MERI MÄKELÄ
SYNTHESIS OF A DIKETOPYRROLOPYRROLE/TETRAFLUOROBENZENE COPOLYMER VIA DIRECT ARYLATION POLYCONDENSATION
Master of Science Thesis

ABSTRACT

TAMPERE UNIVERSITY OF TECHNOLOGY
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The growing demand on the renewable energy sources has increased the interest on utilizing solar power. Inorganic silicon based solar cells are already well known and have extensively been used. Recently, new types have thus been designed: organic solar cells. These devices are based on organic active material layers consisting of donor and acceptor-materials. The active material is often made of a conjugated polymer or fullerene based compounds. Conjugated polymers are able to transport charge along the polymer chain and thus act as a semiconductor. Diketopyrrolopyrrole (DPP) compounds are conjugated polymers that combine good thermal, optical and electrical properties and are therefore promising materials for optoelectronic devices. Furthermore, the properties of DPP compounds can easily be modified and can be produced via straightforward synthesis. Previously DPP compounds were mostly synthesized with cross-coupling methods that required organostannane cross-coupling precursors.

This work includes a theoretical overview of conjugated polymers and one of their applications, namely, organic solar cells. The structure and the operation of the solar cell are described and the requirements for an optimal polymer used in active material are given. As an example of conjugated polymers used in solar cells, DPP compounds and their characteristics are presented. The novel direct arylation method used in the polymerization is described and compared to traditional coupling methods. In addition, microwave assisted heating is introduced.

In the experimental part of the work, a DPP based monomer is synthesized and copolymerized with dibromotetrafluorobenzene. Direct arylation polycondensation was used to produce 3,6-diphenydiketopyrrolopyrrole/tetrafluorobenzene. Results are compared to results obtained by Stille cross-coupling method. Optimal reaction parameters are reported for each step of the monomer and polymer syntheses. The thermal and optical properties of the copolymer were investigated and compared with values found in the literature.

The results show that the copolymer made by direct arylation has good quality and promising properties to be used in organic photovoltaic devices. The copolymer tolerates high temperatures and absorbs light effectively. Reaction conditions leading to good yield and high molecular weight were found for the copolymerization. Because of the utilization of direct arylation, monomer synthesis could be made two steps shorter than with existing methods. Moreover, the reaction parameters were optimized especially in the case of alkylation and purification process. Further studies are suggested especially on the solvent choice and termination mechanism of the copolymerization.

TIIVISTELMÄ

Aurinkoenergian hyödyntäminen sekä samalla uusien aurinkokennojen kehitystyö on viime vuosina lisääntynyt voimakkaasti. Epäorgaaniseen piihin pohjautuvien kennojen lisäksi tutkimuksen kohteena ovat uudentyyppiset, orgaanista materiaalia hyödyntävät aurinkopaneelit.

Orgaanisten aurinkokennojen aktiivisena kerroksena käytetään konjugoituja polymeerejä jotka voivat kuljettaa varausta ja toimia puolijohteen tavoin. Diketopyrrolopyrroli (DPP) yhdisteet ovat esimerkki konjugoidusta rakenteesta, joka voi toimia aktiivisena kerroksena orgaanisessa aurinkokennossa. Hyvien johtavuusominaisuuksien lisäksi DPP polymeerit ovat termisesti kestäviä ja absorboivat valoa aallonpituudella 380–780 nm. DPP yhdisteiden valmistusmenetelmä on yksinkertainen sisältäen vain kaksi reaktiovaihetta ja niiden ominaisuudet ovat helposti muunneltavissa.

Tämän diplomityön teoreettinen osuus alkaa konjugoidun rakenteen sekä sitä hyödyntävien sovellusten kuvauksella. Orgaanisista aurinkokennoista esitellään rakenne ja toimintaperiaate sekä ominaisuudet, joita aktiivisessa kerroksessa käytettäviltä polymeereiltä vaaditaan. Konjugoitujen polymeerien yhtenä ryhmänä esitellään diketopyrrolopyrrolit jotka ovat ominaisuuksiltaan sopivia käytettäväksi aurinkokennojen aktiivisena materiaalina. Polymeroinnissa käytetty suora C-H-aktivaatio menetelmä esitellään ja sitä verrataan perinteisiin kytkentäreaktioihin. Lisäksi verrataan mikroaalto avusteista lämmitystä perinteiseen termiseen lämmitykseen öljyhauteessa. Teoriaosuus päättyy työssä käytettyjen karakterisointimenetelmien esittelyyn.

