the reactivity of **1f**, the dichloride (4.43 g) was used in the next reaction step without purification.

^{1}H NMR ($CDCl_3$): 6,81 (s, 1H) 4.69 (s, 2H), 4.68 (s, 2H), 2.52 (t, J = 7.78, 2H), 1.61-1.51 (m, 2H), 1.32-1.22 (m, 10H), 0.86 (t, J = 7.14, 3H)

*Synthesis of 3-octythiophene-2,5-diylbismethylene N,N-diethyldithiocarbamate (**1g**)*

To a solution of bischloromethyl **1f** (4.43 g, 15 mmol) in ethanol (50 mL), sodium diethyldithiocarbamic acid salt trihydrate (13.61g, 6 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The monomer was obtained after column chromatography (eluent: $CHCl_3$/hexane 1/1) as a yellow oil (75 %, 5.8 g).

^{1}H NMR ($CDCl_3$): 6.75 (s, 1H), 4.65 (s, 2H), 4.58 (s, 2H), 4.01 (q, J = 7.06, 4H), 3.69 (q, J = 7.25, 4H), 2.48 (t, J = 7.70, 2H), 1.59-1.47 (m, 2H), 1.29-1.23 (m, 10H), 0.85 (t, J = 7.10, 3H); ^{13}C NMR ($CDCl_3$): 194.7, 194.5, 141.4, 136.9, 130.5, 129.0, 49.5, 49.3, 46.7, 36.9, 35.2, 31.9, 30.7, 29.5, 29.2, 28.4, 22.7, 14.1, 12.5, 11.6

2.3.2. Precursor polymer synthesis.

Polymerization.

The monomer **1g** (2.8 g, 5.4 mmol) was freeze dried. A solution, with a monomer concentration of 0.4 M, in dry THF (13.5 mL) was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (11 mL of a 1M solution in THF) was added in one go to the stirred monomer solution. The resulting mixture was stirred for 90 minutes under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvents of the combined organic layers were evaporated under reduced pressure and a second precipitation was performed in cold methanol. The polymer **1h** was collected and dried *in vacuo* (yield 56 %, 1.1 g).

UV-Vis: λ_{max} = 261 nm (in film); FT-IR(NaCl disk): 2931, 2846, 1486, 1415, 1268, 1206 cm^{-1}; SEC: M_w = 86 . 10³; PD = 3.1; ^{1}H NMR (CDCl$_3$): 6.57 (br, 1H), 5.46 (br, 1H), 3.96 (br, 2H), 3.66 (br, 4H), 2.27 (br, 2H), 1.21 (br, 18H), 0.85 (br, 3H); ^{13}C NMR (CDCl$_3$): 193.96, 139.5, 138.8, 133.8, 127.6, 52.7, 48.9, 46.6, 31.8, 30.7, 29.5, 29.3, 28.2, 22.6, 14.0, 12.5, 11.5

2.3.3. Conjugated polymer.

Thermal conversion towards O-PTV.

The precursor polymer **1h** (1g, 2.7 mmol) was dissolved in *o*-dichlorobenzene (50 mL) and refluxed for 4.5 h. Afterwards the solution was cooled to room temperature and the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol and dried *in vacuo*. A purple/black solid has been obtained (yield 90 %, 0.54 g).

UV-Vis: λ_{max} = 620 nm (in film); λ_{max} = 582 nm (in CHCl$_3$); FT-IR: 2931, 2846, 1460, 1250, 1016, 926 cm^{-1}; SEC: M_w = 65 . 10³; PD = 2.6; ^{1}H NMR (CDCl$_3$): 6.97 (s, 1H), 5.00 (s, 1H), 2.26 (br, 2H), 1.24 (br, 12H), 0.85 (br, 3H)

2.4. Synthesis of BOP-PTV

2.4.1. Monomer synthesis

*Synthesis of 3,4-bis(4-octylphenyl)thiophene (**2d**)*

A solution of *p*-octylphenyl boronic acid (**2b**) (4.45 g, 19 mmol), dibromothiophene (**2c**) (1g, 4.1 mmol) and potassium fluoride (0.96 g, 17 mmol) was made in a mixture of water and toluene (1/1). Pd(PPh$_3$)$_4$ (0.33 g, 0.029 mmol) was added as a catalyst. The resulting mixture was refluxed for 18 hours. Then an extraction was performed with dichloromethane, the organic layers were dried over MgSO$_4$ and the solvent was evaporated in vacuo. The desired product **2d** was obtained as colorless oil after purification by column chromatography over silica with pentane as an eluent (84%, 7.4 g).

^{1}H NMR ($CDCl_3$): 7.27 (s, 2H), 7.11-7.02 (m, 8H), 2.58 (t, J = 7.87, 4H), 1.64-1.54 (m, 4H), 1.34-1.20 (m, 20H), 0.89 (t, J = 6.93, 3H); ^{13}C NMR ($CDCl_3$): 141.7, 141.5, 133.9, 128.8, 128.1, 123.5, 35.6, 31.9, 31.3, 29.5, 29.35, 29.3, 22.7, 14.1; MS (EI, m/e): 460 (M^+)

*3,4-bis(4-octylphenyl)-2,5-bis(chloromethyl)thiophene (**2e**)*

In a three-necked round bottom flask a mixture of **2d** (3.3 g, 7.1 mmol) and paraformaldehyde (0.58 g, 19 mmol) was made. The mixture was cooled to 0 °C under a nitrogen atmosphere, concentrated HCl (4.0 g, 41 mmol) and acetic anhydride (7.3 g, 71 mmol) were added drop wise. The resulting mixture was heated at 75 °C for 4,5 hours. After cooling down (0 °C) a cold saturated solution of sodium acetate and a solution of sodium hydroxide (2M) were added. The solution was extracted with diethyl ether, dried over $MgSO_4$ and the solvents were evaporated under vacuo. Because of the instability of the product, the crude product **2e** was used in the next reaction step without further purification.

^{1}H NMR ($CDCl_3$): 7.04-6.92 (m, 8H), 4.68 (s, 4H), 2.57 (t, J = 7.94, 4H), 1.63-1.49 (m, 4H), 1.31-1.22 (m, 20H), 0.86 (t, J =7.08, 3H)

*Synthesis of 3,4-bis(4-octylphenyl)thiophene-2,5-diylbismethylene-N,N-diethyl dithiocarbamate (**2f**)*

Compound **2e** (3.96 g, 7.1 mmol) was dissolved in methanol (50 mL), sodium diethyldithiocarbamate trihydrate (4.8 g, 21 mmol) was added as a solid and the mixture was stirred overnight. Subsequently the mixture was extracted with diethyl ether, dried over $MgSO_4$ and the solvent was evaporated under vacuo. The crude product was purified by column chromatography with a mixture of chloroform/pentane (1/1) as an eluent. The dithiocarbamate monomer **2f** was obtained as orange oil (yield: 54 %).

^{1}H NMR ($CDCl_3$): 7.01-6.87 (m, 8H), 4.62 (s, 4H), 4.06-3.95 (m, 4H), 3.77-3.66 (m, 4H), 2.50 (t, J = 7.58, 4H), 1.60-1.51 (m, 4H), 1.32-1.20 (m, 32H), 0.86 (t, J = 7.16, 3H); ^{13}C NMR ($CDCl_3$): 194.6, 141.5, 141.4, 133.0, 132.7, 130.0, 128.0, 49.4, 46.8, 36.2, 35.6, 31.9, 31.2, 29.5, 22.7, 14.1, 12.5

2.4.2. Precursor polymer synthesis.

Polymerization.

The monomer **2f** (0.37 g, 0.48 mmol) was freeze dried. A solution, with a monomer concentration of 0.2 M, in dry THF (2.4 mL) was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (0.6 mL of a 1M solution in THF) was added in one go to the stirred monomer solution. The resulting mixture was stirred for 90 minutes under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvent of the combined organic layers was evaporated under reduced pressure and a second precipitation was performed in pure cold methanol. The polymer **2g** was collected and dried *in vacuo* (yield: 54 %, 0.16 g).

UV-Vis: λ_{max} = 242 nm (in film); IR: 2921; 2862; 1485; 1415; 1266; 1207; SEC: M_w = 186 . 10^3; PD = 2.7; ^{1}H NMR ($CDCl_3$): 7.00-6.68 (br, 8H), 4.07-3.93 (br, 4H), 3.91-3.38 (br, 4H), 2.44 (br, 4H), 1.61-1.40 (br, 24H), 1.32-1.15 (br, 12H), 0.91-0.79 (br, 6H)

2.4.3. Conjugated polymer

Thermal conversion towards BOP-PTV .

The precursor polymer **2g** (0.16 g, 0.25 mmol) was dissolved in *o*-dichlorobenzene (6.2 mL) and stirred for 4,5 h at 150 °C. After being cooled to room temperature, the resulting dark solution was precipitated drop wise in methanol. The conjugated **2h** polymer was filtered off and dried under reduced pressure. A dark blue solid was obtained in a yield of 60 % (87 mg).

UV-Vis: λ_{max} = 596 nm (in $CHCL_3$ solution); λ_{max} = 601 nm, shoulder at 646 nm (in film); FT-IR: 2930; 2850; 1269; 1095; 1030; 934; 802; SEC: $M_w = 53 . 10^3$; PD = 2.1; ^1H NMR ($CDCl_3$): 6.99-6.80 (br, 8H), 2.54 (br, 4H), 1.61-1.48 (br, 4H), 1;31-1.18 (br, 20 H), 0.89-0.82 (br, 6H)

2.5. Device preparation

All devices were made on pre-patterned ITO/Glass samples supplied by Philips. After a standardized cleaning procedure in a wet station, a layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) was spin coated on top of the ITO. This layer has a thickness of 50 to 60 nm. The aqueous PEDOT:PSS solution (CLEVIOS P VP AI 4083 by H.C. Starck) was spin coated in exactly the same way for each substrate (10 seconds at 500 rpm followed by 50 seconds at 1500 rpm).

On top of the PEDOT:PSS, a layer of either BOP-PTV or O-PTV was spin coated inside the glove box. Table 1 shows the spin procedures and concentrations for both polymers. Finally, as a cathode, a metal top contact was evaporated, consisting of 5 nm samarium with 100 nm aluminum on top.

Polymer	**Solvent**	**Conc. (mg/mL)**	**Spin programme (lid, speed (rpm), acceleration (rpm/s), time (s))**
BOP-PTV	$CHCl_3$	15	Close, 300 , 500, 4 Close, 500, 500, 60 Open, 500, 500, 30
O-PTV	*o*-dichlorobenzene	10	Open, 300, 100, 120 Open, 800, 200, 30

Table 1. Applied spin coating procedures and concentrations for both polymers.

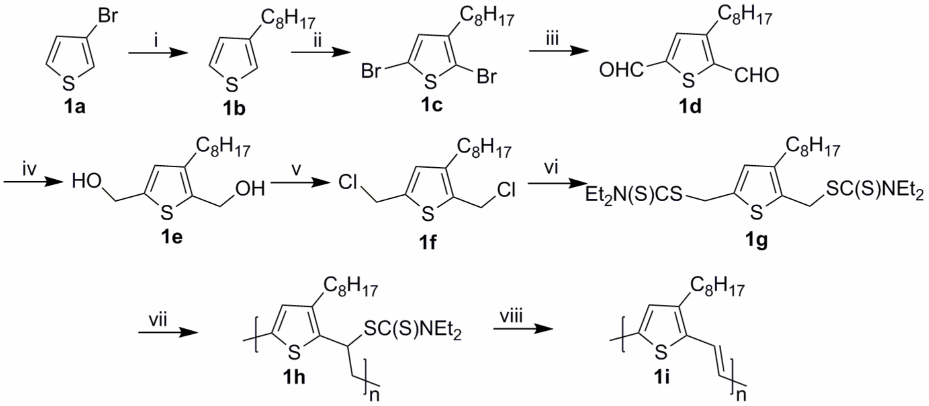
2.6. Device measurements

All measurements were performed in a glove box, under nitrogen atmosphere. Current *versus* voltage characteristics were determined using a Keithly 2400 Source meter. The device current was registered using a Labview program, while sweeping a voltage across the device, going up from 0 V to a positive voltage, then down to -2 V and up again to 0 V. The thicknesses of all spin coated polymers, including the PEDOT:PSS were determined using a Dektak 6M Stylus Profiler.

3. Results and discussion

3.1. Monomer synthesis

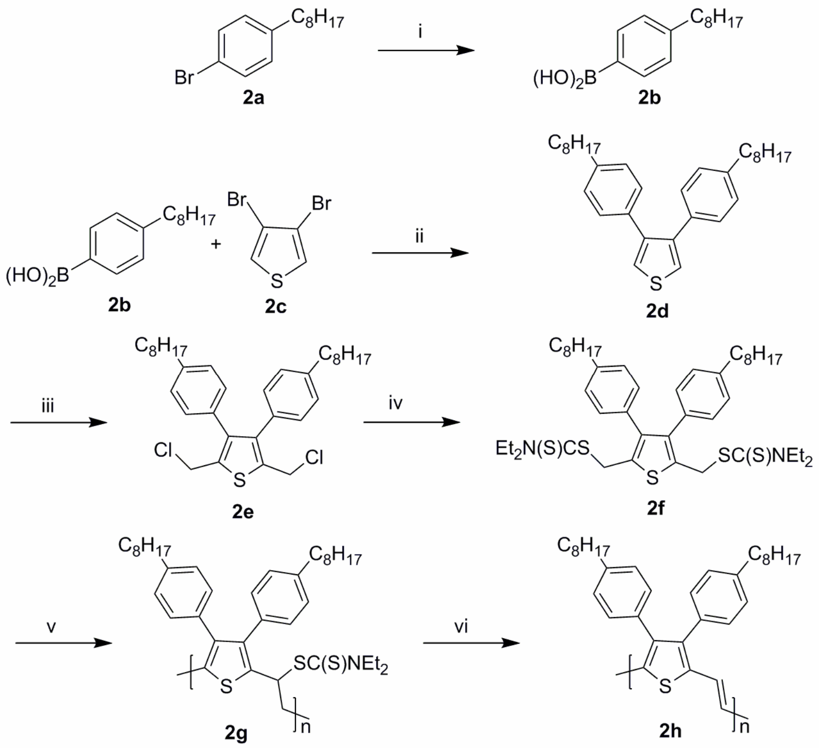
In view of the advantages compared to other routes (e.g., Wessling, xanthate, …), the dithiocarbamate (DTC) route has been chosen as the precursor route of preference to obtain the PTV derivatives. The monomers used were synthesized by two different synthetic pathways in accordance with their substitution profile (mono- or disubstituted backbone).[6,30] The mono substituted PTV (O-PTV) has been synthesized by a six-step synthetic procedure (Scheme 1).



Scheme 1. Synthetic route towards O-PTV: (i) $BrMgC_8H_{17}$, $NiCl_2(dppp)$; (ii) NBS, DMF; (iii) 1. *n*-BuLi, 2. *n*-formylpiperidine; (iv) $LiAlH_4$, THF; (v) $SOCl_2$, THF; (vi) $NaSC(S)NEt_2.3H_2O$, EtOH; (vii) base, THF; (viii) ΔT.

The synthetic scheme starts with substitution of commercially available 3-bromothiophene (**1a**) by a Kumada coupling.[31] Secondly, bromination has been performed.[32] Dialdehyde **1d** was formed by a reaction with *n*-BuLi and *n*-formylpiperidine.[33] Reduction with lithium aluminum hydride, followed by chlorination of the diol with thionyl choride afforded intermediate **1f**.[34] Due to the instability of thiophene **1f**, it has to be converted in situ to the dithiocarbamate monomer **1g**.[6] Monomer purification was performed by column chromatography (silica).

For the BOP-PTV monomer a slightly different pathway has been used (Scheme 2).



Scheme 2. Synthetic pathway towards BOP-PTV: (i) 1. *n*-BuLi, 2. triisopropylborate; (ii) $Pd(PPh_3)_4$, KF, toluene/H_2O; (iii) CH_2O, HCl, Ac_2O; (iv) $NaSC(S)NEt_2.3H_2O$, MeOH; (v) NaHMDS, THF; (vi) ΔT.

The monomer has been formed in a 4 step synthesis. The first step is the synthesis of boronic acid[35] **2b** which is used for the formation of 3,4-di(octylphenyl)thiophene (**2d**) via a Suzuki coupling with dibromothiophene **2c**. Bis(methylenechloride) **2e** has been synthesized by a direct chloromethylation reaction. The last reaction step and purification towards monomer **2f** are identical to the first procedure.

3.2. Polymerization towards the precursor polymer

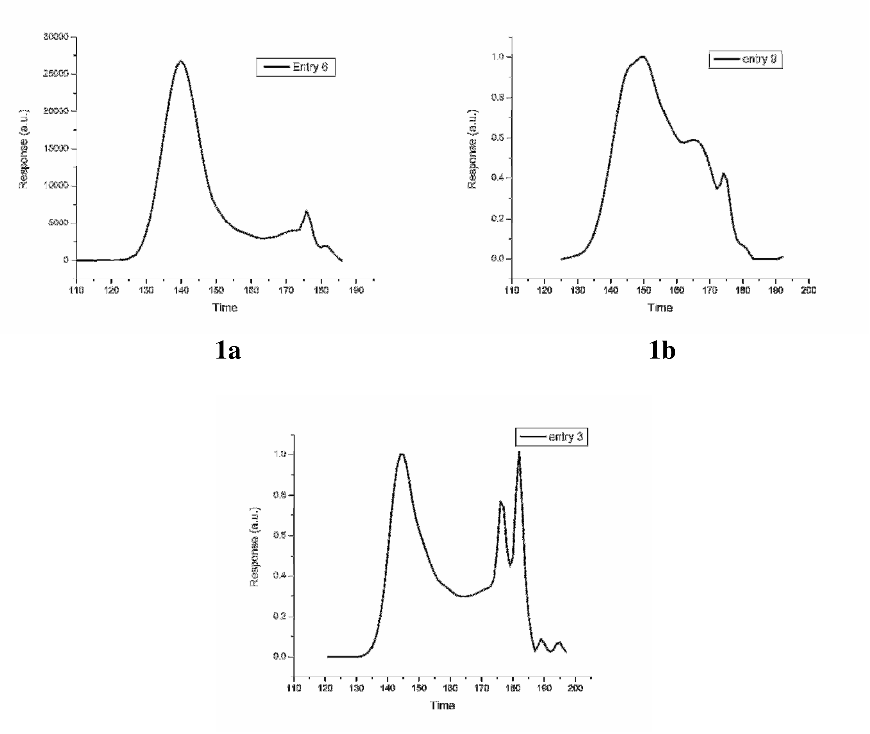
Both monomers were freeze dried to remove any traces of water. The polymerizations have been initiated by different bases. All the other conditions are the same for every reaction; 2 equivalents of base were used, the initial concentration of the monomer was fixed at 0.4 M and all polymerizations were performed at a definite reaction temperature (0 °C) and reaction time of 90 minutes.

To study the influence of the base on the formation of the precursor polymer, 4 different bases have been used: LHMDS, NaHMDS, KHMDS and Na*t*BuO.

The first base which has been tested is LHMDS. For this base, it has already been proven that the formation of high molecular weight materials is possible,[29] but the reproducibility of the polymerization showed to be an important problem. To test the reproducibility, over 20 experiments have been done. All the polymerizations were carried out under exactly the same conditions as described above. All the polymers reached a high molecular weight (table 2) and a moderated yield of 38 % (average of all the experiments), but the achieved weight distribution differed significantly. Basically there are 3 different situations (figure 1): a monomodal distribution (**1a**) (Figure 1), an intermediate situation which can be described as tailing (**1b**) and a bimodal distribution (**1c**). The monomodal distribution only occurred 2 times. Seemingly the polymerization process has the tendency to yield a bimodal distribution or tailing. Both situations appear in approximately the same frequency.

Entry	M_w (10^3)	PD	Yield (%)
1	69	6.5	34
2	241	3.2	43
3	64	2.3	38
4	66	6.4	36
5	115	4.7	39
6	156	3	44
7	56	5.5	42
8	96	2.5	35
9	53	5.1	43
10	83	2	30

Table 2. The polymerization results for the precursor polymer after polymerization with LHMDS.



1a

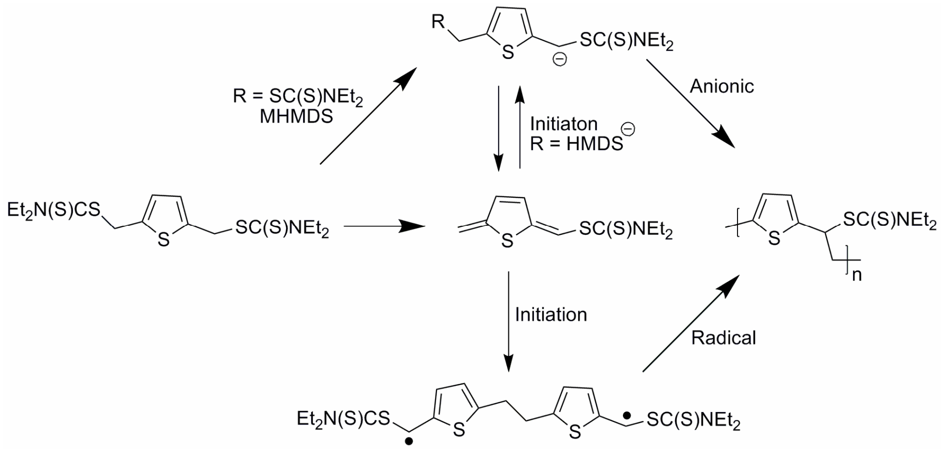
1b

1c

Figure 1. Molecular weight distribution of O-PTV (SEC profiles).

The different molecular weight distributions can be explained by the polymerization mechanism (scheme 3). Polymerization starts with a base induced elimination from the (pre)monomer; the base abstracts a proton and subsequently one of the dithiocarbamate groups is expelled. This leads to the actual monomer, a *p*-quinodimethane system. The actual polymerization can proceed by either an anionic or radical mechanism (scheme 3). In former work it has been shown that the radical polymerization mechanism leads to the high molecular weight fraction and the anionic mechanism results in low molecular weight fractions.[36]

In case of the radical mechanism, the initiator is formed when two *p*-quinodimethane systems combine and a diradical originates. For the anionic mechanism a nucleophile has to be present as an initiator, it is possible that the base interacts as such a nucleophile or that the anionic intermediate towards the *p*-quinodimethane system takes up that role.[36]



Scheme 3. Mechanism of dithiocarbamate monomer polymerization via *p*-quinodimethane system.

To prove that two different polymerization mechanisms are present, two additional experiments have been done.[37] In a first experiment 0.5 equivalents of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been added to a typical reaction mixture (figure 2).[38] Here, the molecular weight has been reduced significantly (M_w: 28 . 10^3; PD: 6.4). This is an indication that the high molecular weights originate from a radical polymerization mechanism, which in this experiment is suppressed by the radical inhibitor, TEMPO. To verify this observation, a reversed addition, meaning that the monomer is added drop wise to a solution of the base, has been done (figure 2). Such an addition should favor the anionic polymerization.[39,40] The experiment confirms this hypothesis, the molecular weight dropped extremely (M_w: 5.5 10^3; PD: 3.1).

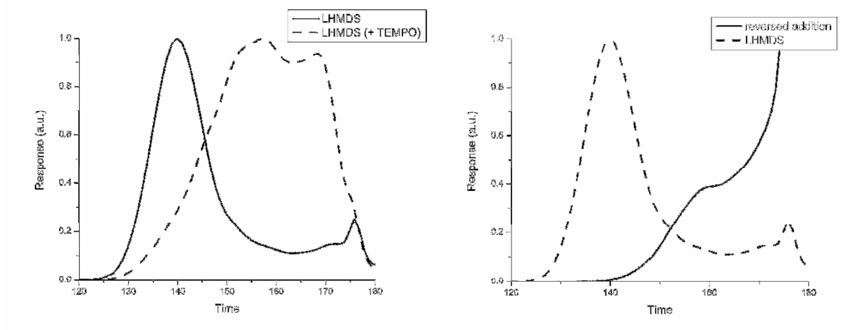


Figure 2. The influence of TEMPO and reversed addition on the molecular weight distribution.

The second base which has been used is the sodium equivalent of LHMDS, NaHMDS (table 3 and figure 3). Its base strength is conditioned by the basicity or the pKa of the parent amine, hexamethyldisilazide. Even so, the results for these polymerizations differ significantly. Also high molecular weights have been reached. But now, all polymerizations have more or less the same bimodal distribution. Another advantage of the change of base is the fact that the yield rises till 52 % (average of the four experiments).

Entry	High molecular weight		Low molecular weight		Yield
	M_w (10^3)	PD	M_w (10^3)	PD	
1	164	2	2.0	1.2	50
2	107	1.9	2.4	1.3	51
3	218	2.8	2.7	1.5	54
4	208	2.6	2.7	1.4	52

Table 3. Polymerization results with NaHMDS.

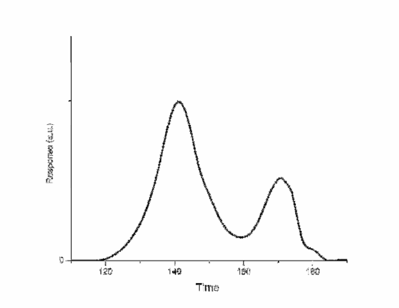


Figure 3. SEC profile (entry 4) for polymerization with NaHMDS.

To complete the sequence lithium-sodium-potassium, also the effect of KHMDS as a base has been tested. Here a monomodal distribution with lower molecular weights (M_W: 14 . 10^3, PD: 3.2) has been achieved, but the yield rises till 64 % (figure 4).

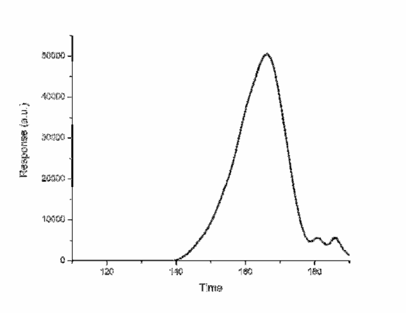


Figure 4. SEC-profile for polymerization with KHMDS.

When we compare the three sterically hindered hexamethyldisilazane bases, the yield goes up through the sequence Li-Na-K. A second phenomenon that can be recognized concerns the molecular weight distribution. The larger the counter ion (Li<Na<K), the more low

molecular weight fractions are formed, so the anionic polymerization mechanism is in favor. A possible explanation can relate the results with differences in solvatation of the cation. The polymerizations are performed in THF, which is a solvent with a low dielectric constant (ε = 7.58)[41], and therefore a weakly dissociating solvent. In such a solvent the nucleophilicity of anions depends on the electrostatic attraction of the cation-anion pair and therefore the charge density on the cation. The larger the cation, the lower the charge density and the more the cation-anion pair will be separated. So the probability of any nucleophile to act as an anionic initiator increases.

Finally also sodium *tert*-butoxide has been tested as a base. Its base strength is lower than LHMDS. This also leads to the formation of lower molecular weights (M_w = 2 . 10^3) (figure 5) under normal reaction conditions (0 °C). The high molecular weight peak is present in a very small amount. From previous experience,[42] it is indeed to be expected that due to the lower base strength, proton abstraction and formation of the *p*-quinodimethane system is much slower. In case of a competition between a radical and an anionic mechanism the competition occurs at the level of initiation kinetics.[39] As the rate of initiation for the radical mechanism scales with the square and for the anionic mechanism in first order in the concentration of the *p*-quinodimethane system, initiation kinetics are for the former more sensitive to concentration of the true monomer than the latter.

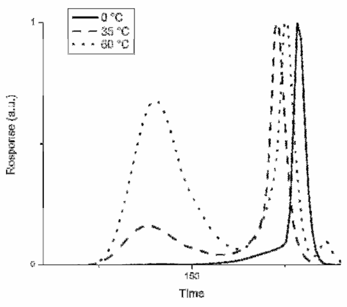


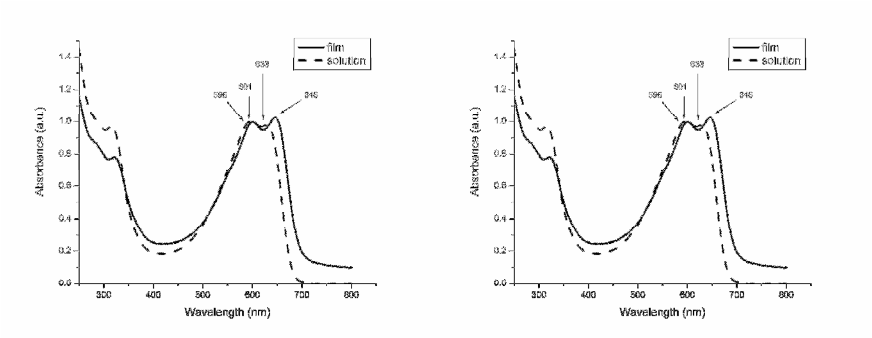
Figure 5. SEC profiles for polymerization at 0 °C, 35 °C and 60 °C.

Consequently this would imply that higher temperatures, leading to a more efficient formation of the true monomer and keeping all other polymerization parameters (time, equivalents base,…) constant, would lead to a more competitive radical polymerization mechanism. Accordingly performing the polymerization reaction at 35 °C and 60 °C results in an increased contribution of the high molecular weight fraction (Figuur 5).

The precursor polymers which are used for further characterization have been made in the same conditions. Both monomers (**1g** and **2f**) were polymerized using sodium hexamethyldisilazide (2M solution in THF) as a base in dry THF at 0 °C for 90 minutes to afford the polymers (**1i** and **2h**). Work-up and purification have been done as described above. The isolated yields range from 56 % for the octyl-precursor polymer to 54 % for the BOP-precursor polymer. Molecular weights were determined by means of SEC in THF against polystyrene standards (Table 4).

3.3. Conversion to the conjugated polymers

The precursor polymers can be converted into their conjugated counterparts by a thermal treatment (scheme 1 and 2). Upon heating, the dithiocarbamate group of the precursor polymer is eliminated to form the conjugated backbone. The thermal conversion has been performed in solution. The precursor polymers are dissolved in *o*-dichlorobenzene and stirred for 4.5 h at 180 °C to form O-PTV and at 150 °C to form BOP-PTV. Polymers are isolated by precipitation of the resulting reaction mixture in MeOH. After isolation the conjugated polymers were characterized by UV/VIS (Figure 6) and SEC (Table 4). Furthermore, the polymers were studied by FT-IR spectroscopy, to be certain that all dithiocarbamate groups disappeared and therefore full conjugation has been realized.



O-PTV **BOP-PTV**

Figure 6. UV-Vis spectra of the conjugated polymers (film and solution).

	M_w	PD
O-PTV precursor polymer	$86 . 10^3$	3.1
O-PTV	$65 . 10^3$	2.6
BOP precursor polymer	$186 . 10^3$	2.7
BOP PTV	$53 . 10^2$	2.1

Table 4. SEC data for the precursor and the conjugated polymers.

3.4. Transport properties

Hole only devices have been made resulting in a hole mobility of 3.10^{-9} m^2/Vs for BOP-PTV and 5.10^{-9} m^2/Vs for O-PTV, which is slightly lower as compared to the hole mobility of 3.10^{-8} m^2/Vs for P3HT, but nevertheless acceptable when compared to other efficient low band gap donors (Figure 7).[8,43-45] Combined with the good transport properties of PCBM no space charge effects are expected, at least for moderately thick films, similar to those used in MDMO-PPV:PCBM blends.

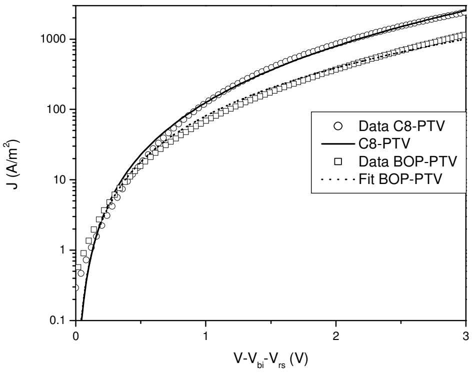


Figure 7. Current density versus voltage, corrected for built in voltage and series resistance of a BOP-PTV and O-PTV hole only device. Data (symbols) are fitted (line) using a space charge limited current with a field dependent mobility.

3.5. Cyclic Voltammetry

The cyclic voltammograms of thin films of BOP-PTV and O-PTV display distinct characteristic irreversible oxidation and reduction processes during the first potential scan. Upon repeated scanning the currents associated with these features significantly reduces, as expected for irreversible electrochemical processes. From the onset potentials of the oxidation and reduction the position of the energy levels can be estimated. For BOP-PTV the onset of oxidation occurs at 0.46 V *vs.* Ag/AgNO$_3$ and the onset of reduction occurs at -1.18 V *vs.* Ag/AgNO$_3$. The corresponding energy level of BOP-PTV for the highest occupied molecular orbital (HOMO) is -5.39 eV and for the lowest unoccupied molecular orbital (LUMO) is -3.75 eV. For O-PTV the onset of oxidation occurs at 0.22 V *vs.* Ag/AgNO$_3$ and the onset of reduction occurs at -1.30 V *vs.* Ag/AgNO$_3$. The corresponding energy level of O-PTV for the highest occupied molecular orbital (HOMO) is -5.15 eV and for the lowest unoccupied molecular orbital (LUMO) is -3.63 eV. The resulting electrochemical band gap of BOP-PTV is 1.64 eV and of O-PTV is 1.52 eV. Although in the same order of magnitude, these values are somewhat lower than the observed optical band gaps (1.78 eV and

1.70 eV, respectively). This is not surprising, since the determination of the onsets of oxidation and reduction for irreversible electrochemical processes may incur some level of error. Notwithstanding, the cyclic voltammetry measurements clearly confirm the occurrence of a lower band gap for O-PTV as compared to BOP-PTV, likely a result of increased conformational disorder due to steric effects of the substituents. In addition, for BOP-PTV both the HOMO and the LUMO are lowered as compared to O-PTV, which reflects the electronic effects of the phenyl substituents (Table 5).

	HOMO	**LUMO**	**E_g (electrochemical)**	**E_g (optical)**
O-PTV	- 5.15	- 3.63	1.52	1.70
BOP-PTV	- 5.39	- 3.75	1.64	1.78

Table 5. CV data for O-PTV and BOP-PTV.

3.6. Solar cells

Solar cells were made by sandwiching the conjugated polymers in between an ITO/PEDOT:PSS anode and a samarium/aluminum cathode. The best obtained performance for bulk heterojunction solar cells with BOP-PTV or O-PTV as donor polymer and PCBM as acceptor material are depicted in figure 8 and table 6. For a 1:4 BOP-PTV:PCBM solar cell spin coated from chloroform the highest achieved efficiency is 0.80 %. This cell has an open circuit voltage (V_{oc}) of 0.67 V and a fill factor of 60% and higher for films with a thickness of more than 200 nm, indicating good charge transport properties of the blend. For a 1:4 O-PTV:PCBM solar cell spin coated from *o*-dichlorobenzene the highest achieved efficiency is 0.92 %. The open circuit voltage (V_{oc}) of O-PTV is 0.47 V, this is 0.2 V less compared to BOP-PTV. This difference in Voc is most likely originated from the differences in the HOMO levels of both polymers. Apparently, the introduction of phenyl substituents results in a lowering of the HOMO energy level, which translates itself in a larger V_{oc}. The difference in short circuit currents can be explained by the differences in absorption of both films, which will be discussed in the next section. Notwithstanding, the short circuit currents (J_{sc}) are low, which results in the observed efficiencies below 1.0 %. Even so the performance of the solar cells made by the optimized polymerization with NaHMDS are significant better than the one made by LHMDS. Girotto et all measured an efficiency of 0.15 %-0.17 % for other 3-alkyl-substituted PTV's.[46] So by optimizing the synthetic route towards the PTV-derivatives, the efficiency of the solar cell has been increased with a factor 4.5.

	V_{oc} (V)	**J_{sc} (A/m^2)**	**FF %**	**Efficiency %**
1:4 O-PTV:PCBM	0.47	52.8	35	0.92
1:1 BOP-PTV:PCBM	0.66	9.1	59	0.34
1:2 BOP-PTV:PCBM	0.67	15.8	57	0.66
1:4 BOP-PTV:PCBM	0.67	18.3	60	0.80

Table 6. Solar cell performance for BOP-PTV:PCBM and O-PTV:PCBM.

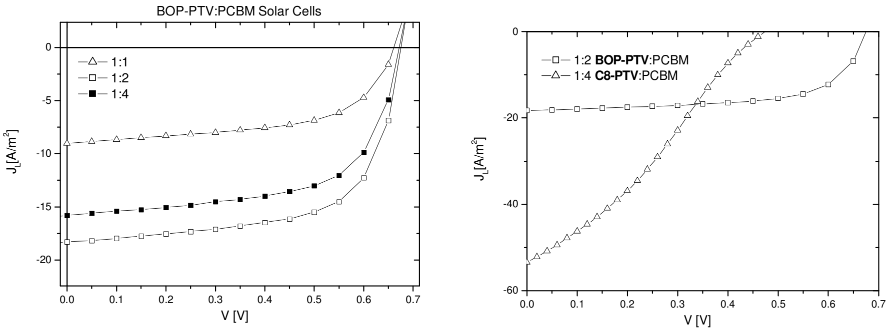


Figure 8. Current density versus voltage of PTV:PCBM solar cells under Illumination of a 1000 W/m^2 simulated solar spectrum.

3.7. Absorption characteristics

To understand the moderate efficiencies for these new low band gap polymers, the absorption characteristics, as well in solution as in thin films, of both PTV derivatives have been studied and compared to P3HT. To this end, thin films of P3HT, BOP-PTV and O-PTV were prepared from the same solvent, *i.e.* chloroform. After measuring the film thickness, the absolute absorbance as a function of the wavelength can be readily determined (Figure 9). Furthermore, the optical band gap can be derived from the low energy side tangent. The band gap and the absolute absorptivity in a thin film are presented in table 7.

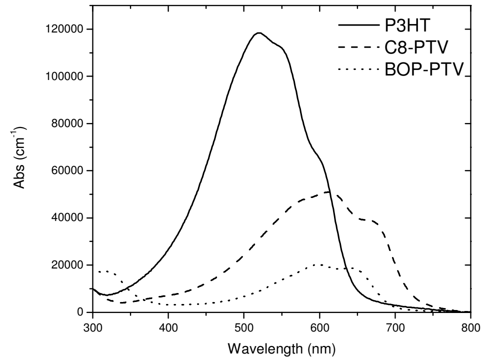


Figure 9. The absolute absorbance in function of the wavelength for spincoated films of P3HT, BOP-PTV and O-PTV.

	Thin film absolute absorptivity (cm^{-1})	Molar attenuation coefficient (M^{-1} cm^{-1})	Optical band gap (eV)
BOP-PTV	20135	10453	1.78
O-PTV	50998	4240	1.70
P3HT	118334	8000	1.90

Table 7. Thin film absolute absorptivities, solution extinction coefficients and optical band gaps of BOP-PTV, O-PTV and P3HT.

The moderate short circuit currents (J_{sc}) of BOP-PTV and O-PTV compared to P3HT can be understood in terms of the absolute absorption maxima. It is noteworthy that the absorptivity of P3HT and O-PTV in a thin film follow the same trend relative to the molar attenuation coefficient. On the other hand where BOP-PTV has the highest molar attenuation coefficient of the three compounds, this does not translate to a high absorptivity. This can be explained in part by the high structural order and even crystalline character of P3HT[47] and the expected nature or rotational disorder of the larger side chains in BOP-PTV. This will be a subject for further research.

4. Conclusions

In conclusion, two new conjugated polymers were synthesized via the dithiocarbamate precursor route. Synthesis of the required substituted thiophene dithiocarbamate monomers was easily achieved. The polymerization has been optimized by the use of 4 different bases. Polymerizations with NaHMDS as a base resulted in polymers with high molecular weights, high λ_{max} values, acceptable polydispersities and more important a good reproducibility. Both polymers were provided with alkyl side chains to guarantee solubility and improve the processing capacities: therefore we have a better solar cell performance than for the unsubstituted PTV. It is demonstrated that these narrow band gap polymers have a sufficiently high hole mobility. Notwithstanding, the short circuit currents (J_{sc}) are still inferior, resulting in low efficiencies. The moderate short circuit currents (J_{sc}) of BOP-PTV and O-PTV compared to P3HT can be explained by their significant lower absorptivity in thin films.

5. Acknowledgements

The authors gratefully acknowledge BELSPO in the frame of network IAP P6/17, and the Fund for Scientific Research, Flanders (Belgium) (FWO) for financial support and for granting Ph.D. fellowships (H.D. & A.P.). The FWO is also gratefully acknowledged for the funding of the project G.0091.07. We also thank the European Science Foundation (ESF) for the received support for the activity entitled 'New Generation of Organic based Photovoltaic Devices'.

6. References

1. Mayer, A. C; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D. *Mater. Today* **2007**, *10*, 28–33.
2. Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.
3. Goris, L.; Loi, M. A.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Polec, I.; Lutsen, L.; Manca, J.; De Schepper, L.; Vanderzande, D. *Synthetic Met.* **2003**, *138*, 249–253.
4. Colladet, K.; Nicolas, M.; Goris, L.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, *7*, 451–452.
5. Shaheen, S. E.; Vangeneugden, D.; Kiebooms, R.; Vanderzande, D.; Fromherz, T.; Padinger, F.; Brabec, D. J.; Sariciftci, N. S. *Synthetic Met.* **2001**, *121*, 1583–1584.
6. Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *Appl. Phys. Lett.* **2006**, *88*, 93511-1–93511-3.
7. Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789–794.
8. Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19–26.
9. Yeon-Beom, L.; Hong-Ku, S.; Seung-Won, K. *Macromol. Rapid Comm.* **2003**, *24*, 522–526.
10. Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Boer, B. *Polym. Rev.,* **2008**, *48*, 531–582.

11. Van De Wetering, K.; Brochon, C.; Nhov, C.; Hadziioannou, G. *Macromolecules* **2006**, *39*, 4289–4297.

12. Vanderzande, D. J.; Issaris, A. C.; Van Der Borght, M. J.; van Breemen, A. J.; de Kok, M. M.; Gelan, J. M. *Macromol. Symp.* **1998**, *125*, 189-203.

13. Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1985**, *4*, 202–203.

14. Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. A. J. *Chem. Mater.* **2009**, *21*, 4669–4675.

15. Helgesen, M.; Krebs, F. C. *Macromolecules* **2010**, *43*, 1253–1260.

16. Harper, K.; West, W. J. W. *Eur. Pat. Appl. No. 182548*, **1985**.

17. Jen, K. Y.; Jow, R.; Eckhardt, H.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 49–53.

18. Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309–311.