Työn kokeellisessa osassa syntetisoitiin tiofeeni-DPP monomeeri, joka polymerisoitiin dibromotetrafluorobentseenin kanssa käyttäen uuden tyyppistä C-H-aktivoitua menetelmää. Sekä monomeerisynteesille että polymerointireaktiolle pyrittiin löytämään optimaaliset reaktio-olosuhteet. Polymerisoinnin tulosta verrattiin kirjallisuudessa esiteltyyn perinteisellä ristiinkytkentä menetelmällä valmistettuun vastaavaan kopolymeeriin. Lopullisen tuotteen optisia ja termisiä ominaisuuksia mitattiin ja niiden perusteella arvioitiin tuotteen sopivuutta käytettäväksi orgaanisissa laitteissa, jotka hyödyntävät auringon valoa.

Tulosten perusteella DA metodilla tuotettua kopolymeeriä voidaan pitää laadullisesti hyvänä ja ominaisuuksiltaan lupaavana: tuote absorboi valoa tehokkaasti ja kestää korkeita lämpötiloja hajoamatta. Lisäksi polymerisointireaktiolle löydettiin sopivat parametrit, joilla yhdistyvät korkea saanto ja hyvä molekyylipaino. Monomeerisynteesiä voitiin C-H-aktivaatio menetelmän ansiosta lyhentää verrattuna aikaisempiin menetelmiin ja reaktio-olosuhteita optimoitiin erityisesti alkylointivaiheen ja puhdistusprosessin osalta. Kopolymeerin laatua voitaisiin mahdollisesti parantaa entisestään optimoimalla liuottimen valinta polymerisointireaktion aikana ja tutkimalla tarkemmin ketjun päättymismekanismia.

PREFACE

In Freiburg, Germany, on 12 August 2014

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TABLE OF CONTENTS

List of symbols and abbreviations

^{1}H	Proton
18-Crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
Br$^-$	Bromide
δ	Chemical shift
CB	Chlorobenzene
CDCl$_3$	Deuterated chloroform
CHCl$_3$	Chloroform
Cl$^-$	Chloride
CMD	Concerted metalation-deprotonation
d	Doublet (NMR)
DA	Direct arylation
DCM	Dichloromethane
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DPP	Diketopyrrolopyrrole
DPPPhF$_4$	DPP-tetrafluorobenzene copolymer
DSC	Differential Scanning Calorimetry
eV	Electronvolt
eq	Molar equivalent
GPC	Gel Permeation Chromatography
H$_2$O	Water
HOMO	Highest occupied molecular orbital
K$_2$CO$_3$	Potassium carbonate
KOBu	Potassium-t-butoxide
I$_2$	Iodine
J	Coupling constant (NMR)
LUMO	Lowest unoccupied molecular orbital
M	Molar concentration, mol dm^{-3}
m	Multiple (NMR)
MgSO$_4$	Magnesium sulfate
MeOH	Methanol
M$_n$	Number average molecular weight
M$_w$	Mass average molecular weight
M$_y$	Viscosity average molecular weight
M$_z$	Size average molecular weight
Na$_2$SO$_3$	Sodium Carbonate
NaCl	Sodium Chloride
NMP	1-Methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance
OFED	Organic Field-Effect Transistor

OPV	Organic photovoltaic
OTf	Trifluoromethanesulfonate, triflate
PCy_3	Tricyclohexylphosphane
$Pd(OAc)_2$	Palladium acetate
PDI	Polydispersity index
PivOH	Pivalic acid, dimethylpropanoic acid
PivOK	Potassium salt of pivalic acid
PPh_3	Triphenylphosphane
ppm	Parts per million
s	Singlet (NMR)
T_g	Glass transition temperature
TGA	Thermal Gravimetric Analysis
Th-DPP	Dithienyl-diketopyrrolopyrrole
TLC	Thin-layer Chromatography
T_m	Melting point
TMS	Tetramethylsilane
TS	Transition state

1 INTRODUCTION

The ever growing world is requiring more and more energy to fulfill the needs of industry and households. There is increasing pressure on renewable energy sources. For example in Germany significant investments have been made and the renewable energy sector is growing faster than expected [1]. Wind power is the most important renewable energy source in Germany, but amount of energy taken from sun light is growing when the solar cell technology has developed. In many European countries use of solar energy is today governmentally supported and the use of solar energy has indeed been growing fast in recent years.

Regardless of the growth, photovoltaics are covering only 9.4 % of the renewable energy supply in Germany, while wind power produces roughly a double amount, 16.8% [1]. The cost of solar energy is about 0.3 USD/KW-h which is still high compared to other renewable energy sources but prices are contracting. In 2011 the capacity of installed solar photovoltaics increased by 70% and prize of solar devices decreases rapidly speeding up by low cost manufacturing in China. Power produced by an inorganic silicon cell made in China costs 0.75 USD/W while Western manufactures need to content to 1,1 USD/W [2]. Lower device prices make solar energy a cost-effective solution also in regions with less net sunlight. At the same time improvements in solar technology are increasing the lifetime and efficiency of the photovoltaics.

The above described trend in solar technology will continue if new, cheaper and more effective materials can be used in cell manufacturing. Solar devices also need to be more versatile, durable and easily available to keep them attracting choice for consumers. Organic solar cells may respond to these requirements by using organic compounds as an active material instead of silicon. This gives rise to a new era of lightweight, rollable and adjustable photovoltaics.

First organic solar cell was presented at the beginning of the 70's. As Koyuncy et al. pointed out, organic semiconductors have several advantages compared to traditional, inorganic solar cells. Organic devices are light in weight, flexible and relatively easy and cheap to produce. Lower material consumption per area leads to lower cost and weight, which makes them attractive for solar cells [3]. The efficiency of best organic solar cells has reached the level of 10 %, which is still much lower compared to inorganic cells, which have power conversion efficiency over 20%. However, organic cells have several advances and potential to improve the effectiveness [4]. The use of polymers gives limitless opportunities to process and adjust the active material and modify it to meet the demands of photovoltaic applications. Lot of research is currently

focused on improving the effectiveness of organic active materials. This means novel polymers, new synthesizing methods and better processing ways.

Among other emerging materials, diketopyrrolopyrrole (DPP) compounds seem to have potential as solar cell polymers. They absorb light efficiently, transport the charge well along the conjugated chain, tolerate high temperatures and are relatively easy to synthesize. However, DPPs are new and quite little discussed in the literature and are usually prepared with traditional coupling methods. This leaves room for closer research and testing new working methods and gives motivation for my thesis.

The goal of this work was to synthesize diketopyrrolopyrrole monomer and co-polymerize it with dibromotetrafluorobenzene using direct arylation polycondensation. Best reaction conditions were investigated for both monomer synthesis and polymerization. Results are compared to the traditional Stille cross-coupling presented in literature [5]. The product, diketopyrrolopyrrole/tetrafluorobenzene, is designed to be used in the active layer in organic solar cells. The work was part of a research done in the working group lead by Dr. Michael Sommer at the Institute for Macromolecular Chemistry, University of Freiburg, Germany. The group is studying novel conjugated polymers to be used in optoelectronic devices.

The thesis consists of a theoretical overview and an experimental part. Conjugated polymers are defined and their application as active materials in organic solar cells is presented. DPP compounds are then introduced as a specific group of conjugated materials. The last two chapters of the theoretical part consider polymerization and characterization methods used to synthesize and examine the DPP copolymer. Experimental part begins with the monomer synthesis and the optimization process. Then the polymerization entries are described and finally polymer properties are studied. Conclusions are made in chapter 8 and last chapter includes detailed description of the syntheses.

2 CONJUGATED POLYMERS

A new group of polymers, conjugated polymers suitable for electronic materials, were presented in 1977 by Heeger, Shirakawa and MacDiarmid [6]. They showed that polyacetylene, the simplest example of conjugated polymers, can transfer charge and act like a semiconductor. It can be also chemically doped after the synthesis to create metallic conduction properties. [7,8] Figure 1 shows the structure of polyacetylene, also called as polyethyne.
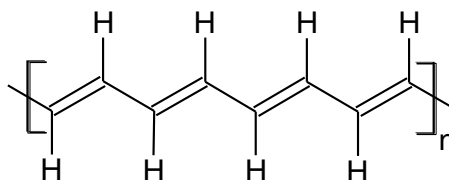
Figure 1. *Polyacetylene, the simplest conjugated polymer.*