19. Yamada, D.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, *00*, 1448–1449.

20. Tokito, S; Momii, T.; Murata, H; Tsutsui, T.; Saito, S. *Polymer* **1990**, *31*, 1137–1141.

21. Tsutsui, T.; Murata, H.; Momii, T.; Yoshiura, K.; Tokito, S.; Saito, S. *Synth. Met.* **1991**, *41*, 327–330.

22. Murase, I.; Ohnishi, T.; Noguchi, *T. Ger. Offen.* No. 3704411, **1987**.

23. Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin solid films* **2004**, *451-452*, 472–579.

24. Henckens, A. *PhD dissertation*, University of Hasselt, Diepenbeek, Belgium, October **2003**.

25. Mitchell, W. J.; Pena, C.; Burn, P. L. *J. Mater. Chem.* **2002**, *12*, 200–205.

26. Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J. *J. SPIE Proc*. **2004**, 52–59.

27. Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Eur. Phys. J.-Appl. Phys.* **2007**, *37*, 237–240.

28. Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2006**, *90*, 2815–2828.

29. Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

30. Banishoeib, F.; Henckens, A.; Fourier, S..; Vanhooyland, G.; Breselge, M.; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, N. S. *Thin solid films* **2008**, *516*, 3978–3988.

31. Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347– 3354.

32. Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner, F.; Gaudl, K. U.; Caro, M. B.; Fischer, P. *J. Chem. Soc. Perk. T. 2* **1993**, 489–494.

33. Frey, J.; Bond, A. D.; Holmes, A. B. *Chem. Commun.* **2002**, 2424–2425.

34. Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925–4932.

35. Wand, M. D.; Thurmes, W. N.; Walba, D. M. *US patent 5380460*, **1995**.

36. Henckens, A.; Duyssens, I.; Lutsen, L.; Vanderzande, D.; Cleij, T. J.; *Polymer* **2006**, *47*, 123–131.

37. Vandenbergh, J.; Wouters, J.; Adriaensens, P. J.; Mens, R.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2009**, *42*, 3661–3668.

38. Hontis, L.; Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1999**, *40*, 6615–6617.

39. Vanderzande, D. J. M.; Hontis, L.; Palmaerts, A.; Van Den Berghe, D.; Wouters, J.; Lutsen, L.; Cleij, T. Proc. of SPIE **2005**, *5937*, 59370Q-1–59370Q-10.

40. Neef, C. J.; Ferraris, J. P. Macromolecules **2000**, *33*, 2311–2314.

41. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Physical Properties and methods of purification* **1986**, 309–311.

42. Adriaensens, P.; Van Der Borght, M.; Hontis, L.; Issaris, A.; van Breemen, A.; de Kok, M.; Vanderzande D.; Gelan, J. *Polymer* **2000**, *41*, 7003–7009.

43. Andersson, L. M.; Zhang, F. L.; Inganas, O. *Appl. Phys. Lett.* **2006**, *89*, 142111.

44. Zhang, F. L.; Mammo, W.; Andersson, L. M. *Adv. Mater.* **2006**, *18*, 2169-2173.

45. Mihailetchi, V. D.; Xie, H.; De Boer,B.; Koster, L. J. A.; Blom, P. W. M. *Adv.Funct. Mater.* **2006**, *16*, 699–708.

46. Girotto, C.; Cheyns, D.; Aernouts, T.; Banishoeib, F.; Lutsen, L.; Cleij, T. J.; Vanderzande, D.; Genoe, J.; Poortmans, J.; Heremans, P. *Org. Electron.* **2008**, *9*, 740–746.

47. Oosterbaan, W. D.; Vrindts, V.; Berson, S.; Guillerez, S.; Douhéret, O.; Ruttens, B.; D'Haen, J.; Adriaensens, P.; Manca, J.; Lutsen, L.; Vanderzande, D. *J. Mater.Chem.* **2009**, *19*, 5424–5435.

Chapter 3: An Efficient Acid induced Conversion of Dithiocarbamate Precursor Polymers into Conjugated Materials

An acid induced conversion method for dithiocarbamate precursor poly(thienylene vinylene) (PTV) and poly(phenylene vinylene) (PPV) derivatives is presented, which has the advantage that it can be executed at moderate temperatures. The lower conversion temperature avoids possible thermal degradation of the polymer chromophore structure and therefore conjugated polymers with a higher effective conjugation length can be obtained. This process was studied using UV-Vis and FTIR spectroscopy. The obtained results indicate that trifluoroacetic acid yields a more defect free structure as compared to benzenesulfonic acid which induces degradation after prolonged reaction times. A tentative mechanism is proposed in which the formation of an intermediate carbenium ion is part of the rate limiting step. It also implicates a competition between elimination and substitution reactions depending on specific reaction conditions.

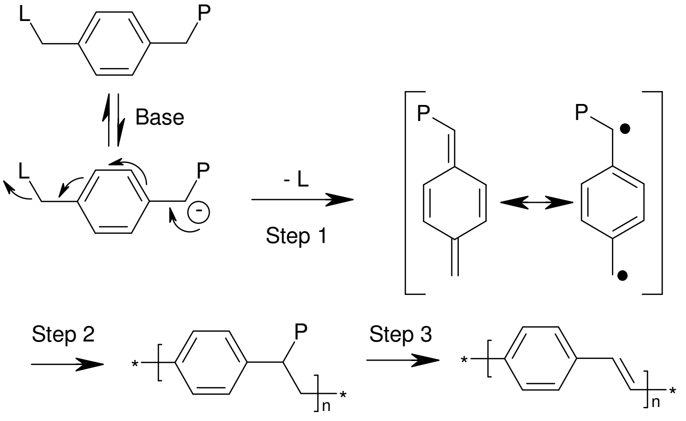
1. Introduction

Nowadays, conjugated polymers find application in various optical and electronic devices such as light emitting diodes (LED),[1] field effect transistors (FET),[2] photovoltaic cells[3] and sensors.[4] Due to their interesting optoelectronic and electrical properties, a considerable amount of research has been performed on poly(arylene vinylene) derivatives.[5,6] These polymers have been typically synthesized via

---

* By H. Diliën, J. Vandenbergh, F. Banishoeib, P. Adriaensens, T. J. Cleij, L. Lutsen, D. Vanderzande for Macromolecules, 2011, accepted

precursor routes in which a *p*-quinodimethane system acts as the actual monomer. This monomer will polymerize into the precursor polymer via a self-initiating radical chain mechanism.[7–11] In a second step, the obtained precursor polymers can be transformed into the conjugated form in situ or ex situ. The major advantage of such precursor routes is the ease by which high molecular weight materials are obtained. Over the last 50 years several different precursor routes have been developed such as: the sulfonium route,[12–15] the Gilch route,[16] the xanthate route,[17–19] and the, in our research group developed, sulphinyl[20,21] and dithiocarbamate route.[22–27] All these routes differ by the identity of the polarizer (P) and leaving (L) functional group in the premonomer structure, the polymerization conditions, whether conversion to the conjugated structure occurs in situ or ex situ and to what extent the conversion is thermal induced or reagent induced (Scheme 1).



Gilch route:	L=P= Cl or Br
Sulfonium route:	L=P= R_2S-
Sulfinyl route:	L= Cl or Br ; P= RS(O)-
Xanthate route:	L=P= RO-C(S)-S-
Dithiocarbamate route:	L=P= R_2N-C(S)-S-

Scheme 1. Precursor Routes towards Poly(*p*-Phenylene Vinylene) Derivatives.

Furthermore, the characteristics of the obtained polymers can vary along the different precursor routes.

For instance, the xanthate precursor route yields typically broad polydispersities (PD) and shows structural defects in the final conjugated system. On the other hand the sulphinyl and the, in this study discussed, dithiocarbamate precursor route lead to the formation of precursor polymers with low structural defect levels.[28,29] Furthermore in case of the sulphinyl route the conversion from the precursor polymer towards the conjugated polymer already starts at 65 °C.[30] However the implementation of the non-symmetrical P and L groups into the premonomer is quite challenging.[31] For the dithiocarbamate precursor route the opposite situation occurs: here the monomer synthesis is rather simple and results into highly stable monomers. However higher conversion temperatures (180 °C) are necessary to reach fully conjugated polymers and therefore degradation of the polymer chromophore structure is a realistic threat.[32] In a serendipitous way, we discovered that the dithiocarbamate functional group in the precursor is eliminated, inducing the formation of the conjugated system, in the presence of acid. Typically a temperature of 70 °C can be used, but also at ambient temperature conversion occurs. Such low conversion temperatures may avoid the degradation of the polymeric chromophore and therefore guarantee the formation of conjugated structures with optimal electronic properties.

Specifically in this study, poly(3-octyl-2,5-thienylene vinylene) (O-PTV) and poly[(2-methoxy-5-(3’,7’-dimethyloctyloxy))-1,4-phenylene vinylene] (MDMO-PPV) have been synthesized using the dithiocarbamate precursor route.[28] Furthermore, to combine the advantages of both the sulphinyl and dithiocarbamate routes, e.g. low conversion temperatures and easy monomer synthesis, a new conversion process for dithiocarbamate precursor polymers has been developed. After synthesis and characterization of the precursor polymer, the thermal conversion as well as the acid induced conversion process towards O-PTV and MDMO-PPV is studied via FT-IR and UV-Vis spectroscopy. Finally, a tentative reaction mechanism is proposed and preliminary results are presented concerning the specific characteristics of the acid induced elimination reaction of dithiocarbamate groups.

2. Experimental section

2.1. General

Unless otherwise stated, all reagents and chemicals were obtained from commercial sources (Acros and Aldrich) and used without further purification. A xanthate precursor towards plane PTV was synthesized according to a literature preocedure.[19] Tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone. NMR spectra were recorded with a Varian Inova 300 spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR using a 5 mm probe. Gas chromatography/mass spectrometry (GC/MS) analyses were carried out with TSQ-70 and Voyager mass spectrometers (Thermoquest); the capillary column was a Chrompack Cpsil5CB or Cpsil8CB. Analytical size exclusion chromatography (SEC) was performed using a Spectra series P100 (Spectra Physics) pump equipped with two mixed-B columns (10 μm, 0.75 cm x 30 cm, Polymer Labs) and a refractive index detector (Shodex) at 70°C. Molecular weight distributions are given relative to polystyrene standards. FT-IR spectra were collected with a Perkin-Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm-1, summation of 16 scans). UV-Vis spectroscopy was performed on a VARIAN CARY 500 UV-Vis-NIR spectrophotometer (scan rate: 600 nm/min). Samples for temperature-dependent thin-film FT-IR and UV-Vis characterization were prepared by dropcasting the precursor polymer from a $CHCl_3$ solution (10 mg/mL) onto NaCl disks or quartz disks. The disks were heated in a Harrick high-temperature cell (heating rate: 2 °C/min), which was positioned in the beam of either the FT-IR or the UV-Vis spectrometer to allow in-situ measurements. Spectra were taken continuously under a continuous flow of N_2 during which the samples were in direct contact with the heating element. “Timebase software” supplied by Perkin-Elmer and “Scanning Kinetics software” supplied by Varian, respectively, were used to investigate regions of interest.

2.2. Synthesis

2.2.1. Monomer synthesis

The synthetic routes towards the MDMO-PPV bisdithiocarbamate premonomer **1** and the O-PTV bisdithiocarbamate premonomer **4** have been reported earlier.[22,33,34]

2.2.2. Polymer synthesis

MDMO-PPV

Synthesis of MDMO precursor PPV ***2***

Premonomer **1** (500 mg, 0.851 mmol) was dissolved in dry THF (4.2 mL) giving a concentration of 0.2 M. The mixture was stirred at 35 °C under a continuous flow of nitrogen. 1,5 equivalents of a LHMDS solution (1 M in THF) were added in one go to the stirred monomer solution. The reaction proceeded for 1.5 hours at 35 °C under a nitrogen atmosphere, and the mixture was subsequently quenched in ice water (100 mL). The excess of base was neutralized with HCl (1 M). The aqueous phase was extracted with $CHCl_3$ (3x40 mL). After combination of the organic phases and evaporation of the solvent, the obtained crude polymer was again dissolved in $CHCl_3$ (2 mL) and precipitated in stirred cold methanol (100 mL). The mixture was filtered and the polymer was collected and dried in vacuo. The residual fractions contained only premonomer and oligomers (yield 64%, 239 mg).

^{1}H NMR ($CDCl_3$): 6.97–6.45 (br m, 2H), 5.87–5.50 (br s, 1H), 4.23–3.05 (br m, 11H), 1.95–1.02 (br m, 16H), 1.02–0.74 (m, 9H); ^{13}C NMR ($CDCl_3$): 195.76, 150.85, 127.68, 114.11, 113.09, 67.10, 56.39, 51.98, 49.08, 46.38, 39.27, 37.54, 36.60, 34.45, 29.91, 27.92, 24.67, 22.69, 22.58, 19.66, 12.47, 11.55; IR (NaCl, cm^{-1}): 2953, 2929, 1504, 1484, 1462, 1413, 1267, 1210, 1140, 1041. SEC: $M_w = 220 \times 10^3$; PD = 2.3.

Thermal conversion of precursor polymer to conjugated MDMO-PPV ***3a***

From a solution of **2** (50 mg, 0.114 mmol) in *o*-dichlorobenzene (25 mL) oxygen was removed by purging for 1h with nitrogen. Subsequently, the solution was heated to 180 °C and stirred for 3 h. After cooling to room temperature, the *o*-dichlorobenzene was evaporated and the crude polymer mixture was dissolved in chloroform (2 mL). The solution was precipitated drop wise in cold methanol (50 mL). The polymer was filtered off, washed with cold methanol and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3a** was obtained as a red polymer. The elimination procedure was performed a second time to ensure complete elimination (yield: 97%, 32 mg).

^{1}H NMR ($C_2D_2Cl_4$): 7.5 (br, 2H) 7.2 (br, 2H) 4.6-3.2 (br m, 5H) 2.1-0.6 (br m; 19H); ^{13}C NMR ($CDCl_3$): 151.4; 127.0, 123.3; 110.5; 108.8; 67.9; 56.4; 39.2; 37.4; 36.6; 30.2; 27.9; 24.6; 22.6; 19.8; IR (KBr, cm^{-1}): 2957, 2925, 2860, 1510, 1469, 1395, 1217, 1028, 872. UV-Vis: λ_{max} (thin film) = 530 nm. SEC: $M_w = 351 \times 10^3$; PD = 3.0.

Benzenesulfonic acid induced conversion of precursor polymer to conjugated MDMO-PPV ***3b***

From a solution of **2** (50 mg, 0.114 mmol) in chlorobenzene (25 mL) oxygen was removed by purging for 1h with nitrogen. Subsequently, the solution was heated to 70 °C and 1.5 equivalents (based on the amount of dithiocarbamate moieties in the precursor polymer) of a benzenesulfonic acid solution (0.342M in chlorobenzene) were added. After stirring for 30 minutes, the excess of acid was neutralized with $NaHCO_3$ and the mixture was extracted with $CHCl_3$. The solvent was evaporated and the crude polymer mixture was redissolved in chloroform (2 mL). The solution was precipitated drop wise in cold methanol (50 mL). The polymer was filtered off, washed with cold methanol and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3b** was obtained as a red polymer (yield: 97%, 32 mg). UV-Vis: λ_{max} (thin film) = 534 nm. SEC: $M_w = 284 \times 10^3$; PD = 4.1.

*Trifluoroacetic acid induced conversion of precursor polymer to conjugated MDMO-PPV **3b***

From a solution of **2** (200 mg, 0.456 mmol) in chlorobenzene (100 mL) oxygen was removed by purging for 1h with nitrogen. Subsequently, the solution was heated to 70 °C and 1.5 equivalents (based on the amount of dithiocarbamate moieties in the precursor polymer) of trifluoroacetic were added. After stirring for 8 hours, the excess of acid was neutralized with $NaHCO_3$ and the mixture was extracted with $CHCl_3$. The solvent was evaporated and the crude polymer mixture was redissolved in chloroform (8 mL). The solution was precipitated drop wise in cold methanol (200 mL). The polymer was filtered off, washed with cold methanol and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3b** was obtained as a red polymer (yield: 98%, 130 mg).

UV-Vis: λ_{max} (thin film) = 538 nm. SEC: $M_w = 385 \times 10^3$; PD = 2.8.

O-PTV

*Synthesis of the octyl precursor PTV **5***

The premonomer **4** (2.8 g, 5.4 mmol) was previously freeze dried. A solution, with a premonomer concentration of 0.4 M, in dry THF (13.5 mL) was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (11 mL of a 1M solution in THF) was added in one go to the stirred monomer solution. The resulting mixture was stirred for 90 minutes under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvent of the combined organic layers was evaporated under reduced pressure and a second

precipitation was performed in pure cold methanol. The precursor polymer **5** was collected and dried in vacuo (yield 56 %, 1.1 g).
^{1}H NMR ($CDCl_3$): 6.57 (br, 1H), 5.46 (br, 1H), 3.96 (br, 2H), 3.66 (br, 4H), 2.27 (br, 2H), 1.21 (br, 18H), 0.85 (br, 3H); ^{13}C NMR ($CDCl_3$): 193.96, 139.5, 138.8, 133.8, 127.6, 52.7, 48.9, 46.6, 31.8, 30.7, 29.5, 29.3, 28.2, 22.6, 14.0, 12.5, 11.5; UV-Vis: λ_{max} = 261 nm (in film); IR: 2931, 2846, 1486, 1415, 1268, 1206 cm^{-1}; SEC: $M_w = 86 \times 10^3$; PD = 3.1.

Thermal conversion of the octyl precursor PTV ***5*** *towards octyl-PTV* ***6a***

The precursor polymer **5** (51 mg, 0.14 mmol) was dissolved in *o*-dichlorobenzene (2.8 mL) and refluxed for 4.5 h. After being cooled, the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol and dried in vacuo. A purple/black solid has been obtained (yield 92 %, 28 mg).
^{1}H NMR ($CDCl_3$): 6.97 (s, 1H), 5.00 (s, 1H), 2.26 (br, 2H), 1.24 (br, 12H), 0.85 (br, 3H); ^{13}C NMR ($CDCl_3$): 140.2, 139.3, 134.4, 128.4, 121.1, 53.3, 37.2, 32.7, 31.6, 30.4, 30.1, 29.0, 23.4, 14.9; UV-Vis: λ_{max} = 548 nm (in solution); IR (cm^{-1}): 2931, 2846, 1460, 1250, 1016, 926; SEC: $M_w = 47 \times 10^3$; PD = 3.3.

Benzenesulfonic acid induced conversion of the octyl precursor PTV ***5*** *towards octyl-PTV* ***6b***

The precursor polymer **5** (30 mg, 0.1 mmol) was dissolved in chlorobenzene (5 mL) and heated till 70 °C before benzenesulfonic acid (0.019 g, 0.12 mmol) was added. The solution was stirred for 10 minutes at 70 °C. After being cooled, the solution was poured into H_2O and extracted with diethyl ether. The solvent was evaporated under reduced pressure and the obtained slurry was precipitated in MeOH, filtered off and dried in vacuo. A purple/black solid was obtained (17 mg, yield 93 %).
UV-Vis: λ_{max} = 580 nm; SEC: $M_w = 72 \times 10^3$; PD = 3.7.

*Trifluoroacetic acid induced conversion of the octyl precursor PTV **5** towards octyl-PTV **6b***

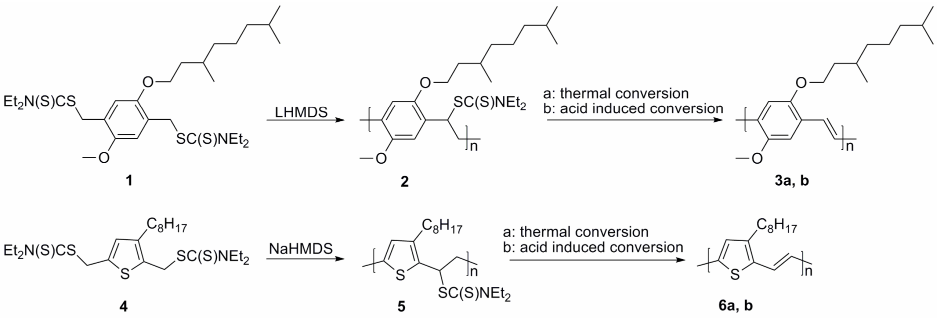
The precursor polymer **5** (36 mg, 0.1 mmol) was dissolved in chlorobenzene (5 mL) and heated till 70 °C before trifluoroacetic acid (0.011 mL, 0.15 mmol) was added. The solution was stirred for 10 minutes at 70 °C. After being cooled, the solution was poured into H_2O and extracted with diethyl ether. The solvent was evaporated under reduced pressure and the obtained slurry was precipitated in MeOH, filtered off and dried in vacuo. A purple/black solid was obtained (21 mg, yield 95 %).

UV-Vis: $\lambda_{max} = 583$ nm (shoulder: 628 nm); SEC: $M_w = 57 \times 10^3$; PD = 3.4.

3. Results and discussion

3.1. Precursor polymers

The synthetic routes towards the MDMO-PPV bisdithiocarbamate premonomer **1** and the O-PTV bisdithiocarbamate premonomer **4** have been reported earlier.[22,33,34] The polymerizations are performed under nitrogen atmosphere. To this end, the monomers are dissolved in dry THF (0.2 M for MDMO-PPV premonomer and 0.4 M for the O-PTV premonomer) and the base is added (Scheme 2).



Scheme 2. Synthesis of MDMO-PPV and O-PTV via the dithiocarbamate precursor route, followed by the thermal or acid induced elimination.

In case of the MDMO-PPV premonomer an amount of 1.5 equivalents of lithium hexamethyldisilazide (LHMDS), for the O-PTV monomer 2.0 equivalents of sodium hexamethyldizilazide (NaHMDS) have been used. After polymerization both reaction mixtures are poured into ice water, neutralized by hydrochloric acid (1M) and extracted with $CHCl_3$. The precursor polymers **2** and **5** are isolated by precipitation in cold methanol.

3.2. In-situ thermal conversion in thin film

To examine the conversion conditions for dithiocarbamate precursor polymers, the thermal elimination was studied in thin films by in situ UV-Vis and FT-IR spectroscopy. Thin films were obtained by dropcoating a solution of the precursor polymers in $CHCl_3$ on quartz or NaCl disks, these films have been placed into a Harrick high-temperature cell under a continuous nitrogen flow, which was positioned in the beam of either the UV-Vis or the FT-IR spectrometer, respectively. The thin precursor polymer films were heated at 2 °C/min from ambient temperature to 200 °C and spectra were collected at different temperatures.

Upon heating, a new absorption band appears in the UV-Vis absorption spectra, associated with the formation of the conjugated system. Concomitantly, the absorption band associated with the precursor polymer decreases. For MDMO-PPV the precursor band is situated at 288 nm (figure 1a). The absorption maximum (λ_{max} 460 nm) at 134 °C is lower as compared to this observed (λ_{max} 490 nm) after cooling to room temperature due to the thermochromic effect.[26] The elimination process can be more thoroughly analyzed by plotting the absorption profiles at 460 and 288 nm as a function of temperature (Figure 1b). In these profiles an increase of the absorbance at 460 nm can be noticed between 95 °C and 130 °C under these heating conditions (2 °C/min). In the same temperature range, a decrease in the absorbance at 288 nm takes place.

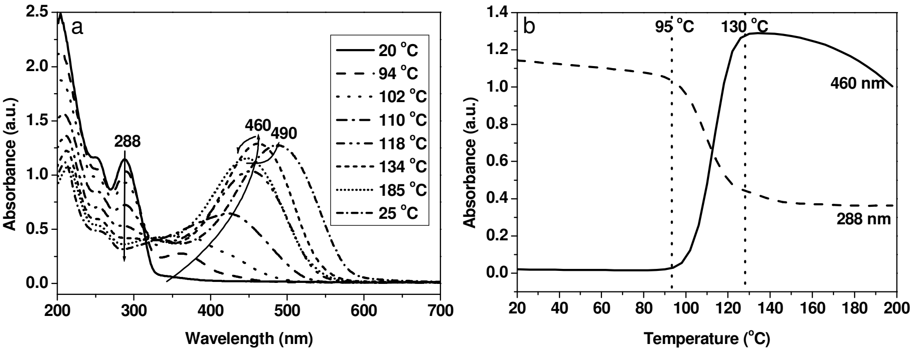


Figure 1. a) UV-Vis spectra of precursor polymer **2** at different temperatures. b) UV-Vis absorbance profiles at 288 nm and 460 nm at different temperatures for **2**.

For the O-PTV a similar behaviour is observed. The absorption at 275 nm, corresponding to the precursor polymer, decreases during the reaction. Simultaneously the absorption consistent with the conjugated system appears around 560 nm. From the absorbance profiles, it can be concluded that under these heating conditions (2 °C/min) the formation of the conjugated system starts above 100 °C.

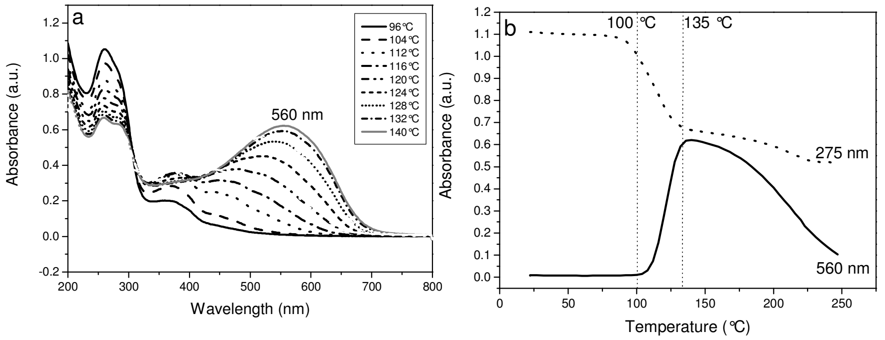


Figure 2. a) UV-Vis spectra of **5** at different temperatures. b) UV-Vis absorbance profiles at 275 nm and 560 nm at different temperatures for **5**.

These processes can also be monitored using in situ FT-IR spectroscopy. Using this technique, upon heating a decrease is observed of the absorption bands at 1205, 1266, 1414 and 1486 cm^{-1}, which can be assigned to vibrations of the dithiocarbamate functional group. At the same time, a new absorption band appears (at 965 cm^{-1}, for MDMO-PPV)[35] which originates from the *trans*-vinylene double bonds formed during thermal elimination. Concerning MDMO-PPV it can be noticed from the FT-IR transmission profiles at 965 and 1266 cm^{-1}, that the elimination starts at 105 °C and is completed at 145 °C, under the heating conditions used. These results are consistent with the UV-Vis profiles.

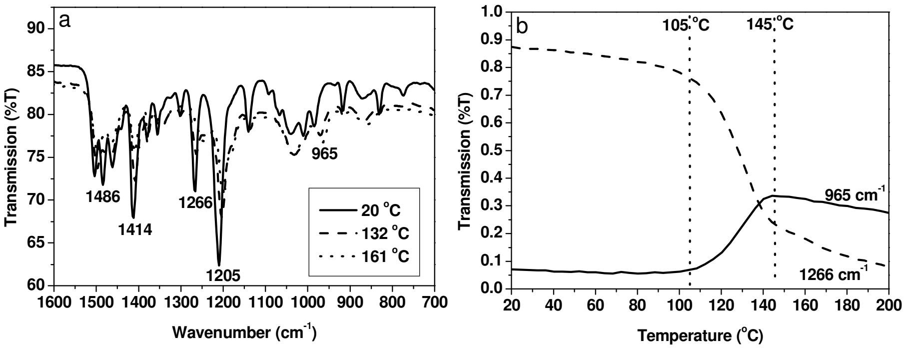


Figure 3. a) FT-IR spectra of **2** at different temperatures. b) IR absorption profiles at 965 cm^{-1} and 1266 cm^{-1} at different temperatures for **2**.

Also for O-PTV the disappearance of the dithiocarbamate functional group and the formation of the trans-vinylene double bond (at 926 cm^{-1}) can be observed (figure 4a) using FT-IR spectroscopy. From the absorption profiles, results are obtained totally consistent with the UV-Vis profiles (figure 4b).

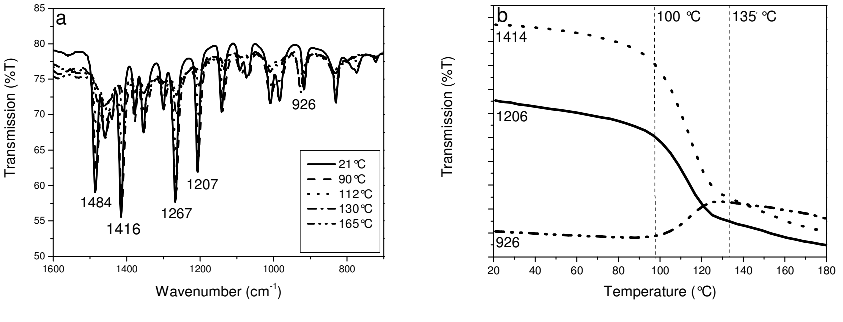


Figure 4. a) FT-IR spectra of **5** at different temperatures. b) IR absorption profiles at 926 cm^{-1}, 1206 cm^{-1} and 1414 cm^{-1} at different temperatures for **5**.

3.3. Thermal conversion in solution

The dithiocarbamate precursor polymers can also be converted into their conjugated form by means of a thermal conversion in solution, which is typically done at a temperature of 180 °C. To determine the time period necessary for a complete conversion in solution, the polymers are dissolved in *o*-dichlorobenzene (o-DCB) and heated at 180 °C. Samples were taken with regular intervals and studied with UV-Vis spectroscopy (Figure 5, a and b). From these spectra it can be concluded that the MDMO-PPV precursor polymer is fully converted under these heating conditions within 60 minutes.

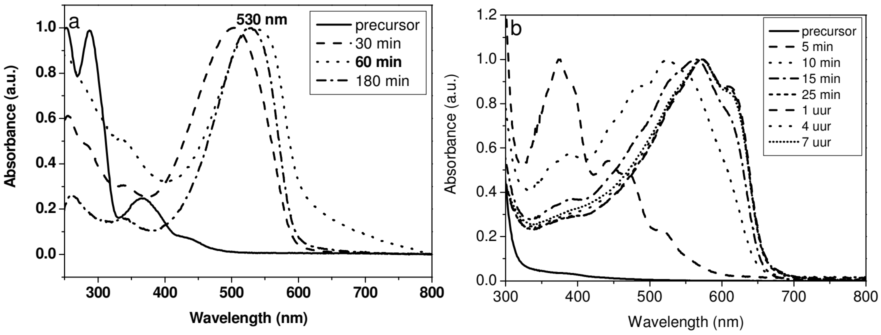


Figure 5. UV-Vis absorption spectra for the thermal conversion (180 °C, *o*-DCB) in solution of a) MDMO precursor PPV and b) octyl precursor PTV.

In case of the O-PTV precursor, the conversion proceeds faster. Already after 25 minutes, the maximum wavelength (573 nm) has been reached (Figure 5b). However, elimination at 180 °C may lead to degradation of the polymer chromophore structure (conjugated system).[32] Prolonged heating (> 4 hours) of the O-PTV leads to a blue shift in the UV-Vis spectra, which is indicative for a thermal degradation of the conjugated system. This underlines the necessity to find alternative conversion processes to avoid detrimental degradation of the conjugated system.

3.4. Acid induced conversion

Recently a haphazard observation in our research group showed that dithiocarbamate precursor polymers have the tendency to change color in “acid” solvents, e.g. chloroform.[36] As this might refer to a partial conversion of the precursor polymer to the conjugated form, a study of the influence of acids on the conversion of dithiocarbamate precursor polymers was started.

The acid induced elimination is studied in solution using UV-Vis spectroscopy. Hereto, the precursor polymers are dissolved in chlorobenzene (CB) and heated at 70 °C in the presence of 1,5 equivalents of either benzenesulfonic acid or trifluoroacetic acid and the reaction is followed by taking samples at regular time intervals. When no further changes in the UV-Vis spectra are observed, the reaction mixture is neutralized and extracted with $CHCl_3$. If possible (sufficient quantity) the polymers are isolated by precipitation in cold methanol.

When the MDMO-PPV precursor is treated with benzenesulfonic acid, the conversion seems to be very fast. It takes only 30 minutes to convert the precursor polymer and reach the maximum absorption wavelength (Figure 6a). This is not the case for the conversion with trifluoroacetic acid. Here it takes about 7 hours before the conversion is complete (Figure 6b).

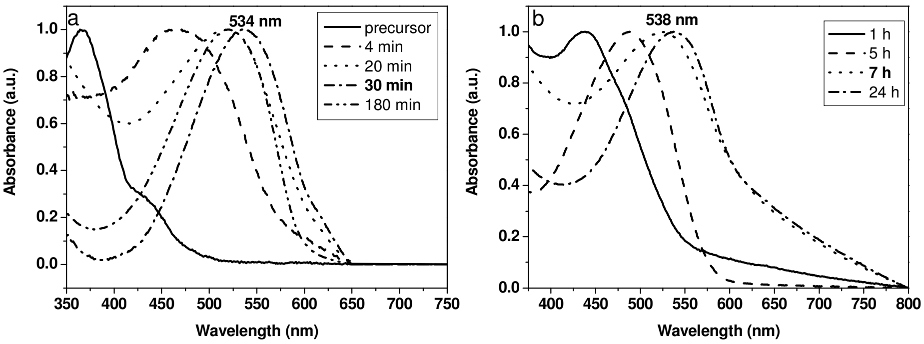


Figure 6. UV-Vis absorption spectra for the acid induced conversion (70 °C in CB) of MDMO precursor PPV with a) benzenesulfonic acid and b) trifluoroacetic acid.

The distinction between these two experiments can simply be explained by the acid strength, e.g. benzenesulfonic acid has a pKa value of -6.5 (at 25 °C). Trifluoroacetic acid is a much weaker acid with a pKa value of 0.5 (at 25°C). The obtained absorption maxima (λ_{max}) are similar (534 and 538 nm) to those obtained after thermal elimination (530 nm).

In case of precursor O-PTV, the acid induced conversion with benzenesulfonic acid is extremely fast, the new absorption maximum is reached almost instantaneously, already after 10 minutes the maximum value of 580 nm has been reached (Figure 7a).

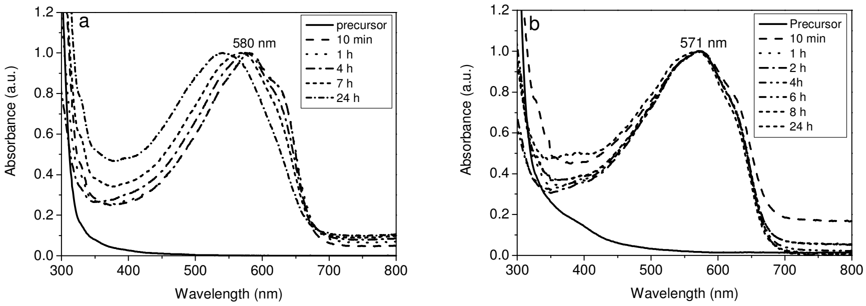


Figure 7. UV-Vis absorption spectra for the acid induced conversion (70 ° in CB) of octyl precursor PTV with a) benzenesulfonic acid and b) trifluoroacetic acid.

If the weaker trifluoroacetic acid is used the reaction is still very fast (Figure 7b). Upon addition of the acid, an instant color change (from orange to purple) occurs. Already the first sample (after 10 minutes) shows a fully conjugated polymer.

For longer reaction times however, a clear difference between the two acids can be observed. With benzenesulfonic acid as reagent, it can be stated that the absorption maximum after 7 hours and especially after 24 hours (figure 7a) shows a clear hypsochromic shift, which is probably due to partial degradation of the polymer. A similar effect is observed for MDMO-PPV when benzenesulfonic acid is used (figure 6a, spectrum at 180 minutes). So, in the case of benzenesulfonic acid, it is very

important to avoid long exposure to acid to avoid degradation of the conjugated system. In the case of trifluoroacetic acid the degradation process is much slower and is not observed within a time frame of 24 hours (figures 6b and 7b). Seemingly because of the lower acidity, the kinetic separation between the elimination process and the degradation process is large enough to limit the reaction to the first process.
Next, the conversion process of precursor O-PTV is studied at room temperature for which the conversion with benzenesulfonic acid was still quit fast. The maximal absorption wavelength reached is however about 50 nm lower than the one at 70 °C (Figure 8). Longer exposure to acid only leads to degradation. A very similar result was obtained when using trifluoroacetic acid at room temperature. Seemingly at room temperature a side reaction limits the extent to which the conjugation in the O-PTV system develops.

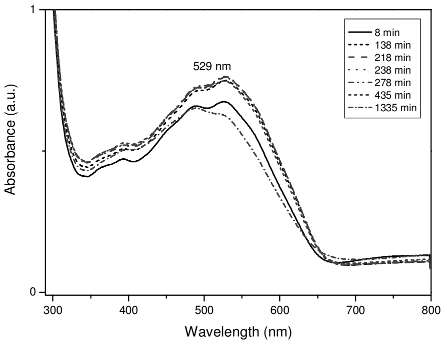
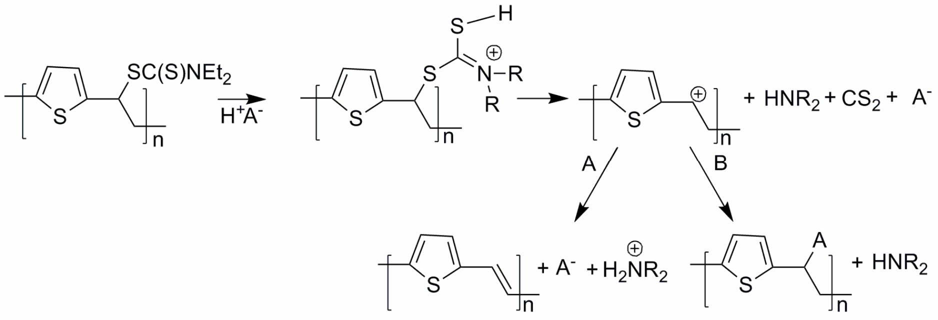


Figure 8. UV-Vis spectra for the acid induced conversion of octyl precursor PTV with benzenesulfonic acid at room temperature.

To achieve a deeper understanding of the acid induced elimination of the dithiocarbamate functional group in the corresponding precursor polymers a mechanistic scheme is proposed as presented in scheme 3.

This mechanism assumes as a first step the protonation of the dithiocarbamate group converting it to a better leaving group. Next the dithiocarbamate group is expelled and decomposes in carbon disulphide and a secondary amine. At the same time a carbenium ion is formed in the precursor polymer structure. This opens a path for two competitive reactions, e.g. an elimination reaction (A) forming a double bond and a substitution reaction (B) with the conjugated base of the acid used, onto the carbenium ion site. In the former reaction the secondary amine will trap the proton liberated during the elimination reaction. This implies that the acid does not act as a catalyst but is effectively consumed. Given this mechanism it should be expected that higher temperatures favour elimination, lower temperature or added nucleophiles would make the substitution reaction more competitive.[37]



Scheme 3. Proposed mechanism for the acid induced conversion reaction of DTC precursor polymers.

To test the latter effect a nucleophile reagent, i.e. 1 equivalent of octanethiol, has been added at room temperature to the reaction mixture with trifluoroacetic acid (Figure 9). Here, it can be observed that the conjugated system did not develop fully, even if the mixture was allowed to react for 24 hours. It may be assumed that the addition of octanethiol favours a nucleophilic substitution and creates a collection of oligomeric conjugated fragments.

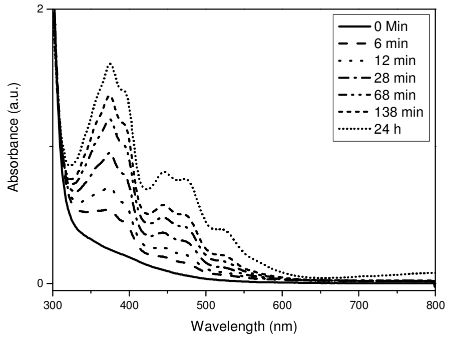


Figure 9. UV-Vis spectra of the trifluoroacetic acid induced conversion of octyl precursor PTV at room temperature, in the presence of octanethiol.

Another experiment evaluates the influence of the acid concentration. On addition of only 0.3 equivalents of trifluoroacetic acid instead of 1.5 (Figure 10), it is observed that the conjugation length is limited again to oligomeric fragments of the conjugated system.[38] This demonstrates that the acid is effectively consumed during the conversion and does not act as a catalyst.

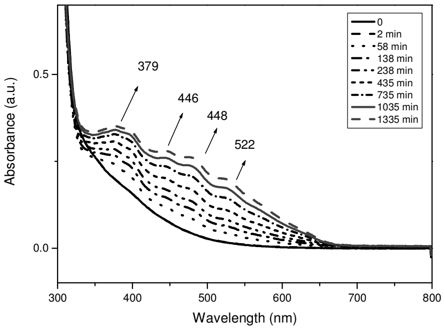
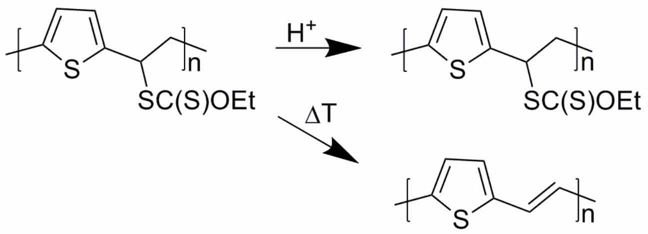


Figure 10. UV-Vis spectra of the acid induced conversion of octyl precursor PTV with 0.3 equivalents of trifluoroacetic acid.

Consistent with the proposed reaction mechanism in Scheme 3 the acid induced conversion of the PTV precursor polymer is much faster than for the PPV precursor polymer. If it is assumed that the reaction proceeds via an intermediate carbenium ion, this carbenium ion will be stabilized by the aromatic core next to it. In the case of PTV, the aromatic core is a thiophene unit which is much more electron rich than the core of the PPV precursor polymer. Therefore the thiophene ring gives raise to a better stabilization of the intermediate and so a faster reaction.

To explore the unique character of this conversion method for dithiocarbamate precursor polymers, a comparison with another precursor route has been performed. A xanthate precursor towards plain PTV[19] has been converted in the presence of 1.5 eq. benzenesulfonic acid at room temperature in CB and the reaction is monitored by UV-Vis spectroscopy in solution (Scheme 4). The spectra (Figure 11a) only show the absorption band of the precursor polymer and there is no indication for the formation of the conjugated system. For comparison, the results from in situ UV-Vis spectroscopy for a thermal elimination of a thin film of the xanthate precursor polymer are shown in Figure 11b. A film of the precursor polymer has been heated with a ramping temperature of 2 °C/ min from room temperature up to 350 °C. Clearly said behavior, i.e. acid induced elimination, is only displayed for the dithiocarbamate precursor polymers and is unprecedented in literature for this class of functional groups. Future work is in progress in which we focus on a detailed NMR study using ^{13}C labeled PTV's to unravel details of the defect structures present in thermal and acid induced converted PTV precursors. Furthermore a study has been started to gain a deeper insight in the chemistry of dithiocarbamate functional groups using model compounds. This work will be reported in due time.



Scheme 4. The acid induced and thermal conversion of a xanthate precursor polymer.

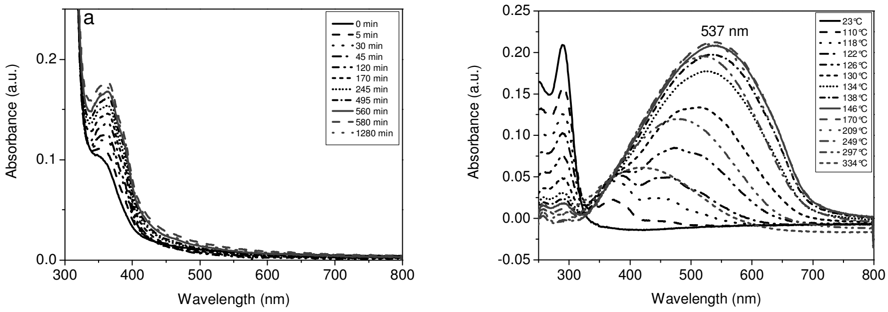


Figure 11. a) UV-Vis spectra of the benzene sulfonic acid induced conversion of the xanthate precursor polymers, at room temperature in CB. b) In situ UV-vis experiment of thermal conversion of xanthate precursor polymer.

4. Conclusion

Two conversion processes for dithiocarbamate precursor polymers have been studied and compared, the thermal conversion and the acid induced conversion. The acid induced conversion allows lowering the conversion temperature from 180 °C to 70 °C. The nature (strength) of the acid is of importance to avoid degradation and therefore defects. By tuning the reaction conditions, the competition between an elimination and a substitution reaction can be controlled in favor of elimination. Finally a mechanistic framework is presented to explain the main features observed for the acid induced elimination.

5. Acknowledgement

The authors would like to thank H. Penxten for the in situ UV-vis and FT-IR measurements. The authors gratefully acknowledge the Fund for Scientific Research-Flanders (FWO) and Belspo in the frame of network IAP P6/27, initiated by the Belgian State Prime Minister’s Office, for financial support. We also want to thank the IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for the financial support via the IWT-SBO project 060843 “Polyspec”.

6. References

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403–428.

2. Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Dev.* **2001**, *45*, 11–27.

3. Helgesen, M. ; Sondergaard, R. ; Krebs, F. C. *J. Mater. Chem.* **2010**, *20*, 36–60.

4. MacDiarmid, W.; Zhang, W.; Huang, Z.; Wang, P. C.; Huang, F.; Xie, S. *Polym. Prepr.* **1997**, *11*, 333–334.

5. Li, A.-K. ; Janarthanan, N. ; Hsu, C.-S. *Polym. Bull.* **2000**, *45*, 129–135.

6. Cacialli, F. ; Daik, R. ; Feast, W. J. ; Friend, R. H. ; Lartigau, C. *Opt. Mater.* **1999**, *12*, 7. Denton, F. R.; Lathi P. M.; Karasz F. E. *J. Pol. Sc. A Pol. Chem.* **1992***, 30,* 2223–2231.

8. Issaris, A.; Vanderzande, D.; Gelan J. *Polymer* **1997**, *38*, 2571–2574.

9. Hontis, L.; Vrindts, V.; Lutsen, L.; Vanderzande, D.; Gelan J. *Polymer* **2001,** *42*, 5793–5796.

10. Wiesecke, J. ; Rehahn, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 567–570.

11. Schwalm, T. ; Wiesecke, J. ; Immel, S. ; Rehahn, M. *Macromolecules* **2007**, *40*, 8842–8854.

12. Harper, K.; West, W. J. W. *Eur. Pat. Appl. No. 182548*, **1985**.

13. Jen, K. Y.; Jow, R.; Eckhardt, H.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 49–53.

14. Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309–311.

15. Wessling, R. A. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 55–66.

16. Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci.* **1966**, *4*, 1337–1349.

17. Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376–378.

18. Kesters, E.; Gillissen, S.; Motmans, F.; Lutsen, L.; Vanderzande D. *Macromolecules* **2002**, *35,* 7902–7910.

19. Mitchell, W. J.; Pena, C.; Burn, P. L. *J. Mater. Chem.* **2002**, *12*, 200–205.

20. van Breemen, A. J. J. M.; Issaris, A. C. J.; de Kok, M. M.; Van Der Borght, M. J. A. N.; Adriaensens, P. J.; Gelan, J. M. J. V.; Vanderzande, D. J. M. *Macromolecules* **1999**, *32*, 5728–5735.

21. Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin solid films* **2004**, *451-452*, 472–579.

22. Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J.; Aernouts, T.; Poortmans, J. *SPIE Proc.* **2004**, 52–59.

23. Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J. *Macromolecules* **2005**, *38*, 19–26.

24. Henckens, A.; Duyssens, I.; Lutsen, L.; Vanderzande, D.; Cleij, T. J. *Polymer* **2006**, *47*, 123–131.

25. Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Eur. Phys. J.-Appl. Phys.* **2007**, *37*, 237–240.

26. Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2006**, *90*, 2815–2828.

27. Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

28. Roex, H.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **2003**, *36,* 5613–5622.

29. Vandenbergh, J.; Wouters, J.; Adriaensens, P. J.; Mens, R.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2009**, *42*, 3661–3668.

30. Kesters, E.; Vanderzande, D.; Lutsen, L.; Penxten, H.; Carleer, R. *Macromolecules* **2005,** *38*, 1141–1147.

31. van Breemen, A. J. J. M.; Vanderzande, D. J. M.; Adriaensens, P. J.; Gelan, J. M. J. V. *J. Org. Chem.* **1999**, *64*, 3106–3112.

32. Breban, L.; Lutsen, L.; Vanhoyland, G.; D'Haen, J.; Manca, J.; Vanderzande, D. *Thin Solid Films* **2006,** *511–512*, 695–700.

33. Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925–4932.

34. Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T.J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, *43*, 10231–10240.

35. Chambon, S.; Rivaton, A.; Gardette, J. -L.; Firon, M.; Lutsen, L. *J. Polym. Sci: Part A: Polym. Chem.* **2007**, *45*, 317–331.

36. Stability of $CHCl_3$: Stable under ordinary conditions of use and storage. pH decreases on prolonged exposure to light and air due to formation of HCl. *Chloroform*; MSDS No. c2915; Mallinckrodt Baker: Phillipsburg, NJ, 07/02/09 http://www.jtbaker.com/msds/englishhtml/c2915.htm (accessed 01/04/11).

37. McMurry, J. *Organic Chemistry*, 6th ed., Thomson, London, **2004**.

38. Jestin, I. ; Frère, P. ; Blanchard, P. ; Roncali, J. *Angew. Chem. Int. Ed.* **1998**, *37*, 942–945.

Chapter 4: Exploring the DTC conversion chemistry by the synthesis and study of model compounds

Dithiocarbamate esters have been successfully used for their applications in organic electronics. Crucial in this context is the transformation of the dithiocarbamate precursor polymers into their conjugated forms, this by elimination of the dithiocarbamate groups. Thermal induced elimination has been used, but this can also lead to degradation of the chromophores. Therefore, a new conversion method was developed induced by acids. Remarkably, it has been noticed that the conjugated system did not always develop fully. This could be due to the presence of a competitive substitution reaction next to the elimination. To investigate the specific reaction mechanism of the elimination of the dithiocarbamate groups and its competitive substitution reaction, multiple model compounds have been made and investigated.

1. Introduction

Although dithiocarbamate compounds look very exotic, their salt complexes with metal ions have already been used for a very long time in several applications, for example as fungicide and herbicide[1-3], as

---

* by H. Diliën, P. J. Adriaensens, T. J. Cleij, L. Lutsen, D. Vanderzande for Tetrahedron, 2011, in preparation

catalyst during the vulcanization of rubbers[4-6], as antioxidant for lubricants[7,8], and for their antiviral[9-11] and antitumor[12,13] behaviour.
In contrast, the use and characteristics of dithiocarbamate esters are less known. First, they have been extensively studied in the context of Reversible Addition-Fragmentation chain Transfer (RAFT) polymerizations.[14-20] Unfortunately, dithiocarbamate groups show low chain transfer coefficients and therefore they are not very efficient as functional group concerning RAFT reactions.[21,22] Furthermore, dithiocarbamate groups have been successfully explored as iniferter (Initiator-chain transfer-terminator).[23-28] In this context, the dithiocarbamate group will initiate a controlled radical polymerization reaction upon heating or irradiation. At last, dithiocarbamate esters have been successfully used for the synthesis of dithiocarbamate precursor polymers and their conversion into conjugated polymers. The latter show great potential for applications in organic electronics.[29-32]

Typically dithiocarbamate ester groups in said precursor polymers can be eliminated thermally.[33-36] Unfortunately, high temperatures, which can induce degradation of the chromophores, have to be applied. Auspiciously another conversion mechanism has been explored by our research group. It has been observed that dithiocarbamate groups are sensitive towards acids.[37] This property has been exploited to adopt the conversion mechanism, and especially to lower the applied temperatures. Remarkably, it has been noticed that the conjugated system did not always developed fully. This could be due to the presence of a competitive substitution reaction next to the elimination reaction. To investigate the specific reaction mechanism of the elimination of the dithiocarbamate groups and its competitive substitution reaction, multiple model compounds have been synthesized. Use of these model compounds in different reaction conditions will deepen our understanding of the chemistry at hand.

2. Experimental section

2.1 General

All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise.

Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone. $SOCl_2$ was previously purified via a vacuum distillation. The precursor polymer for octyl-PTV was synthesized according literature procedures.[32]

2.2 Techniques

^{1}H NMR & ^{13}C NMR spectra were taken on a Varian Inova 300 spectrometer. For all synthesized substances spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm and 77.7 ppm (relatively to TMS) was used as reference for ^{1}H NMR and ^{13}C NMR spectra respectively. GC/MS analyses were carried out on TSQ – 70 and Voyager mass – spectrometers (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB. Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). Ultraviolet visible spectroscopy (UV-Vis) was performed on a VARIAN CARY 500 UV-Vis-NIR spectrophotometer. In situ UV-Vis measurements were performed with a modular Ocean Optics spectrometer, consisting of a balanced deuterium/halogen light source (Mikropack DH-2000-BAL UV-Vis-NIR), a fiber optic dip probe arrangement (path length 2 mm) and a USB2000 miniature fiber optics spectrometer. For the actual transmission measurements, the transmission dip probe was fitted into the temperature controlled reaction vessel.

2.3. Synthesis

Synthesis of model compound **1b**:

A solution of **1a** (3 g, 27 mmol) in a 1:1 mixture of methanol and CH_2Cl_2 was made. The solution was then cooled to 0 °C and $NaBH_4$ (1.5 g, 40 mmol) was added as a solid. The mixture was stirred overnight and afterwards quenched by the addition of H_2O (50 mL), followed by an extraction with Et_2O. The organic layers were dried over $MgSO_4$ and the obtained compound was purified by column chromatography on silica gel with hexane as a solvent. The alcohol **1b** was obtained as colourless oil in a yield of 93 % (2.9 g).

^1H NMR ($CDCl_3$): 7.27 (dd, J_1 = 5.0, J_2 = 1.3, 1H), 7.00 (m, 1H), 6.96 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 4.82 (d, J = 3.5, 2H), 1.79 (s, 1H).

^{13}C NMR ($CDCl_3$): 144.2, 127.0, 125.6, 125.5, 59.3.

Synthesis of 2-(chloromethyl)thiophene **1c**:

A solution of alcohol **1b** (2.6 g, 23 mmol) in dry THF (40 mL) was made in a three-necked round bottom flask. A solution $SOCl_2$ (6.0 g, 50 mmol) in dry THF (20 mL) was added drop wise at 0 °C and the reaction mixture has been stirred for 30 minutes at room temperature. The resulted reaction mixture was quenched with $NaHCO_3$ and extracted with CH_2Cl_2. The crude product was distilled by vacuum distillation to get colourless oil (1.8 g, 17 mmol) in a good yield (75 %).

^1H NMR ($CDCl_3$): 7.30 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 7.07 (dd, J_1 = 3.5, J_2 = 1.2, 1H), 6.94 (dd, J_1 = 5.1, J_2 = 3.5, 1H), 4.80 (s, 1H).

^{13}C NMR ($CDCl_3$): 140.2, 127.8, 127.0 (2C), 40.5.

Synthesis of model compound **1d**:

To a solution of the chloride **1c** (1.64 g, 12.3 mmol) in ethanol (30 mL), diethyldithiocarbamic acid sodium salt trihydrate (7.0 g, 40 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The model

compound **1d** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (2.8 g, 11 mmol) in a yield of 93 %.
^{1}H NMR ($CDCl_3$): 7.14 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 7.01 (dd, J_1 = 3.5, J_2 = 1.2, 1H), 6.88 (dd, J_1 = 5.1, J_2 = 3.5, 1H), 4.75 (s, 2H), 3.98 (q, J = 7.3, 2H), 3.65 (q, J = 7.3, 2H), 1.23 (2t, J_1 = 7.3, 6H).
^{13}C NMR ($CDCl_3$): 194.4, 139.2, 127.3, 127.0, 125.6, 49.8, 47.1, 36.7, 12.8, 11.9.

Synthesis of keton **2c**:
A solution of thiophene **2a** (10 g, 0.12 mol) and 1-propionyl chloride **2b** (13.2 g, 0.14 mol) in toluene was stirred at room temperature. $AlCl_3$ (19.0 g, 0.14 mol) was added as a solid in a time frame of 10 minutes. Next the reaction mixture was refluxed for 30 minutes. The solution was cooled to room temperature and quenched carefully with a 2M HCl solution. The resulting reaction mixture was extracted with toluene, washed with HCl, NaOH and H_2O and dried over $MgSO_4$. The crude product was purified by distillation to give colourless oil (13.0 g, 93 mmol, 77 %).
^{1}H NMR ($CDCl_3$): 7.69 (dd, J_1 = 3.7, J_2 = 1.2, 1H), 7.60 (dd, J_1 = 5.0, J_2 = 1.2, 1H), 7.11 (dd, J_1 = 5.0, J_2 = 3.7, 1H), 2.93 (q, J = 7.2, 2H), 1.22 (t, J = 7.2, 3H).
^{13}C NMR ($CDCl_3$): 194.6, 144.8, 133.9, 132.2, 128.7, 33.3, 9.2.
MS (EI, m/e): 140 (M^+).

Synthesis of alcohol **2d**:
A solution of **2c** (10.2 g, 73 mmol) was made in a mixture of CH_2Cl_2 and MeOH (1/1). The mixture was cooled to 0 °C and $NaBH_4$ (5.5 g, 0.15 mol) was added as a solid. The resulted solution was stirred for 12 hours at room temperature. The reaction was quenched with NH_4Cl and extraction has been carried out by Et_2O and dried over $MgSO_4$. The crude product was purified by flash column chromatography to give colourless oil (10.0 g, 70 mmol, 96 %).

^{1}H NMR ($CDCl_3$): 7.23 (dd, J_1 = 2.2, J_2 = 1.7, 1H), 6.97-6.94 (m, 2H), 4.83 (t, J = 6.6, 1H), 1.95-1.78 (m, 2H), 0.95 (t, J = 7.7, 3H).
^{13}C NMR ($CDCl_3$): 127.3, 126.6, 125.2, 124.5, 72.4, 32.9, 10.8.
MS (EI, m/e): 142 (M^+).

Synthesis of chlorine **2e**:
In a three-necked round bottom flask, the alcohol **2d** (1.5 g, 11 mmol) was added drop wise to a stirred solution of $SOCl_2$ (2.50 g, 21 mmol) in THF (60 mL). The reaction mixture was stirred under nitrogen atmosphere for 1 hour. The solution was cooled to 0 °C and quenched carefully with a $NaHCO_3$ solution. The resulting reaction mixture was extracted with Et_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Due to unstable nature of the product **2e** (1.42 g, 8.8 mmol), the crude product has been used without further purification or characterization.
^{1}H NMR ($CDCl_3$): 7.22 (dd, J_1 = 2.5, J_2 = 1.99, 1H), 6.94-6.91 (m, 2H), 5.08 (t, J = 7.0, 1H), 2.26-2.10 (m, 2H), 1.04 (t, J = 7.2, 3H).

Synthesis of model compound **2f**:
To a solution of the chloride **2e** (0.55 g, 3.4 mmol) in ethanol (20 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.1 g, 14 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The model compound **2f** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (160 mg, 0.59 mmol) in a yield of 17 %.
^{1}H NMR ($CDCl_3$): 7.18 (dd, J_1 = 5.2, J_2 = 1.3, 1H), 7.04 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 6.92 (dd, J_1 = 3.5, J_2 = 5.2, 1H), 5.37 (dd, J_1 = 9.3, J_2 = 6.1, 1H), 3.99 (q, J = 6.8, 2H), 3.68 (q, J = 6.8, 2H), 2.33-2.16 (m, 1H), 2.11-1.94 (m, 1H), 1.24 (t, J = 6.8, 6H), 0.99 (t, J = 7.4, 3H).
^{13}C NMR ($CDCl_3$): 194.8, 145.3, 127.3, 126.3, 125.3, 53.5, 50.1, 47.4, 31.5, 13.3, 13.0, 12.3.

MS (EI, m/e): 273 (M^+).

Characterization of ethers **2g**:

^1H NMR ($CDCl_3$): isomer 1: 7.28 (dd, J_1 = 5.0, J_2 = 1.3, 2H), 6.96 (dd, J_1 = 5.0, J_2 = 3.4, 2H), 6.88 (dd, J_1 = 3.4, J_2 = 1.3, 2H), 4.36 (t, J = 6.8, 2H), 1.95-1.77 (m, 2H), 1.77-1.60 (m, 2H), 0.81 (t, J = 7.3, 6H) isomer 2: 7.17 (dd, J_1 = 4.9, J_2 = 1.2, 2H), 6.88 (dd, J_1 = 4.9, J_2 = 3.5, 2H), 6.84-6.82 (m, 2H), 4.60 (t, J = 6.5, 2H), 2.04-1.74 (m, 2H), 0.81 (t, J = 7.7, 6H).

MS (EI, m/e): 266 (M^+).

Synthesis of alkene **3b**:

A suspension of Zn powder (6.9 g, 0.1mol) was made in anhydrous THF (200 mL). This suspension was stirred at -10 °C under nitrogen atmosphere. $TiCl_4$ (10 g, 0.05 mol) was added drop wise to this suspension. The resulted mixture was heated at reflux temperature for 1h. Afterwards the mixture was cooled to room temperature, the aldehyde **3a** was added slowly and the reflux was continued for 4 h. The mixture was poured into a K_2CO_3 (10%) solution, extracted with Et_2O and the organic layers were dried over $MgSO_4$. The product was purified by means of column chromatography with petroleum ether as a solvent. The product **3b** was obtained as a colourless powder (1.37 g, 13 %).

^1H NMR ($CDCl_3$): 7.18 (dt, J_1 = 5.0, J_2 = 1.1, 2H), 7.06 (s, 2H), 7.04 (dd, J_1 = 3.6, J_2 = 1.1, 2H), 6.99 (dd, J_1 = 5.0, J_2 = 3.6, 2H).

^{13}C NMR ($CDCl_3$): 143.0, 128.3, 126.7, 125.0, 122.1.

MS (EI, m/e): 192 (M^+).

Synthesis of alcohol **3c**:

A mixture of $TiCl_4$ (0.49 g, 2.6 mmol) and $NaBH_4$ (0.20 g, 5.2 mmol) in DME was stirred at room temperature for 1 hour. Alkene **3b** (0.5 g, 2.6 mmol) was added and the mixture was allowed to stir at room temperature for 14 hours. The reaction was quenched with H_2O. The resulting reaction mixture was extracted with Et_2O and dried over

$MgSO_4$. The solvent was evaporated and the product was found in a low yield (5 %).

^1H NMR ($CDCl_3$): 7.26 (dd, J_1 = 4.7, J_2 = 1.9, 1H), 7.11 (dd, J_1 = 5.1, J_2 = 1.1, 1H), 6.93-6.88 (m, 2H), 6.86 (br d, J = 3.5, 1H), 6.79 (br d, J = 3.6, 1H), 5.15 (t; J = 6.8, 1H), (d, J = 3.6, 2H).

MS (EI, m/e): 210 (M^+).

Synthesis of **3g**:

A solution of thiophene **2a** (10 g, 0.12 mol) and 2-thiophene acetyl chloride **3f** (23.9 g, 0.15 mol) in toluene was stirred at room temperature. $AlCl_3$ (19.8 g, 0.15 mol) was added as a solid in a time frame of 10 minutes. Next the reaction mixture was refluxed for 30 minutes. The solution was cooled to room temperature and quenched carefully with a 2M HCl solution. The resulting reaction mixture was extracted with toluene, washed with HCl, NaOH and H_2O and dried over $MgSO_4$. The crude product was purified by distillation to give colourless oil (6.6 g, 32 mmol, 29 %).

^1H NMR ($CDCl_3$): 7.79 (dd, J_1 = 3.7, J_2 = 1.1, 1H), 7.65 (dd, J_1 = 5.0, J_2 = 1.1, 1H), 7.21 (dd, J_1 = 3.7, J_2 = 2.9, 1H), 7.13 (dd, J_1 = 3.8, J_2 = 5.0, 1H), 6.95-6.94 (m, 2H), 4.38 (s, 2H).

^{13}C NMR ($CDCl_3$): 189.5, 143.8, 135.9, 135.1, 133.4, 128.9, 127.57, 127.55, 125.8, 40.8.

MS (EI, m/e): 208 (M^+).

Synthesis of **3c**:

A solution of **3g** (1 g, 4.8 mmol) was made in a mixture of CH_2Cl_2 and MeOH (1/1). The mixture was cooled to 0 °C and $NaBH_4$ (0.36 g, 9.6 mmol) was added as a solid. The resulted solution was stirred for 12 hours at room temperature. The reaction was quenched with NH_4Cl and extraction has been carried out by Et_2O and dried over $MgSO_4$. The crude product was purified by flash column chromatography to give colourless oil (0.95 g, 4.5 mmol, 94 %).

^{1}H NMR ($CDCl_3$): 7.25 (dd, J_1 = 4.7, J_2 = 1.7, 1H), 7.17 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 6.99-6.92 (m, 3H), 6.86 (dd, J_1 = 3.4, J_2 = 1.0, 1H), 5.14 (dd, J_1 = 6.9, J_2 = 5.6, 1H), 3.32 (dd, J_1 = 2.4, J_2 = 0.8, 2H).
^{13}C NMR ($CDCl_3$): 147.6, 140.0, 127.4, 127.2, 127.1, 125.3, 125.1, 124.6, 71.4, 40.5.
MS (EI, m/e): 209 (M^+).

Synthesis of **3d**:
In a three-necked round bottom flask, the alcohol **3c** (0.95 g, 4.5 mmol) was added drop wise to a stirred solution of $SOCl_2$ (1.18 g, 9.9 mmol) in THF (60 mL). The reaction mixture was stirred under nitrogen atmosphere for 30 minutes. The solution was cooled to 0 °C and quenched carefully with a $NaHCO_3$ solution. The resulting reaction mixture was extracted with Et_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Due to unstable nature of the product **3d** (1.0 g, 4.4 mmol), the crude product has been used without further purification or characterization.

Model compound **3e**:
To a solution of the chloride **3d** (1.0 g, 4.4 mmol) in ethanol (25 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.9 g, 18 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The model compound **3e** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (1.24 g, 3.6 mmol) in a yield of 59 %.
^{1}H NMR ($CDCl_3$): 7.19 (dd, J_1 = 5.2, J_2 = 1.3, 1H), 7.06 (dd, J_1 = 5.0, J_2=1.3, 1H), 6.99 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 6.90 (dd, J_1 = 5.2, J_2 = 3.5, 1H), 6.84 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 6.81 (dd, J_1 = 3.5 ,J_2 = 1.3, 1H), 5.62 (dd, J_1 = 9.9, J_2 = 4.7, 1H), 4.01 (q, J = 6.9, 2H), 3.84 (dd, J_1 = 14.8, J_2 = 4.7, 1H), 3.69 (q, J = 6.9, 2H), 3.43 (dd, J_1 = 14.8, J_2 = 9.9, 1H), 1.26 (t, J = 6.9, 3H), 1.25 (t, J = 6.9, 3H).

^{13}C NMR ($CDCl_3$): 194.2, 143.1, 141.3, 127.4, 127.2, 127.1, 126.9, 125.7, 124.7, 52.9, 50.0, 47.4, 38.8, 13.2, 12.3.

Test reactions acid induced conversion on model compounds **2f**:
Model compound **2f** (0.1 g, 0.37 mmol) was dissolved in chlorobenzene and heated till 70 °C. Trifluoroacetic acid (0.06 g, 0.54 mmol) was added and the reaction mixture was allowed to stir for 24 hours. The reaction was quenched by addition of H_2O. An extraction with Et_2O was performed and the resulting mixture was dried over $MgSO_4$. The reaction mixture was followed during the reaction and at the end of the reaction, with TLC and GC/MS.

Test reactions acid induced conversion on model compounds **3e**:
Model compound **3e** (0.02 g, 0.059 mmol) was dissolved in chlorobenzene and heated till 70 °C. Trifluoroacetic acid (0.01 g, 0.088 mmol) was added and the reaction mixture was allowed to stir for 24 hours. The reaction was quenched by addition of H_2O. An extraction with Et_2O was performed and the resulting mixture was dried over $MgSO_4$. The reaction mixture was followed during the reaction and at the end of the reaction with TLC and GC/MS.

Synthesis of 3-octylthiophene **4b**
A solution of 3-bromothiophene **4a** (56 g, 0.343 mol), diethyl ether (100 ml) and Ni(dppp)Cl_2 (2,243 g, 3.43 mmol) was made in a three-necked flask under vacuum. Octyl magnesium bromide (206 ml of a 2.0 M solution in diethyl ether) was added drop wise via a cannula at 0 °C. After complete addition the mixture was stirred at room temperature overnight. Next, the solution was neutralized by addition of diluted HCl (2 M) and extracted with diethyl ether. The organic layer was dried over $MgSO_4$. The obtained product was purified via flash chromatography using diethyl ether as eluent to give an orange oil in a yield of 97 % (109 g).

^{1}H NMR ($CDCl_3$): 7.22 (dd, J_1 = 4.9, J_2 = 3.1, 1H), 7.92 (dd, J_1 = 4.9, J_2 = 1.3, 1H), 7.91 (dd, J_1 = 3.1, J_2 = 1.3, 1H), 2.61 (t, J = 7.7, 2H), 1.60 (p, J = 7.7, 2H), 1,36-1,21 (m, 10H), 0.87 (t, J = 6.4, 3H).
^{13}C NMR ($CDCl_3$): 143.6, 128.7, 125.5, 120.3, 32.6, 31.3, 31.0, 30.2, 30.12, 30.06, 23.4, 14.8.
MS (EI, m/e): 196 (M^+).

Synthesis of chlorine **4c**
A mixture of 3-octylthiophene **4b** (5.0 g, 25 mmol) and paraformaldehyde (0.84 g, 28 mmol) was made and cooled to 0 °C under a nitrogen atmosphere. First a 12 M HCl solution (6.3 mL, 28 mmol) was added drop wise, afterwards acetic anhydride (12.0 mL, 127 mmol) was also added. The reaction was stirred for 16 hours at room temperature. The resulting reaction mixture was cooled till 0 °C and quenched with NaAc and NaOH (2M), extracted with diethyl ether and dried over $MgSO_4$. Because of the unstable nature of chlorine **4c**, the product has been used without further purification or characterization.

Synthesis of model compound **4d**
The chlorine **4c** was dissolved in ethanol and the sodium dithiocarbamate salt was added as a solid. The resulting mixture was stirred for two hours, extracted with diethyl ether and dried over $MgSO_4$. The product was purified with column chromatography over alumina with hexane/EtOAc as eluent. The product **4d** was obtained as orange oil (2.5 g, 27 %)
^{1}H NMR ($CDCl_3$): 7.09 (d, J = 5.1, 1H), 6.81 (d, J_1 = 5.1, 1H), 4.67 (s, 2H), 4.01 (q, J = 7.4, 2H), 3.68 (q, J = 7.4, 2H), 2.58 (t, J = 7.7, 2H), 1.57 (p, J = 7.7, 2H), 1.36-1.21 (m, 16 H), 0.87 (t, J = 6.8, 3H).
^{13}C NMR ($CDCl_3$): 195.0, 141.8,131.0, 129.1, 124.2, 49.7, 47.1, 35.5, 32.3, 31.2, 29.9 (2X), 29.7, 28.8, 23.1, 14.6, 12.9, 12.0.
FT-IR (cm^{-1}): 3061.15 (υ(CH)), 2955.06 (υ_{as}(–CH_3)), 2926.75 (υ_{as}(-CH_2-)), 2870.46 (υ_s(–CH_3)), 2853.92 (υ_s(-CH_2-)), 1485.99 (υ(C(S)-N),

1416.13 (υ(S-CH$_2$)), 1268.67 (υ(C(S)-N), 1206.96 (υ(C=S)), 719.44($\delta_{\beta r}$(-CH$_2$-)).

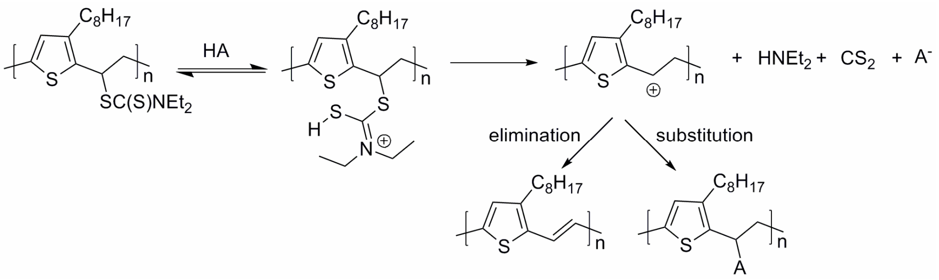
Test reactions acid induced conversion on model compound **4d**
Model compound **4d** (50 mg, 0.14 mmol) was dissolved in chlorobenzene and heated till 60 °C. Trifluoroacetic acid (0.28 mmol) and octanol (or octanethiol) (0.28 mmol) were added and the reaction mixture was allowed to stir for 24 hours. The reaction was quenched by addition of H_2O. An extraction with CH_2Cl_2 was performed and the resulting mixture was dried over $MgSO_4$. The reaction mixture was followed during the reaction and at the end of the reaction with TLC and GC/MS.

NMR experiments on model compound **4d** (solvent effect)
Model compound **4d** (4 mg, 0.01 mmol) was dissolved in chloroform, N-methylformamide (NMF), dimethylsulfoxide (DMSO) and toluene respectively. Trifluoroacetic acid (100 µL, 1.3 mmol) and octanethiol (15 µL, 0.08 mmol) were added. The reaction was followed in situ by ^{1}H-NMR spectroscopy at 55 °C.

NMR experiments on model compound **4d** (effect of the nucleophile)
Model compound 4d (4 mg, 0.01 mmol) was dissolved in chloroform. Benzenesulfonic acid (25 mg, 0.16 mmol) and octanethiol (15 µL, 0.08 mmol) or octanol (14 µL, 0.08 mmol) were added. The reaction was followed in situ by ^{1}H-NMR spectroscopy at 55 °C.

3. Results & discussion

The efficient thermal and acid induced conversion of dithiocarbamate groups in precursors toward Poly(2,5-Thienylene Vinylene) (PTV) and Poly(Phenylene Vinylene) (PPV) derivatives, has been investigated by us in recent years.[31,35,37] For the acid induced conversion, it was observed that the desired conjugated system did not always develop fully. This can be explained by the presence of a competitive substitution reaction next to the earlier observed elimination reaction. Indeed, taken the reaction mechanism proposed for the acid induced conversion of dithiocarbamate groups (scheme 1), it can be expected that such substitution reaction can occur. This reaction mechanism starts with the protonation of the dithiocarbamate group which induces the elimination of the latter. This will result into the formation of a carbenium ion. In a next step, as well elimination as substitution can occur depending on the presence of a nucleophile.

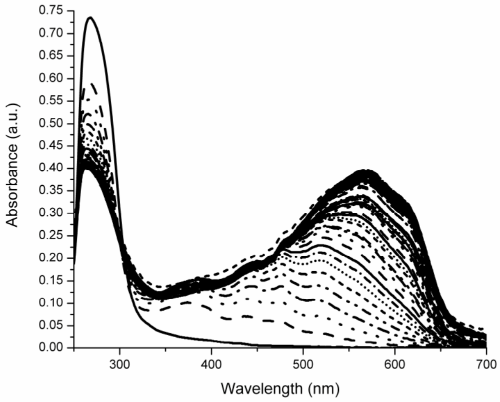


Scheme 1. Proposed reaction mechanism for the acid induced conversion of dithiocarbamate groups.

3.1. In situ UV-Vis spectroscopy

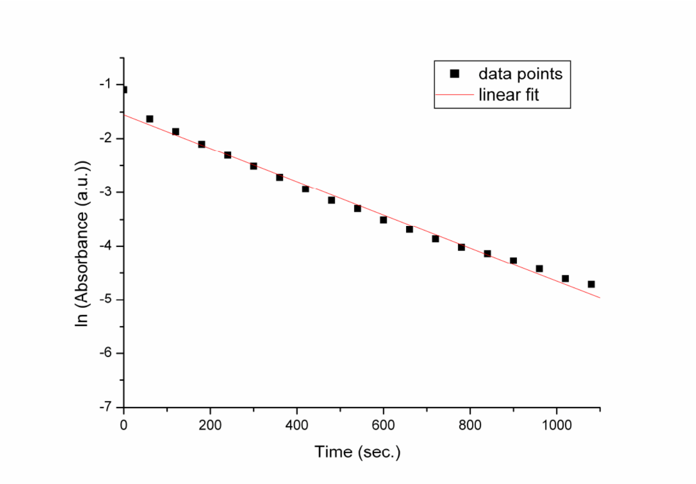
In a first phase the reaction has been monitored on the precursor polymer level. The acid induced conversion reaction has been followed in situ by means of UV-Vis spectroscopy. The purpose of the experiment is to determine the order of the reaction. To be sure that the concentration of the acid (which diminishes during the reaction) does not interfere in the reaction equations, an excess of acid was used.

The precursor polymer was dissolved in $CHCl_3$ and heated till 50 °C. When the reaction mixture reached the proper temperature, 1500 equivalents of acid have been added. During the reaction the absorption band of the precursor polymer at 267 nm was followed for 15 minutes (graph 1).



Graph 1. UV-Vis profiles of acid induced conversion of octyl-PTV.

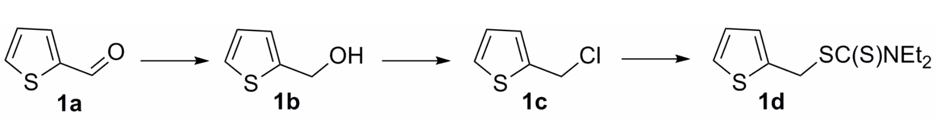
It is observed that this band decreases during the reaction. The formation of the conjugated system can also be followed during the measurement. The conjugated system has a λ_{max} value of 570 nm with a shoulder at 615 nm. The collection of the data indicate that in this time period the conjugated system and thus the conversion is driven virtually to completion. To determine the order of the reaction, the change in absorption, which is equivalent with the change of the concentration of the isolated thiophene chromophore, was plotted versus time. When the ln of the absorbance is plotted versus time (graph 2) a graph is obtained that can be fitted to a linear function ($R^2 = 0.988$). This indicates that the reaction follows first order kinetics ($k = 3{,}21 \,.\, 10^{-3}\ s^{-1}$). It should be mentioned that, because of the excess of acid, the reaction conditions enforce pseudo-first order kinetics. This means that all dithiocarbamate groups convert independably of each other. Furthermore, the obtained linear dependence is consisted with the proposed mechanism in scheme 1, in which the formation of the carbenium ion intermediate is rate determining.



Graph 2. Linear fit of (ln) absorbance at 267 nm.

3.2. Synthesis of model compounds

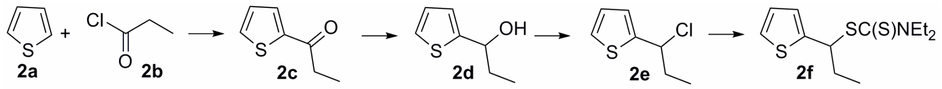
Further insight into the reaction mechanism was pursued by using three model compounds **1d**, **2f** and **3e**, which can undergo the elimination and/or substitution reaction envisaged. For the synthesis of the first model compound **1d** a quite easy synthetic strategy has been used (scheme 2). This three step pathway starts with the reduction of 2-thiophenecarboxaldehyde **1a** towards alcohol **1b**. This alcohol has been chlorinated by $SOCl_2$. The chlorinated product **1c** is unstable, therefore it cannot be purified by column chromatography. However it is possible to purify the compound by vacuum distillation. At last a substitution reaction with the dithiocarbamate salt yields the first model compound **1d**.[38]



Scheme 2. The synthesis of the first model compound **1d**.

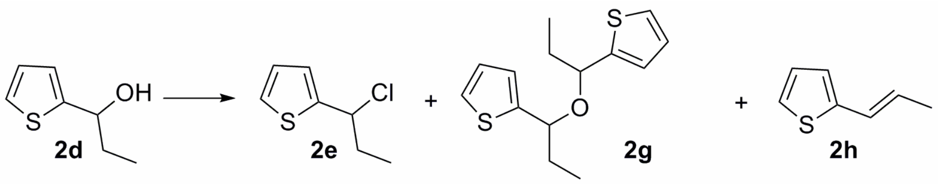
For the synthesis of the second model compound a four step reaction pathway has been performed (scheme 3). The first step is a Friedel-

Crafts reaction between thiophene **2a** and propionyl chloride **2b** to form keton **2c**.[39] Afterwards, this keton has been reduced towards its corresponding alcohol **2d**. The third step should be a straightforward chlorination by $SOCl_2$. Here the same procedure as adopted during the synthesis of dithiocarbamate monomers has been used.[32,38] The reaction has been performed several times under these conditions (THF, 1.2 eq $SOCl_2$, 2h, R.T.). Unfortunately not only the desirable product **2e** (in a very little amount) is formed, but also a lot of unreacted alcohol **2d,** alkene **2h** and two isomers of ether **2g** have been found (scheme 4). Due to the unstable nature of the chlorine **2e**, all the reaction mixtures are analyzed by NMR and GC-MS analysis on the crude reaction mixture. To isolate and separate the two ether isomers **2g** a purification by column chromatography has been done with a mixture of hexane and ethylacetate (90/10) as eluent.



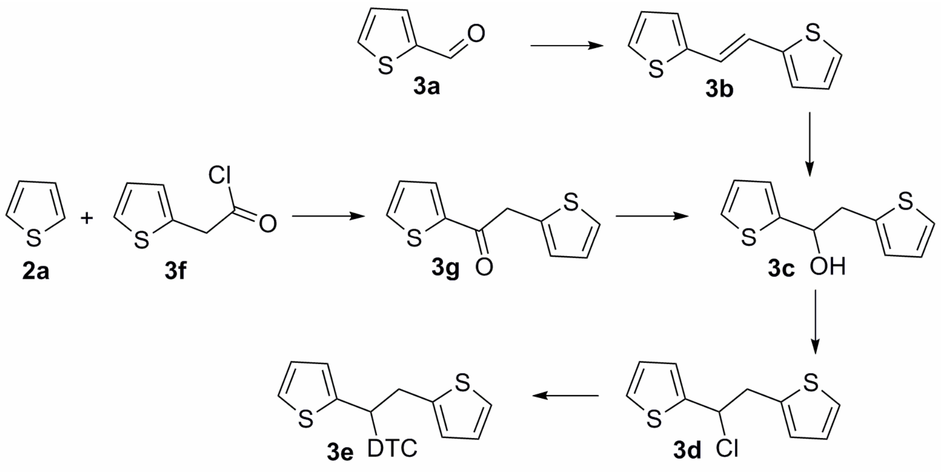
Scheme 3. The synthesis of the second model compound **2d**.

To avoid the side products **2g** and **2h**, several different reaction conditions have been tested. First the influence of the solvent has been investigated. Besides THF and CH_2Cl_2, also a reaction without solvent has been tested. The reactions in CH_2Cl_2 leaded towards more unreacted alcohol **2d** than reactions performed in THF. In the reaction without solvent, no unreacted alcohol **2d** or ethers **2g** have been found. In the latter case, the formation of a large amount of alkenes **2h** was observed (59/41 ratio based on NMR), next to the desired product **2e**. The influence of the amount of $SOCl_2$ has been investigated and showed 2 equivalents to be the optimum. In a next phase the reaction time has been studied, a reaction has been monitored while samples were taken every 30 minutes for 7 hours. Additional samples have been taken after 12 and 14 hours. These samples were analyzed by NMR spectroscopy. It can be stated that the optimal reaction time is 30 minutes. Longer reaction times are leading towards more alkene **2h**. This can be explained by the unstable nature of the chlorine **2e**. The longer the reaction time the more eliminated product **2h** will appear. The amount of ethers formed during the reaction is already present after 30 minutes and this amount does not change with longer reaction times. This can be an indication that the ethers are formed at the start of the reaction, when both the starting product **2d** and the reacted product **2e** are present in the reaction mixture. To avoid the formation of the ethers **2g,** a reversed addition has been done. The alcohol **2d** has been added drop wise to a solution of $SOCl_2$ in THF. This change in reaction conditions avoided the formation of ethers completely. After optimization of the reaction conditions a big batch of chlorine **2e** has been made, because of its unstable nature it hasn't been purified but substitution, with the dithiocarbamate salt, towards model compound **2f** has been done directly.



Scheme 4. Chlorination with $SOCl_2$.

In order to make model compound **3e** another strategy (scheme 5), based on the $NaBH_4$-$TiCl_4$ oxidation on stilbene derivatives, has been tried.[40,41] Here $NaBH_4$ and $TiCl_4$ were stirred for 1 hour at room temperature to form $Ti(BH_4)_3$, the thiophene dimer **3b** has been added and the resulted mixture has been stirred for 14 h at room temperature. Here, not only the starting product has been found, also 1,2-di(thiophen-2-yl)ethane and the desired alcohol **3c** have been obtained (scheme 5), unfortunately the latter only in a yield of 5 %.