Conjugation is defined as a system that consists of alternating double and single bonds and therefore has a delocalized π-electron system. Carbon atoms have alternating bond lengths and are bound together with sigma bonds and with π-bonds created by carbon p_z orbitals. [9,10,11] Electrons in the π-orbitals can delocalize along the conjugated bonds [12]. Molecules containing conjugated system are more stable than the corresponding non-conjugated ones. The increased stability is due to hybridization: alternating single and double bonds make the sp^2 orbitals to overlap and form a stronger bond. Furthermore, molecular orbitals have lower energy in conjugated system thus lowering the resonance energy and stabilizing the molecular. [13]

Conjugated polymers are intrinsically conductive, since the charge is able to move along the main chain. Charge is moving along the polymer chain in a fast wave-like movement and also by hopping between polymer chains that are packed next to each other [14]. Conjugated polymers are activated with oxidizing or reducing process only and doping changes not only the conductive properties but also the optical and magnetic properties of the polymer [15]. This differentiates conjugated polymers from conductive polymers that have been made electrically conductive by adding particles of metal or other conducting species.

Doping of the conjugated polymer chain means that amount of electrons in the polymer chain is modified. The process is reversible and can be repeated several times without damaging the polymer. All conjugated polymers can be doped with p- or n-type redox doping. If doping is done by partly oxidizing the conjugated chain of the polymer, it is called p-doping. Positive charge is delocalized by π-electron system and electrons

can move in the polymer chain. Thus the polymer becomes a p-type semiconductor. Correspondingly, partly reduction of the conjugated chain is called n-doping and the product is n-type semiconductor. Doping can be done chemically by adding an oxidizing or reducing agent or electrochemically with electric current. Furthermore, doping can be done without a doping ion. High energy radiation, such as UV-light, can give the electrons required energy to go over the band gap. This photo-doping causes charges that delocalize to polymer chain. However, the radiation energy must be greater than the energy difference in the band cap of the polymer. [16] When conjugated polymers are used in the organic solar cells, light is enough to induce electron movement [7, p. 14].

Earlier conjugated polymers were regarded only as pigments because of their ability to absorb energy from the UV- and visible light. Light carries energy as photons and can therefore excite π-electrons to higher molecular orbitals. Conjugated compounds with delocalized π-electron system contain valence electrons with low excitation energy level and are therefore easily excitable. [18]

After the unique properties of polyacetylene were published, research on other conjugated polymers, for example polyaniline, polythiophene and polypyrrole (Figure 2) began.
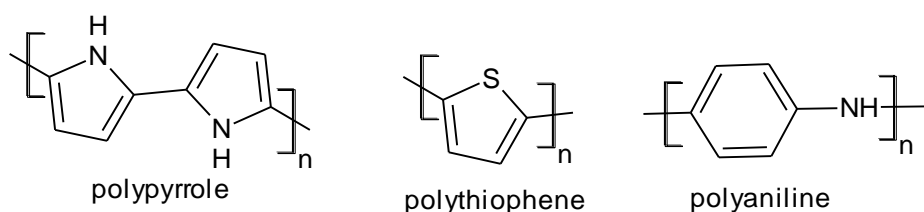
Figure 2. *Examples of conjugated polymers.*

These compounds are more stable and easier to process compared to polyacetylene, which is insoluble and rather unstable [7,11]. The development of new or well modified conjugated polymers and copolymers has been the goal in polymer chemistry in recent years. Since 1990 conjugated polymers have been used in commercially available diodes and later in polymer LEDs. Today they are widely used in electronic organic applications, such as OLEDs for lighting and flat panels or organic field-effect transistors for disposable electronics. Conjugated polymers have also used as sensors, heaters, photo detectors and electrochromic cells. [19]

3 ORGANIC SOLAR CELLS

Conjugated polymers fulfill the two most important requirements set to photovoltaic device materials: they absorb light effectively and are able to carry charge. Therefore they are used in active material of organic solar cells.