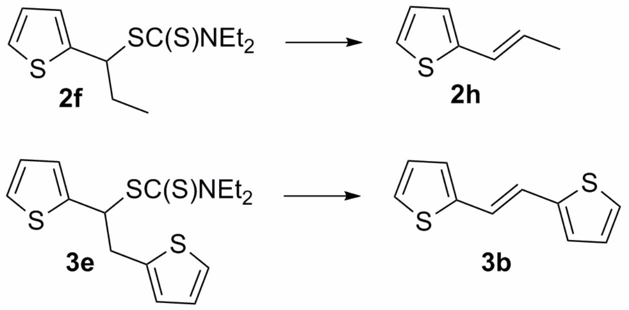


Scheme 5. Synthesis of model compound **3e** via $NaBH_4$-$TiCl_4$ oxidation and Friedel Crafts reaction (DTC = -SC(S)NEt_2).

To gain higher yields, a different pathway based on the synthesis of the second model compound **2f** has been investigated (scheme 5). First a Friedel-Crafts reaction between thiophene **2a** and the acid chloride **3f** has been performed to form the keton **3g**.[39] In a next step the keton **3g** has been reduced towards alcohol **3c** with $NaBH_4$ as a reducing agent. This alcohol **3c** will be chlorinated by $SOCl_2$. Due to the unstable nature of the chlorine **3c**, this product has been substituted with the dithiocarbamate salt immediately, to form model compound **3e**. On account of the experience gained from the chlorination of the second model compound **2f,** and possibly because of the more sterical hindered compound **3c**, the formation of ethers could be avoided. It is worthwhile mentioning that also some eliminated product **3b** has been retrieved. This can be formed during work-up of the chlorine **3d** or can be, due to degradation during column chromatography, caused by the acidity of the used silica.

3.3. Test reactions on model compounds 1d, 2f and 3e

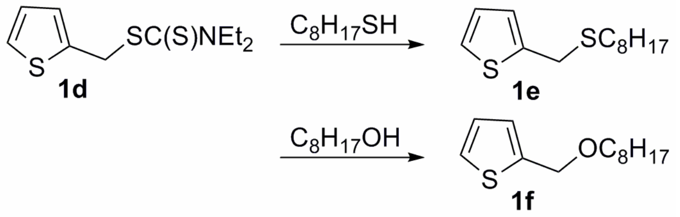
Since all model compounds have finally been synthesized properly, they can be used to investigate the acid induced conversion of the dithiocarbamate groups and the competition between the elimination and substitution reaction in detail. First model compound **2f** and **3e** are tested in the same conditions as the dithiocarbamate precursor polymers were converted (scheme 6).[37] These polymers have been dissolved in dichlorobenzene and heated to 70 °C, then 1.5 equivalents of benzenesulfonic acid or trifluoroacetic acid have been added and reacted for 10 minutes. When these conditions were applied on the model compounds **2f** and **3e** no reaction occurred. Even when the reagents where allowed to react for 24 hours only the starting compounds have been retrieved.



Scheme 6. Test reactions for the acid induced elimination on model compound **2f** and **3e**.

To test whether the inability to eliminate the dithiocarbamate group is inherent for the model compound or due to reaction conditions, model compound **3e** was also converted at higher temperature. In the normal polymer conditions for thermal conversion (1 hour reaction time, 180 °C, *o*-dichlorobenzene) only the starting product has been found. So the reaction was left for a longer time and after 3 hour a partial elimination occurred. 20 Hours later the model compound was totally converted towards compound **3b**. To verify if the acid can have an influence on the elimination two additional tests have been done. For the first test, the polymer conditions (70 °C, 1h) were used, but this time an excess of benzenesulfonic acid (10 eq) was added. Here a partial elimination took place. For the second experiment (1,5 eq. of benzenesulfonic acid, *o*-dichlorobenzene) the temperature was raised till 130 °C and the compound was allowed to stand overnight. Here a partial elimination arose as well. To be sure that this was not only due to the higher temperature, an experiment with the same reaction conditions (reaction overnight, *o*-dichlorobenzene, 130 °C) but without the acid was set up as well. Here no conversion occurred at all.

In a next phase the first model compound **1d** has also been explored. On this model compound it is not possible to perform an elimination. But substitution with nucleophiles should be possible. So the model compound was dissolved in chlorobenzene, 1.5 equivalents of benzenesulfonic or trifluoroacetic acid and 2 equivalents of respectively octanethiol and octanol have been added (scheme 7). The reactions were heated towards 70 °C and were allowed to stir for 16 hours. After work-up, there was no sign of reactivity, only starting product has been found.

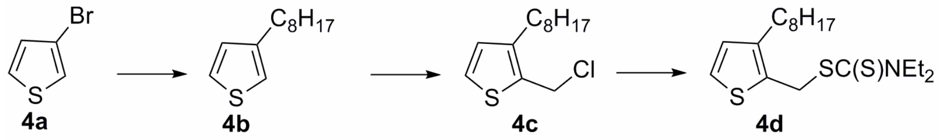


Scheme 7. Test reactions concerning the substitution reaction on model compound **1d**.

All these experiments indicate that conversion on the model compounds is possible but much slower than conversion on the polymer level. So, something in the polymer structure should have an influence on the conversion of the dithiocarbamate groups. To investigate this idea, the difference between the polymer chain and the model compounds has to be examined. There is one specific difference between them, the presence of side chains on the thiophene core on the polymer level. The synthesis of two different model compounds **4d** en **5d** has been started for this reason.

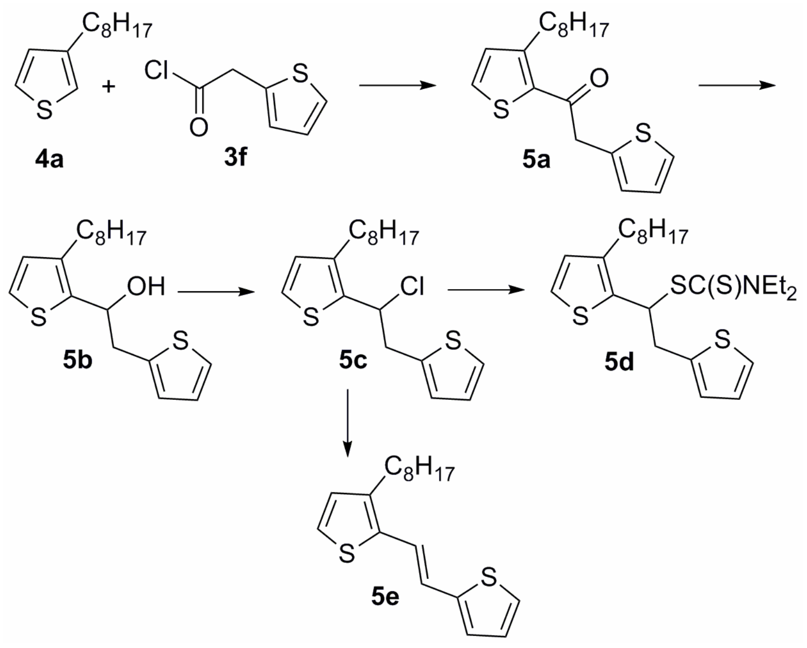
3.4. Synthesis of model compounds with side chains

For the synthesis of model compound **4d**, on which the substitution reaction can be tested, a three step pathway has been followed (scheme 8). First, the octyl side chain will be introduced by a Kumada coupling.[42] Next a chloromethylation reaction will be done on the 3-octylthiophene **4b**. Here the reaction conditions, normally used to chloromethylate the 2- and 5 positions of the thiophene,[43] had to be optimized. To get the dichloromethylated product, the reaction is heated towards 70 °C and allowed to stay at this temperature for 4 hours. In case of mono chloromethylation the temperature will be lowered till room temperature but the reaction time will be elongated till 16 hours. In a last phase the chlorine **4c** was substituted by a dithiocarbamate. Purification of model compound **4d** by column chromatography over silica was not possible. Degradation of the product occurred, which is already a sign for its acid sensitivity. Although the product is stable on an alumina column, purification was quite difficult. Nevertheless, eventually product **4d** has been obtained.



Scheme 8. The synthesis of model compound **4d**.

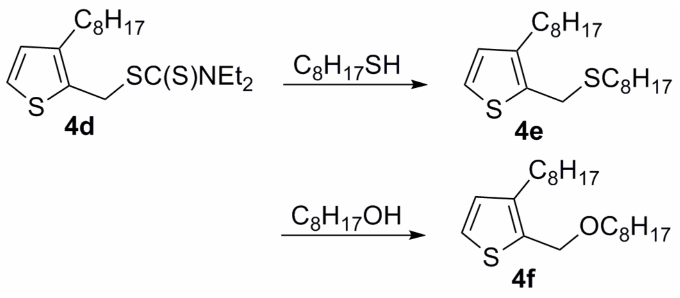
To test the influence of the side chains during the elimination reaction, the synthesis of model compound **5d** has also been started. Here a similar reaction pathway as towards model compounds **2f** and **3e** has been set up (Scheme 9). The first Friedel-Crafts reaction was successful, and keton **5a** could be obtained in a moderate amount. This keton **5a** has been reduced towards the alcohol **5b,** and in a next step chlorination and substitution with the dithiocarbamate salt has been performed. Unfortunately, not the desired model compound **5d** but the eliminated product **5e** has been found at the end of the reaction sequence. So the optimal chlorination conditions for the model compounds **2f** and **3e** could not be transferred towards model compound **5d**. The reaction has been repeated several times but the elimination reaction could not be avoided. This can already been seen as an indication that the substituents on the thiophene core have an influence on the elimination reaction.



Scheme 9. The synthesis of model compound **5d** via Friedel-Crafts reaction.

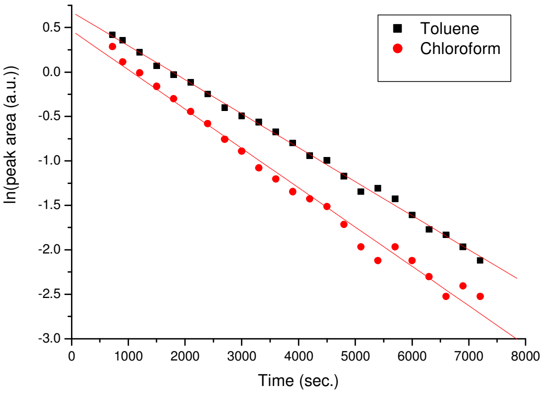
3.5. Test reactions on model compound 4d

The influence of the side chain on the conversion reaction has been tested by performing the substitution reaction on model compound **4d** in the same conditions as done on model compound **1d** which did not give any reaction at all (scheme 10). First, when the reaction has been performed with trifluoro acetic acid as an acid and octanol as a nucleophile, the starting product and some unreacted alcohol has been found. Moreover the ester derivative from trifluoro acetic acid and the alcohol has been formed. So it seems that trifluoro acetic acid has more tendency to react with the nucleophile than as an acid.



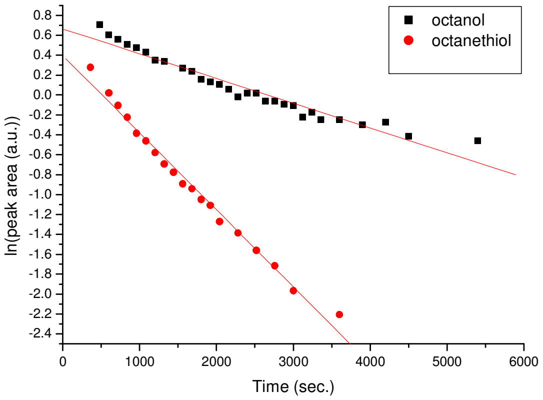
Scheme 10. Test reactions model compound **4d**.

Therefore, the same reaction has been tried with octanethiol as a nucleophile. In this case substitution is possible. This substitution reaction has been followed by means of in situ ^{1}H-NMR spectroscopy. Furthermore, the influence of the solvent on the reaction speed has been tested with four different solvents, i.e. toluene, chloroform, DMSO and NMF (graph 3). The reactions in toluene and chloroform seem to proceed with approximately the same velocity ($k_{toluene}$ = 3,82 . 10^{-4} s^{-1} with $R^2 = 0.998$, $k_{chloroform}$ = 4,43 . 10^{-4} s^{-1} with $R^2 = 0.994$). However, when NMF or DMSO have been used as solvents, no reaction occurred at all. This phenomenon can be explained by the polarity of the different solvents which can be expressed by their dielectric constants ($\varepsilon_{chloroform}$ = 4.8; $\varepsilon_{toluene}$ = 2.4; ε_{DMSO} = 46.5; ε_{NMF} = 182.4).[44] Chloroform and toluene can be considered to be more apolar solvents with more or less the same polarity, DMSO and NMF are (very) polar solvents. The rate of the reaction is in this case influenced by the charge density on the reactants and the transition state. The charges on the transition state become more dispersed in comparison to the case in the reactant. Therefore increasing solvent polarity decreases the reaction rate.[45]



Graph 3. The influence of different solvents on the substitution reaction.

Finally, the influence of the nucleophile on the reaction speed has been tested. Here two nucleophiles, octanol and octanethiol have been compared. Because trifluoroacetic acid and octanol seem to react towards the corresponding ester, these reactions have been performed with benzenesulfonic acid. Again both reactions have been followed by in situ ^{1}H-NMR spectroscopy (graph 4) and the decrease of the concentration of the starting product has been monitored ($k_{octanol} = 2{,}49 \cdot 10^{-4}\ s^{-1}$ with R² = 0.971, $k_{octanethiol} = 7{,}75 \cdot 10^{-4}\ s^{-1}$ with R² = 0.993).



Graph 4. The influence of different nucleophiles on the substitution reaction.

It can be stated that the reaction speed for both nucleophiles are in the same order of magnitude for both nucleophiles, which differ enormously in nucleophilic strength. This observation supports the proposed reaction mechanism (scheme 1), the rate limiting step will be the formation of the carbenium ion and not the substitution of the nucleophile.

From these experiments, we can conclude that the electron donating side chain accelerates the conversion of the dithiocarbamate groups. This is consistent with a stabilizing effect of the electron donating side chain on the carbenium ion intermediate. Consistent with this assumption, the type of nucleophile seems not to influence the reaction speed.

4. Conclusions

To conclude, it can be stated that dithiocarbamate groups can undergo elimination by heating in combination with acids. This property is exploited in the synthesis of poly(arylene vinylene) derivatives via the dithiocarbamate precursor route. The mechanism of the acid induced conversion has been investigated using model compounds. Elimination as well as substitution reactions are observed for the dithiocarbamate group. The results obtained are consistent with a mechanism which involves in the rate determining step the formation of a carbenium ion intermediate via an acid induced elimination of the dithiocarbamate group. Consequently electron donor substituents increase the kinetics substantially and secondly the kinetics for the substitution reaction show no influence of the type of nucleophile that is used.

5. Acknowledgements

The authors gratefully acknowledge BELSPO in the frame of network IAP P6/17 for the financial support and for granting a Ph.D. fellowship (H.D.). The FWO is also gratefully acknowledged for the funding of the project G.0091.07. We also want to thank the European Science Foundation (ESF) for the received support for the activity entitled 'New Generation of Organic based Photovoltaic Devices'.

6. References

[1] Hester; W. F. *U.S. pat.* 2,317,765 **1943**.

[2] Rafin, C.; Veignie, E.; Sancholle, M.; Postal, D.; Len, C.; Villa, P.; Ronco, G. *J. Agric. Food Chem.* **2000**, *48*, 5283–5287.

[3] Len, C; Postal, D.; Ronco, G.; Villa, P.; Goubert, C.; Jeufrault, E.; Mathon, B.; Simon, H. *J. Agric. Food Chem.* **1997**, *45*, 3–10.

[4] Nieuwenhuizen, P. J. *Appl. Catal. A-Gen.* **2001**, *207*, 55–68.

[5] Nieuwenhuizen, P. J. ; Ehlers, A. W.; Haasnoot, J. G.; Janse, S. R.; Reedijk, J.; Baerends, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 163–168.

[6] Sullivan, F. A. V.; Lindaw, A. C. US Pat. 3215703 **1965**.

[7] Denton, W. M.; Thompson, S. A. M. Inst. Petrol. Rev. 1966, 20, 46–54.

[8] Holubec, A. M. *U. S. Pat.* 3876550 **1975**.

[9] Uchide, N.; Ohyama, K. J. antimicrob. Chemoth. **2003**, *52*, 8–10.

[10] Gaudernak, E.; Seipelt, J.; Triendl, A.; Grassauer, A.; Kuechler, E. *J. Virol.* **2002**, 6004–6015.

[11] Krenn, B. M.; Gaudernak, E.; Holzer, B.; Lanke, K.; Van Kuppeveld, F. J. M., Seipelt, J. *J. Virol.* **2009**, *83*, 58–64.

[12] Huang, W.; Ding, Y.; Miao, Y.; Liu, M. Z.; Li Y.; Yang G. F. Eur. *J. Med. Chem.* **2009**, *44*, 3687–3696.

[13] Milacic, V.; Chen, D.; Ronconi, L.; Landis-Piwowar, K. R.; Fregona, D.; Dou, Q. P. *Cancer R.* **2006**, *66*, 10478–10486.

[14] Schilli, C.; Lanzendörfer, M. G., Müller, H. E. *Macromolecules*, **2002**, *35*, 6819–6827.

[15] Zhou, D.; Zhu, X.; Zhu, J.; Hu, L.; Cheng, Z. *J. Appl. Polym. Sci.* **2006**, *103*, 982–988.

[16] Thang, S. H.; Chong, Y. K. Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, *40*, 2435–2438.

[17] Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977–6980.

[18] Schilli, C.; Lanzendörfer, M. G.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 6819–6827.

[19] Malepu, V.; Petruczok, C. D.; Tran, T.; Zhang, T.; Thopasridharan, M.; Shipp, D. A. *Controlled/Living Radical Polymerization: Progress in RAFT, DT, NMP, OMRP* **2009**, 37–47.

[20] Kwak, Y.; Nicolaÿ, R.; Matyjaszewski, K. *Aust. J. Chem.* **2009**, *62*, 1384–1401.

[21] Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410.

[22] Moad, G.; Chen, M.; Häussler, M.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Chem.* **2010**, 10.1039/c0py00179a, published online

[23] Durmaz, Y. Y.; Karagoz, B.; Bicak, N.; Yagci, Y. *Polym. Int.* **2008**, *57*, 1182–1187.

[24] Otsu, T. J. Polym. Sci. Part A: Polym. Chem. **2000**, *38*, 2121–2136.

[25] Garcia-Con, L. M.; Whitcombe, M. J.; Piletska, E. V.; Piletsky, S. A.. *Angew. Chem. Int. Ed.*, **2010**, *49*, 4075–4078.

[26] Lee, H. J.; Matsuda, T. *J. Biomed. Mater. Res.* **1999**, *47*, 564–567.

[27] Ward, J. H.; Peppas, N. A. *Macromolecules* **2000**, *33*, 5137–5142.

[28] Luo, N.; Hutchison, B.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci. Pol. Chem.* **2002**, *40*, 1885–1891.

[29] Vandenbergh, J.; Wouters, J.; Adriaensens, P. J.; Mens, R.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. J. M. *Macromolecules*, **2009**, *42*, 3661–3668.

[30] Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande D. *Eur. Phys. J. Appl. Phys.* **2007**, *37*, 237–240

[31] Henckens A.; Duyssens, I.; Lutsen, L.; Vanderzande, D.; Cleij, T. J. *Polymer* **2006**, *47*, 123–131.

[32] Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, 10231–10240.

[33] Chande, M. S. J. Indian Chem. Soc. **1979**, *56*, 386.

[34] Padmanaban, G.; Nagesh, K.; Ramakrishnan, S. *J. Polym. Sci. Part A: Polym. Chem.***2003**, *41*, 3929–3933.

[35] Henckens, A. Colladet, K.; Fourier, S., Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. Macromolecules **2005**, *38*, 19–26.

[36] Ahmed, S.; Baker, L. A.; Grainger, R. S.; Innocenti, P.; Quevedo, C. E. *J. Org. Chem.* **2008**, *73*, 8116-8119.

[37] Diliën, H.; Vandenbergh, J.; Banishoeib, F.; Adriaensens, P. J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. Acid induced conversion of dithiocarbamate precursor polymers into conjugated materials, *Macromolecules* **2011**, accepted.

[38] Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19–26.

[39] Kieseritzky, F.; Hellberg, J.; Wang, X.; Inganäs, O. *Synthesis* **2002**, *9*, 1195–1200.

[40] Kano, S.; Tanaka, Y.; Hibino, S. *J. Chem. Soc. Chem. Commun.* **1980**, 414–415.

[41] Kumar, K. S. R.; Baskaran, S.; Chandrasekaran, S.; *Tetrahedron Lett.* **1993**, *34*, 171–174.

[42] Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347– 3354.

[43] Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, 572–579.

[44] Reichardt, C. *Solvents and solvent effects in Organic Chemistry* **1990**, 407–410.

[45] Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry* **2006**, 643–647.

Chapter 5: Identification and quantification of defect structures in Poly(2,5-Thienylene Vinylene) derivatives prepared via the dithiocarbamate precursor route by means of NMR spectroscopy on ^{13}C-labeled polymers

During the last decades several synthetic routes towards the low band gap polymer poly(2,5-thienylene vinylene) (PTV) and derivatives have been studied. This study describes an extensive NMR characterization of ^{13}C-labeled 3-octyl-PTV and its precursor polymer prepared via the dithiocarbamate route which is, since stable monomers are available, a promising route towards PTV derivatives. By introducing ^{13}C-labeled vinylene carbons, we were able to characterize these polymers in a quantitative way, taking the end groups and structural polymerization defects, which disturb the conjugated system, into account. Several NMR techniques and the synthesis of model compounds were used to fully assign the proton and carbon chemical shifts. Moreover, the classically used thermal conversion of the precursor towards the conjugated polymer has been compared to a smoother, acid induced elimination procedure.

1. Introduction

During the last two decades rapid strides have been made in the field of conjugated polymers. Their semi-conductor properties allow their use in all kinds of electronic devices, such as organic field effect transistors,[1,2,3]

---

* by H. Diliën, S. Chambon, T. J. Cleij, L. Lutsen, D. Vanderzande, P. J. Adriaensens for Macromolecules, 2011, submitted

biosensors,[4] light emitting diodes[5,6,7] and photovoltaic cells.[8-13] The main advantage of such organic semi-conductors is that their structure and thus their electro-optical properties can be tuned virtually to any combination of specifications needed for a dedicated application. For example, in polymeric bulk heterojunction solar cells the mismatch between the absorption spectrum of the active layer and the solar emission spectrum can be decreased by focusing on the design and synthesis of different classes of low band gap materials.[14-22] In this context poly(2,5-Thienylene Vinylene) (PTV) derivatives have been considered as a promising class of low band gap polymer.[23-28] The most efficient synthetic routes toward PTV's make use of the polymerization behavior of quinodimethane systems. They can be obtained via a base induced elimination in a premonomer of type **1g** (scheme 1 and 2). On formation of the quinodimethane system, a fast polymerization reaction yields high molecular weight precursor polymers which can be converted in situ or ex situ to the conjugated structure. Substantial research efforts have been devoted to the optimization of these synthetic pathways towards PTV derivatives, e.g. the Wessling,[29,30,31] xanthate,[32,33] sulphinyl[34,35] and dithiocarbamate[36,37] routes. The dithiocarbamate (DTC) route towards PTV, developed in our lab, has as main advantage that the premonomer is much more stable as compared to the premonomers of the other precursor routes and therefore allows the polymerization of better defined precursor polymers.

In this paper a thorough investigation is presented into the detection and identification of defect structures and end groups in 3-octyl-PTV (O-PTV) precursor polymers and their converted, still soluble, conjugated O-PTV polymers. Hereto, ^{13}C-labeled polymers were prepared by introducing ^{13}C labels in the premonomers. Quantitative NMR-techniques and model compounds allowed for the identification of said defects. Moreover, the precursor polymer was converted to the conjugated polymer by a thermal as well as acid induced conversion process. Comparison of the results obtained indicates that the acid induced conversion proceeds smoother than the thermal induced one.

2. Experimental section

2.1. Materials

All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone.

2.2. Analytical

^{1}H and ^{13}C NMR spectra were taken on a Varian Inova 300 or 400 spectrometer from solutions in deuteroform (D 99.8%). The chemical shifts were calibrated by means of the (remaining) proton and carbon resonance signals of $CDCl_3$ (7.24 and 77.7 ppm for ^{1}H and ^{13}C, respectively). The T_{1C} relaxation decay times were determined via the inversion-recovery method. To quantify the amount of structural defects and end groups from the ^{13}C NMR spectra, the summed integration of three signals of the side chain (carbon atoms 17, 18 and 19) was taken as an internal reference to which the other resonances were normalized. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by Size Exclusion Chromatography (SEC). Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10 µm, 0.75 x 30 cm, Polymer Labs) and a relative index (RI) detector (Shodex). GC/MS analyses were carried out on a TSQ – 70 and Voyager mass – spectrometer (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB.

Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans).

Ultraviolet visible spectroscopy (UV-Vis) was performed on a Varian cary 500 UV-Vis-NIR spectrophotometer (interval: 1 nm, scan rate: 600 nm/min, continuous run from 200 to 700 nm).

TLC analyses were made on Merck aluminium sheets, 20 x 20 cm, covered with silica gel 60 F_{254}.

2.3. Synthesis and characterization

*A) Synthesis of the ^{13}C-labeled monomer (**1g**):*

The synthesis of 3-octylthiophene **1b** and 3-octyl-2,5-di-bromothiophene **1c** has been described elsewhere.[38]

Synthesis of 3-octyl-2,5-thiophenedicarboxaldehyde **1d**

In a three-necked round bottom flask a solution of 2,5-dibromo-3-octylthiophene **1c** (4.3 g, 12 mmol) in THF (100 mL) was stirred under nitrogen atmosphere at -78 °C. A solution of *n*-butyl lithium (16.7 mL, 27 mmol of a 1.6 M solution in hexane) was slowly added with a cannula, the mixture was stirred for 30 minutes and afterwards ^{13}C enriched DMF (2.0 g, 0.27 mol), previously distilled, was slowly added. The resulting mixture was stirred for 12 hours at room temperature. HCl (2 M, 50 mL) was added to quench the excess of *n*-BuLi followed by extraction with chloroform. The organic layers were dried over $MgSO_4$ and the obtained compound was purified by column chromatography on silica gel with chloroform/hexane (1/1) as a solvent. The dialdehyde **1d** was obtained as orange oil (1.8 g, yield 58 %).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 10.12 (d, $^1J_{H\text{-}13C} = 180$, 1H), 9.95 (d, $^1J_{H\text{-}13C} = 180$, 1H), 7.63 (d, J = 3.5, 1H), 2.97 (t, J = 8.1, 2H), 1.73-1.62 (m, 2H), 1.41-1.20 (m, 10H), 0.86 (t, J = 7.3, 3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 184.1, 183.7, 152.7, 148.9, 144.3, 138.2, 32.5, 31.9, 30.0, 29.9, 29.8, 29.2, 23.3, 14.8.

MS (EI, m/e): 254 (M^+).

Synthesis of 3-octyl-2,5-bis(hydroxymethyl)thiophene **1e**

In a three-necked round bottom flask a mixture of $LiAlH_4$ (0.54 g, 14 mmol) in dry THF (50 mL) was made under argon atmosphere. This slurry was cooled to 0 °C and the di-aldehyde **1d** (1.8 g, 7.1 mmol) in THF (50 mL) was slowly added with a dropping funnel. When the addition was completed the slurry was heated at reflux temperature for 5 hours. Afterwards the mixture was placed in an ice bath and quenched very careful with water and an aqueous 15 % NaOH solution. The solution was extracted with diethyl ether, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The diol **1e** was obtained as a yellow oil in a yield of 96 % (1.7 g).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.76 (d, $^3J_{H\text{-}13C} = 3.2$, 1H), 4.73 (d, J = 144, 2H), 4.70 (d, J = 144, 2H), 2.52 (t, J = 8.0, 2H), 1.57-1.48 (m, 2H), 1.34-1.19 (m, 10H), 0.85 (t, J = 6.4, 3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 142.6, 140.9, 137.8, 128.3, 60.9, 58.4, 32.5, 32.3, 31.7, 30.1, 29.9, 28.9, 23.3, 14.8.

MS (EI, m/e): 224 (M^+ - hydroxyl functions, M^+ is not stable).

Synthesis of 3-octyl-2,5-bis(chloromethyl)thiophene **1f**

To a cooled (0 °C), stirred solution of diol **1e** (1.7 g, 6.8 mmol) in THF (30 mL) was slowly added a solution of $SOCl_2$ (2.16 g, 18 mmol) in THF (40 mL). The temperature of the reaction mixture was allowed to increase to RT under continuous stirring for 1 hour. Then, the mixture was cooled down again to 0 °C and a saturated sodium carbonate solution was added drop wise until neutral. The mixture was extracted with diethyl ether and dried over $MgSO_4$. The solvent was evaporated and the highly reactive dichloride **1f** was obtained as an orange oil. Because of the high reactivity of **1f**, the dichloride was used in the next reaction step without purification or characterization.

Synthesis of 3-octyl-2,5-diylbismethylene N,N-diethyldithiocarbamate **1g**

To a solution of **1f** (2.08 g, 4.0 mmol) in ethanol (50 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.61 g, 16 mmol) was added as solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The monomer **1g** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (2.5 g, 67 %).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.75 (d, J = 3.3, 1H), 4.65 (d, J = 146, 2H), 4.58 (d, J = 146, 2H), 4.01 (q, J = 6.8, 4H), 3.68 (q, J = 6.8, 4H), 2.48 (t, J = 8.0, 2H), 1.59-1.49 (m, 2H), 1.33-1.22 (m, 16H), 0.85 (t, J = 6.8, 3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 195.3, 195.0, 141.9, 137.8, 131.4, 129.6, 49.9, 47.3, 32.5, 31.2, 30.1, 29.8, 29.1, 23.3, 14.7, 13.1, 12.2.

MS (CI, m/e): 517 (M^+).

*B) Synthesis of the ^{13}C-labeled precursor polymer **1h***

The monomer **1g** (0.93 g, 1.8 mmol) was previously freeze dried. A solution, with a monomer concentration of 0.4 M in dry THF was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (3.6 mL of a 1.0 M solution in THF) was added in one go to the stirring monomer solution. The resulting mixture was stirred for 90 minutes under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvent of the combined organic layers was evaporated under reduced pressure and a second precipitation was performed in pure cold methanol. The polymer **1h** was collected and dried *in vacuo* (0.45 g, yield 67 %)**.** The polymer has been purified by multiple reversed precipitations (the polymer was solved in $CHCl_3$ and MeOH was added drop wise till the high molecular weight fraction precipitated) to collect the high molecular weight fraction (180 mg = precursor polymer **1D** (large batch)).

Precursor polymers **1A**, **1B** and **1C** are made with the same procedure. Polymers **1A** and **1B** are the low and high molecular weight fractions from a same small batch, respectively. Precursor polymer **1C** is the isolated high molecular weight fraction of another small batch.

IR (in cm^{-1}): 2931, 2846, 1486, 1415, 1268, 1206

SEC: $M_w = 188 . 10^3$; PD = 3.4 (batch **1D**)

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.49 (1H), 5.35 (1H), 3.96 (2H), 3.66 (2H), 3.17 (2H), 2.28 (2H), 1.40-1.05 (18H), 0.85 (3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 194.7, 140.2, 139.3, 134.4, 128.4, 53.3, 49.8, 47.4, 37.2, 32.7, 31.6, 30.4, 30.1, 29.0, 23.4, 14.9, 13.4, 12.3.

*C) Synthesis of the ^{13}C-labeled polymer **1i***

Thermal conversion

The precursor polymer **1h** (60 mg, 0.16 mmol) was dissolved in *o*-dichlorobenzene (5 mL) and refluxed for 1 h. After being cooled, the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol and dried *in vacuo*. A purple/black solid was obtained (25 mg, yield 70 %).

UV-Vis: $\lambda_{max} = 574$ nm (shoulder: 611 nm)

SEC: $M_w = 48 . 10^3$; PD = 2.2

^{1}H NMR ($CDCl_3$): See chemical shifts of **1h** except for the signals of the dithiocarbamate group which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 6.8-6.9 ppm.

^{13}C NMR ($CDCl_3$): See chemical shifts of **1h** except for the dithiocarbamate signals which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 121 ppm.

Acid induced conversion

The precursor polymer **1h** (60 mg, 0.16 mmol) was dissolved in *o*-dichlorobenzene (5 mL) and heated till 70 °C before trifluoroacetic acid (0.018 mL, 0.24 mmol) was added. The solution was stirred for 10 minutes at 70 °C. After being cooled, the solution was poured into H_2O and extracted with diethyl ether. The solvent was evaporated under reduced pressure and the obtained slurry was precipitated in MeOH, filtered off and dried *in vacuo*. A purple/black solid was obtained (34 mg, yield 97 %).

UV-Vis: λ_{max} = 574 nm (shoulder: 614 nm)

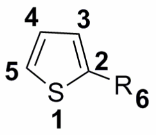
SEC: $M_w = 109 . 10^3$; PD = 2.8

^1H NMR ($CDCl_3$): See chemical shifts of **1h** except for the signals of the dithiocarbamate group which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 6.8-6.9 ppm.

^{13}C NMR ($CDCl_3$): See chemical shifts of **1h** except for the dithiocarbamate signals which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 121 ppm.

D) Synthesis of model compounds for end groups

The chemical shifts of the model compounds are assigned using the numbering system in the next figure.



Model compound **2a**: 2-thiophene-carbaldehyde (commercially available):

^1H NMR ($CDCl_3$, δ in ppm, J in Hz): 9.91 (d, J = 1.2, 1H, **6**), 7.77 (dd, J_1 = 3.9, J_2 = 1.2, 1H, **5**), 7.75 (dt, J_1 = 4.9, J_2 = 1.2, 1H, **3**), 7.20 (dd, J_1 = 4.9, J_2 = 3.9, 1H, **4**).

^{13}C NMR ($CDCl_3$, δ in ppm): 183.7 (**6**), 144.6 (**2**), 137.0 (**3**), 135.8 (**5**), 129.0 (**4**).

Model compound **2b**: 2-thiophene methanol

A solution of **2a** (3 g, 27 mmol) in a 1:1 mixture of methanol and CH_2Cl_2 was cooled to 0 °C and $NaBH_4$ (1.5 g, 40 mmol) was added as a solid. The mixture was stirred overnight and afterwards quenched by the addition of H_2O (50 mL), followed by an extraction with Et_2O. The organic layers were dried over $MgSO_4$ and the obtained compound was purified by column chromatography on silica gel with hexane as a solvent. The alcohol **2b** was obtained as a colorless oil in a yield of 93 % (2.9 g).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.27 (dd, J_1 = 5.0, J_2 = 1.3, 1H, **5**), 7.00 (m, 1H, **3**), 6.96 (dd, J_1 = 5.0, J_2 = 3.5, 1H, **4**), 4.82 (d, J = 3.5, 2H, **6**), 1.79 (s, 1H, **6'**).

^{13}C NMR ($CDCl_3$, δ in ppm): 144.2 (**2**), 127.0 (**3**), 125.6 (**4**), 125.5 (**5**), 59.3 (**6**).

Model compound **2c** 2-thiophene-carboxylic acid (commercially available):

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 12.50 (s, 1H, **6**), 7.89 (dd, J_1 = 3.8, J_2 = 1.2, 1H, **3**), 7.64 (dd, J_1 = 5.0, J_2 = 1.2, 1H, **5**), 7.13 (dd, J_1 = 5.0, J_2 = 3.8, 1H, **4**).

^{13}C NMR ($CDCl_3$, δ in ppm): 168.8 (**6**), 135.8 (**3**), 134.8 (**5**), 133.5 (**2**), 128.8 (**4**).

E) Synthesis of model compounds for structural defects in the precursor polymer

Synthesis of 2-(chloromethyl)thiophene **2g**:

A solution of $SOCl_2$ (6.9 g, 58 mmol) in dry CH_2Cl_2 (40 mL) was made in a three-necked round bottom flask. A solution of the alcohol **2b** (3 g, 26 mmol) in dry THF (20 mL) was added drop wise at 0 °C and the reaction mixture has been stirred for 30 minutes at room temperature. The resulting reaction mixture was quenched with $NaHCO_3$ and extracted with CH_2Cl_2. The crude product was distilled by vacuum distillation to get a colorless oil (3.0 g, 23 mmol) in a good yield (88%).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.30 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 7.07 (dd, J_1 = 3.5, J_2 = 1.2, 1H), 6.94 (dd, J_1 = 5.1, J_2 = 3.5, 1H), 4.80 (s, 2H).

^{13}C NMR ($CDCl_3$, δ in ppm): 140.2, 127.8, 127.0 (2C), 40.5.

Model compound **2d**:

A three-necked round bottom flask was filled with dry THF and sodium (0.9 g, 40 mmol). 2-(chloromethyl)thiophene **2g** (0.5 g, 3.8 mmol) was added drop wise to this dispersion. The reaction mixture was stirred overnight. Afterwards the reaction was quenched by the addition of ethanol (50 mL) and H_2O (50 mL). The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. The product **2d** was obtained as an oil (0.14 g, 0.7 mmol) after column chromatography (eluent: hexane) in a yield of 20 %.

^{1}H-NMR ($CDCl_3$, δ in ppm, J in Hz): 7.14 (dd, $J_1 = 5.1$, $J_2 = 1.2$, 2H), 6.93 (dd, $J_1 = 5.1$, $J_2 = 3.6$, 2H), 6.82 (dd, $J_1 = 3.6$, $J_2 = 1.2$, 2H), 3.21 (s, 4H).

^{13}C-NMR ($CDCl_3$, δ in ppm): 144.3, 127.4, 125.3, 124.0, 32.8.

MS (EI, m/e): 194 (M^+)

Synthesis of **2j**:

A solution of thiophene **2i** (10 g, 0.12 mol) and 2-thiophene acetyl chloride **2h** (23.9 g, 0.15 mol) in toluene was stirred at room temperature. $AlCl_3$ (19.8 g, 0.15 mol) was added as a solid in a time frame of 10 minutes and the reaction mixture was refluxed for 30 minutes. The solution was cooled to room temperature and quenched carefully with a 2M HCl solution. The resulting reaction mixture was extracted with toluene, washed with HCl, NaOH and H_2O and dried over $MgSO_4$. The crude product was purified by distillation to give a colorless oil (6.6 g, 32 mmol, 29 %).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.79 (dd, $J_1 = 3.7$, $J_2 = 1.1$, 1H), 7.65 (dd, $J_1 = 5.0$, $J_2 = 1.1$, 1H), 7.21 (dd, $J_1 = 3.7$, $J_2 = 2.9$, 1H), 7.13 (dd, $J_1 = 3.8$, $J_2 = 5.0$, 1H), 6.95-6.94 (m, 2H), 4.38 (s, 2H).

^{13}C NMR ($CDCl_3$, δ in ppm): 189.5, 143.8, 135.9, 135.1, 133.4, 128.9, 127.57, 127.55, 125.8, 40.8.

MS (EI, m/e): 208 (M^+).

Synthesis of **2k**:
A solution of **2j** (1 g, 4.8 mmol) was made in a mixture of CH_2Cl_2 and MeOH (1/1). The mixture was cooled to 0 °C and $NaBH_4$ (0.36 g, 9.6 mmol) was added as a solid. The resulted solution was stirred for 12 hours at room temperature. The reaction was quenched with NH_4Cl and extraction has been carried out by Et_2O and dried over $MgSO_4$. The crude product was purified by flash column chromatography to give a colorless oil (0.95 g, 4.5 mmol, 94 %).
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.25 (dd, J_1 = 4.7, J_2 = 1.7, 1H), 7.17 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 6.99-6.92 (m, 3H), 6.86 (dd, J_1 = 3.4, J_2 = 1.0, 1H), 5.14 (dd, J_1 = 6.9, J_2 = 5.6, 1H), 3.32 (dd, J_1 = 2.4, J_2 = 0.8, 2H).
^{13}C NMR ($CDCl_3$, δ in ppm): 147.6, 140.0, 127.4, 127.2, 127.1, 125.3, 125.1, 124.6, 71.4, 40.5.
MS (EI, m/e): 209 (M^+).

Synthesis of **2l**:
In a three-necked round bottom flask, the alcohol **2k** (0.95 g, 4.5 mmol) was added drop wise to a stirred solution of $SOCl_2$ (1.18 g, 9.9 mmol) in THF (60 mL). The reaction mixture was stirred under nitrogen atmosphere for 30 minutes. The solution was cooled to 0 °C and quenched carefully with a $NaHCO_3$ solution. The resulting reaction mixture was extracted with Et_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Due to the unstable nature of the product **2l** (1.0 g, 4.4 mmol), the crude product has been used without further purification or characterization.

Model compound **2e**:
To a solution of the chloride **2l** (1.0 g, 4.4 mmol) in ethanol (25 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.9 g, 18 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The model

compound **2e** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (1.24 g, 3.6 mmol) in a yield of 59 %.

^{1}H-NMR ($CDCl_3$, δ in ppm, J in Hz): 7.19 (dd, J_1 = 5.2, J_2 = 1.3, 1H), 7.06 (dd, J_1 = 5.0, J_2 = 1.3, 1H), 6.99 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 6.90 (dd, J_1 = 5.2, J_2 = 3.5, 1H), 6.84 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 6.81 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 5.62 (dd, J_1 = 9.9, J_2 = 4.7, 1H), 4.01 (q, J = 6.9, 2H), 3.84 (dd, J_1 = 14.8, J_2 = 4.7, 1H), 3.69 (q, J = 6.9, 2H), 3.43 (dd, J_1 = 14.8, J_2 = 9.9, 2H), 1.26 (t, J = 6.9, 3H), 1.25 (t, J = 6.9, 3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 194.2, 143.1, 141.3, 127.4, 127.2, 127.1, 126.9, 125.7, 124.7, 52.9, 50.0, 47.4, 38.8, 13.2, 12.3.

Synthesis of model compounds for structural defects in the conjugated polymer

Synthesis of **2m**:

A suspension of Zn powder (6.9 g, 0.1 mol) was made in anhydrous THF (200 mL). This suspension was stirred at -10 °C under nitrogen atmosphere. $TiCl_4$ (10 g, 0.05 mol) was added drop wise to this suspension. The resulted mixture was heated at reflux temperature for 1h. Afterwards the mixture was cooled to room temperature, the aldehyde **2a** was added slowly and the reflux was continued for 4 h. The mixture was poured into a K_2CO_3 (10%) solution, extracted with Et_2O and the organic layers were dried over $MgSO_4$. The product was purified by means of column chromatography with petroleum ether as eluent. The product **2m** was obtained as a colorless powder (1.37 g, 13 %).

^{1}H-NMR ($CDCl_3$, δ in ppm, J in Hz): 7.18 (dd, J_1 = 5.0, J_2 = 1.1, 2H), 7.06 (s, 2H), 7.04 (dd, J_1 = 3.6, J_2 = 1.1, 2H), 6.99 (dd, J_1 = 5.0, J_2 = 3.6, 2H).

^{13}C-NMR ($CDCl_3$, δ in ppm): 143.0, 128.3, 126.7, 125.0, 122.1.