3.1 Working principle

Organic photovoltaic device (OPV) is a system that uses organic molecules to absorb light and produce electricity. Active layer is sandwiched between two electrodes and it consists of organic materials instead of inorganic silicon. Organic layer has two phases: donor, an electron donator, and electron withdrawing acceptor. Conjugated materials are commonly used in both roles. Polypyrrolopyrrole, polythiophene and porphyrin are examples of donor materials. Acceptor is typically made of fullerene or perylene compounds [4,17].

Electrostatic forces take place in organic layer, when the absorbed light creates exitons. Exitons are hole-charge pairs which can decompose into free charge carriers. Absorbed light gives the donor material a photon in a way that the exiton in the Highest Occupied Molecular Orbital (HOMO) has enough energy to climb up to the Lowest Unoccupied Molecular Orbital (LUMO). The material with the higher LUMO is called donor and an energy drop is needed between the donor's LUMO and the acceptor's LUMO. The exitons diffuse to the donor-acceptor interface where electron transfer is possible and the exitons can decompose to electrons and holes. Figure 3 presents the charge transfer between molecular orbitals. [3,17]
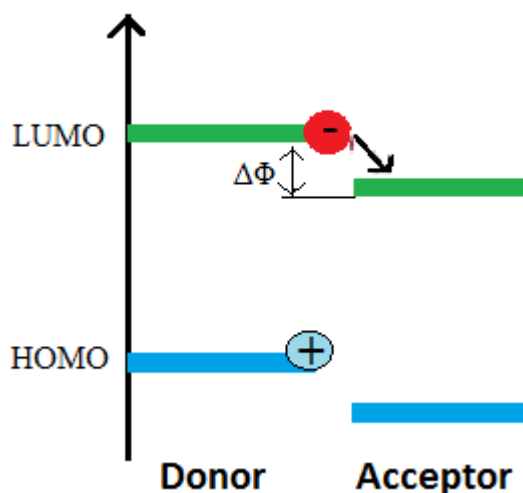
Figure 3*. Exiton decomposes to charges and electron is transferred to acceptor at the donor-acceptor interface. Potential difference between LUMO levels is marked with ΔΦ. Modified from* [3].

When the exiton has decomposed, excited electrons can jump from the LUMO-orbital of donor to the LUMO-orbital of the acceptor. Holes move to the donors HOMO orbital. Acceptor has now the negative charges which can travel along the conjugated polymer chain and finally reach the cathode. Holes are transferred by the polymer chain of the donor and collected in anode. Thus voltage difference is created between anode and cathode. [3,17,20]

3.2 Structure

Structure of the organic solar cell is based on substrate in which other layers are coated on top of each other. Structure and typical materials of organic solar cell are presented in Figure 4. The substrate can be rigid or flexible and it needs to be translucent to let the sun light in the cell. Glass substrate is commonly used for simple test devices. Looking from the sun-side anode is the topmost followed by a buffer and active layers. Indium-tin oxide (ITO) serves usually as the anode [12]. Finally metal cathode is placed on top of the active layer. Typical cathode materials are aluminum, calcium and barium [21,22]. Work function of calcium is well suitable for task but it is unstable, so Al-Ca mixture is often used.
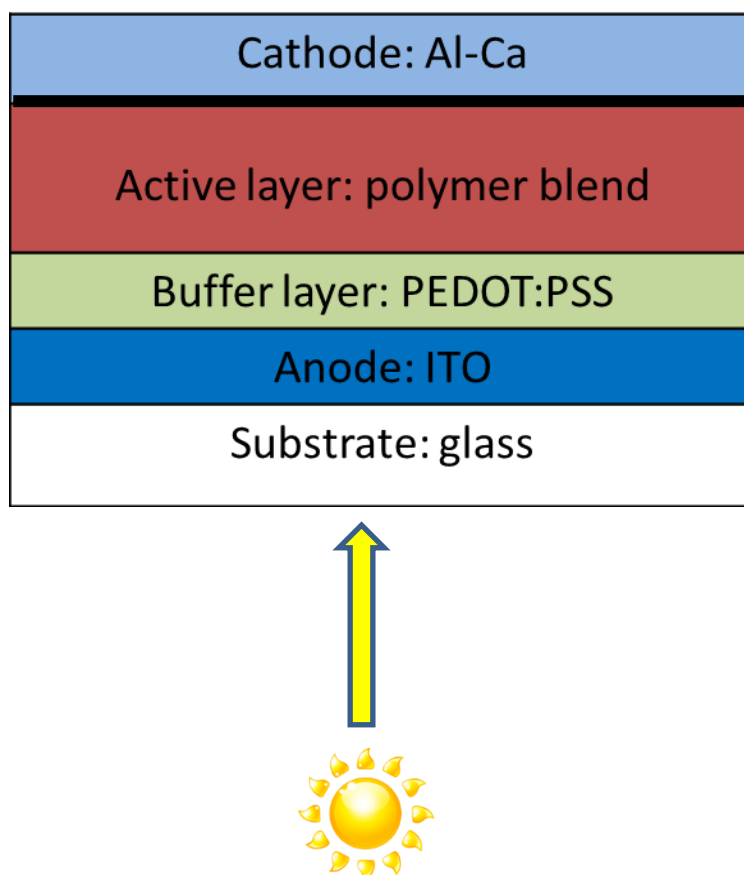
Figure 4. *Structure of a typical organic solar cell.*

A buffer layer, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or molybdenum oxide (MnO_x), is usually added between the electrode and the active layer. Anode buffer layer (ABL) is used to improve the interaction between anode and the active layer. This layer can be passed through by the holes but not by the electrodes, which improves the charge transfer in the cell. Hole transfer is most effective when the LUMO level of the donor matches with the work function of the electrode. Alternatively, a thin film of buffer material can be used to decrease the energy difference. In many cases the work function of PEDOT:PSS matches better with donor's LUMO level and thus mitigates the hole transport from donor to anode. Correspondingly, cathode puffer layers such as zinc oxide or titanium oxide can be used to improve the electron transfer from acceptor to cathode. It can also protect the metallic cathode from oxidizing and mixing with active layer. However, cathode buffer layer is less frequently used than ABL. [17,20,23]

At least three different cell structures can be used in active layer. First organic solar cells were single layer devices, which used only one organic compound as active material. Efficiency of the early devices was very low and the next step was to use two compounds with different electrical properties in active material layers. This so-called bilayer heterojunction device has donor and acceptor materials on top of each other.

Exitons decompose in the interlayer and charges are then carried in opposite directions towards electrodes.

After all, efficiency of bilayer devices was quite low and in 1995 Yu and Heeger presented improved structure: bulk heterojunction material [24]. In bulk heterojunction devices donor and acceptor materials are blended in one active layer, so that the diffusion distance of a single exiton is smaller and cell works more effectively. This polymer blend can be prepared by dissolving both polymers in same solvent and spin-coating the mixture. Phase-separation takes place during the spin-coating giving a bulk heterojunction. The drawback is that recombination of the exitons is more probable in blend where hole and electron can meet and dissociate while traveling to electrodes [3,4]. Structure of both bulk heterojunction and bilayer heterojunction are shown in Figure 5.
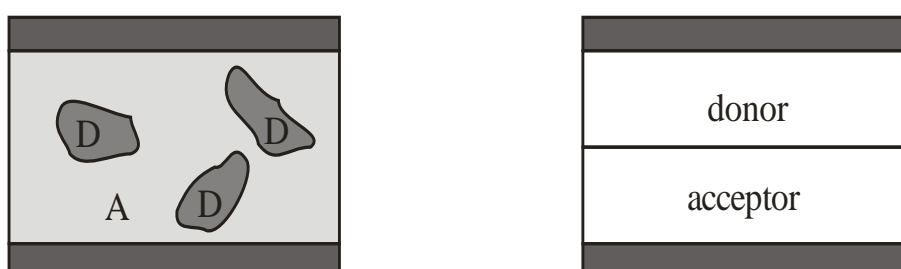
Figure 5. *Two structure of the active material. In bulk heterojunction (a) donor (D) and acceptor (A) are blended in one layer. Bilayer heterojunction (b) has separated donor and acceptor layers on top of the each other.*

In an ideal cell each exiton reach the donor-acceptor interface within the diffusion range and all charge carriers are collected by electrodes. In bulk heterojunction solar cells the donor and the acceptor are mixed and charge develop can be affected by active layer morphology. Fine particle size and proper mixing of the donor and the acceptor gives a large interface for the exitons to decompose. On the other hand, if the mixing is too fine cell efficiency is lost because of weaker charge transport capability. The best result can be obtained with a coarser morphology that gives balance between charge composing and transferring. [4,25]

3.3 Conjugated polymers in the active layer

The active layer may be fully or partly composed of conjugated polymers. Different types of devices based on either small molecules or conjugated polymers or combination of these two have been introduced. An example of the mixed type is a device, where conjugated polymers are connected with fullerene. This approach has been successfully used in organic solar cells over a decade [26]. However, it seems that fullerene-based cells have already been pushed to their theoretical limit and thus for better efficiency, new materials have to be introduced [3].