MS (EI, m/e): 192 (M^+).

3. Results and discussion

3.1. Synthesis of the ^{13}C-labeled monomer (1g)

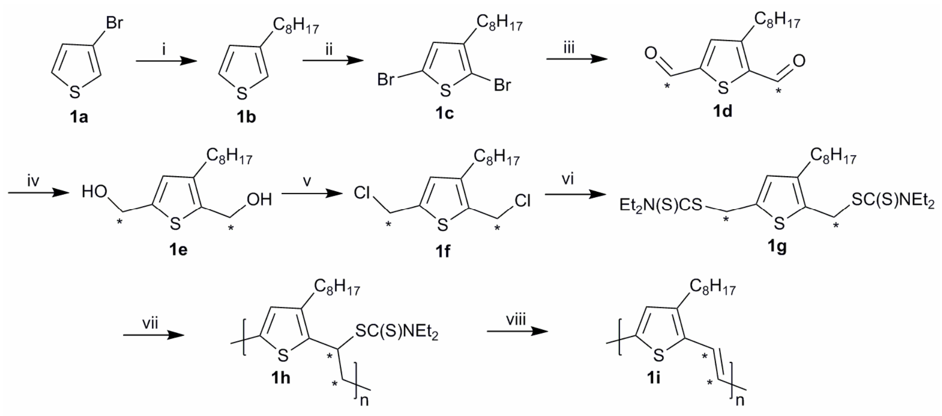
The first two steps in the synthesis of the ^{13}C-labeled monomer for octyl-PTV (O-PTV) are exactly the same as for the non labeled variant (scheme 1).[38] First, the substitution of 3-bromothiophene **1a** by means of a Kumada coupling[39] has been performed, followed by bromination of the α-positions of the thiophene **1b**.[40] In the third step of the reaction pathway, the ^{13}C label was incorporated. This was done by a metal-halogen exchange under the influence of *n*-BuLi, followed by addition of ^{13}C enriched DMF, which results into the ^{13}C-labeled dialdehyde **1d**.[41] Thereafter, the dialdehyde **1d** was reduced with lithium aluminum hydride ($LiAlH_4$), followed by chlorination of the diol **1e** with thionyl choride ($SOCl_2$).[42] Due to the instability of the product **1f**, it must be converted in situ towards the bis(dithiocarbamate) monomer **1g**.[23] The monomer **1g** was purified using column chromatography with hexane/chloroform (50/50) as an eluent.

3.2. Synthesis of the ^{13}C-labeled O-PTV precursor polymer (1h)

The optimized polymerization route towards the precursor polymer has been reported earlier.[38,43] The polymerization of the precursor polymers has been accomplished under influence of sodium bis(trimethylsilyl)amide (NaHMDS) (scheme 1). Several precursor polymer batches were prepared and purified by means of reversed precipitation in order to separate the low from the high molecular weight fractions towards characterization by GPC and quantitative NMR (see later in the characterization part).

3.3. Synthesis of the ^{13}C-labeled O-PTV (1i)

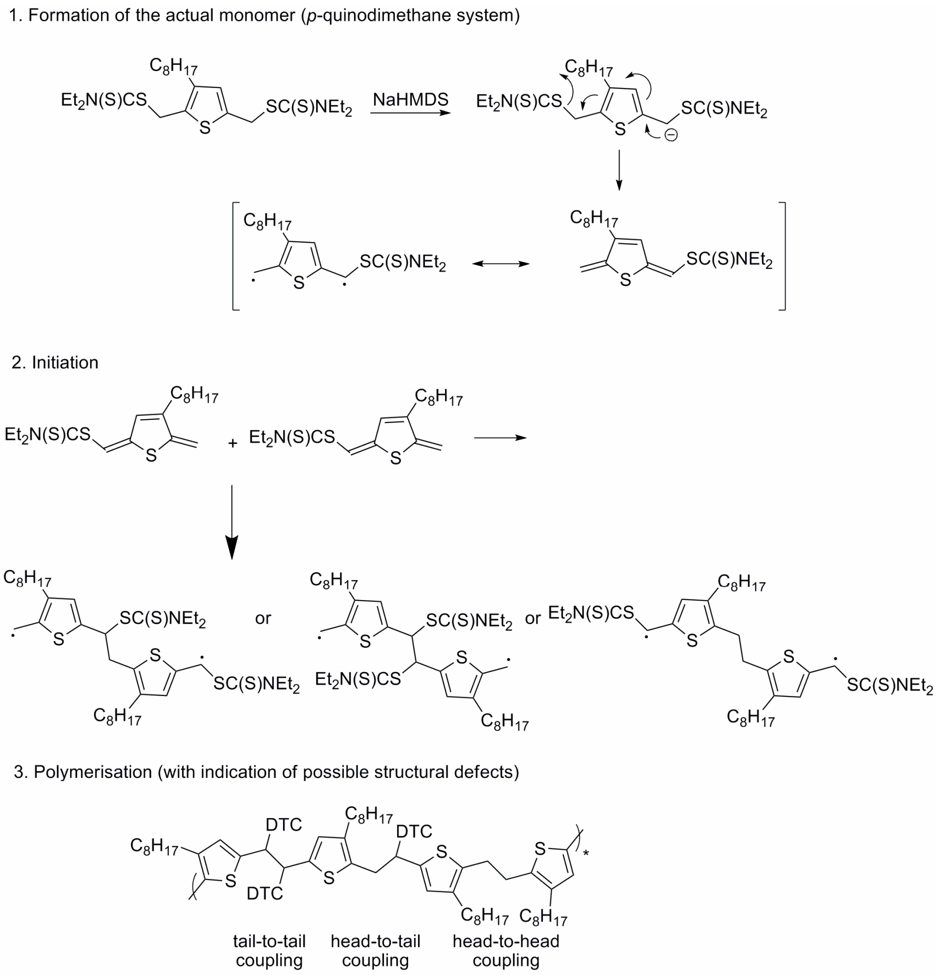
To investigate and compare two different conversion mechanisms towards the conjugated state in more detail, a large batch of precursor polymer (**1D**) has been divided in two equal parts of which one part was converted thermally while a smoother acid induced method was used for the other part (scheme 1).[44] The resulting O-PTV polymers were studied by quantitative NMR spectroscopy.



Scheme 1. Synthetic route towards ^{13}C-labeled O-PTV: (i) $BrMgC_8H_{17}$, $NiCl_2(dppp)$; (ii) NBS, DMF; (iii) 1. BuLi, 2. ^{13}C enriched DMF; (iv) $LiAlH_4$, THF; (v) $SOCl_2$, THF; (vi) $NaSC(S)NEt_2.3H_2O$, EtOH; (vii) NaHMDS, THF; (viii) ΔT or CF_3COOH.

3.4. Characterization of the ^{13}C-labeled precursor polymer

The first step in the polymerization pathway is the formation of the actual monomer, a quinodimethane system (scheme 2), by a base induced 1,6-elimination from the premonomer. Then, a self-initiating radical polymerization reaction is triggered by the recombination of two quinodimethane systems yielding the initiating species, a diradical.[45,46] In this way intrinsic defects can be formed in the central part of the precursor polymer. Consequently, the propagation occurs by addition of quinodimethane systems on both sides of the initiator. Due to the non-symmetric nature of the monomer, three different ways of monomer addition can take place for the growing polymer chain. More specific, next to the normal head-to-tail addition which will lead to the formation of double bonds upon conversion to the conjugated state, head-to-head and tail-to-tail additions can take place, which are considered as structural defects.[47-50]



Scheme 2. Polymerization mechanism for the DTC precursor route.

In order to identify and quantify the amount of structural defects present in the main chain, four different ^{13}C enriched O-PTV precursors were studied by ^{13}C NMR (**1A, 1B, 1C, 1D**) of which the molecular weights are listed in Table 1.

	GPC			NMR			
Polymer	M_n (g mol^{-1}) x10^3	PD	Average number of repetition units	183.5 ppm	162.3 ppm	59.7 & 61.5 ppm	Average number of repetition units
Precursor O-PTV							
1A	7.4	6.2	20	2.2%	9.3%	9.0%	10
1B	13.7	5.0	37	1.2%	4.4%	4.9%	19
1C	24	3.5	65	1.4%	2.0%	2.5%	34
1D	55	3.4	149	0.3%	1.1%	1.3%	74
O-PTV							
Thermal	22	2.2	100	0.4%	1.0%	1.0%	83
Acid	39	2.8	177	0.4%	0.7%	0.8%	105

Table 1. Average number of repetition units in the precursor and conjugated O-PTV polymers as calculated by GPC and NMR (Molecular weight of the repetition units is 369 and 220 Da for the precursor and conjugated polymer, respectively).

Figure 1 presents the chemical structure and carbon numbering for precursor O-PTV.

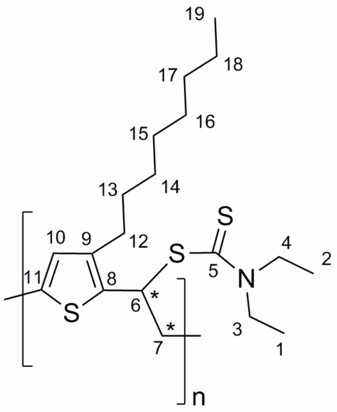


Figure 1. Chemical structure of precursor O-PTV including a carbon numbering scheme for the assignment of the resonances in the ^{13}C-NMR spectra.

Analysis of the proton-decoupled ^{13}C spectrum, DEPT and INADEQUATE experiments allowed us to assign the NMR signals as presented in Table 2. The chemical shift assignment of the carbon nuclei of the octyl side chain is based on the T_{1C} relaxation decay times. For mobile side chains it can be stated that, the closer the carbon is situated towards the side chain end, the longer its relaxation decay time will be due to less restricted conformational motions.

Carbon atom	**Chemical shift ^{13}C (ppm)**	**T_{1C} (s)**	**Chemical shift ^{1}H (ppm)**
C1/C2	12.3/13.4		1.05-1.40
C3/C4	47.4/49.8		3.66/3.96
C5	194.7		
C6	53.3		5.35
C7	37.2		3.17
C8/C11/C9	134.4/139.3/140.2		
C10	128.4		6.49
C12	29.0	0.21	2.28
C13	31.6	0.41	1.05-1.40
C14/C15	30.4	0.52	1.05-1.40
C16	30.1	0.76	1.05-1.40
C17	32.7	1.32	1.05-1.40
C18	23.4	1.85	1.05-1.40
C19	14.9	2.80	0.85

Table 2. Chemical shift assignment of the proton and carbon NMR signals of precursor O-PTV.

However, next to the signals described in Table 2, some remaining carbon signals were detected in the ^{13}C spectra (Figure 2). Based on their intensities, these signals have to arise from ^{13}C-labeled carbons situated in end groups or in structural defects in the main chain. The carbonyl signals around 183.5 and 162.3 ppm do not show a $^{1}J_{C\text{-}C}$ coupling and therefore have to represent end groups. Table 1 shows a decrease in their intensity with increasing M_n confirming that it concerns end group signals. DEPT spectra indicate that the 162.3 ppm signal originates from a quaternary carbon while the 183.5 ppm signal represents a methine carbon. The resonances at 59.7 and 61.5 ppm are methylene carbons (DEPT) and show the same trend, i.e. their intensity increases with decreasing molecular weight (see insets of figure 2) and no ${}^{1}J_{C\text{-}C}$ coupling is observed. The assignment of these end group signals to aldehyde (183.5 ppm), carboxylic acid (162.3 ppm) and methylol (59.7 and 61.5 ppm) functional groups will be discussed later on. By means of quantitative ${}^{13}C$ NMR spectroscopy, the amount of all end groups was determined and the number of repetition units was calculated and compared to that obtained by GPC as presented in Table 1. As the GPC measurements are calibrated against polystyrene standards it is not unusual that the GPC results show an overestimation of the molecular weights.

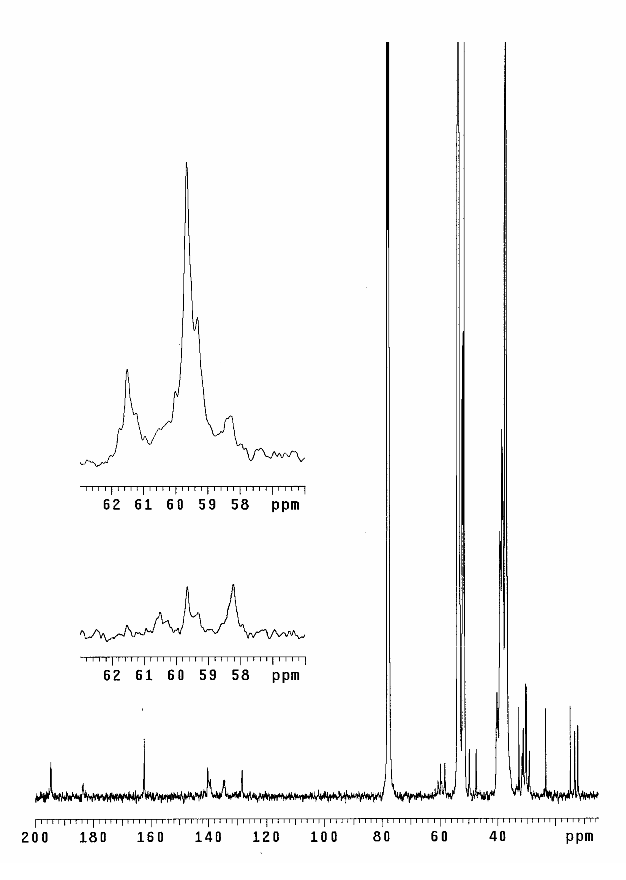
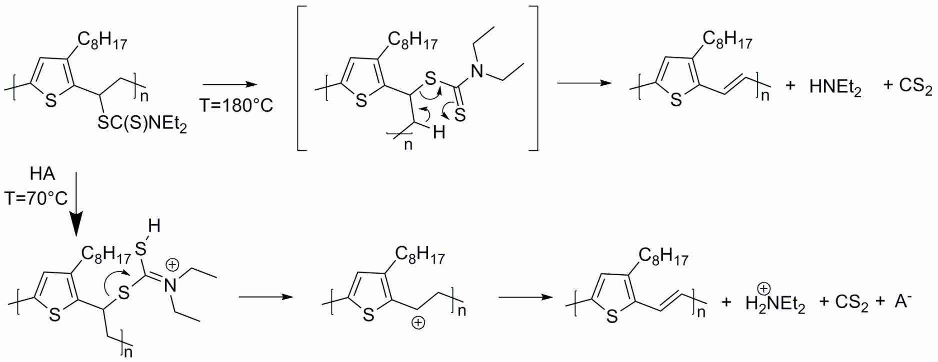


Figure 2. ${}^{13}C$ NMR spectrum of precursor polymer **1D** (top inset = polymer **1A**, bottom inset = polymer **1D**).

3.5. Characterization of the ^{13}C-labeled conjugated O-PTV

The thermal conversion of the precursor polymer to the conjugated state can be accomplished by heating a solution of precursor O-PTV in dichlorobenzene at a typical temperature of 180 °C. The mechanism is presented below as a concerted mechanism although a stepwise (radical) mechanism cannot be excluded (scheme 3). However, since these high temperatures may lead to thermal degradation, an acid induced conversion method has been developed that allows to convert the precursor O-PTV at much lower temperatures (typically 70 °C).[44]



Scheme 3. Thermal and acid induced conversion of precursor O-PTV.

At first glance the NMR spectra of the converted polymers seem to be very similar (Figure 3 and 4). The ^{13}C spectra indicate that the polymer is fully converted, i.e. no trace of the signal of the C6 carbon bearing the dithiocarbamate group (53.3 ppm) is detected anymore and the resonance characteristic of the double bond appears around 120 ppm. The resonances at 183.5, 162.3, 61.5 and 59.7 ppm are still present in the ^{13}C NMR spectrum which confirms their assignment to end groups. The amount of end groups is presented in Table 1. Two independent characterization techniques, i.e. GPC and NMR, demonstrate that the average number of repetition units is higher in acid converted O-PTV as compared to thermally converted O-PTV. Note that the higher M_n found for acid converted O-PTV, as compared to the O-PTV precursor, can be explained by a difference in hydrodynamic volume for GPC and an error margin of around 0.3% for the NMR quantification.

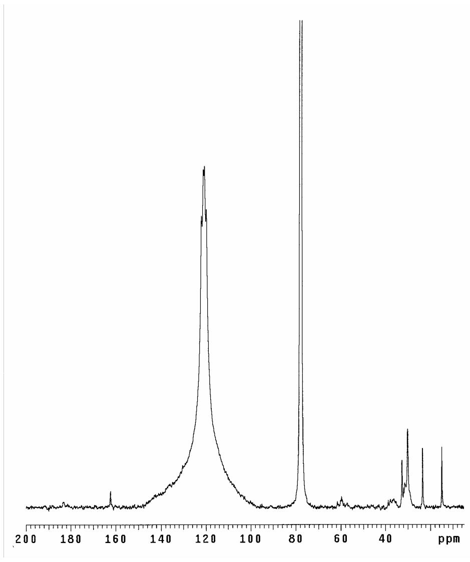


Figure 3. ^{13}C NMR spectrum of the acid converted O-PTV.

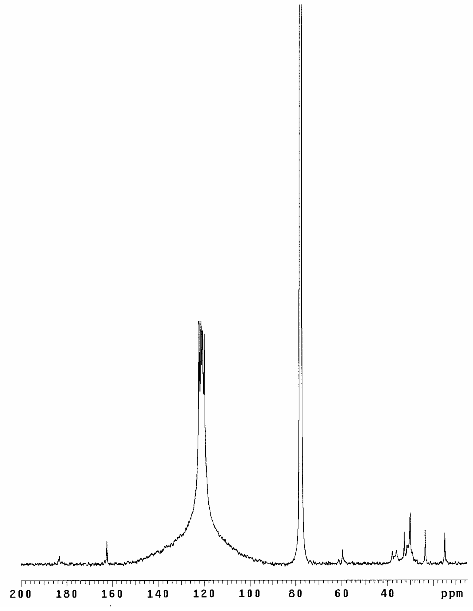
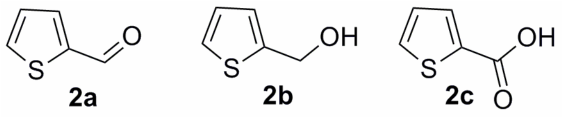


Figure 4. ^{13}C NMR spectrum of the thermally converted O-PTV.

3.6. Identification of end groups and structural defects

3.6.1. End groups

While the ^{13}C chemical shifts of the signals at 183.5 and 162.3 ppm are pointing to aldehyde and carboxylic end groups, the chemical shifts at 61.5 and 59.7 ppm point to methylol end groups. In order to confirm this assignment, model compounds **2a**, **2b** and **2c** (figure 5) have been fully characterized by NMR (see experimental section).



2a **2b** **2c**

Figure 5. Model compounds for end groups.

The assignment of the resonance at 183.5 ppm to an aldehyde group is confirmed by means of the model compound **2a**. Further oxidation towards a carboxylic acid would not be unexpected. Model compound **2c** shows a resonance at 168.8 ppm which confirms the assignment of the 162.3 ppm resonance to a carboxylic acid function. The methylol model compound **2b** was synthesised and presents a ^{13}C-resonance at 59.3 ppm which allows to assign the signals at 59.7 and 61.5 ppm to methylol end groups.

3.6.2. Structural defects

With the end groups and regular head-to-tail polymer signals determined, only some very small signals remain undefined, i.e. a signal for the precursor polymer at 58.2 ppm and two for the conjugated polymer around 36-38 ppm (remark that the chemical shift difference is too large to assign them to a doublet as a result of $J_{13C\text{-}13C}$ coupling). Since the intensity of these undefined signals, arising from ^{13}C-labeled carbons, is very small, it demonstrates that the amount of structural head-to-head and tail-to-tail polymerization defects has to be very small.

To get chemical shift information regarding the possible structural units in the precursor and conjugated polymers, several model compounds have been made. Towards the identification of structural defects at the precursor polymer level, two different model compounds **2d** (for head-to-head coupling) and **2e** (for normal head-to-tail) have been synthesized (figure 6). The synthesis of model compound **2f** for the tail-to-tail coupling has been explored extensively, but without success. The first model compound **2d** has been synthesized by the well-known Wurtz-coupling of 2-(chloromethyl)thiophene **2g** (scheme 4).[51] This chloride **2g** has been made by a two step synthesis from 2-thiophene-carbaldehyde **2a**. After a reduction with $NaBH_4$, the alcohol **2b** has been converted into the chloride **2g** by $SOCl_2$.[52]

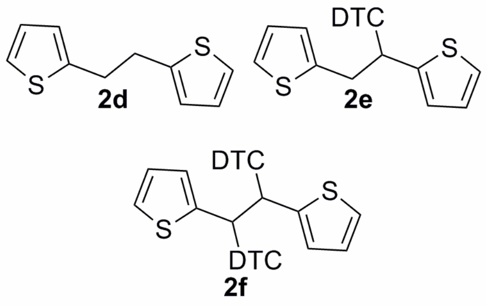
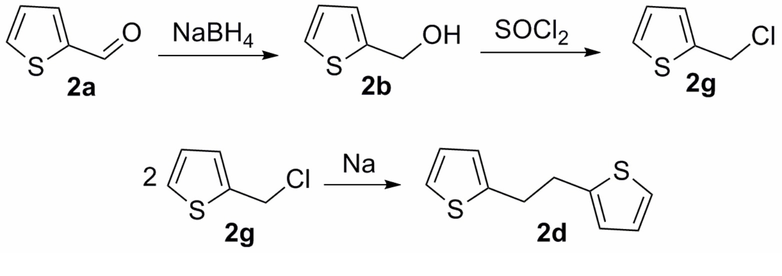
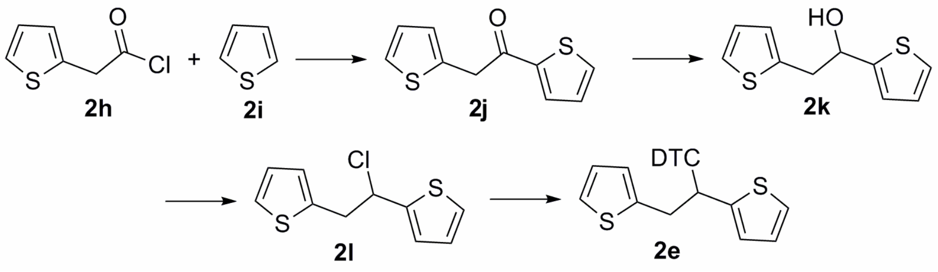


Figure 6. Model compounds for possible structural units in the precursor polymer.



Scheme 4. Synthesis of model compound **2d**.

The second model compound **2e** has been synthesized by a four step pathway (scheme 5). After a Friedel-Crafts reaction between 2-thiopheneacetylchloride **2h** and thiophene **2i,** the resulting keton **2j** has been reduced to the alcohol **2k** by $NaBH_4$ in an almost quantitative yield.[53] In a next step the alcohol **2k** was transformed into a rather unstable chloride **2l** which was immediately converted into model compound **2e** via a substitution reaction with diethyldithiocarbamic acid sodium salt.[23,52]



Scheme 5. Synthesis of model compound **2e**.

Three additional structural units can appear at the level of the conjugated O-PTV (figure 7).

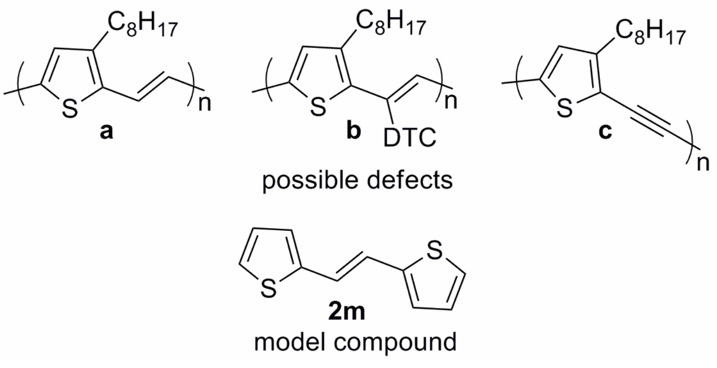
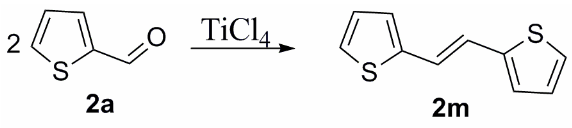


Figure 7. Additional structural units possible in O-PTV (a,b,c) and model compound for a head-to-tail unit after conversion (**2m**).

The model compound **2m** contains the double bond present in the structural unit obtained upon elimination of a normal head-to-tail unit. This model compound has been synthesized by a McMurry coupling of 2-thiophene carbaldehyde **2a** under influence of Zn and $TiCl_4$ (scheme 6).[53] The elimination of dithiocarbamate groups out of a tail-to-tail structural unit can lead to defects as presented in figure 7 for a partial elimination (**b**) and double elimination (**c**). The latter would show a triple bond resonance signal that would be easily observed in the ^{13}C-NMR spectra around 90 ppm and which is not detected.



Scheme 6. Synthesis of model compound **2m**.

Regarding the undefined signal at 58.2 ppm in the ^{13}C spectrum of the precursor polymer, its relative intensity is not influenced by the molecular weight. This suggests that the corresponding carbon atom resides in the main chain. However, since the signal appears as a singlet, the corresponding ^{13}C atom should be linked to a chemically identical ^{13}C atom, explaining why no $J_{C\text{-}C}$ coupling is observed. It can be expected that C6 / C7 of a tail-to-tail addition would have a resonance at this position (Figure 8).

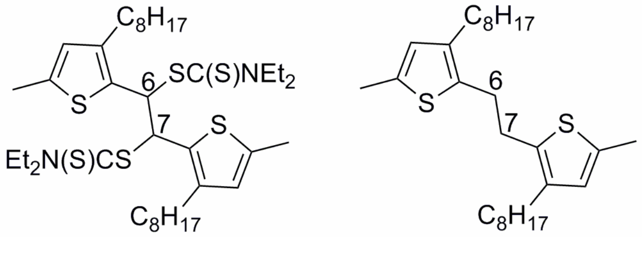


Figure 8. Chemical structure of tail-to-tail (left) and head-to-head (right) defects in precursor O-PTV.

Moreover, the observations that a) DEPT spectra indicate that this signal corresponds to a CH group and b) this signal disappears in the conjugated polymer are strong indications to assign the resonance at 58.2 ppm to a tail-to-tail defect.

The model compound **2d** shows a methylene signal at 32.8 ppm. Since no signal was detected at this position in the ^{13}C spectrum of the precursor polymer, no direct evidence for head-to-head defects was found at the precursor level. It can however not be excluded that the position of this methylene signal is slightly shifted downfield in the precursor polymer and so would end up in the foot of the huge C7 signal (37.2 ppm) of the normal head-to-tail units. The ^{13}C spectrum of converted O-PTV (see below) should make this clear.

The chemical shifts of the bridge methylene and methine carbon resonances of model compound **2e** (38.8 and 52.9 ppm) are in good agreement with those of C7 and C6 in normal head-to-tail units of the precursor O-PTV (37.2 and 53.3 ppm).

Regarding the two undefined signals in the ^{13}C spectrum of the conjugated polymer at 36-38 ppm, DEPT spectra indicate that these resonances correspond to CH_2 groups. These methylene signals might arise from units of incomplete elimination (represented by model compound **2e**) or from head-to-head defects (represented by model compound **2d**). However, incomplete elimination can be excluded since no signal appears from the dithiocarbamate group bearing methine carbon around 53.3 ppm. Moreover, since no $J_{13C\text{-}13C}$ coupling is observed, these resonances are assigned to head-to-head defects. As discussed above, these resonances were not observed for the precursor O-PTV as they were masked by the huge C7 signal of normal head-to-tail structural units.

Regarding the 58.2 ppm signal in the precursor spectrum, assigned to tail-to-tail defects, no characteristic signal of a triple bond is detected in the spectra of the converted polymers (around 90 ppm). This indicates that no full elimination of the tail-to-tail defects occurs, leaving a structural unit as indicated in Figure 7 (**b**) of which the carbon signals will end up in the huge signal of the ^{13}C-labeled olefinic carbons of the normal head-to-tail units.

The amount of defects has been calculated from the ^{13}C NMR spectra. For the head-to-head defects, measured via the spectra of O-PTV, an amount of 0.6 % is found. The amount of tail-to-tail defects, measured via the spectrum of the precursor O-PTV, is rather similar, i.e. in the order of 0.6 %. Therefore, it can be definitely concluded that the dithiocarbamate precursor route is an excellent route towards PTV-based polymers with a very low amount of structural defects.

Last but not least, the ^{13}C NMR spectra clearly demonstrate that the relative intensity of the methylene carbon signal of head-to-head defects (2 x 0.6%) is much smaller than this of the carbons in end groups. This indicates that the initiation unit of the polymerization reaction cannot be a head-to-head unit solely, as the amount of carbons in end groups and in methylene groups of head-to-head units should than be identical. For substituted PTV's prepared via the DTC route, it can be expected that towards the formation of the actual monomer, the long octyl side chains will stimulate the base to abstract an acid proton at the opposite site of the premonomer due to steric hindrance (scheme 2).[54] During the next initiation step, two of these *p*-quinodimethane systems can than combine in three different ways of which the head-to-tail initiation seems to be preferential. This can explain the low amount of head-to-head (and tail-to-tail) structural units in these polymers.

4. Conclusions

This study describes an extensive structural characterization of ^{13}C-labeled 3-octyl-PTV and its precursor polymer, prepared via the dithiocarbamate route, by means of several NMR techniques and model compounds. Aldehydes, carboxylic acids and methylol groups have been detected as polymerization end groups. It is further demonstrated that the dithiocarbamate precursor route is an excellent route towards PTV-based polymers with a minor amount of structural defects, i.e. head-to-head and tail-to-tail structural defects are found in an amount as low as 0.6%. This probably because, due to steric constraints caused by the side chains, the head-to-tail initiation is preferential in the polymerization reaction of substituted PTV derivatives. Last but not least, with respect to the conversion of the precursor polymer to its conjugated state, it is shown that thermal degradation can be avoided by using a smooth, acid induced elimination procedure.

5. Acknowledgement

We gratefully acknowledge Belspo in the frame of network IAP P6/27. We also thank the EU for the FP6-Marie Curie-RTN ‘SolarNtype’ (MRTN-CT-2006-035533) and the IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for the financial support via the SBO-project 060843 ‘PolySpec’. Last but not least, the support of the Fund for Scientific Research-Flanders (FWO) via the projects, G.0252.04N and G.0091.07N is acknowledged.

6. References

[1] Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377.

[2] Hu, P. A.; Li, K.; Chen, W.; Peng, L.; Chu, D.; O-Neill, W. *J. Micromech. Microeng.* **2010**, *20*, 075032/1–075032/7.

[3] Kano, M.; Minari, T.; Tsukagoshi, K. Appl. Phys. Express **2010**, *3*, 051601/1–051601/3.

[4] Gerard, M.; Chaubey, A.; Malhotra, B. D. *Biosens. Bioelectron.* **2002**, *17*, 345–359.

[5] Burroughes, J. H.; Bradley, D. D. C.; Brown, A; Marks, R. N.; Mackay, K; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.

[6] Gomez, E. D.; Lee, S. S.; Kim, C. S.; Loo, Y-L. *Molecular and Organic Electronic Devices* **2010**, 109–152.

[7] Chen, Z.; Liu, Q.; Singh, S. P.; Zen, A. *PCT Int. Appl.* **2010**, W0210096010 A1 20100826.

[8] Spanggaard, H.; Sariciftci, F. C. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 125–146.

[9] Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338.

[10] Gevorgyan, S. A.; Krebs, F. C. *Molecular and Organic Electronic Devices* **2010**, 291–309.

[11] Kietzke, T. *Molecular and Organic Electronic Devices* **2010**, 253–289.

[12] Servaites, J. D.; Ratner, M. A.; Marks, T. J. *Appl. Phys. Lett.* **2009**, *95*, 163302/1– 163302/3.

[13] Zhang, C.; Tong, S. W.; Jiang, C.; Kang, E. T.; Chan, D. S. H.; Zhu, C. Appl. Phys. Lett. 2008, *92*, 083310/1–083310/3.

[14] Winder, C.; Sariciftci, N.S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.

[15] Goris, L.; Loi, M. A.; Cravino, A.; Neugebauer, H.; Sariciftci, N.S.; Polec, I.; Lutsen, L.; Manca, J.; De Schepper, L.; Vanderzande, D. *Synthetic Met*. **2003**, *138*, 249–253.

[16] Colladet, K.; Nicolas, M.; Goris, L.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, *7*, 451–452.

[17] Shaheen, S.E.; Vangeneugden, D.; Kiebooms, R.; Vanderzande, D.; Fromherz, T.; Padinger, F.; Brabec, D.J.; Sariciftci, N.S. *Synthetic Met.* **2001**, *121*, 1583–1584.

[18] Hou, J.; Chen, H-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586–15587.

[19] Chen, C.-P.; Chan, S-H.; Chao, T-C.; Ting, C.; Ko, B-T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833.

[20] Mei, J.; Heston, N. C.; Vasilyeva, S. V.; Reynolds, J. R. *Macromolecules* **2009**, *42*, 1482–1487.

[21] Chen, C-P.; Chan, S-H.; Chao, T-C.; Ting, C.; Ko, B-T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833.

[22] Bundgaard, E.; Krebs, F. C. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 954–985.

[23] Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19–26.

[24] Yeon-Beom, L.; Hong-Ku, S.; Seung-Won, K. *Macromol. Rapid Comm.* **2003**, *24*, 522–526.

[25] Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Boer, B. *Polym. Rev.,* **2008**, *48*, 531–582.

[26] Kim, J. Y.; Qin, Y.; Stevens, D. M.; Ugurlu, O.; Kalihari, V.; Hillmyer, M. A.; Frisbie, C. D. *J. Phys. Chem. C* **2009**, *113*, 10790–10797.

[27] Gavrilenko, A. V.; Matos, T. D.; Bonner, C. E.; Sun, S-S.; Zhang, C.; Gavrilenko, V. I. *J. Phys. Chem.* **2008**, *112*, 7908–7912.

[28] Van De Wetering, K.; Brochon, C.; Ngov, C.; Hadziioannou, G. *Macromolecules* **2006**, *39*, 4289–4297.

[29] Jen, K. Y.; Jow, R.; Eckhardt, H.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1987**, 56, 49–53.

[30] Yamada, D.; Tokito, S. H.; Tsutsui, T; Saito, S *J. Chem. Soc., Chem. Commun.* **1987**, 00, 1448–1449.

[31] Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Poly. Comm.* **1987,** 28 (8), 229-231.

[32] Mitchell, W. J.; Pena, C.; Burn, P. L. *J. Mater. Chem.* **2002**, *12*, 200–205.

[33] Kesters, E.; Gillissen, S.; Motmans, F.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2002**, *35*, 7902–1910.

[34] van Breemen, A. J. J. M.; Issaris, A. C. J.; de Kok, M. M.; Van Der Borght, M. J. A. N.; Adriaensens, P. J.; Gelan, J. M. J. V.; Vanderzande, D. J. M. *Macromolecules* **1999**, *32*, 5728–5735.

[35] Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin solid films* **2004**, 451-452, 472–579.

[36] Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J. *J. SPIE Proc*. **2004**, 52–59.

[37] Banishoeib, F.; Henckens, A.; Fourier, S.; Vanhooyland, G.; Breselge, M; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, N. S. *Thin Solid Films* **2008**, 516 (12), 3978-3988.

[38] Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, 10231–10240.

[39] Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347–3354.

[40] Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner, F.; Gaudl, K.U.; Caro, M.B.; Fischer, P. *J. Chem. Soc. Perk. T. 2* **1993**, 489–494.

[41] Frey, J.; Bond, A. D.; Holmes, A. B. *Chem. Commun.* **2002**, 2424–2425.

[42] Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925–4932.

[43] Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

[44] Diliën, H.; Vandenbergh, J.; Banishoeib, F.; Adriaensens, P. J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. Acid induced conversion of dithiocarbamate precursor polymers into conjugated materials, *Macromolecules* **2011**, accepted.

[45] Issaris, A.; Vanderzande, D.; Gelan J. *Polymer* **1997**, *38*, 2571–2574.

[46] Hontis, L.; Vrindts, V.; Lutsen, L.; Vanderzande, D.; Gelan J. *Polymer* **2001,** *42*, 5793–5796

[47] Hontis, L.; Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1999**, *40*, 6615–6617.

[48] Schwalm, T.; Wieskcke, J.; Immel, S.; Rehahn, M. *Macromolecules* **2007**, *40*, 8842–8854.

[49] Hontis, L.; Vrindts, V.; Vanderzande, D.; Lutsen L. *Macromolecules* **2003,** *36,* 3035-3044

[50] Adriaensens, P.; Van der Borght, M.; Hontis, L.; Issaris, A.; van Breemen, A.; de Kok M.; Vanderzande, D.; Gelan, J. *Polymer* **2000**, *41*, 7003–7009.

[51] Davis, M.C. *Synthetic Commun.* **2005**, *35*, 2079–2083.

[52] Kieseritzky, F.; Hellberg, J.; Wang, X.; Inganäs, O. *Synthesis* **2002**, *9*, 1195–1200.

[53] Chen, B.; Wu, Y.; Wang, M.; Wang, S.; Sheng S.; Zhu, W.; Sun, R.; Tian, H. *Eur. Polym. J.* **2004**, *40*, 1183–1191.

[54] Vandenbergh, J.; Wouters, J.; Adriaensens, P. J.; Mens, R.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. J. M. *Macromolecules*, **2009**, *42*, 3661–3668.

Chapter 6: Joint theoretical-experimental NMR study of small thiophene based model compounds as a guideline for the assignment of structural defects in poly(thienylene vinylene) (PTV) based conjugated polymers

In the field of plastic electronics low band gap conjugated polymers like poly(thienylene vinylene) (PTV) and derivatives like poly(3-octyl thienylene vinylene) (O-PTV) are a promising class of materials which can be obtained with high molecular weight via the so called dithiocarbamate precursor route. This paper describes the full NMR chemical shift assignment of a series of model compounds related to possible structural defects that can appear during the polymerization of PTV's (e.g. head-to-head and tail-to-tail defects) from a joint experimental-theoretical point of view. Also model compounds for possible end groups are presented. This information, combined with the NMR characterization of PTV's of which the vinylene carbons are ^{13}C-labeled, will allow to identify and quantify the amount of structural defects and end groups. Besides, since little literature information is available regarding the proton and carbon NMR chemical shifts of this kind of thiophene derivatives, the results also provide interesting input for NMR chemical shift prediction software.

1. Introduction

In the field of plastic electronics various classes of conjugated polymers have been studied.[1-6] To overcome the mismatch between the absorbance

---

* By H. Diliën, L. Marin, E. Botek, B. Champagne, V. Lemaur, D. Beljonne, R. Lazzaroni, T. J. Cleij, L. Lutsen, D. Vanderzande, P. J. Adriaensens for Journal of Physical Chemistry, 2011, in preparation

window of the semi-conducting polymer and the solar spectrum, low band gap materials have been investigated thoroughly.[7-13] Since these materials absorb light of longer wavelengths, poly(thienylene vinylene) (PTV) based polymers are promising materials.[14-20] The synthesis of PTV derivatives is however very challenging. Two different strategies are applied, i.e. condensation reactions[21,22] which lead to low molecular weight polymers and precursor routes.[23-32] It has been presented earlier that the dithiocarbamate precursor route is the only route which allows to create stable monomers for polymerization.[33-37] In ongoing work, the precursor route towards poly(3-octyl thienylene vinylene) (O-PTV) is being explored extensively by NMR spectroscopy. This in order to identify and quantify the polymer end groups and possible structural defects due to e.g. head-to-head or tail-to-tail monomer additions in the polymerization process. Therefore, ^{13}C-labeled vinylene carbons are introduced into the polymer which remains, due to the long octyl side chains, soluble in several organic solvents.[38] Unfortunately, literature does not provide a lot of information concerning the complete assignment of proton and carbon chemical shifts of these defects. Therefore, a joint experimental-theoretical NMR study has been set up based on several relevant model compounds. The results also provide interesting input for NMR chemical shift prediction software, since few experimental data on this type of compounds is available.

Also the regioregularity of O-PTV is evaluated on basis of predicted carbon chemical shifts. According to literature, poly(thienylene vinylene) derivatives which were prepared via a condensation reaction are 100 % regioregular. One claims that the regioregularity can be determined by ^{1}H and ^{13}C NMR spectroscopy.[22,39] Therefore, the most stable geometrical conformations of relevant trimers will be determined by theoretical calculations, followed by prediction of their chemical shifts. The theoretical results are compared with experimental data at the level of the conjugated polymer.

2. Experimental section

2.1. General

All the commercially available chemicals were purchased from Acros or Sigma-Aldrich and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone. All reactions were carried out under inert atmosphere.

2.2. Techniques

^{1}H and ^{13}C NMR spectra were taken on a Varian Inova 300 or 400 spectrometer from solutions in deuteroform (D 99.8%). The chemical shifts were calibrated by means of the (remaining) proton and carbon resonance signals of $CDCl_3$ (7.24 and 77.7 ppm for ^{1}H and ^{13}C, respectively). Quantitative 1D NMR experiments are complemented with other pulssequences like APT (Attached Proton Test), 2D-HETCOR (Heteronuclear Correlation Spectroscopy) and 2D-INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment). The latter is used for some compounds to assign the carbon-backbone. GC/MS analyses were carried out on TSQ – 70 and Voyager mass – spectrometers (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB. Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans).

2.3. Synthesis

Model compounds **2c, 2f** and **2h** were commercially available. The synthesis of model compounds **1b**, **1c, 1d, 2d, 2e** and **2g** [38] as well as these of **2a** and **2b**[40] has been reported earlier.

Model compound **1b**:

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.19 (dd, J_1 = 5.2, J_2 = 1.3, 1H), 7.06 (dd, J_1 = 5.0, J_2=1.3, 1H), 6.99 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 6.90 (dd, J_1 = 5.2, J_2 = 3.5, 1H), 6.84 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 6.81 (dd, J_1 = 3.5 ,J_2 = 1.3, 1H), 5.62 (dd, J_1 = 9.9, J_2 = 4.7, 1H), 4.01 (q, J = 6.9, 2H), 3.84 (dd, J_1 = 14.8, J_2 = 4.7, 1H), 3.69 (q, J = 6.9, 2H), 3.43 (dd, J_1 = 14.8, J_2 = 9.9, 1H), 1.26 (t, J = 6.9, 3H), 1.25 (t, J = 6.9, 3H).

^{13}C NMR ($CDCl_3$, δ in ppm): 194.2, 143.1, 141.3, 127.4, 127.2, 127.1, 126.9, 125.7, 124.7, 52.9, 50.0, 47.4, 38.8, 13.2, 12.3.

Model compound **1c**:

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.14 (dd, J_1 = 5.1, J_2 = 1.2, 2H), 6.93 (dd, J_1 = 5.1, J_2 = 3.6, 2H), 6.82 (dd, J_1 = 3.6, J_2 = 1.2, 2H), 3.21 (s, 4H).

^{13}C NMR ($CDCl_3$, δ in ppm): 144.3, 127.4, 125.3, 124.0, 32.8.

Model compound **1d**:

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.18 (dd, J_1 = 5.0, J_2 = 1.1, 2H), 7.06 (s, 2H), 7.04 (dd, J_1 = 3.6, J_2=1.1, 2H), 6.99 (dd, J_1 = 5.0, J_2 = 3.6, 2H).

^{13}C NMR ($CDCl_3$, δ in ppm): 143.0, 128.3, 126.7, 125.0, 122.1.

Model compound **2a**:

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.14 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 7.01 (dd, J_1 = 3.5, J_2 = 1.2, 1H), 6.88 (dd, J_1 = 5.1, J_2 = 3.5, 1H), 4.75 (s, 2H), 3.98 (q, J = 7.3, 2H), 3.65 (q, J = 7.3, 2H), 1.23 (2t, J_1 = 7.3, 6H).

^{13}C NMR ($CDCl_3$, δ in ppm): 194.4, 139.2, 127.3, 127.0, 125.6, 49.8, 47.1, 36.7, 12.8, 11.9.

Model compound **2b**:

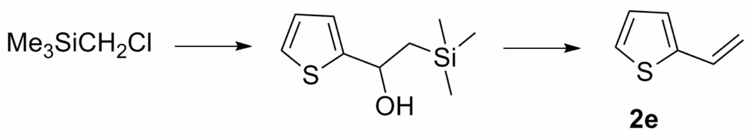
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.09 (d, J = 5.1, 1H), 6.81 (d, J_1 = 5.1, 1H), 4.67 (s, 2H), 4.01 (q, J = 7.4, 2H), 3.68 (q, J = 7.4, 2H), 2.58 (t,

J = 7.7, 2H), 1.57 (p, J = 7.7, 2H), 1.36-1.21 (m, 16 H), 0.87 (t, J = 6.8, 3H).
^{13}C NMR ($CDCl_3$, δ in ppm): 195.0, 141.8, 131.0, 129.1, 124.2, 49.7, 47.1, 35.5, 32.3, 31.2, 29.9 (2X), 29.7, 28.8, 23.1, 14.6, 12.9, 12.0.

Model compound **2c**:
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.19 (dd, J_1 = 5.2, J_2 = 1.2, 1H), 7.02 (dd, J_1 = 5.2, J_2 = 3.4, 1H), 6.89 (m, 1H), 2.62 (d, J = 1.2, 3H).
^{13}C NMR ($CDCl_3$, δ in ppm): 139.8, 127.3, 125.6, 123.5, 15.2.

Model compound **2d**:
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.22 (dd, J_1 = 4.9, J_2 = 3.1, 1H), 6.92 (dd, J_1 = 4.9, J_2 = 1.3, 1H), 6.91 (dd, J_1 = 3.1, J_2 = 1.3, 1H), 2.61 (t, J = 7.7, 2H), 1.60 (p, J = 7.7, 2H), 1,36-1,21 (m, 10H), 0.87 (t, J = 6.37, 3H).
^{13}C NMR ($CDCl_3$, δ in ppm): 143.6, 128.7, 125.5, 120.3, 32.6, 31.3, 31.0, 30.2, 30.12, 30.06, 23.4, 14.8.

Synthesis of model compound **2e**:



Step 1: 1-(thiophen-2-yl)-2-(trimethylsilyl)ethanol
Chloromethyl-trimethylsilane (6.1g, 50.0 mmol) was added drop wise to a suspension of magnesium turnings (1.25g, 50 mmol) in dry THF (150 mL) and the mixture was allowed to react under reflux for 4h. To the freshly prepared Grignard solution, cooled at -78°C, thiophene-2-carbaldehyde (5.32g, 47.5 mmol) was added drop wise. The mixture was allowed to react for 1h at -78°C, then at room temperature, overnight. The reaction mixture was poured in 50 mL cold NH_4Cl solution (10%, vol.); the organic layer was washed with H_2O, $NaHCO_3$ (10%, vol.), dried over anhydrous Na_2SO_4 and the solvent removed under reduced

pressure. Purification of the crude product by vacuum distillation afforded the pure alcohol as colorless oil (8.72g, 87% yield).

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.21 (dd, J_1 = 4.9, J_2 = 1.4, 1H), 6.94 (dd, J_1 = 3.5, J_2 = 1.4, 1H), 6.91 (dd, J_1 = 4.9, J_2 = 3.5, 1H), 5.12-5.04 (m, 1H), 1.95 (d, J = 4.42, 1H), 1.30 (dd, J_1 = 7.38, J_2 = 6.04, 2H), 0.02-0.00 (m, 9H).

MS (EI, m/e): 200 (M^+).

Step 2: Synthesis of 2-vinyl thiophene **2e**

Concentrated sulfuric acid (6 drops) was added to a solution of 1-(thiophen-2-yl)-2-(trimethylsilyl)ethanol (2.0g, 10 mmol) in dry THF (10 mL) and then mixture was allowed to react under reflux for 2h. The reaction was quenched by the addition of cold NH_4Cl solution (10%, vol.) and the aqueous phase was extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the pure title compound **2e** in a quantitative manner.

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.16 (dd, J_1 = 3.6, J_2 = 1.9, 1H), 6.95 (dd, J_1 = 3.6, J_2 = 1.9, 1H), 6.94 (t, J = 3.6, 1H), 6.81 (dd, J_1 = 10.9, J_2 = 17.3, 1H), 5.57 (d, J = 17.5, 1H), 5.14 (d, J = 10.9, 1H).

^{13}C NMR ($CDCl_3$, δ in ppm): 143.7, 130.5, 128.0, 126.5, 125.0, 113.9.

MS (EI, m/e): 110 (M^+).

Model compound **2f**:

^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 9.91 (d, J = 1.2, 1H), 7.77 (dd, J_1 = 3.9, J_2 = 1.2, 1H), 7.75 (dt, J_1 = 4.9, J_2 = 1.2, 1H), 7.20 (dd, J_1 = 4.9, J_2 = 3.9, 1H).

^{13}C NMR ($CDCl_3$, δ in ppm): 183.7, 144.6, 137.0, 135.8, 129.0.

Model compound **2g**:

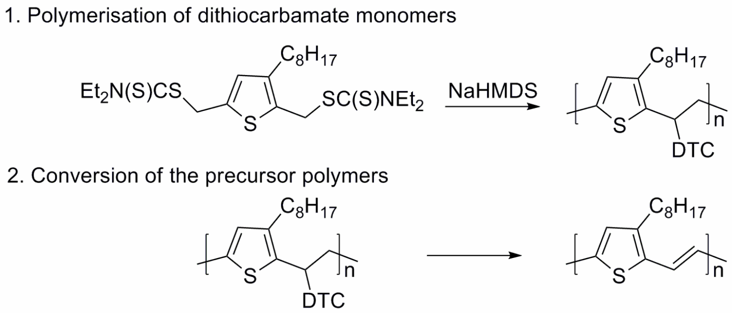
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.27 (dd, J_1 = 5.0, J_2 = 1.3, 1H), 7.00 (m, 1H), 6.96 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 4.82 (d, J = 3.5, 2H), 1.79 (s, 1H).

^{13}C NMR ($CDCl_3$, δ in ppm): 144.2, 127.0, 125.6, 125.5, 59.3.

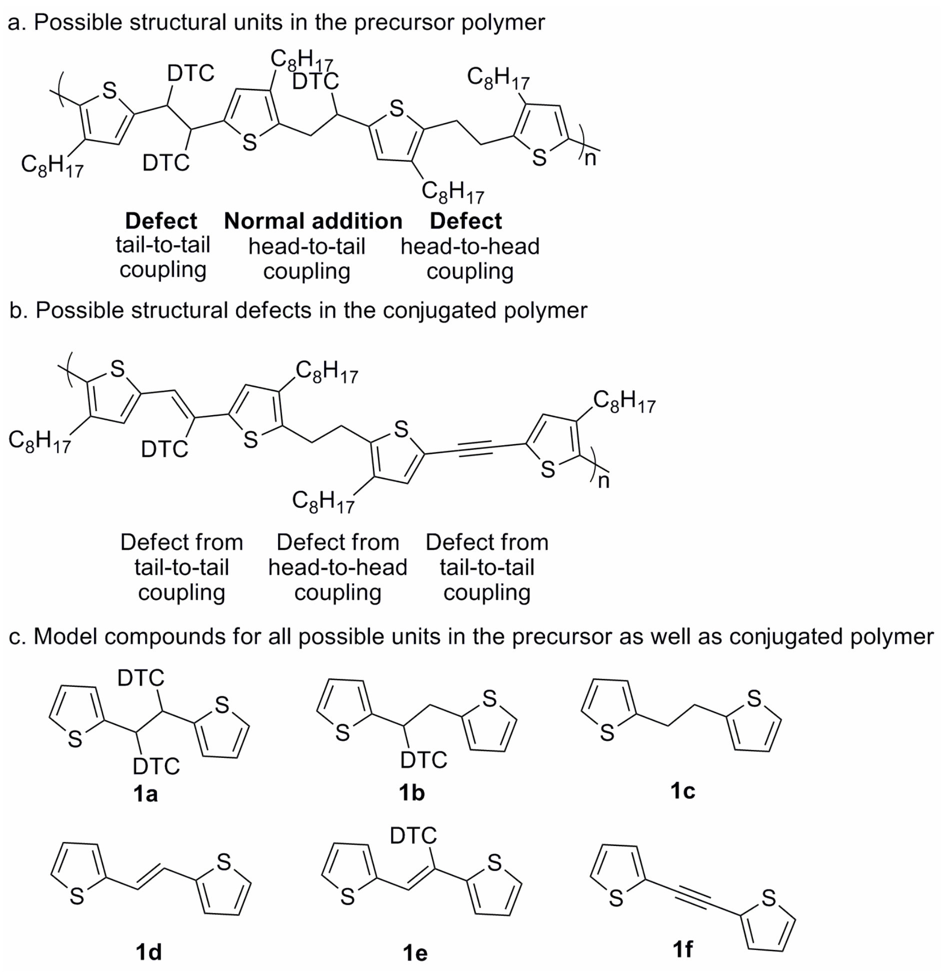
Model compound **2h**:
^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 12.50 (s, 1H), 7.89 (dd, J_1 = 3.8, J_2 = 1.2, 1H), 7.64 (dd, J_1 = 5.0, J_2 = 1.2, 1H), 7.13 (dd, J_1 = 5.0, J_2 = 3.8, 1H).
^{13}C NMR ($CDCl_3$, δ in ppm): 168.8, 135.8, 134.8, 133.5, 128.8.

3. Results and discussion

Scheme 1 describes the polymerization of 3-octylthiophene dithiocarbamate monomers towards O-PTV via the so called dithiocarbamate precursor route.[33] The first step consists in the formation of the so-called precursor polymer by normal head-to-tail addition of monomers. However, several structural defects can appear as a result of head-to-head and tail-to-tail additions (Figure 1). In a second step, the precursor polymer is converted into the conjugated state by means of an elimination reaction.[41] The structures of possible defects in the conjugated polymer are represented in figure 1b. In order to identify the NMR chemical shifts of all these structural units in the precursor as well as conjugated polymer a joint theoretical-experimental study has been performed via a series of model compounds (figure 1c).



Scheme 1. Polymerization of 3-octyl dithiocarbamate monomers towards O-PTV. (DTC = DiThioCarbamate = $-SC(S)NEt_2$)



a. Possible structural units in the precursor polymer

b. Possible structural defects in the conjugated polymer

c. Model compounds for all possible units in the precursor as well as conjugated polymer

Figure 1. Possible structural defects in O-PTV.

3.1. Model compounds for possible structural units in the precursor and conjugated O-PTV

In the precursor polymer three structural units can appear which are represented by model compounds **1a**, **1b** and **1c**. Two of them are described from a theoretical as well as an experimental point of view, i.e. the model compound representing the normal head-to-tail units (**1b**) and the structural defect resulting from a head-to-head monomer addition (**1c**). The synthesis of these two model compounds was reported earlier.[38] The NMR characterization of these model compounds is described later on. The third possible unit in the precursor polymer is a tail-to-tail defect (**1a**) for which the chemical shifts will be predicted from theoretical calculations.

In the conjugated PTV polymer, six different situations can appear. Next to **1c**, the structural unit **1b** can remain present due to an incomplete conversion of normal head-to-tail units towards a trans double bond (**1d**). Model compound **1d** has been synthesized and the NMR shifts have been determined. Structures **1a** and **1e** can appear in the conjugated polymer due to incomplete elimination of a tail-to-tail defect. Elimination of both dithiocarbamate groups of a tail-to-tail defect results in the formation of triple bonds as in **1f**. Due to sterical hindrance, model compounds **1a** and **1e** were not experimentally available. The chemical shifts of these model compounds will be predicted from theoretical calculations.

3.2. Reference compounds for DFT theoretical modeling

To provide experimental data for the DFT calculations, several previously synthesized,[38,40] model compounds have been fully characterized with ^{1}H and ^{13}C NMR techniques (**2a-2h**) (figure 2). Based on this chemical shift information, the chemical shifts of all model compounds for structural units, but especially these of compounds **1a**, **1e** and **1f** will be determined by theoretical calculations.

.

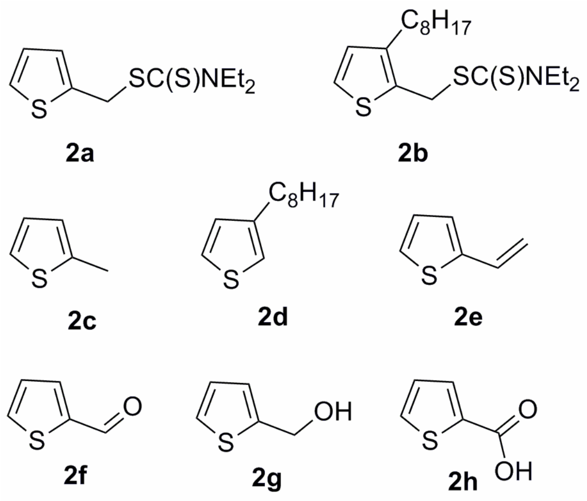


Figure 2. Reference compounds for DFT theoretical modeling.

3.3. NMR characterization of the reference compounds

In the next paragraphs the assignment of the proton and carbon chemical shifts of these model compounds will be discussed based on experimental NMR information. All the thiophene structures will be numbered as indicated in figure 3.

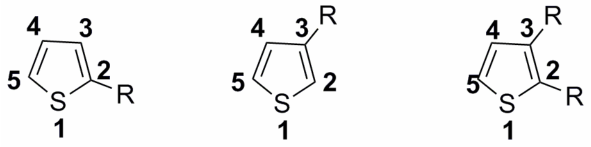


Figure 3. Numbering of the thiophene structures.

The chemical shift assignment of the carbon atoms of 2-thiophene carbaldehyde **2f** (figure 4) has been accomplished by means of 2D-INADEQUATE. Starting from the aldehyde carbon at 183.69 ppm, the carbon resonances of C2, C3, C4 and C5 could be assigned to the signals at 144.61, 137.04, 128.96 and 135.78 ppm, respectively. The corresponding proton shifts were assigned by HETCOR, i.e. H-3 appears at 7.77 ppm (dd, J_1 = 3.9, J_2 = 1.2, 1H), H-5 at 7.75 ppm (dt, J_1 = 4.9, J_2

= 1.2, 1H) and H-4 can be assigned at 7.20 ppm (dd, $J_1 = 4.9$, $J_2 = 3.9$, 1H).

Figure 4. Assignment of the chemical shifts of 2-thiophene carboxaldehyde **2f**.

The chemical shifts of 2-thiophene methanol **2g** (figure 5) were assigned by means of selective proton decoupling. First the proton coupling between H-3 and the two benzylic protons was removed by selective decoupling of the benzylic protons at 4.82 ppm (d, J = 3.5 Hz, 2H). By this H-3 could be assigned to the signal at 7.00 ppm (m, 1H). The other protons are assigned based on their coupling constants. H-4 appears at 6.96 ppm (dd, $J_1 = 5.0$ Hz, $J_2 = 3.5$ Hz, 1H) and H-5 is assigned at 7.27 ppm (dd, $J_1 = 5.0$ Hz, $J_2 = 1.3$ Hz, 1H). The carbon shifts have been assigned by APT and HETCOR.

Figure 5. Assignment of the chemical shift of 2-thiophene methanol **2g**.

The signals of 2-thiophene carboxylic acid **2h** (figure 6) are assigned by means of 2D-INADEQUATE. Starting from the carboxylic carbon at 168.8 ppm, the carbon resonances of C2, C3, C4 and C5 could be assigned to the signals at 133.5, 135.8, 128.8 and 134.8 ppm, respectively. The corresponding proton shifts were assigned by HETCOR, i.e. H-3 can be attributed to 7.89 ppm (dd, $J_1 = 3.8$, $J_2 = 1.2$, 1H), H-5 to 7.64 ppm (dd, $J_1 = 5.0$, $J_2 = 1.2$, 1H) and H-4 to 7.13 ppm (dd, $J_1 = 5.0$, $J_2 = 3.8$, 1H).

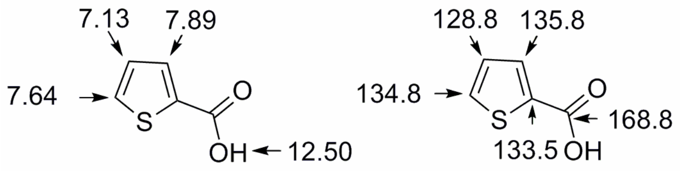


Figure 6. Assignment of the chemical shift of 2-thiophene carboxylic acid **2h**.

For the signal assignment of 2-methyl thiophene **2c** (figure 7), the methyl proton situates at 2.62 ppm (d, J = 1.2 Hz, 3H). By selective decoupling of these methyl protons, the coupling with H-3 disappears. Therefore, H-3 can be assigned to 6.89 ppm (m, 1H). H-4 could then be assigned to 7.02 ppm (dd, $J_1 = 5.2$ Hz, $J_2 = 3.4$ Hz, 1H), and H-5 appears at 7.19 ppm (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz, 1H). The carbon shifts have been assigned by APT and HETCOR.

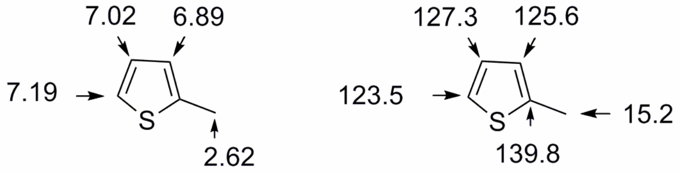


Figure 7. Assignment of the chemical shifts of 2-methyl thiophene **2c**.

As an intermediate conclusion, it can be stated that for 2-substituted thiophenes the $^3J_{H5\text{-}H4}$ coupling is always larger than the $^3J_{H3\text{-}H4}$ coupling and offers a criterium for signal assignment for this type of compounds.

For the signal assignment of the chemical shifts of 3-octyl thiophene **2d** (figure 8), a somewhat more extensive study was necessary. First, the methylene protons of the side chain closest to the thiophene ring were selectively irradiated. This resulted in the disappearance of the coupling with H-2 and H-4, resulting is the assignment of H5 at 7.22 ppm (dd, $J_1 = 4.9$ Hz, $J_2 = 3.1$ Hz, 1H). The corresponding carbon shift could be assigned by HETCOR. C3 is the only quaternary carbon in the structure, so this could be assigned by APT at 143.6 ppm. Starting from C3 or C5, C2 and C4 were further assigned via INADEQUATE to the signals at 120.3 ppm and 128.7 ppm respectively. The corresponding proton shifts were determined by HETCOR (H2: 6.91 ppm (dd, J_1 = 3.1 Hz, J_2 = 1.3 Hz, 1H), H4: 6.92 ppm (dd, J_1 = 4.9 Hz, J_2 = 1.3 Hz, 1H)). Also the carbons of the alkyl side chain were assigned on basis of the INADEQUATE experiment. By this all the carbons are determined and the corresponding proton shifts are assigned by HETCOR.

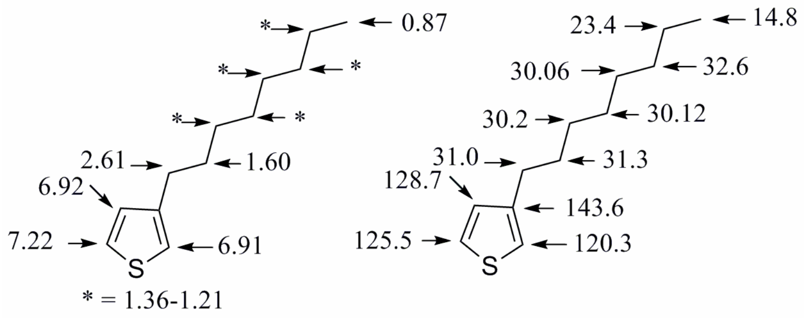


Figure 8. Assignment of the chemical shifts of 3-octyl thiophene **2d**.

For the signal assignment of 2-vinyl thiophene **2e** (figure 9), the quaternary and CH_2 carbons could be assigned by APT. Knowing two of the six carbons, the other four could be derived from the INADEQUATE 2D-spectrum. The corresponding protons were determined by HETCOR.

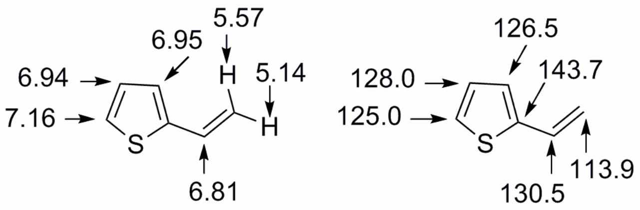


Figure 9. Assignment of the chemical shifts of 2-vinyl thiophene **2e**.

For the signal assignment of the thiophene dimer **1d** (figure 10) first the quaternary carbon has been assigned by means of APT (143 ppm).

Furthermore, the protons from the double bond are easy to recognize, because they are the only protons which are represented by a singlet (7.06 ppm). The aromatic protons are assigned based on their coupling constants and all the according carbons are determined by the HETCOR spectrum.

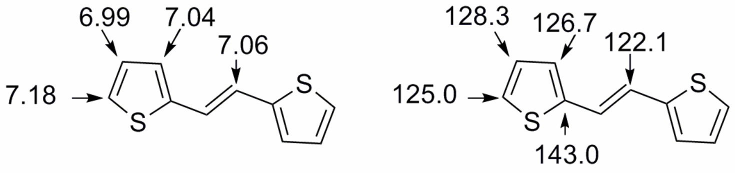


Figure 10. Assignment of the chemical shifts of thiophene dimer **1d**.

The determination of the chemical shifts of model compound **1b** (figure 11) was more complicated. First the quaternary, methylene and methyl carbons have been determined by APT. The quaternary carbon of the dithiocarbamate group appears at 194.2 ppm. Both quaternary carbons of the aromatic rings have been determined on 143.1 and 141.3 ppm; their assignment follows. The chemical shifts at 50.0 and 47.4 ppm arise from the methylene carbons next to the nitrogen of the dithiocarbamate group (hindered rotation around the N-C=S bond). The signal at 38.8 ppm corresponds to the bridge methylene group. The remaining aliphatic CH signal at 52.9 ppm can be adapted to the bridge methine carbon and the two CH_3 signals at 12.3 and 13.2 ppm are from the dithiocarbamate group. All the corresponding proton shifts have been determined via the HETCOR spectrum. At last, all the aromatic signals had to be assigned. First the proton coupling constants were determined allowing to position these protons on the thiophene rings. For the signal assignment of the protons to the appropriate thiophene rings a homonuclear ^1H-^1H NOE experiment has been done (selective proton irradiation at 5.62 ppm results in a clear NOE effect at 6.99 ppm). The corresponding carbon signals have been assigned by HETCOR. Finally, the quaternary carbons have been assigned by means of a long-range 2D HETCOR experiment (based on the $^2J_{C\text{-}H}$ and $^3J_{C\text{-}H}$ couplings between the quaternary carbons and the assigned H-2 and H-3 protons).

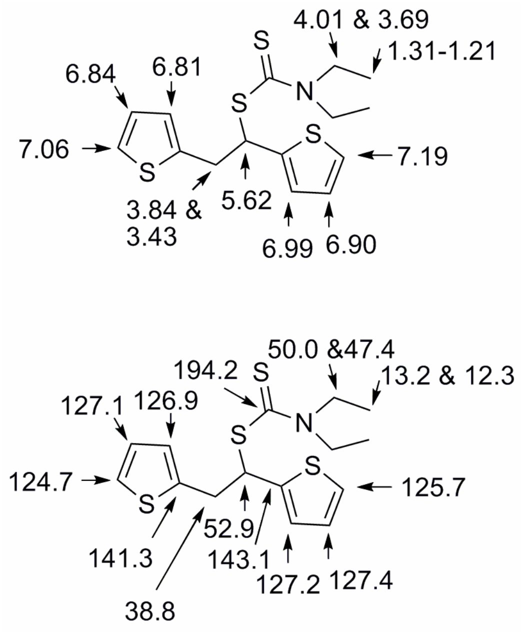


Figure 11. Assignment of the chemical shifts of model compound **1b**.

For the signal assignment of model compound **1c** (figure 12), first an APT spectrum was taken allowing to assign the quaternary and CH_2 carbons to 144.3 and 32.8 ppm, respectively. Furthermore, the aromatic protons were assigned by means of their coupling constants. The central proton on the ring was found at 6.93 ppm with coupling constants of 5.1 en 3.6 Hz. The position of the other protons was determined via the J-coupling (H-3: J_1 = 3.6 Hz and H-5: J_1 = 5.1 Hz) and confirmed by means of long range HETCOR. A $^2J_{C\text{-}H}$ coupling between the quaternary carbon at 144.3 ppm and the proton at 6.82 ppm was observed. The corresponding carbon and proton signals have been assigned by means of HETCOR.

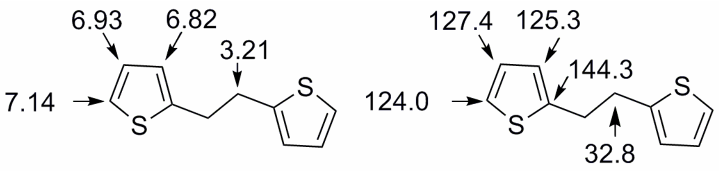


Figure 12. Assignment of the chemical shifts of model compound **1c**.

The signal assignment of model compound **2a** (figure 13) has also been started with APT to assign the quaternary carbons. The aliphatic protons and carbons can be assigned based on their chemical shift and HETCOR information. This leaves only the aromatic protons and carbons. Also here, the coupling constants are very helpful: H-4 can be assigned to the signal at 6.88 ppm based on coupling constants of 5.1 and 3.5 Hz, H-3 (J_1 = 3.5 Hz) and H-5 (J_1 = 5.1 Hz) to signals at 7.01 and 7.14 ppm. Again, the assignment of H-3 was confirmed by means of a long range HETCOR.

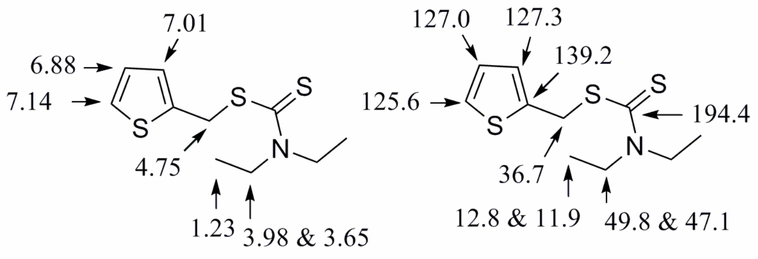


Figure 13. Assignment of the chemical shifts of model compound **2a**.

For the determination of the chemical shift of model compound **2b** (figure 14) the same strategy as for model compound **2a** was followed and by which all the aliphatic protons/carbons (except for the octyl tail) were determined. For the assignment of the signals of the octyl tail and the dithiocarbamate group, the chemical shifts have been compared with the ones of model compound **2d** and **2a**, respectively. In a next phase the two aromatic quaternary carbons were assigned by heteronuclear ^{1}H-^{13}C NOE experiments (selective proton irradiation at 4.67 ppm results in a clear NOE for the carbon signal at 131.0 ppm). At last the other two aromatic signals have been assigned by means of homonuclear ^{1}H-^{1}H NOE experiments (selective proton irradiation at 2.58 ppm results in a NOE effect for the proton signal at 6.81 ppm).

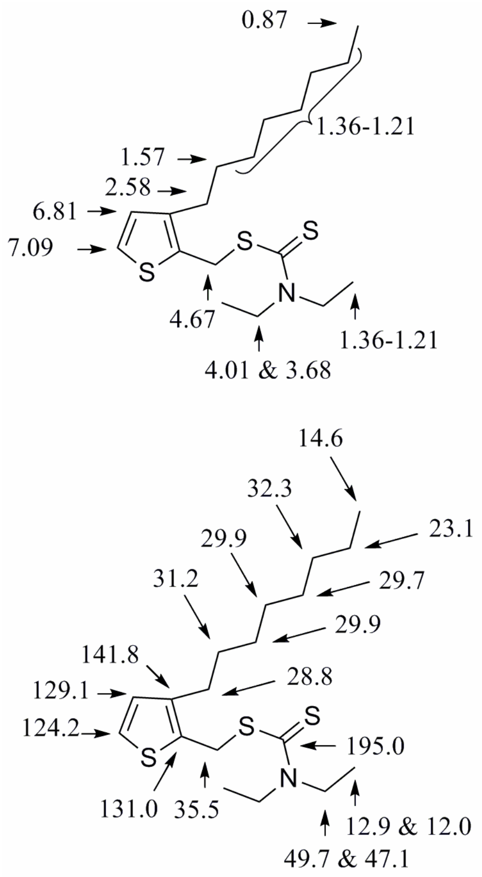


Figure 14. Assignment of the chemical shifts of model compound **2b**.

3.4. Theoretical DFT calculations of the NMR chemical shifts of model compounds representing structural defects in the O-PTV polymers.

Because little information is available in literature regarding the proton and carbon NMR chemical shifts of thiophene derivatives, theoretical calculations of the chemical shifts of all model compounds is ongoing. Especially for the model compounds which are not experimentally accessible, i.e. **1a, 1e** and **1f**. This in order to situate or confirm the chemical shifts of these, possibly appearing structural defects, in the ^{13}C-labeled polymers.

This theoretical DFT study is being accomplished by Prof. Dr. B. Champagne and Dr. E. Botek from FUNDP (Namur).

Moreover, experimental data regarding the NMR chemical shifts of this type of thiophene derivatives is also very interesting for the further refinement of NMR chemical shift prediction software.

3.5. Regioregularity

In literature, it is claimed on basis of ^{1}H and ^{13}C NMR spectroscopy that poly(thienylene vinylene) derivatives which are prepared via a condensation reaction are 100 % regioregular.[22,39] In order to find a criterium to determine the regioregularity of O-PTV, a joint experimental-theoretical NMR study towards the determination of the chemical shifts of the following four model compounds is proposed (figure 15). The theoretical calculations for these model compounds are ongoing to find out if the experimental synthesis is worthwhile.

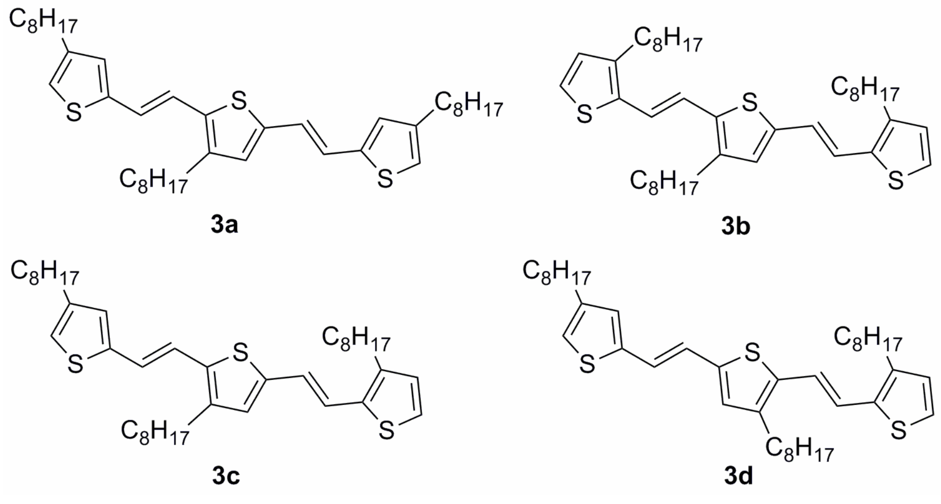


Figure 15. Different model compounds to study the regioregularity.

First the most stable conformers will be determined by Prof. Dr. R. Lazzaroni, Dr. V. Lemaur and Dr. D. Beljonne from the university of Mons. Afterwards, this information will be used to calculate the ^{1}H and ^{13}C chemical shifts by Prof. Dr. B. Champagne and Dr. E. Botek from FUNDP (Namur).

The calculated chemical shifts will then be evaluated with respect to their dependency on the regioregularity. If the chemical shift of an aromatic or olefinic carbon atom is dependent on the position of the octyl side chains on the thiophene core, it can be used as a criterium to describe the regioregularity at the level of the polymers.[42]

4. Conclusions

In this chapter several model compounds are discussed which have been synthesized and fully characterized by different NMR techniques in order to obtain chemical shift information regarding the regioregularity and identity of structural defects in PTV based polymers. As an interesting fact, it has been noticed that for 2-substituted thiophenes the $^{3}J_{H5-H4}$ coupling is always larger than the $^{3}J_{H3-H4}$ coupling and offers a criterium for signal assignment. The obtained chemical shift information will be used to calculate the chemical shifts of model compounds **1a**, **1e**, **1f, 3a**, **3b**, **3c** and **3d** (in cooperation with the university of Namur and Mons). This chemical shift information will be very useful to verify the structural defects on the polymer level and to determine the degree of regioregularity of the polymers. Furthermore, the experimental NMR results will also be interesting to further refine chemical shift prediction software.

5. Acknowledgement

We gratefully acknowledge BELSPO in the frame of the IAP P6/27 network, the IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for the financial support via the SBO-project 060843 ‘PolySpec’. We also want to thank the EU for the FP6-Marie Curie-RTN ‘SolarNtype’ (MRTN-CT-2006-035533). Furthermore, the support of the Fund for Scientific Research-Flanders (FWO projects G.0161.03N, G.0252.04N and G.0091.07N) is acknowledged.

6. References

[1] Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377.

[2] Gerard, M.; Chaubey, A.; Malhotra, B. D. *Biosens. Bioelectron.* **2002**, *17*, 345–359.

[3] Burroughes, J. H.; Bradley, D. D. C.; Brown, A; Marks, R. N.; Mackay, K; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.

[4] Spanggaard, H.; Sariciftci, F. C. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 125–146.

[5] Sariciftci, N. S. *Mater. Today* **2004**, 36–40.

[6] de Boer, B.; Facchetti, A. *Polym. Rev.* **2008**, *48*, 423–431.

[7] Dhanabalan, A.; van Duren, J. K. J.; van Hal, P. A.; van Dongen, J. L. J.; Janssen, R. A. J. *Adv. Funct. Mat.* **2001**, *11*, 255–262.

[8] Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985.

[9] Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; de Boer, B. *Polym. Rev.* **2008**, *48*, 531–582.

[10] Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.

[11] Goris, L.; Loi, M. A.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Polec, I.; Lutsen, L.; Manca, J.; De Schepper, L.; Vanderzande, D. *Synthetic Met.* **2003**, *138*, 249–253.

[12] Colladet, K.; Nicolas, M.; Goris, L.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, *7*, 451–452.

[13] Shaheen, S. E.; Vangeneugden, D.; Kiebooms, R.; Vanderzande, D.; Fromherz, T.; Padinger, F.; Brabec, D. J.; Sariciftci, N. S. *Synthetic Met.* **2001**, *121*, 1583–1584.

[14] Gravilenko, A. V.; Matos, T. D.; Bonner, B. E.; Sun, S.-S.; Zhang, C.; Gravilenko, V. I. *J. Phys. Chem.* **2008**, *112*, 7908–7912.

[15] Xie, H.-Q.; Liu, C.-M.; Guo, J.-S. *Eur. Polym. J.* **1996**, *32*, 1131–1137.

[16] Fuchigami, H.; Tsumura, A.; Koezuka, H. *Appl. Phys. Lett.* **1993**, *63*, 1372–1374.

[17] Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19–26.

[18] Yeon-Beom, L.; Hong-Ku, S.; Seung-Won, K. *Macromol. Rapid Comm.* **2003**, *24*, 522–526.

[19] Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Boer, B. *Polym. Rev.,* **2008**, *48*, 531–582.

[20] Smith, A. P.; Smith, R. R.; Taylor, B. E.; Durstock, M. F. *Chem. Mater.* **2004**, *16*, 4687–4692.

[21] Van De Wetering, K.; Brochon, C.; Nhov, C.; Hadziioannou, G. *Macromolecules* **2006**, *39*, 4289–4297.

[22] Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214–3221.

[23] Harper, K.; West, W. J. W. *Eur. Pat. Appl. No. 182548*, **1985**.

[24] Jen, K. Y.; Jow, R.; Eckhardt, H.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 49–53.

[25] Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309–311.

[26] Yamada, D.; Tokito, S.; H.; Tsutsui, T; Saito, S *J. Chem. Soc., Chem. Commun.* **1987**, *00*, 1448–1449.

[27] Tokito, S; Momii, T.; Murata, H; Tsutsui, T.; Saito, S. *Polymer* **1990**, *31*, 1137–1141.

[28] Tsutsui, T.; Murata, H.; Momii, T.; Yoshiura, K.; Tokito, S.; Saito, S. *Synth. Met.* **1991**, *41*, 327–330.

[29] Murase, I.; Ohnishi, T.; Noguchi, *T. Ger. Offen.* No. 3704411, **1987**.

[30] Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin solid films* **2004**, *451-452*, 472–579.

[31] Henckens, A. *PhD dissertation*, University of Hasselt, Diepenbeek, Belgium, October **2003**.

[32] Mitchell, W. J.; Pena, C.; Burn, P. L. *J. Mater. Chem.* **2002**, *12*, 200–205.

[33] Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T.J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, 43, 10231–10240.

[34] Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J. *J. SPIE Proc*. **2004**, 52–59.

[35] Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Eur. Phys. J.-Appl. Phys.* **2007**, *37*, 237–240.

[36] Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2006**, *90*, 2815–2828.

[37] Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

[38] Diliën, H.; Chambon, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Adriaensens, P. J. Identification and quantification of defect structures in Poly(2,5-Thienylene Vinylene) derivatives prepared via the dithiocarbamate precursor route by means of NMR spectroscopy on ^{13}C-labeled polymers *Macromolecules*, **2011**, submitted.

[39] Zhang, C.; Matos, T.; Li, R.; Sun, S.-S.; Lewis, J. E.; Zhang, J.; Jiang, X. *Polym. Chem.* **2010**, 663–669.

[40] Diliën, H; Adriaensens, P.J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Exploring the DTC chemistry by the synthesis and study of model compounds* **2011**, in preparation.

[41] Diliën, H.; Vandenbergh, J.; Banishoeb, F.; Adriaensens, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. J. M. An Efficient Acid induced Conversion of Dithiocarbamate precursor polymers into Conjugated Materials *Macromolecules* **2010**, accepted.

[42] Zhang, C.; Matos, T.; Li, R.; Sun, S-S.; Lewis, J. E.; Zhang, J.; Jiang, X. *Polym. Chem.* **2010**, 663–669.

Chapter 7: Synthesis and characterization of dihexyl-PTV

Poly(3,4-dihexyl-(thienylene vinylene)) has been obtained via the dithiocarbamate precursor route. First, the monomer has been synthesized via an efficient three step reaction pathway involving a chloromethylation step. In a next step the monomer has to be polymerized towards its precursor polymer. This polymerization step has been optimized for this sterically more hindered monomer. Finally, the influence of number the side chains on the mobility of PTV materials in organic thin-film transistors has been tested.

1. Introduction

Low band gap materials have gained a lot of interest in the context of organic electronics, because of their improved resemblance with the solar spectrum.[1-5] Well known and studied examples of these materials are the oligothienylenevinylenes based on 3,4-dihexylthiophene.[6-9] These components are not only interesting because of their electronic and photovoltaic applications or their use as molecular wires, but also because they have been used to model the electronic and electrochemical properties of their corresponding polymers. Nonetheless, on the polymer level, e.g. poly(3,4-dihexyl-(thienylene vinylene)) limited studies have been performed. The 3,4-dihexyl-PTV has been synthesized in our research group and studied in solar cells.[10-12] Solar cells made by these PTV derivatives demonstrated very promising results. Their efficiencies

---

* By H. Diliën, M. Spijkman, D. De Leeuw, T. J. Cleij, L. Lutsen, D. Vanderzande for Polymer, 2011, status: in preparation

were four times greater than these of solar cells made from monosubstituted PTV derivatives. As a result, the idea arose that the regioregularity or the defect level (due to the polymerization mechanism) in these materials should have a big influence on the devices behaviour. Hence, these materials are synthesized once again, after optimization of the polymerization[13] and the conversion reaction.[14] Moreover the dithiocarbamate precursor route has been examined by a detailed NMR study.[15] This study revealed that former route is especially suitable to synthesis poly(thienylene)vinylene derivatives with a low amount of defects and high molecular weights. The only drawback of this route is the synthetic pathway towards the monomers. Unfortunately this is quite demanding and time consuming. Hence a shorter synthetic pathway, including a direct chloromethylation step, has been investigated.

2. Experimental section

2.1. General

All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone.

2.2. Techniques

^{1}H NMR and ^{13}C NMR spectra were taken on a Varian Inova 300 spectrometer. For all synthesized substances spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm and 77.7 ppm (relatively to TMS) was used as reference for ^{1}H NMR and ^{13}C NMR spectra respectively. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by Size Exclusion Chromatography (SEC). Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10 µm, 30 cm, Polymer Labs) and a relative index (RI) detector (Shodex). GC/MS analyses were carried out on TSQ – 70 and Voyager mass – spectrometers (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB. Ultraviolet visible spectroscopy (UV-Vis) was performed on a VARIAN CARY 500 UV-Vis-NIR spectrophotometer. Electrical measurements were performed with an Agilent 4155C semiconductor parameter analyzer at ambient conditions.