Purely polymer based solar cells are under research due to their easier processability and variability. If the active layer contains polymers only, it is possible to process

as solutions using simple and cheaper techniques. Spin-coating, ink printing and spray coating are commonly used ways to produce the thin active layer. Additionally, important parameters can be tuned after synthesis and during the cell preparation [27]. Properties of the conjugated polymers can be modified by varying energy levels, band gap, crystallinity and charge mobility. [3,4,25]

As a summary, active layer have four main tasks to make the organic photovoltaic device working. First, exitons should be generated then diffused to donor-acceptor interface and separated to charges. Finally charges should be transported to anode and cathode. To fulfill these assignments the conjugated polymer used in the active layer has many requirements. Polymer need to show good electrical and optical properties and physical properties should be suited for processing. In addition, it should be stable in air, also during high temperatures and UV-scattering. High molecular weight and regioregularity improve the device performance [28]. One important parameter is solubility to common solvents: polymers should be soluble so that proper film-formation is attainable and cell synthesis is possible in commercial scale.

For the donor material, absorption band should be broad and in the lower wavelength. Polymers that absorb light in the near-UV area receive higher energy radiation and thus more photons, as presented by Figure 6. Polymers, that absorbs red light and thus appears blue for the human eye, are absorbing in the area of 700-1000 nm. Therefore blue shifting polymers are effective materials in solar cells.
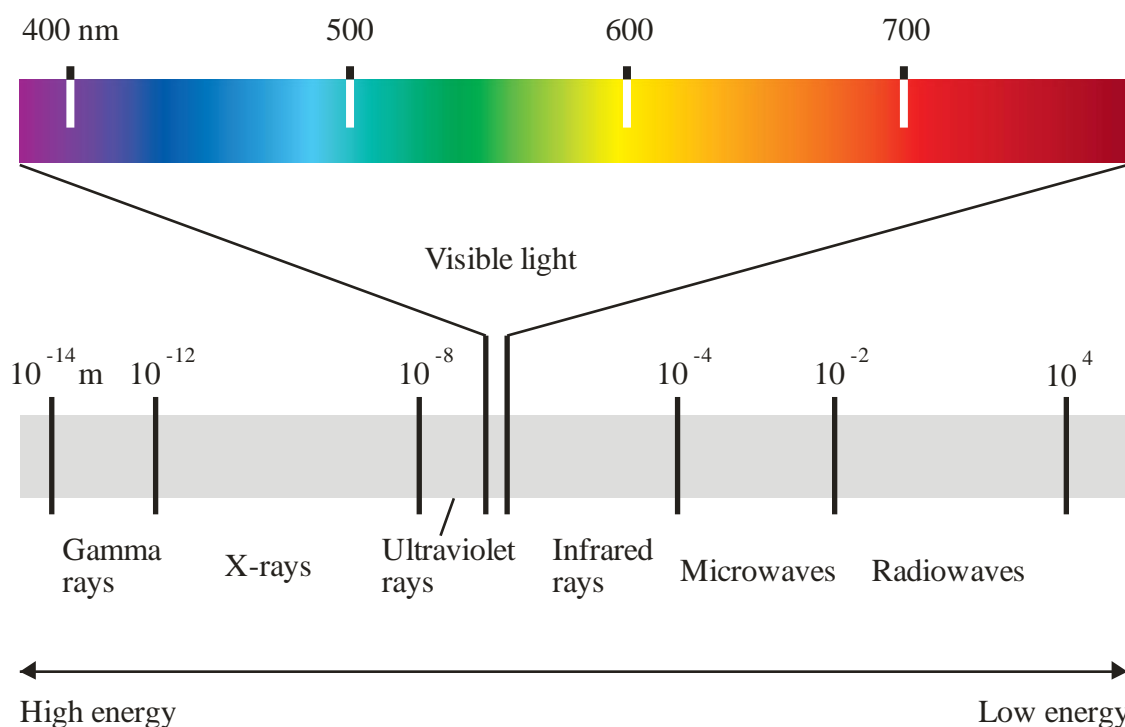
Figure 6. *Electromagnetic spectrum. Polymers with the absorption band at the red area of visible light absorb more energy from the sun light.*