2.3. Synthesis

Synthesis of 3,4-dihexyl thiophene **1b**

A solution of 3,4-dibromothiophene **1a** (9.3 g, 39 mmol), diethyl ether (100 ml) and Ni(dppp)Cl_2 (0.2 g, 0.39 mmol) has been made in a three-necked flask under vacuum. Hexyl magnesium bromide (100 ml of a 2.0 M solution in diethyl ether) was added drop wise via a cannula at 0 °C. After complete addition the mixture was refluxed overnight. Then the solution was neutralized by addition of diluted HCl (2 M) and extracted with diethyl ether, the organic layer was dried over $MgSO_4$. The obtained product **1b** was purified via flash chromatography using diethyl ether as eluens to give an orange oil in a yield of 98 %(10 g, 39 mmol).

^1H NMR ($CDCl_3$): 6.87 (s, 2H), 2.48 (t, J = 7.44, 4H), 1.60 (q, J = 7.41, 4H), 1.42-1.26 (m, 12H), 0.88 (t, J = 6.80, 6H).

^{13}C NMR ($CDCl_3$): 142.5, 120.5, 32.5, 30.4, 30.1, 29.6, 23.4, 14.8.

MS (EI, m/e): 252 (M^+)

Synthesis of 2,5-bis(chloromethyl)-3,4-dihexylthiophene **1f**

A mixture of 3,4-dihexylthiophene **1b** (1 g, 3.9 mmol) and paraformaldehyde (0.3 g, 11 mmol) was made and cooled to 0 °C under a nitrogen atmosphere. First a 12 M HCl solution (1.9 mL, 22 mmol) was added drop wise. Afterwards acetic anhydride (3.7 mL, 39 mmol) was also added. The reaction was stirred for 24 hours at room temperature. The resulting reaction mixture was cooled till 0 °C and quenched with NaAc and NaOH (2M), extracted with diethyl ether and dried over $MgSO_4$. Because of the unstable nature of chlorine **1f**, the product has been used without further purification or characterization.

Synthesis of monomer **1g**

The chlorine **1f** (1.8 g, 3.1 mmol) was dissolved in ethanol and the sodium dithiocarbamate salt (3.5 g, 15.6 mmol) was added as a solid. The resulting mixture was stirred for four hours, extracted with diethyl ether and dried over $MgSO_4$. The product was purified with column chromatography over silica with hexane/chloroform (50/50) as eluent. The product **1g** was obtained as orange oil (2.3 g, 78 %).

^1H NMR ($CDCl_3$): 4.61 (s, 4H), 4.01 (q, J = 7.42, 4H), 3.69 (q, J = 7.00, 4H), 2.47 (t, J = 7.58, 4H), 1.50-1.41 (m, 4H), 1.32-1.20 (m, 24H), 0.87 (t, J = 6.79, 6H).

^{13}C NMR ($CDCl_3$): 194.3, 140.6, 129.6, 48.8, 46.2, 35.2, 31.1, 29.1, 27.0, 22.1, 13.6, 12.0, 11.1.

Polymerization of monomer **1g**

The monomer **1g** (0.94 g, 1.6 mmol) was freeze dried. A solution, with a monomer concentration of 0.4 M, in dry THF (4.1 mL) was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium tert-butoxide (NatBuO) (10 mL of a 1M solution in THF) was added in one go to the stirred monomer solution. The resulting mixture was stirred for 90 minutes under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvents of the combined organic layers were evaporated under reduced pressure and a second precipitation was performed in cold methanol. The polymer was purified (isolation of the high molecular weight fraction) by a biobeads column. The polymer **1h** was collected and dried *in vacuo* (yield 15 %, 0.1 g: only the highest molecular weight fraction).

SEC: $M_w = 60 . 10^3$; PD = 3.2

^{1}H NMR ($CDCl_3$): 5.62-5.33 (br s, 1H), 4.15-3.86 (br q, 2H), 3.84-3.54 (br q, 2H), 3.55-3.44 (br, 2H), 2.59-1.96 (m, 4H), 1.53-1.02 (m, 22H), 0.95-0.75 (br t, 6H).

Acid induced conversion towards dihexyl-PTV **1i**.

The precursor polymer **1h** (0.1g, 0.24 mmol) was dissolved in chlorobenzene (6.7 mL) and heated till 70 °C. Trifluoro acetic acid (0.03 mL, 0.35 mmol) was added and the resulted mixture was stirred for 10 minutes at 70 °C. Afterwards the solution was cooled to room temperature, quenched with water and extracted with chloroform. The solvent has been removed and the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol and dried *in vacuo*. A purple/black solid has been obtained (yield 89 %, 0.058 g).

UV-Vis: λ_{max} = 590 nm, shoulder at 631 nm (in THF)

SEC: $M_w = 22 . 10^3$; PD = 3.2

^{1}H NMR ($CDCl_3$): 5.25-5.60 (br s, 2H), 2.24-2.36 (br m, 4H), 1.05-1.60 (br m, 16H) 0.91-0.82 (br t, 6H).

Synthesis of 3-octyl-PTV (O-PTV).

The synthetic procedures concerning the O-PTV precursor polymer was reported earlier.[13] The conversion of this precursor polymer towards the conjugated form was done by the acid induced conversion.

Acid induced conversion towards O-PTV.

The precursor O-PTV (118 mg, 0.32 mmol) was dissolved in chlorobenzene (9.1 mL) and heated till 70 °C. Trifluoro acetic acid (0.035 mL, 0.48 mmol) was added and the resulted mixture was stirred for 10 minutes at 70 °C. Afterwards the solution was cooled to room temperature, quenched with water and extracted with chloroform. The solvent has been removed and the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol and dried *in vacuo*. A purple/black solid has been obtained (yield 76 %, 0.053 g).

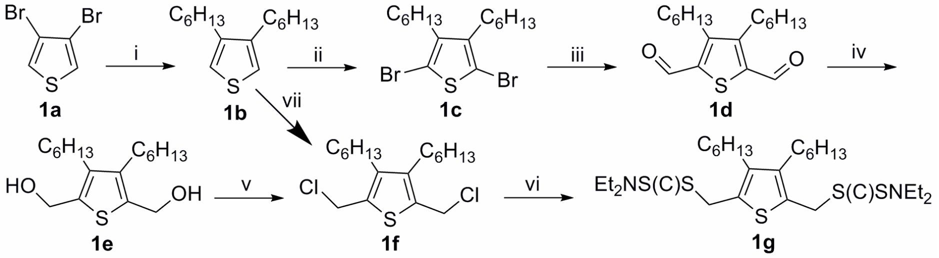
UV-Vis: λ_{max} = 575 nm, shoulder at 613 nm (in THF)
SEC: M_w = 52 . 10^3; PD = 2.3
^{1}H NMR ($CDCl_3$): 6.49 (br, 1H), 2.28 (br, 2H), 1.40-1.05 (br, 12H), 0.85 (br, 3H).

3. Results & discussion

3.1. Synthesis

3.1.1. Monomer synthesis

In this chapter the synthesis of the symmetric dihexyl-PTV has been optimized. In earlier work, 3,4-dihexyl-PTV has been made by a six step synthesis in which the dialdehyde is a key intermediate (scheme 1).[10,11,12] Unfortunately, this route is very time consuming. Not only because of the number of reaction steps but also because of the difficult purification of the crude reaction mixture. The latter consist of a mixture of starting product **1c**, desired product **1d** and its mono aldehyde derivative. Consequently, a shorter reaction pathway has been considered which involves a direct chloromethylation on **1b** (scheme 1).



Scheme 1. Synthesis of dihexyl-PTV monomer **1g** via dialdehyde: (i) $BrMgC_8H_{17}$, $NiCl_2(dppp)$; (ii) NBS, DMF; (iii) 1. *n*-BuLi, 2. *n*-formylpiperidine; (iv) $LiAlH_4$, THF; (v) $SOCl_2$, THF; (vi) $NaSC(S)NEt_2.3H_2O$, EtOH; (vii) CH_2O, HCl, Ac_2O

This shorter three step pathway makes use of the same reaction as the former reaction sequence, namely a Kumada coupling under influence of a nickel catalyst (Ni(dppp)Cl_2) to introduce both side chains. To stimulate the introduction of both side chains the used temperatures are raised from room temperature till reflux conditions. After introduction of the side chains a direct chloromethylation can be performed. By this reaction three reaction steps can be skipped and the dichloride **1f** can be formed immediately. Due to the unstable nature of this dichloride, the crude reaction mixture has always been used in the next reaction step without further purification or characterization. The chloromethylation reaction has previously been used for the synthesis of PPV polymers.[16] Unfortunately the same reaction conditions are not favourable for the synthesis of the PTV monomers. The reaction always resulted in a black slurry which was very difficult to purify and consequently the obtained yields were very low (< 20 %).

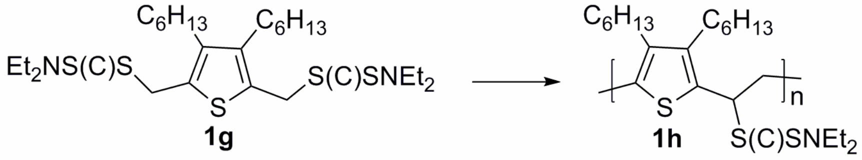
It can be expected that the reaction conditions are to extreme for the electron rich thiophene structure. Maybe the used temperatures during the reaction (75 °C) are too high and can induce all kinds of unfavoured side reactions. Another possible cause can be the large amount of acid (5,7 eq. of HCl), formaldehyde (2,7 eq.) or the excess of acetic anhydride (10 eq.). Therefore, different reaction conditions have been tested and the chloromethylation reaction has been optimized (table 1). As indicated in table 1 the number of equivalents acid, formaldehyde and acetic anhydride were already optimal. Only the temperature and time had to be adapted. Lowering the temperature till room temperature could avoid side reactions or the decomposition of the compound but the reaction remained incomplete. To obtain disubstitution a longer reaction time of 24 hours had to be applied. In a last phase the dichloride **1f** has been substituted with the dithiocarbamate salt to gain the dihexyl monomer **1g**. This crude reaction mixture has been purified by column chromatography with hexane/chloroform (50/50) as a mixture.

Entry	Time (h)	Temperature (°C)	Equivalents formaldehyde	Equivalents HCl	Equivalents acetic anhydride	Result
1	3.5	75	2.7	5.7	10	Black mixture: decomposition
2	3.5	R.T.	2.7	2	10	Monosubstitution and starting product
3	3.5	50	2.7	2	10	Black mixture: decomposition
4	3.5	0	2.7	5.7	10	Monosubstitution, small amount of disubstitution
5	3.5	R.T.	2.7	5.7	4	Mixture monosubstitution and starting product, small amount of disubstitution
6	3.5	R.T.	2.0	5.7	10	Monosubstitution, small amount of disubstitution
7	5	R.T.	2.7	5.7	10	Monosubstitution, small amount of disubstitution
7	16	R.T.	2.7	5.7	10	Mixture mono and disubstitution
8	24	R.T.	2.7	5.7	10	Mainly disubstition

Table 1. Optimization of the chloromethylation conditions.

3.1.2. Synthesis of the polymer

Once monomer **1g** has been synthesized, it has to be polymerized towards the precursor polymer **1h** (scheme 2). In earlier work, we optimized the polymerization conditions for the synthesis of mono-substituted PTV derivatives.[13] Here, sodium hexamethyldizilazide (NaHMDS: 2 equivalents) has been used as a base. The reaction has been stirred for 90 minutes at 0 °C. When these reaction conditions were applied on the dihexyl monomer **1g**, only low molecular weight polymers were formed (table 2).



Scheme 2. Polymerization towards precursor polymer **1h**.

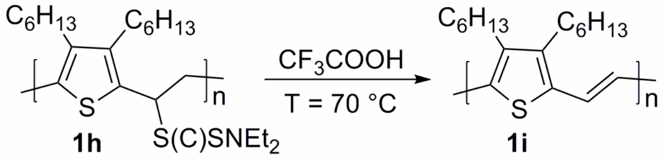
It has been stated earlier,[13] that lithium hexamethyldisilazide (LHMDS) can yield higher molecular weights than NaHMDS. Indeed, higher molecular weights have been formed, but they are much lower than achieved with the monosubstituted monomer (average of 174 . 10^3 Dalton). These observations can be explained due to the introduction of an additional side chain, the steric hindrance on the monomer has been increased. Therefore the abstraction of a proton in the monomer **1g** by the base is much more difficult and the reaction will be slowed down. Also NatBuO has been tested as a base; here even higher molecular weights could be formed. This can be explained due to the more bulky side chains on LHMDS compared to NatBuO. Due to these results NatBuO has been selected as the base of choice to polymerize the dihexyl monomers.

At last also the temperature effect has been studied. To investigate whether temperature has an influence on the polymerization reaction with NaHMDS, the reaction temperature has been raised till 30 °C. Because of this adaptation the molecular weight increased a lot. The increased steric hindrance of the side groups can be neutralized by the raise of temperature.

Entry	Base	Temperature (°C)	M_w (.10³)	PD
1	NaHMDS	0	7	1.9
2	NaHMDS	30	79	2.5
3	LHMDS	0	51	1.8
4	NatBuO	0	78	2.8

Table 2. Polymerization results of dihexyl monomer.

Finally, the precursor polymer has been converted into its conjugated form by the acid induced conversion method (scheme 3).[14]



Scheme 3. Acid induced conversion towards dihexyl-PTV **1i**.

3.2. Field-effect transistors

Due to the symmetric nature of the dihexyl-PTV monomer, there is no issue on regioregularity of the side chains possible in the polymer structure. To test whether the degree of regioregularity has an influence on the performance of these materials in devices, organic thin-film transistors (TFT) have been made from dihexyl-PTV and, a previously synthesized, O-PTV. A polymer film was applied on a TFT substrate by spincoating, from a 10 mg/mL solution in *o*-dichlorobenzene. The substrate consisted of a Si gate with 200 nm of thermally annealed SiO_2 as the gate dielectric. Au source and drain contacts were defined by standard photolithography. After spincoating the substrate was annealed overnight at 120 °C in a nitrogen atmosphere to remove traces of solvent. Afterwards the transistors were measured in air without encapsulation. The resulting mobilities are 1 x 10^{-5} cm²/Vs for the dihexyl-PTV and 5 x 10^{-4} cm²/Vs for the O-PTV. These mobilities are lower compared to those of unsubstituted PTV,[17] which can be explained by the steric hindrance due to the side chains on the substituted PTV derivatives. The mobility of the monosubstituted O-PTV is higher than the one obtained by the disubstituted dihexyl-PTV. So future research should be focused on the synthesis of monosubstituted PTV derivatives.

4. Conclusions

In this study, a much shorter and efficient synthetic pathway towards the dihexyl-PTV monomer has been explored. Furthermore, the polymerization of this, more steric hindered, monomer has been optimized. Finally, transistors have been made from this material, as well as from O-PTV. These results have been compared, and it can be concluded that the number of side chains on the thiophene core has a big influence on the mobility of the materials. To gain materials with high mobilities, disubstituted derivatives are less suitable then monosubstituted, this is probably due to the increased steric hindrance.

5. Acknowledgements

The authors gratefully acknowledge BELSPO in the frame of network IAP P6/17 for the financial support and for granting Ph.D. fellowships (H.D.). The FWO is also gratefully acknowledged for the funding of the project G.0091.07. We want to thank the European Science Foundation (ESF) for the received support for the activity entitled ‘New Generation of Organic based Photovoltaic Devices’. We also thank the European programme ONE-P (no. 212311) for financial support and T. Geuns (MiPlaza Eindhoven) for technical assistance.

6. References

[1] Mayer, A. C.; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D *Mater. Today* **2007**, *10*, 28–33.

[2] Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.

[3] Goris, L.; Loi, M. A.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Polec, I.; Lutsen, L.; Manca, J.; De Schepper, L.; Vanderzande, D. *Synthetic Met.* **2003**, *138*, 249–253.

[4] Colladet, K.; Nicolas, M.; Goris, L.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, *7*, 451–452.

[5] Kroon, R.; Lenes, M.; Hummelen, J.C.; Blom, P. W. M.; De Boer, B. *Polym. Rev.* **2008**, *48*, 531–582.

[6] Roncali, J.; Jestin, I.; Frère, P.; Levillain, E.; Sievenard, D. *Synthetic Met.* **1999**, *101*, 667–670.

[7] Marineau, C.; Blanchard, P.; Rondeau, D.; Delaunay, J.; Roncali, J. *Adv. Mater.* **2002**, *14*, 283–287.

[8] Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem. Int. Ed.* **1998**, 942–945.

[9] Jestin, I; Frère, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150–8158.

[10] Banishoeib, F.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Eur. Phys. J.-Appl. Phys.* **2007**, *37*, 237–240.

[11] Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energ. Mat. Sol. C.* **2007**, *91*, 1026–1034.

[12] Banishoeib, F.; Henckens, A.; Fourier, S..; Vanhooyland, G.; Breselge, M.; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L.H.; Neugebauer, H.; Sariciftci, N.S. *Thin solid films* **2008**, *516*, 3978–3988.

[13] Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, 10231–10240.

[14] Diliën, H.; Vandenbergh, J.; Banishoeib, F.; Adriaensens, P. J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. Acid induced conversion of

dithiocarbamate precursor polymers into conjugated materials, *Macromolecules* **2011**, accepted.

[15] Diliën, H; Chambon, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Adriaensens, P. J. Identification and quantification of defect structures in Poly(2,5-Thienylene Vinylene) derivatives prepared via the dithiocarbamate precursor route by means of NMR spectroscopy on ^{13}C-labeled polymers*,* *Macromolecules* **2011**, submitted.

[16] Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925–4932.

[17] Huitema, H. E. A.; Gelinck, G. H.; van der Putten, J. B. P. H.; Kuijk, K. E.; Hart, K. M.; Cantatore, E.; de Leeuw, D. M. *Adv. Mater.* **2002**, *14*, 1201–1204.

Chapter 8: Perspectives

In this chapter, the synthetic strategy for three new conjugated polymers is presented. First, the synthesis of two polymers with electron withdrawing side chains will be explored, in order to lower the HOMO and LUMO energy levels. Furthermore, the improvement of the morphology of the polymers has been tested via an alternative for the BOP-PTV. Here a more planar structure, which can introduce more stacking between the polymers, and therefore improve the morphology, will be proposed.

1. Introduction

Recently, a lot of research efforts have been spend on the study of organic photovoltaic solar cells. Especially solar cells with an active layer showing a bulk-heterojunction have been made.[1-6] Here, an electron donating conjugated polymer will be blend with an electron acceptor, which is most of the time PCBM. Already a broad range of conjugated polymers have been tested, including poly(thienylene vinylene).[7] The obtained efficiencies where quite low, compared with P3HT. To increase the efficiencies of these solar cells, there are three strategies which can be followed.[8,9] A first strategy is to lower the band gap. The obtained low band gap polymers have a higher photon flux and therefore the J_{sc} can be increased (figure 1).[10]

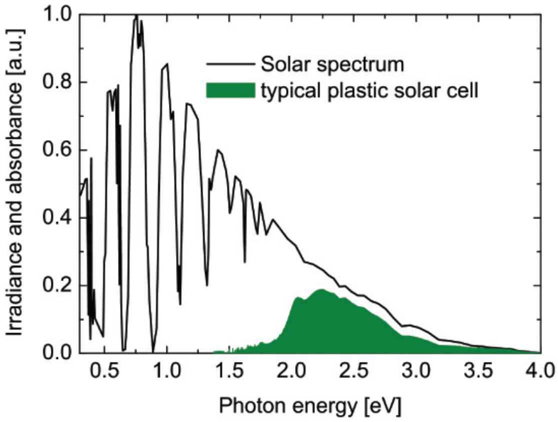


Figure 1. Solar spectrum.

Another strategy is to optimize the V_{oc}, the theoretical highest possible value can be calculated from the difference between the HOMO level of the donor and the LUMO level of the acceptor. So, changing the V_{oc} can be done by lowering the HOMO and LUMO values of the conjugated polymer. A third strategy is to optimize the morphology of the thin films, which will have an influence on the fill factor (interface effect) and on the absorptivity of the films. In this chapter, the synthetic strategy of three new polymers is presented. First, it has been tried to lower the HOMO and LUMO levels of the electron donating polymer by the introduction of electron withdrawing side chains, e.g. a pentafluorophenyl group or an ester function. For the last polymer, it has been tried to optimize the morphology by the synthesis of an alternative for the BOP- PTV, by introducing a more planar structure.

2. Synthesis of “electron poor” PTV derivatives

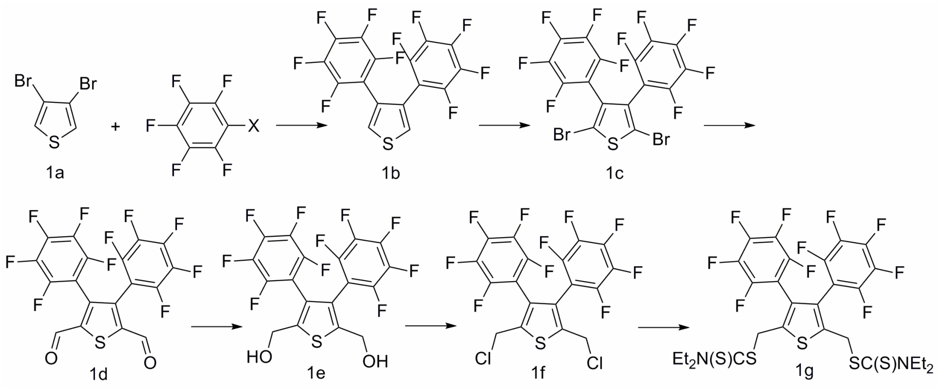
2.1 Fluor containing PTV derivatives

To enhance the efficiencies of devices, one of the options for improvement is to adapt the HOMO and LUMO levels of the polymers.

Electron withdrawing groups will lower both HOMO and LUMO levels to fit them better to these of the frequently used PCBM. In this case fluor containing groups are used as electron withdrawing groups. It has already been proven that this kind of groups can have numerous advantages. These kind of groups are already studied in PPV derivatives and polythiophenes.[11,12] The relationship between the poor stability of PPV towards photo-oxidation and the level of the LUMO energy has been investigated. It has been stated that the stability against photo-oxidation can be enhanced by lowering the HOMO energy level of the polymers, which should also effect the lifetimes of the devices made with these materials.[11] The second subject, that has been studied concerns the LUMO energy level, which is too high to make PPV a good electron acceptor. The introduction of fluor containing side groups indeed lowered the LUMO level, so better electron injection was observed.[11] In this chapter, this strategy will be applied on PTV derivatives. The thiophene core will be substituted with a pentafluorophenyl side chain, to test whether this really lowers the LUMO energy level, and the synthetic strategy of the other PTV derivatives can be applied. In a latter stage the introduction of alkyl side chains, to enhance processability, can be considered.

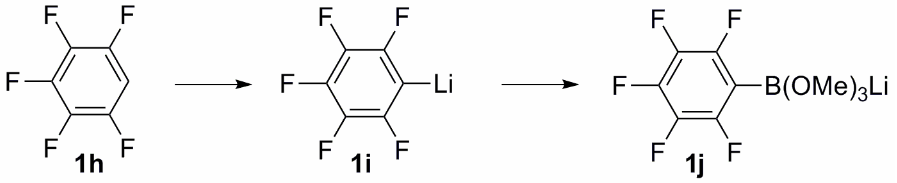
2.1.1. Results & discussion

For the synthesis of the poly[di-3,4-(pentafluorophenyl)-2,5-thienylenevinylene] monomer a six step synthesis has been designed (scheme 1). In a first step the pentafluor aromatic side chain will be introduced. Next the thiophene core will be brominated, followed by the formation of a dialdehyde. Furthermore, the dialdehyde will be reduced towards an alcohol, which will by chlorinated and in a last step substituted with the dithiocarbamate salt.



Scheme 1. Synthesis of the fluor containing PTV derivatives.

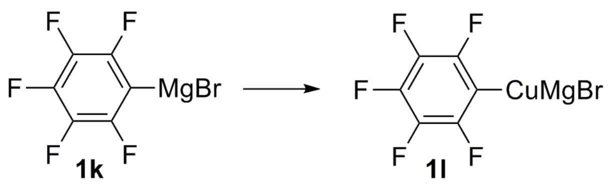
The introduction of the side groups will be done by a Suzuki coupling[13] between 3,4-dibromothiophene **1a** and a boronic ester salt **1j**. First the boronic ester salt **1j** has to be synthesized. This by the formation of a lithium salt **1i** under influence of *n*-BuLi, which has to be reacted with B(OMe)$_3$ toward boronic ester salt **1j** (scheme 2).[14] This salt is very hygroscopic and sensitive towards air. Therefore isolation of the salt, to characterize the product wasn't possible and the salt has been used immediately in the following Suzuki reaction. Unfortunately after reaction a large amount of starting products, and only a small amount of the monosubstituted thiophene derivatives **1b,** has been isolated.



Scheme 2. Synthesis of the boronic ester salt.

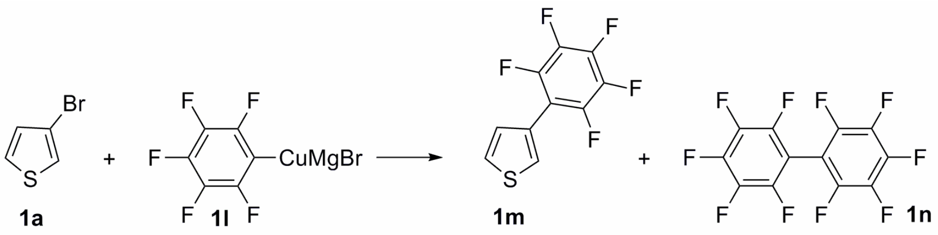
In a second attempt to introduce the side chains, the frequently used Kumada coupling, between the 3,4-dibromothiophene **1a** and the commercial available Grignard reagens **1k** under influence of a nickel catalyst has been tried.[15] Unfortunately, only starting products have been retrieved. No reaction occured at all.

In a third attempt to induce a coupling between the pentafluorophenyl side chain and the 3,4-dibromothiophene **1a**, a Normant reagens **1l** has been used. This Normant reagens has been made by insertion of Cu (from freshly purified Cu(I)Br) into Grignard reagens **1k** (scheme 3).[16] Here reaction did occur. Unfortunately less than 1 % of the reaction mixture resulted in the disubstituted thiophene **1b**. 40 % of the reaction resulted in the monosubstituted product. Some starting product and Wurtz coupled product **1n** appeared as well. So it is possible to introduce the pentafluorobenzyl side chains. To force the introduction of two side chains the number of equivalents of Normant reagens has been increased, just as the reaction time. But still it seemed to be very demanding, probably because of the extensive steric hindrance. Therefore, it was decided to synthesize the monosubstituted thiophene **1m** (scheme 4).



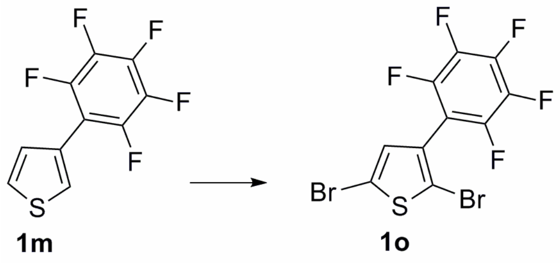
Scheme 3. Synthesis of the Normant reagent.

To exclude the Wurtz coupled product **1n**, multiple different reaction conditions have been tested. But the change of reaction temperature (30 °C - 90 °C) or solvent (toluene, THF, Et_2O) didn't change a thing. After analysis, it has been determined that a great amount of the Wurtz coupled product **1n** was already present in the commercial available grignard reagens **1k**. Purification of the reaction mixture has been tried by column chromatography, distillation and recrystallization, but unfortunately none of these techniques were suitable to purify the mixture. Because of the inert nature of the perfluorobiphenyl **1n,** it was decided to start the next reaction without further separation of the products.



Scheme 4. Synthesis of the mono substituted PTV derivative.

In a next step, the crude reaction mixture has been brominated by NBS (scheme 5). The same conditions as for the former mono substituted derivative (O-PTV) have been used. Unfortunately, only 5 % of the reaction mixture consisted of the dibrominated thiophene **1o**. The main fraction of the reaction mixture (44%) contained two mono substituted isomers. Furthermore, 12 % of starting material **1m** has been found and of course the Wurtz coupled product **1n**. The reaction has been performed for multiple times with prolonging the reaction time, but the results were more or less the same. Therefore, other reaction conditions have been tried. Also NBS has been used, but the solvent has been changed from DMF to a mixture of sulfuric acid and trifluoro acetic acid.[17,18] Here, 20 % of the dibrominated product has been formed. No monobrominated product or starting product **1m** has been found. However, a great amount of tribrominated product has been detected as well. Even after multiple optimization steps the tribrominated product couldn't be avoided.



Scheme 5. Bromination of mono substituted PTV derivative.

2.1.2. Conclusion

Because of the problems with the Wurtz coupled product, tribromination, the price of fluor reagent **1k** and especially the great amount of time spent on the optimization of the synthesis, it has been decided to leave this synthetic route. Nevertheless, the fluor containing PTV derivatives are a very innovative idea to lower the HOMO and LUMO levels of the PTV polymers.

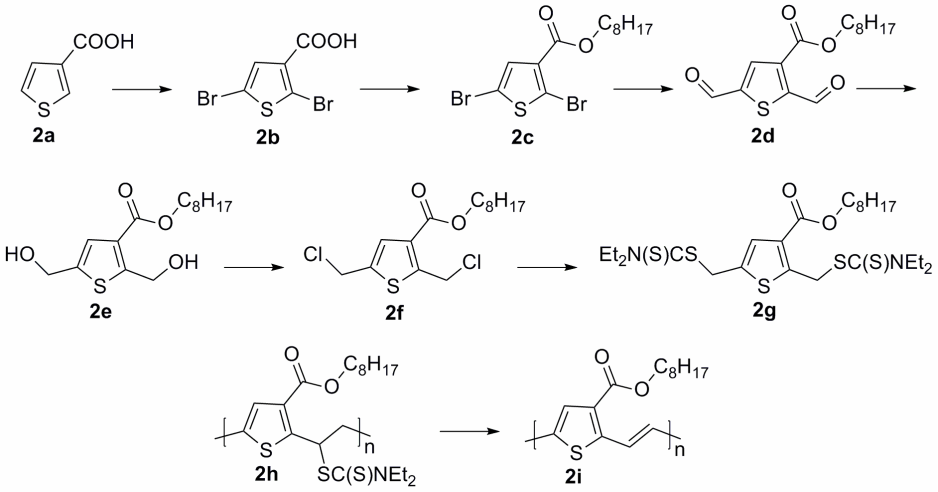
2.2 P3CTV

In our search for possibilities to lower the energy levels of PTV polymers, functionalization of the thiophene core with an ester unit is an option as well. Here, Huo and coworkers synthesized poly(3-carboxylated-2,5-thienylenevinylene) (P3CTV) via Stille coupling.[19] Due to the introduction of the electron withdrawing group the LUMO energy level was set on -3.56 and the power conversion efficiency raised towards 2.01 %. Another interesting fact concerning these materials is that PTV's are considered to be nonluminescent materials.[20,21] After introduction of the carbonyl derivative a photoluminescence peak at 724 nm appeared, this can indicate that the excitated state will have an longer lifetime and therefore a better charge transfer to PCBM will be possible. This can be a second reason why the power conversion efficiency increased.

Because of the rather low molecular weights ($M_w = 17 . 10^3$) which were achieved following the Stille coupling procedure, it was decided to try to make P3CTV via the dithiocarbamate precursor route developed in our research group. This in order to increase the molecular weights of the polymer.

2.2.1. Results & discussion

The polymer P3CTV will be synthesized according to the well known synthetic pathway for mono substituted PTV derivatives (via a dialdehyde as a key intermediary, scheme 6).[7] The first two steps were described by Hou and coworkers, these synthetic procedures have been tested.[19] First a bromination has to be performed, our normal bromination conditions with NBS will not be strong enough to brominate the electron poor thiophene **2a**. Therefore molecular Br_2 will be used.



Scheme 6. Synthesis of P3CTV.

When the described conditions were used (5 eq. Br_2, 15u, 60 °C), the reaction mixture mainly contained the tribrominated derivated (56 %). The desired 2,5-dibromothiophene-3-carboxylic acid **2b** was also present in a yield of 40 %. It was impossible to separate these two compounds by recrystallization. Therefore it was decided to optimize the reaction conditions for this bromination. After several reactions, it can be stated that the number of equivalents of Br_2 have to be lowered to 2.1 equivalent and the reaction time has to be shortened from 15 to 7 hours. When these conditions were used the dibrominated compound **2b** was obtained with only 2 % of mono brominated side product, tribromination was completely prevented. In a next step the carboxylic acid will be transformed into an ester in a two step reaction. First, an acid chloride will be formed under influence of $SOCl_2$. Next the ester will be formed by addition of an excess of *n*-octanol. Subsequent, the aldehyde **2c** has been formed via reaction with *n*-BuLi and *n*-formylpiperidine. Regrettably, the product has been obtained in a very low yield (21%). Historically, the dialdehyde **2c** has to be reduced by reaction with $LiAlH_4$. Unfortunately, this can also reduce the ester function itself. Therefore, reduction with $NaBH_4$, which is a milder reductans, has been tried. Here the analysis of the reaction mixture was very difficult. Not only traces of starting product were found, also an amount of octanol has been detected. Here the idea rised that trans esterification occurred. The reaction has been done in MeOH as a solvent, so the methanol and octanol can exchange on the ester function. To avoid this problem, the solvent has been switched to octanol in all further reactions. This induced some new problems, because of the high boiling point of octanol (195 °C), the solvent has to be distilled by vacuum distillation during work-up. After work-up none of the desired alcohol has been found, but it is not clear if this is due to the failing reaction conditions or to the high temperatures during work-up. Unfortunately, because of the low yield of the dialdehyde **2c,** and the problems with the reduction of the aldehyde, further reaction steps were abandoned.

2.2.2. Conclusion

The synthesis of poly(3-carboxylated-2,5-thienylenevinylene) (P3CTV) via the dithiocarbamate route could have been a great progress into the development of higher efficiencies for solar cells made from PTV derivatives, this due to lower HOMO and LUMO energy levels and increased photoluminescence. Unfortunately, the synthesis of the polymers has not been finished due to a lack of time. A solution for the reduction of the dialdehyde has to be found. If this problem would be managed, the route towards this potential, very interesting PTV will be open.

3. Alternative for BOP-PTV

Earlier, it was stated that BOP-PTV is a promising material because of its good value for the HOMO and LUMO levels, but the short circuit currents are quite low compared to the frequently used P3HT.[7] This because of the fact that the absorptivity of P3HT in thin films is much higher due to the structural order and the crystalline character of these films.[22] BOP-PTV does not have any crystalline character, probably because of the rotational disorder of the benzyl side chains. To circumvent this, it has been decided to "freeze" the side chains. The phenyl rings will be covalently connected (figure 2), so a more plane structure will appear, and stacking of the chains can be improved.

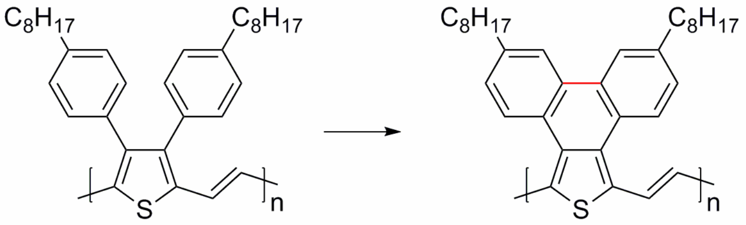
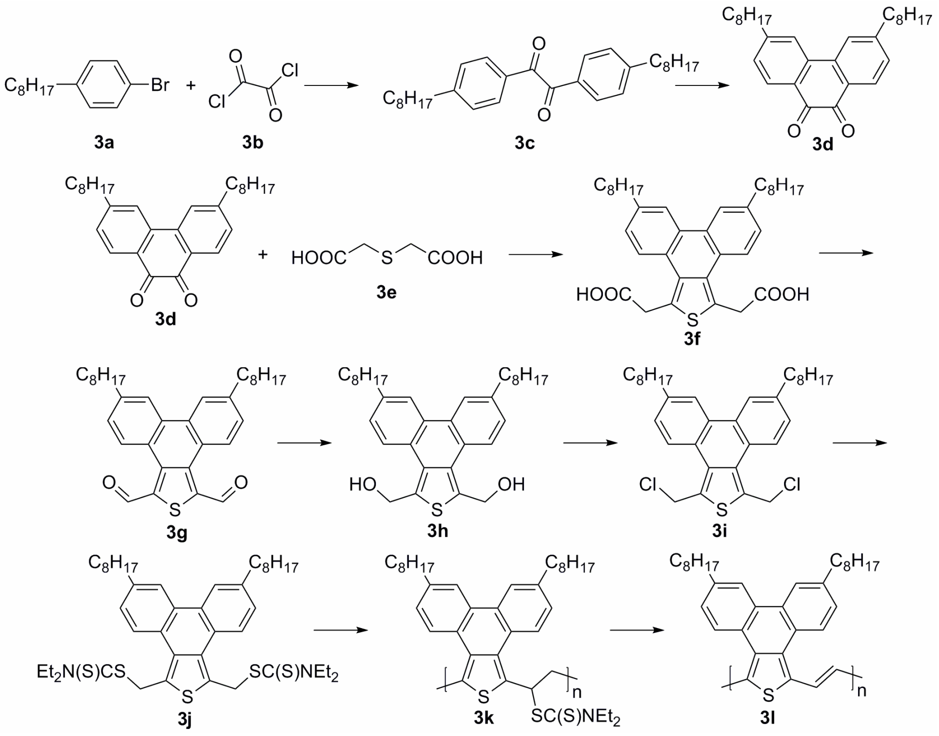


Figure 2. An alternative for BOP-PTV.

3.1. Results & discussion

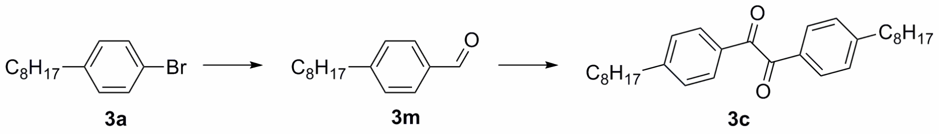
To synthesis a BOP-PTV with "frozen" side chains a nine step synthetic pathway has been developed (scheme 7). The last six steps are very familiar to the reactions used during the normal PTV synthesis of mono substituted derivatives. The first reaction concerns a Grignard reaction between the Grignard reagent of 1-bromo-4-octylbenzene **3a** and oxalylchloride **3b**.[23] Next, ring closure will be induced under influence of C_8K.[25,26] And at last the thiophene ring will be formed by a condensation between diketon **3d** and 2,2'-thiodiacetic acid **3e**.[26,27]

As indicated earlier, the first reaction will be a coupling between oxalylchloride **3b** and the Grignard reagent of 1-bromo-4-octylbenzene **3a** under influence of a Ni catalyst.[23] Unfortunately none of the desired diketon **3c** has been formed. The resulted reaction mixture consisted mainly of octylbenzene. This indicates that the Grignard reagent did form during the reaction, but coupling did not occur. Therefore, coupling has been tried with other organometal reagents, namely a mixture of CuBr and LiBr.[28,29] Now, the desired diketon **3c** did formed in a yield of 32 %. Besides the desired product **3c** also 20 % of octylbenzene and some Wurtz coupled product of the latter have been observed. Purification of the reaction mixture has been tried by means of column chromatography, but this seemed to be very difficult. For this reason, and the low yield which was obtained, another coupling method have been tried.



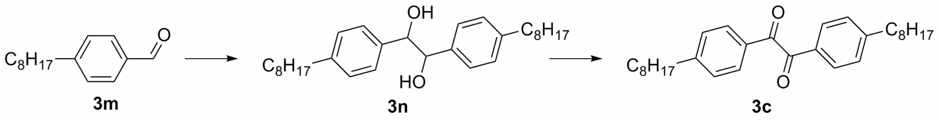
Scheme 7. The synthesis of PTV **3l**.

Alternatively, a two step pathway to make the diketon via aldehyde **3m,** has been tried (scheme 8). First, 4-octylbenzaldehyde has been synthesized via metal-halogen exchange. Subsequently the lithium compound will be substituted with *n*-formylpiperidine to form compound **3m**. Next, a benzoin condensation will be performed to form diketon **3c**.[30,31] Here, the diketon **3c** has been formed in a yield of 22 %.



Scheme 8. Synthesis of diketon **3c**.

Also a three step pathway towards compound **3c** has been checked (scheme 9). The diol will be formed under influence of aluminum and $HgCl_2$, regrettably only in a yield of 22%.



Scheme 9. Alternative synthesis for diketon **3c**.

3.2. Conclusion

The formation of diketon **3c** is possible, but the reaction has to be optimized to increase the gained yields. Consequently, a very promising route remains open for future research.

4. Experimental section

4.1. General

All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise.

Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone. $SOCl_2$ was previously purified via a vacuum distillation.

Cu(I)Br was purified by stirring in acetic acid for 24 h, this to reduce Cu(II) to Cu(I). Next, Cu(I)Br was filtered off and washed frequent with ethanol and finally with diethyl ether, to remove Cu(II)Br_2 and acetic acid. Finally the CuBr was dried in a vacuum oven at 75 °C.

4.2. Techniques

^{1}H NMR & ^{13}C NMR spectra were taken on a Varian Inova 300 spectrometer. For all synthesized substances spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm and 77.7 ppm (relatively to TMS) was used as reference for ^{1}H NMR and ^{13}C NMR spectra respectively. GC/MS analyses were carried out on TSQ – 70 and Voyager mass – spectrometers (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB. Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans).

4.3. Synthesis

Synthesis of 3-(perfluorophenyl)thiophene **1m**
A solution of Grignard reagens **1k** (10.4 mL, 5.2 mmol) and CuBr (2.95 g, 21 mmol) was made in dry THF. The mixture was stirred for 1 hour at room temperature. 3-bromothiophene **1a** (0.5 g, 3.0 mmol) was added together with 75 mL toluene. The resulted mixture was stirred at 90 °C for 16 hours. Afterwards, the reaction was quenched with HCl and filtered over silica to remove the excess of CuBr. The resulted mixture was extracted with diethylether and the solvents were removed under reduced pressure. 1.35 g of crude product was obtained.
^{1}H NMR ($CDCl_3$): 7.65-7.62 (m, 1H), 7.44 (dd, $J_1 = 5.03$, $J_2 = 3.00$, 1H), 7.36-7.31 (m, 1H).
MS (EI, m/e): 250 (M^+)

Synthesis of 2,5-dibromo-3-(perfluorphenyl)thiophene **1o**

A solution of 3-(perfluorophenyl)thiophene **1m** (0.6 g, 2.4 mmol) was made in DMF in the absence of light and cooled to 0 °C. A solution of NBS (0.94 g, 5.3 mmol) in DMF was added slowly to former solution. The mixture was stirred for 72 hours. Afterwards the reaction was poured in a NaOH solution (2,5 M) and stirred at 0 °C. The resulted reaction mixture was extracted with Et_2O, washed with NaOH and NaCl, dried over $MgSO_4$. The mixture was purified by column chromatography over silica with pentane as eluent. 120 mg of crude product was obtained (still contained some Wurtz coupled product).

^{1}H NMR ($CDCl_3$): 6.91 (s, 1H).

MS (EI, m/e): 408 (M^+)

Synthesis of 2,5-dibromothiophene-3-carboxylic acid **2b**

Thiophene-3-carboxylic acid **2a** (10.0 g, 78 mmol) has been solved in acetic acid. Bromine (5.4 mL, 167 mmol) was added at room temperature and the resulted mixture was stirred at 60 °C for 7 hours. Afterwards the reaction was poured into ice water, and a white precipitate formed. This precipitation was filtered and recrystallised in a mixture of water and ethanol (60/40). Here white needle shaped crystals has been formed in a yield of 46 % (10.3 g).

^{1}H NMR ($CDCl_3$): 7.38 (s, 1H).

^{13}C NMR ($CDCl_3$): 166.0, 132.7, 131.5, 122.0, 112.4.

FT-IR (cm^{-1}): 1696.99 (υ(C=O)), 1529.00 (υ(C=C)), 1438.56 (δ_β(-OH)), 1252.11 (υ(C-O)), 905.96 (δ_γ(O-H))

MS (EI, m/e): 286 (M^+)

Synthesis of octyl-2,5-dibromothiophene-3-carboxylate **2c**

The carboxylic acid **2b** (1.0 g, 6.6 mmol) was solved in $SOCl_2$ (9.0 mL, 0.12 mol). The mixture was heated at 80 °C for 6 hours. Afterwards the excess of $SOCl_2$ was distilled. A mixture of *n*-octanol (8.6 mL, 54.4 mmol) and dry pyridine (18.2 mL, 0.226 mol) was added drop wise to the resulted product. The mixture was stirred for 16 hours at 60 °C.

After cooling to room temperature, the resulted reaction mixture was poured into a solution of ice water with HCl (2,5 M). Afterwards, the reaction was extracted with diethyl ether, washed with a $NaHCO_3$ solution and dried over $MgSO_4$. After removing the solvent under reduced pressure, the product **2c** was obtained in a yield of 65 % (0.93 g).

^{1}H NMR ($CDCl_3$): 7.32 (s, 1H), 4.24 (t, J = 6.54, 2H), 1.77-1.64 (m, 2H), 1.46-1.20 (m, 10H), 0.86 (t, J = 7.34, 3H).

^{13}C NMR ($CDCl_3$): 161.6, 132.7, 132.4, 119.6, 112.0, 66.2, 32.5, 29.9, 29.8, 29.2, 26.7, 23.3, 14.8

FT-IR (cm^{-1}): 3117.32 (υ(CH)), 2949.00 ($\upsilon_{as}(–CH_3)$), 2917.96 ($\upsilon_{as}(-CH_2-)$), 2866.07 ($\upsilon_s(–CH_3)$), 2849.17 ($\upsilon_s(-CH_2-)$), 1731.59 (υ(C=O)), 1525.90 (υ(C=C)), 1473.76 ($\delta_{\beta s}(-CH_2-)$), 1378.88 ($\delta_s(-CH_3)$) , 1153.59 (υ_{as}(C-O-C)), 1023.95 (υ_s(C-O-C)), 586.95 (υ(C-Br))

MS (EI, m/e): 398 (M^+)

Synthesis of octyl-2,5-diformylthiophene-3-carboxylate **2d**

In a three-necked round bottom flask a solution of ester **2c** (0.25 g, 0.63 mmol) in THF was stirred under nitrogen atmosphere at -78 °C. A solution of *n*-butyl lithium (0.9 mL, 1.4 mmol of a 1.6 M solution in hexane) was slowly added, the mixture was stirred for 30 minutes and afterwards *n*-formylpiperidine (0.15 g, 1.4 mmol), freshly distilled, was slowly added. The resulting mixture was stirred for 12 hours at room temperature. HCl (2M) was added to quench the excess of *n*-BuLi followed by extraction with chloroform. The organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. The obtained compound was purified by column chromatography on silica gel with ethylacetate/hexane (1/9) as a solvent. The dialdehyde **2d** was obtained as orange oil (40 mg, 21 %).

^{1}H NMR ($CDCl_3$): 10.72 (s, 1H), 9.98 (s, 1H), 8.20 (s, 1H), 3.65 (t, J = 6.57, 2H), 1.62-1.50 (m, 2H), 1.35-1.22 (m, 10H), 0.86 (t, J = 7.06, 3H).

Synthesis of 4-octylbenzaldehyde **3m**:

A solution of bromine **3a** (1 g, 3.7 mmol) in THF was stirred under nitrogen atmosphere and cooled towards -78 °C. A solution of *n*-butyl lithium (2.6 mL, 4.1 mmol of a 1.6 M solution in hexane) was slowly added, the mixture was stirred for 30 minutes and afterwards freshly distilled *n*-formylpiperidine (0.5 mL, 4.1 mmol), was added. The resulting mixture was stirred for 12 hours at room temperature. The reaction was quenched with HCl (2M) followed by extraction with chloroform. The organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. The obtained compound was purified by column chromatography on silica gel with chloroform/hexane (1/1) as a solvent. The aldehyde **3m** was obtained as orange oil (610 mg, 80 %).

^{1}H NMR ($CDCl_3$): 9.95 (s, 1H), 7.78 (d, J = 7.94, 2H), 7.32 (d, J = 7.94, 2H), 2.66 (t, J = 7.81, 2H), 1.67-1.54 (m, 2H), 1.35-1.22 (m, 10H), 0.85 (t, J = 6.51, 3H).

Synthesis of diketon **3c** via Grignard reagent:

A solution of LiBr (0.32 g, 3.7 mmol) was made in THF under nitrogen atmosphere. This solution was added to a stirred suspension of freshly purified CuBr (0.27 g, 1.9 mmol) in THF. The mixture was stirred at room temperature till it became homogeneous. Then, it was cooled towards 0 °C. Meanwhile, a Grignard reagent from bromine **3a** was prepared. Some I_2 crystals were added to a suspension of Mg (63 mg, 2.6 mmol) in THF. The bromine **3a** (0.5 g, 1.9 mmol) was added drop wise and the mixture was allowed to stir at reflux temperatures for 15 minutes. Subsequently, this mixture was added to the stirred mixture of lithium and cupper salts. Immediately, oxalylchloride (0.07 mL, 0.77 mmol) was added to this resulted mixture and it was stirred for another 15 minutes at 0 °C. Next, the reaction mixture was quenched with a saturated NH_4Cl solution, extracted with ethylacetate and dried over Na_2SO_4. The product was obtained in a yield of 33 % (based on GC/MS analysis)

^{1}H NMR ($CDCl_3$): 7.89 (d, J = 7.85, 4H), 7.43 (d, J = 7.19, 4H), 2.72-2.57 (m, 4H), 1.69-1.55 (m, 4H), 1.41-1.21 (m, 20H), 0.96-0.83 (br t, 6H)
MS (EI, m/e): 434 (M^+)

Synthesis of diketon **3c** via aldehyde **3m**:
A solution of 5-(2-hydroxylethyl)-3,4-dimethylthiazolium iodide (26 mg, 9 10^{-5} mol) was made in ethanol. Triethylamine (0.1 mL, 0.8 mmol) and aldehyde **3m** (0.1 g,0.5 mmol) were added and the mixture was refluxed for 24 hours. The mixture was extracted with chloroform, washed with HCl, $NaHCO_3$ and water. Furthermore, the reaction was dried over $MgSO_4$ and the solvent was removed in vacuo. The product was obtained as a pale yellow oil (22 %, 0.05 mmol).
^{1}H NMR ($CDCl_3$): 7.92 (d, J = 7.93, 4H), 7.20 (d, J = 8.27, 4H), 2.66-2.57 (m, 4H), 1.66-1.51 (m, 4H), 1.33-1.18 (m, 20H), 0.86 (t, J = 6.26, 6H).

Synthesis of diol **3n**
A solution of 4-octylbenzaldehyde **3m** (0.1 g, 0.46 mmol) and $HgCl_2$ (0.9 mg, 3.4 10^{-6} mol) was made in a mixture of ethanol and toluene (50/50). Aluminum (0.025 g, 91 mmol) was added and the reaction mixture was heated till reflux temperatures for 90 minutes. Afterwards, the reaction was cooled to 0 °C and the reaction was quenched with a saturated NaCl and a HCl solution (2.5 M). The resulted reaction mixture was extracted with diethyl ether and washed with HCl, NaHCO3 and NaCl. The product was obtained as a yellow oil (12 mg, 0.027 mmol).
^{1}H NMR ($CDCl_3$): 8.02 (d, J = 8.18, 4H), 7.26 (d, J = 8.18, 4H), 2.59 (t, J = 7.46, 4H), 1.69-1.54 (m, 4H), 1.37-1.20 (m, 20H), 0.88 (t, J = 7.09, 6H).

5. Conclusions

In this chapter, the synthetic pathway for three different polymers, have been designed, in order to increase the efficiencies of organic solar cells. Two of these polymers have electron withdrawing side chains to lower the HOMO and LUMO levels. The third polymer will be an alternative for BOP-PTV, the morphology of thin films could by improved by the introduction of more planar side chains, this because of the better stacking of the polymers. Unfortunately, there was not enough time to finish all these synthetic pathways. But the synthetic strategy is already present, so three routes towards three very promising PTV derivatives are still open for the future work.

6. References

[1] Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533–4542.

[2] Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *Appl. Phys. Lett.* **2006**, *88*, 093511-1–093511-3.

[3] Dhanabalan, A.; van Duren, J. K. J.; van Hal, P. A.; van Dongen, J. L. J.; Janssen, R. A. J. Adv. Funct. Mater., 2001, 11, 255–262.

[4] Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mat.* **2001**, 11, 15–26.

[5] Spanggaard, H.; Krebs, F. C. *Sol. Energ. Mat. Sol. C.* **2004**, *83*, 125–146.

[6] Mayer, A. C.; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D. *Mater. Today* **2007**, *10*, 28–33.

[7] Diliën, H.; Palmaerts, A.; Lenes, M.; de Boer, B.; Blom, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, *43*, 10231–10240.

[8] Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater* **2006**, *18*, 789–794.

[9] Zhou, H.; Yang, L.; Stoneking, S.; You, W. *Appl. Mat. Interfaces* **2010**, *2*, 1377–1383.

[10] Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *SPIE Newsroom* **2007**, 10.1117.

[11] Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Chem. Commun.* **2007**, 1003–1022.

[12] Thomas, S.; Zhang, C.; Sun, S-S. *J. Polym. Sci. Pol. Chem.* **2005**, *43*; 4280–4287.

[13] Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *J. Fluorine Chem.* **2003**, *122*, 195–199.

[14] Adonin, N. Y.; Bardin, V. V.; Flörke, U.; Frohn, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2638–2646.

[15] Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347– 3354.

[16] Chen, Z.; Huang, C.; O'Shea, S.; Loh, K. P. *patent* **2006**, WO 2006/093467.

[17] Zou, Y.; Hou, J.; Yang, D.; Li, Y. *Macromolecules* **2006**, *39*, 8889–8891.

[18] Zhan, X.; Tan, Z.; Domerq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 7246–7247.

[19] Hou, L.; Chen, T. L.; Zhou, Y.; Hou, J.; Chen, H-Y.; Yang, Y.; Li, Y. *Macromolecules* **2009**, *42*, 4377–4380.

[20] Brasset, A. J.; Colaneri, N. F.; Bradley, D. D. C.; Lawrence, R. A.; Friend, R. H.; Murata, H.; Tokito, S.; Tsutsui, T.; Saito, S. *Phys. Rev. B* **1990**, *41*, 10586–10594.

[21] Hwang, I-W.; Xu Q-H.; Soci, C.; Chen B.; Jen A. K-Y.; Moses, D.; Heeger, A. J. *Adv. Funct. Mat.* **2007**, *17*, 563–568.

[22] Oosterbaan, W. D.; Vrindts, V.; Berson, S.; Guillerez, S.; Douhéret, O.; Ruttens, B.; D'Haen, J.; Adriaensens, P.; Manca, J.; Lutsen, L.; Vanderzande, D. *J. Mater. Chem.* **2009**, *19*, 5424–5435.

[23] Mc Eachern, A.; Soucy, C.; Leitch, L. C.; Arnason, J. T.; Morand, P. *Tetrahedron* **1988**, *44*, 2403–2412.

[24] Tamarkin, D.; Rabinovitz, M. *J. Org. Chem* **1987**, *52*, 3472–3474.

[25] Tamarkin, D.; Benny, D.; Rabinovitz, M. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 642–643.

[26] Agarwal, N.; Hung, C-H.; Ravikanth, M. *Tetrahedron* **2004**, *60*, 10671–10680.

[27] Koparir, M.; Cansiz, A.; Cetin, A. *Heteroatom Chem.* **2005**, *16*, 503–506.

[28] Dierschke, F.; Müllen, K. *Macromol. Chem. Phys.* **2007**, *208*, 37–43.

[29] Babudri, F.; Flandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron. Lett.* **1995**, *36*, 7305–7308.

[30] Lee, C. K.; Gong, J. S.; Sin, K. S.; Jun, J-G. *Bull. Korean Chem. Soc.* **1993**, *14*, 29–31.

[31] Stetter, H.; Kuhlmann, H.; Haese, W. *Org. Synth.* **1993**, *8*, 620.

If you're not failing every now and again,
It's a sign you're not doing anything very innovative.

Summary

Poly(thienylene vinylene) polymers seem to be very promising materials for application in solar cells. Because of their low band gap behaviour, their absorption spectrum resembles better the emission spectrum of the sun than commonly used materials as poly(phenylene vinylene) (PPV). In this thesis the synthesis, polymerization and solar cell behaviour of PTV materials have been investigated. All these materials have been made via the dithiocarbamate precursor route, which was previously developed in our research group. For this dithiocarbamate route, the polymerization step has been optimized and the conversion step has been studied extensively. All the chapters (except for chapter 1 and 8) are presented as a manuscript for publication.

In **chapter 1**, a general introduction has been given. First an overview of conjugated polymers and the use of low band gap materials have been described. Furthermore, all parameters which influence the band gap of materials have been reported. Later on, an historical overview of the use of PTV derivatives has been presented with special attention for the dithiocarbamate route and its conversion mechanism. Finally, a short description of solar cells, the photovoltaic principle and their characteristics has been given.

Two new conjugated polymers, i.e. poly(3-octyl-2,5-thienylene vinylene) (O-PTV) and poly(bis-octylphenyl-2,5-thienylene vinylene) (BOP-PTV), have been synthesized in **chapter 2**. The polymerization protocol of the monomers, via the dithiocarbamate route, has been optimized by the use of different bases. Therefore, high molecular weight polymers, with a low polydispersity and more important, reproducible results have been achieved with NaHMDS as a base. Furthermore, the obtained (conjugated) polymers have been fully characterized and used as p-type material in solar cells, in cooperation

with the University of Groningen. Because of the optimization of the polymerization the efficiency raised till almost 1%.

In **chapter 3**, the conversion of dithiocarbamate precursor polymers has been investigated, this as well for PTV as PPV derivatives. It has been discovered that these precursor polymers are sensitive towards acids. Due to the addition of strong organic acids, the conversion temperatures can be lowered till 70 °C and therefore degradation of the chromophore can be prevented. Moreover a competition between an elimination and substitution reaction has been reported. This substitution reaction could be used for post polymerization functionalization.

Chapter 4 explores the dithiocarbamate route via model compounds. The competition between the elimination reaction and the substitution reaction has been monitored. The reaction kinetics have been studied, the reaction follows first order kinetics in the substrate concentration and the substituents on the thiophene core have a major influence on the reaction kinetics.

In a next stage the structure of polymers obtained via the dithiocarbamate route, was explored in detail. **Chapter 5** describes the synthesis of a ^{13}C labeled O-PTV which has been studied by quantitative ^{13}C NMR spectroscopy. During this study the structural defects and the end groups of the polymer have been determined and the difference between the acid and the thermal conversion has been investigated. From this study it can be stated that the dithiocarbamate route is an excellent route to prepare polymers with a low amount of defects in the polymer chain.

For the attribution of the chemical shifts of the structural defects, multiple model compounds have been made. In **chapter 6** the attribution of all the NMR chemical shifts of the model compounds have been reported. Unfortunately, not all desired model compounds were synthetically available. Therefore the remaining chemical shifts will be theoretically calculated in cooperation with the University of Mons & Namur.

Chapter 7 describes the synthesis of 3,4-dihexyl PTV. The synthetic pathway has been shortened till a three step synthesis. Furthermore, the reaction conditions of the polymerization step had to be optimized due to the increased steric hindrance of the monomer. Finally, the obtained dihexyl PTV's have been incorporated into organic thin film transistors to measure the mobility of the materials.

In **chapter 8**, the synthetic strategy for three new conjugated polymers has been designed. Unfortunately, these synthetic routes could not be finished during this PhD. So these routes, towards promising low band gap materials, are still open for future work.

As a **general conclusion** it can be stated that poly(thienylene vinylene) derivatives are low band gap materials. Their HOMO and LUMO values are determined and fit well to those demanded for the energy levels of PCBM and the electrodes in solar cells. The polymerization conditions of PTV monomers have been optimized and therefore the efficiencies in solar cells increased with a factor of four. Unfortunately the gained efficiencies are still low compared to other systems. This will probably be due to the morphology of the active layer blend. Furthermore, the dithiocarbamate route has been studied in detail. First, a new conversion mechanism for dithiocarbamate precursor polymers has been developed. This leads towards the use of lower temperatures during conversion and therefore qualitative better conjugated systems. The structural defects and end groups have been determined by quantitative NMR studies on a ^{13}C labeled O-PTV. It can be stated that the dithiocarbamate route is an excellent route to make conjugated polymers with a low amount of defects. As a main conclusion it can be stated that poly(thienylene vinylene) polymers, made via the dithiocarbamate route are still promising materials. But effort has to be made to optimize their film forming properties and corresponding morphologies. This can be done on the level of the solar cells or at the molecular level by tuning the side chains.

Samenvatting

Poly(thienyleen vinyleen) polymeren lijken veelbelovende materialen te zijn voor toepassingen in organische electronica. Vooral als p-type materiaal in zonnecellen lijken ze geschikt omwille van hun *low band gap* karakter. Low band gap materialen vertonen een verbeterde overlap van hun absorptie spectrum met het emissiespectrum van de zon, dit vergeleken met andere veelgebruikte polymeren (bv. PPV derivaten). De (in deze thesis beschreven) materialen werden allen gesynthetiseerd via de, in onze onderzoeksgroep ontwikkelde, dithiocarbamaat route. Dit is de enige route die, omwille van de electronrijke thiofeen structuur, toelaat om stabiele monomeren te synthetiseren en vervolgens een gecontroleerde polymerisatie uit te voeren. In een volgend stadium moeten de precursor polymeren omgezet worden in hun geconjugeerde vorm. Ook deze conversie stap werd uitgebreid bestudeerd.

In **hoofdstuk 1** wordt een overzicht gegeven van geconjugeerde materialen en hun toepassingen. Verder wordt er meer in detail ingegaan op low band gap polymeren, hun eigenschappen en de mogelijkheden om hun band gap te *tunen*. Uiteindelijk wordt een historisch overzicht gegeven van de synthese en het gebruik van PTV derivaten, waarna specifiek de dithiocarbamaat route en het bijhorende conversie mechanisme belicht wordt. Tot slot, zal de opbouw van een zonnecel, het fotovoltaïsch principe en de belangrijkste karakteristieken van zonnecellen onder de loep genomen worden.

In **hoofdstuk 2** wordt de synthese van twee nieuwe PTV derivaten, nl. O-PTV en BOP-PTV beschreven. De polymerisatie condities voor de overeenkomstige monomeren werden geoptimaliseerd door het gebruik van verschillende basen. Het gebruik van NaHMDS, als base, leidde tot hoge moleculaire gewichten, redelijk lage polydispersiteiten en voornamelijk reproduceerbare resultaten. Beide materialen werden tevens gebruikt als p-type materiaal in zonnecellen, dit in samenwerking met de universiteit van Groningen. Omwille van de optimalisatie van het polymerisatie mechanisme kan de efficiëntie van de zonnecellen opgedreven tot bijna 1 %. Dit is een mooie vooruitgang vergeleken met de 0.15-0.2 % bekomen via andere syntheseomstandigheden.

In het **derde hoofdstuk** wordt het conversie mechanisme van zowel PTV als PPV derivaten onder de loep genomen. Enkele jaren geleden werd ontdekt dat dithiocarbamaat precursor polymeren gevoelig waren voor de aanwezigheid van zuren. Door de additie van sterke organische zuren tijdens de conversie, kunnen de gebruikte temperaturen verlaagd worden tot 70 °C. Hierdoor kan degradatie van de polymeerketens voorkomen worden en zullen kwalitatief betere conjugeerde polymeer ketens ontstaan. Tevens werd er ontdekt dat het geconjugeerde systeem zich niet altijd volledig ontwikkelt, wat kan toegeschreven worden aan het voorkomen van een competitieve substitutiereactie.

In **hoofdstuk 4**, wordt deze competitie onderzocht aan de hand van modelverbindingen. Tevens werd ontdekt dat het conversiemechanisme eerste orde kinetica volgt voor het substraat en dat de substituenten op de thiofeenring een grote invloed hebben op de reactiesnelheid.

Vervolgens werd de dithiocarbamaat route en meer bepaald de structurele defecten en eindgroepen die tijdens de polymerisatie ontstaan in detail bestudeerd. **Hoofdstuk 5** geeft de synthese van een ^{13}C gelabeld polymeer weer. Dit polymeer werd vervolgens bestudeerd via kwantitatieve ^{13}C metingen waardoor de verschillende defecten en eindgroepen in het polymeer bepaald konden worden. Verder werd ook het verschil tussen de twee conversiemechanismes bestudeerd. Uit dit hoofdstuk kan besloten worden dat de dithiocarbamaat route uitermate geschikt is om PTV polymeren te synthetiseren met een zeer laag percentage aan defecten.

Het volgende hoofdstuk, **hoofdstuk 6**, kan gezien worden als een ondersteuning van hoofdstuk 5. Hiertoe werden verschillende modelverbindingen gesynthetiseerd en geanalyseerd. Dit om de NMR chemische shiften van mogelijke defect-structuren en eindgroepen te bepalen. Helaas was het niet mogelijk om voor elk defect een model verbindingen te synthetiseren. Daarom zullen de chemische shiften van de ontbrekende modelverbindingen theoretisch berekend worden in samenwerkingen met de universiteiten van Namen en Bergen.

Hoofdstuk 7 beschrijft de synthese van 3,4-dihexyl PTV. Deze synthese werd geoptimaliseerd en ingekort tot een vlotte drie stapssynthese. Vervolgens werd ook de polymerisatie geoptimaliseerd voor dit, sterisch meer gehinderd, monomeer.

In **hoofdstuk 8** wordt de synthesestrategie voor drie nieuwe *low band gap* polymeren beschreven. Al deze polymeren hebben het potentieel om de efficiëntie van zonnecellen te verhogen. Spijtig genoeg was het niet mogelijk al deze syntheses te finaliseren. De weg naar deze veel belovende polymeren ligt dus nog open.

Als **algemeen besluit** kunnen we stellen dat poly(thienyleen vinyleen) derivaten kunnen beschouwd worden als *low band gap* materialen. De HOMO en LUMO posities van deze polymeren komen goed overeen met deze vereist ten opzichte van de energieniveaus van PCBM en deze van de gebruikte elektrodes in zonnecellen. De polymerisatie condities van de PTV monomeren zijn geoptimaliseerd en hierdoor verhoogde de efficiëntie van de, uit deze materialen gemaakte, zonnecellen enorm. Helaas waren deze efficiënties nog niet hoog genoeg om in competitie te kunnen gaan met andere systemen, wat waarschijnlijk te wijten is aan de morfologie van donor acceptor blends in de actieve laag. In een tweede deel van de thesis werd de dithiocarbamaat route in verder detail bestudeerd. Ten eerste werd een nieuw conversiemechanisme voor dithiocarbamaat precursor polymeren ontwikkeld. Hierdoor kunnen lagere temperaturen gebruikt worden tijdens de conversie en bijgevolg zullen er zich ook kwalitatief betere geconjugeerde systemen ontwikkelen. De structurele defecten en eindgroepen zijn bepaald door kwantitatieve NMR metingen op ^{13}C gelabelde polymeren. Uit dit onderzoek kan vastgesteld worden dat de dithiocarbamate route een zeer geschikte route is om geconjugeerde polymeren te synthetiseren met een laag percentage aan defecten. Uit het voorgaande kunnen we besluiten dat poly(thienyleen vinyleen) polymeren, gesynthetiseerd via de dithiocarbamaat route, nog steeds potentieel hebben om gebruikt te worden in zonnecellen, maar dat verder onderzoek vereist is naar de optimalisatie van de filmvormende eigenschappen van de materialen en de resulterende morfologie. Dit kan bewerkstelligd worden zowel op het niveau van de zonnecel als op het moleculair niveau.

List of publications and contribution

1. A deeper insight into the dithiocarbamate precursor route. Optimization of the synthesis of soluble poly(thienylene vinylene) derivatives.

- article writing
- all synthetic work, characterization of the molecules
- Solar cells & devices: Arne Palmaerts & Martijn Lenes

2. An Efficient Acid induced Conversion of Dithiocarbamate Precursor Polymers into Conjugated Materials

- article writing
- synthesis, characterization & analysis of the parts concerning PTV-derivatives
- PPV-derivatives: Joke Vandenbergh

3. Exploring the DTC chemistry by the synthesis and study of model compounds.

- article writing
- all synthetic work, characterization & analysis

4. Identification and quantification of defect structures in Poly(2,5-Thienylene Vinylene) derivatives prepared via the dithiocarbamate precursor route by means of NMR spectroscopy on ^{13}C-labeled polymers.

- article writing
- all synthetic work
- NMR spectroscopy in cooperation with S. Chambon and P. Adriaensens

5. Joint theoretical-experimental NMR study of small thiophene based model compounds as a guideline for the assignment of structural defects in poly(thienylene vinylene) (PTV) based conjugated polymers

- article writing
- all synthetic work
- NMR spectroscopy in cooperation with P. Adriaensens
- theoretical calculations: E. Botek (FUNDP), B. Champagne (FUNDP) and V. Lemaur, D. Beljonne, R. Lazzaroni; university of Namur and Mons respectively

6. Synthesis and characterization of dihexyl PTV

- article writing
- all synthetic work, characterization & analysis
- FET measurements: Mark-Jan Spijkman and Dago De Leeuw; Philips Research and Groningen University

List of abbreviations

^{13}C NMR	Carbon 13 nuclear magnetic resonance spectroscopy
^{1}H NMR	Hydrogen 1 nuclear magnetic resonance spectroscopy
Ag	Silver
$AgNO_3$	Silver nitrate
Al	Aluminium
$AlCl_3$	Aluminium chloride
AM	Air mass
APT	Attached Proton Test
Au	Gold
$B(OMe)_3$	Trimethylborate
BELSPO	Belgian Federal Science Policy Office
BOP-PTV	Bi(octylphenyl) PTV
Br_2	Bromine
C_8K	Graphite-potassium intercalate
$CDCl_3$	Deuterated chloroform
CF_3COOH	Trifluoro acetic acid
CH_2Cl_2	Dichloromethane
$CHCl_3$	Chloroform
CH_3CN	Acetonitrile
Cu	Cupper
CuBr	Cupper bromide
DEPT	Distortionless Enhancement by Polarization Transfer
DME	Dimethoxyethane
DMF	Dimethylformamide
DNA	Desoxyribo Nucleic Acid
DTC	Dithiocarbamate
dppp	(Diphenylphosphino)propane
ε	Molar attenuation coefficient

EI	Electron impact
Eg	Energy gap/ band gap
Eq	Equivalents
ESF	European Science Foundation
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
EU	European Union
eV	electron volt
FET	Field effect transistor
FF	Fill factor
FT-IR	Fourier transform-infrared
FWO	Fonds Wetenschappelijk Onderzoek
GC/MS	Gas chromatography-mass spectrometry
GPC	Gel permeation chromatography
H_2O	Water
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
HETCOR	Heteronuclear correlation
$HgCl_2$	Mercury chloride
HOMO	Highest Occupied Molecular Orbital
I_2	Iodine
I_{sc}	Short circuit current
IAP	Interuniversity Attraction Poles
INADEQUATE	Incredible Natural Abundance Double Quantum Transfer Experiment
IR	Infrared
ITO	Indium Tin Oxide
J_{sc}	Short circuit current
K	Potassium
K_2CO_3	Potassium carbonate
KHMDS	Potassium hexamethyldisilazane
KtBuO	Potassium tert-butoxide
λ	Wavelength

LDA	Lithium diisopropylamide
LED	Light emitting diode
LHMDS	Lithium hexamethyldisilazane
Li	Lithium
$LiAlH_4$	Lithium aluminium hydride
LiBr	Lithium bromide
LiF	Lithium fluoride
LUMO	Lowest Unoccupied Molecular Orbital
M	Molar
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
M^+	Molecular ion
MDMO-PPV	poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]
MeOH	Methanol
Mg	Magnesium
$MgSO_4$	Magnesium sulphate
MPP	Maximum Power Point
MS	Massa spectroscopy
Na	Sodium
NaAc	Sodium acetate
$NaBH_4$	Sodium borohydride
$NaHCO_3$	Sodium bicarbonate/ sodium hydrogen carbonate
NaHMDS	Sodium hexamethyldisilazane
NaOH	Sodium hydroxide
$NaSO_4$	Sodium sulphate
NatBuO	Sodium tert-butoxide
NBS	N-Bromosuccinimide
n-BuLi	*n*-Butyl lithium
NH_4Cl	Ammonium chloride
Ni	Nickel
$Ni(dppp)Cl_2$	[1,3-bis(diphenylphosphino)-propane] dichloronickel(II)

NMR	Nuclear magnetic resonance
O_2	Oxygen
OLED	Organic light emitting diode
O-PTV	Octyl-PTV
OPV	Organic photovoltaics
p	para
P3CTV	Poly(3-carboxylated thienylenevinylene)
P3HT	Poly(3-hexylthiophene)
PCBM	[6,6]-phenyl-C_{61}-butyric acid methyl ester
PCE	Power Conversion Efficiency
PD	Polydispersity
$Pd(PPh_3)_4$	Tetrakis (triphenylphosphine) Palladium
PEDOT	Poly(3,4-ethylenedioxythiophene)
PET	Polyethylene Terephthalate
pK_a	Acid dissociation constant
PITN	Poly(isothianaphthene)
ppm	Parts per million
PPV	Poly(phenylene vinylene)
PSS	Poly(styrenesulfonate)
PTE	Poly(2,5-thienylene-ethylene)
PTV	Poly(thienylene vinylene)
RFID	Radio frequency identification
RI	Relative index
R.T.	Room temperature
SBO	Strategisch BasisOnderzoek
SEC	Size exclusion chromatography
$SOCl_2$	Thionyl chloride
T_1c	^{13}C spin-lattice relaxation time
$TBAPF_6$	Tetrabutylammonium hexafluorophosphate
TEA	Triethylamine
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran

$TiCl_4$	Titanium chloride
TLC	Thin Layer Chromatography
TMS	Tetramethylsilaan
UV-Vis	Ultraviolet Visible
UV-Vis-NIR	Ultraviolet Visible Near Infrared
V_{oc}	Open circuit voltage
Zn	Zink
λ_{max}	Wavelength of maximum absorbance

Dankwoord

Aan het einde gekomen van deze toch wel “lijvige” bundel, wordt het wel eens tijd om terug te blikken op deze laatste vier jaren. In juli 2006, leken vier jaar nog een ellelange tijd, maar uiteindelijk tikten de dagen sneller en sneller weg. Wanneer ik uiteindelijk in de zomer van 2010 begon mijn data neer te pennen in dit werk, leek een proefschrift ook wel een verschrikkelijk eenzame bezigheid. Maar ik besef maar al te goed dat je dit niet alleen doet. Daarom zou ik de verschillende mensen in mijn omgeving, die mij deze vier jaren hebben gesteund, gemotiveerd en hulp hebben geboden waar nodig, graag even in de bloemetjes willen zetten.

Allereerst, zou ik mijn promotor willen bedanken, Prof. Dr. Dirk Vanderzande. In de eerste plaats om mij de kans te geven dit project te starten. De intensieve begeleiding tijdens de voorbereidingen van het project, daarbijhorende IWT aanvraag en de beroemde “minuut”. Ik zal nooit je omschrijving van een doctoraat vergeten: “Wij bieden je een kompas, alle benodigdheden en een eindpunt,... de weg daarnaartoe zoek je zelf”. Hierdoor werd er mij een grote vrijheid, maar ook een grote mate van verantwoordelijkheid gegeven waaruit ik zeker veel geleerd heb. Ik heb mijn kompasje gegrepen, mijn weg gewandeld (ook al was ik af en toe te “negatief” in jouw ogen, in mijn ogen “realistisch” ☺) en mijn doel bereikt!

Verder gaat mijn dank, en niet in het minst, uit naar Prof. Dr. Peter Adriaensens. Peter, bedankt om mij in te leiden in de “wondere wereld der NMR”. Ik ben meer en meer gaan beseffen wat voor een rijke, uitgebreide en vruchtbare techniek NMR kan zijn. Hieruit vloeiden, vele leerrijke sessies in het NMR lokaal (die ook een aangename verkoeling brachtten tijdens de zomermaanden), tevens bedankt voor de nauwkeurige verbeteringen van de bijhorende papers.

Een woordje van dank gaat tevens uit naar Prof. Dr. Thomas Cleij. Thomas bedankt voor je, zowel praktische als intellectuele, hulp met verschillende metingen/technieken. Ook je grote relativeringsvermogen, de vele gastvrije babybezoekjes, bbq en overheerlijke dineetjes zullen mij zeker bijblijven. Al deze dingen brachten een grote gezelligheid in onze groep.

Natuurlijk mag ik de nieuwe telgen in ons proffenkorps niet vergeten, Wouter Maes en Thomas Junkers. Mischien spijtig dat jullie hier pas in mijn laatste jaar aankwamen. Het laatste jaar voelden we een nieuwe frisse wind waaien in ons labo,... wat ik zeker apprecieerde. Ik wens jullie dan ook beiden veel succes om onze “pool” van jong gemotiveerd talent verder in goede banen te leiden. In dit rijtje hoort ook Laurence Lutsen thuis. Bedankt Laurence voor het snel oplossingen van onze vele praktische problemen, snelle bestellingen, raad tijdens PhD meetings,...

En dan nu een woordje van welgemeende dank voor de meest aanwezige mensen, wiens hulp mischien niet de grootste, maar zeker de veelvuldigste en waarschijnlijk wel de belangrijkste was. Motivatie, geluk, succes,... schuilt meestal in kleine dingen en het zijn net die kleine dingen die je nodig hebt om elke dag opnieuw tot een mooie, leerrijke en interesante dag te maken. Beste collegae, ik zal nooit de toffe, gezellige en ook wel “uitgelate” sfeer op “den bureau” vergeten. De vele bouw-, verbouw-, baby-,... perikelen brachten een aangename afwisseling na vele uren in een toch wel “stinkend” labo (al kon dit op ons bureautje ook wel eens gebeuren, lang leve de kikkers!) First, I’d like to thank Fateme: Fateme thank you for introducing me into PTV synthesis, all your practical knowledge and tips gave me a very good start during my first year. Verder natuurlijk ook een woordje van dank aan onze “harde” labokern: Iris, Veerle en Wibren die voor continuiteit in het labo zorgt. Jullie hebben door de jaren heel veel mensen zien komen en gaan en telkens weer helpen jullie ons met al de kleine en grote dingen die hier heel nieuw waren/zijn voor ons allemaal. Wibren bedankt voor het klaarstaan bij vragen, de vele gezamelijke IAP meetings,... Iris veel succes met de geboorte van je nieuwe spruit. Hopelijk moet je hier niet meer lang op wachten als je dit leest, Elise zal dol gelukkig zijn met haar nieuwe broer. Veerle, ook Gijsje zou blij zijn met een (enkele) speelkameraadje(s), maar dat zal wel in orde komen! Ook bedankt voor je organisatorische hulp bij doctoraatsfeesten, GPC’s, ... En dan nu een plaatsje voor mijn lotgenoten, partners in crime, doctors in spe,... met wie ik hier jaren lief, leed en soms vele frustraties heb gedeeld. Sarah, bedankt voor onze vele “praatjes” in het labo, dikwijls waren we er “eenzaam met ons twee” maar daar hebben we ons toch altijd mooi doorgeslaan. Ook onze extramuros activiteiten: de tiramisufabricaties, kook- en haaravondjes, autoritjes,... zullen mij bijblijven. En natuurlijk jouw stralend hoogtepunt als prachtige bruid. Sarah, vergeet niet wat er normaal allemaal volgt na zo'n trouw he... ☺. Hierbij zijn we beland aan ons meest aanwezige lid van het labo, onze Fré, Fredje, Fritsel, Fred Flinstone of wat ik nog allemaal verzonnen heb de laatste jaren. Fré bedankt voor de toffe sfeer in de groep, de Borat imitaties, het opvullen van "elke" stilte ☺ en de vele "geanimeerde" discussies. Als we Frederik vermelden is natuurlijk Inge ook niet ver weg. Inge nog veel succes met de "opvoeding" van Fré, je zal je handjes nog vol hebben, maar ik heb er alle vertrouwen in dat jullie daar samen wel gaan uitkomen. Dus nu wachten wij allemaal vol ongeduld op de housewarming, bruiloft, babyborrel,... En het moet niet noodzakelijk in die volgorde zijn hoor! Wie ook mijn hele "loopbaan" hier prominent aanwezig was is Joke, met wie ik vele treinritjes naar alle uithoeken van het land heb gedeeld. Joke bedankt voor de vele toffe gesprekken, gezamelijke congresbezoeken, je motivatie om van onze groep een echte groep te maken (mede door de lunchmeetings) en je altijd eerlijke en oprechte meningen en opmerkingen. Veel succes met het grote verbouwavontuur en in je verder professionele carriere. Natuurlijk ook vele blijken van dank aan de jongere garde in het labo, Ans (veel inrichtplezier gewenst), Lidia, Matthias, Suleyman, Toon (waarvan ik nogal aparte kuistechnieken heb geleerd ☺) en Tom. Nog veel succes in jullie volgende jaren hier, breng dat maar allemaal tot een mooi einde zodat ik af en toe nog eens terug kan komen voor een mooie receptie en bijhorend feestje. En niet te vergeten, de mannen waarvoor de BIO in onze groepsnaam moest verschijnen. Erik en Gunter, ook al zitten jullie wat verder weg verstopt, toch hebben jullie een plaatsje in onze groep veroverd. Jullie levenswijsheid en organisatievermogen hebben zeker ook een inbreng gehad in mijn jaren hier.

Natuurlijk is er ook nog een plaatsje voor de mensen die ons hier reeds "verlaten" hebben maar die zeker ook hun stempeltje gedrukt hebben op mijn doctoraat: Sylvain (bedankt voor de vele NMR-metingen, Maldi-tof experimenten,... en nog veel plezier gewenst op al je lange reizen), Arne (bedankt voor de metingen van de zonnecellen), Wouter (en de toffe lessen in onze MAO-pakjes), Jan (ik zal nog wel eens voor taartjes zorgen), Raoul, Kristof, Jimmy, Zarina, Burak, Lien, Ine, Julliete, Brecht, Bert,.... het zijn er veel te veel om op te noemen. In dit rijtje horen ook de vele bachelor studenten thuis die elk ook een, al is het maar steentje, hebben bijgedragen aan mijn thesis. Bedankt, Dominique, Raphaël, Dennis, Geert-Jan en Pieter (ook veel succes met je start in onze groep!). Als we het over studenten hebben komen we natuurlijk naadloos bij het didactische team! Hilde, Gène en Rita, die altijd klaar staan om ons te ondersteunen waar nodig in onze didactische taken. Merci! En dan nu de mensen die vele metingen hebben gedaan op mijn producten de laatste jaren, bedankt Huguette voor al de IR en UV-Vis spectra, Iris en Veerle voor de GPC's, Koen voor de NMR-spectra en al onze kleine en grote herstellingen, Christel voor de bestellingen, Tim onze "glasblower" voor de vele herstellingen en natuurlijk tenslotte Jan "de massaman" voor de vele GC/MS analyses en de deskundige uitleg hierbij.

Een niet onbelangrijk plaats in dit lijstje is ook het IAP, wat zorgde voor mijn vierjarige financiering en de vele samenwerkingen met andere universiteiten. Ik kreeg de kans in-situ UV-Vis metingen te doen aan de VUB o.l.v. Prof. Dr. Guy van Assche. Aan de Universiteit van Gent kon in de groep van Prof. Dr. Filip Du Prez in situ IR metingen doen en een inwijding krijgen in ATRP, waarvoor ook mijn grote dank aan Bart Dervaux en Stijn D'hollander voor hun hulp. Verder werden mijn moleculen ook onderworpen aan theoretische berekeningen, waarvoor ik Edith Botek, Benoit Champagne en Roberto Lazzeroni wil bedanken. Mijn tocht bracht me ook tot op IMEC waar ik Afshin Hadipour wil bedanken voor het verifieren van onze zonnecel resultaten. Tevens een welgemeend woordje van dank voor de snelle FET-metingen van Mark-Jan Spijkman.

Tenslotte wil ik al mijn vrienden en familie bedanken voor hun onrechtstreekse bijdragen aan mijn doctoraat. En als allerlaatste, zou ik graag de drie belangrijkste mensen in mijn leven bedanken. Vooreerst mijn ouders, die al 27 jaar elk minuut van de dag voor mij klaarstaan, zelfs al sta ik al een tijdje op eigen benen. Ze hebben mij altijd onvoorwaardelijk gesteund in al mijn beslissingen, door hen heb ik mij ontwikkeld tot wie ik nu ben. En last but not least, is er een speciaal plaatsje voorzien voor Jon, met wie ik nu al bijna 10 jaar een perfect "team" vorm. Jon, het blijkt dat onze enorme tegenstellingen soms, elkaar perfect aanvullen. Bedankt om er altijd voor mij te zijn, mij tot rust te brengen, mij mezelf te laten zijn en nog zoveel meer...

En met deze woorden, kan ik een toch wel mooie periode in mijn leven afsluiten. Een periode waarin ik, letterlijk en figuurlijk, vele brandjes heb geblust, waarin ik gegroeid ben door al de mensen rondom mij en waaraan ik vele herinneringen zal hebben.

Bedankt Allemaal!

Hanne

There is no failure. Only feedback.