The most common problem in organic solar cells is ineffective charge development and transport from the active layer to the electrodes [4]. HOMO and LUMO energy levels and thus band gap plays important role in exiton splitting and charge transfer. Band gap is defined as the energy difference between donor's LUMO and acceptor's HOMO. For the most effective conjugated polymers the band gap is lower than 2.0 eV and they are called low band gap polymers. The band gap can be tuned by using push-pull technique: the polymer chain consists of alternating electron withdrawing and electron repelling units [29]. Suitable donor-acceptor combination leads to small band gap and easier activation of the electrons in donor material. However, the energy difference between LUMO levels of the donor and the acceptor should not be too small because then the whole exiton could hop to the acceptor. The donor-acceptor ratio is also important: in one study best efficiency was achieved with five times more acceptor polymer than donor polymer. [27]

Good photostability of the polymer is required because the lifetime of a cell depends strongly on photostability of the active layers. Furthermore, control over morphology and self-assembly is vital in order to achieve long term stability of the device. Self-assembly is a process, in which molecules take a defined structure without outside guidance. Figuratively speaking the nanostructure builds itself. Morphology refers to the structure and arrangement of the molecules and it is dependent of the polymer structure. Highly crystalline polymers show good self-assembling abilities and well-ordered morphology. [27] Planar main chain of the polymer enables better π-π-stacking and more ordered morphology. If the backbone of the polymer is fully conjugated and rigid, crystallinity and thus morphology is are further improved. [4,25,29]

Morphology can be adjusted during the processing period for example by varying annealing temperature and time. Along with thermal treatments, the type solvent is crucial. Use of low-boiling point solvent, such as chloroform, gives the blend less time to self-assemble and leads to finer phase separation. More harsh morphology is preferred for clear phase separation and so for better charge mobility. Morphology is especially important in heterojunction cells, where donor and acceptor are blended. [4,27]

4 DPP COMPOUNDS

Diketopyrrolopyrrole (DPP) compounds represent a quite recently found group of conjugated molecules. They consist of 2,5-diketopyrrolo-[3,4-c]pyrrole core and aryl substituents, for example phenylene, thiophene or furan. Example of the structures is shown in Figure 7.

difuranyl-DPP diphenyl-DPP diphenyl-DPP
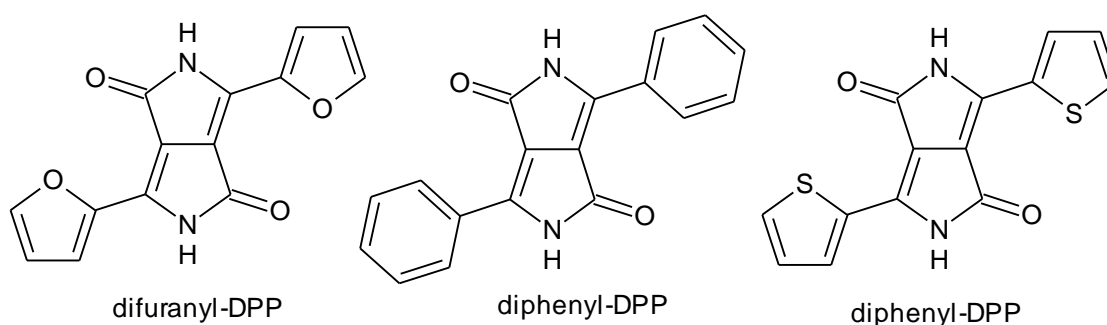
Figure 7. *Structures of the 2,5-diketopyrrolo-[3,4-c]pyrroles with different aryl substituents.*

4.1 Background

The first 2,5-diketopyrrolo-[3,4-c]pyrrole compound was synthesized as early as 1974. Farnum et al. [30] synthesized diphenyl-DPP by accident and in diminutive yield. In 1983 Iqbal et al. developed the reaction further and patented a simple synthetic pathway to produce diphenyl-DPP in high yield [31].

Because of their bright color, DPP compounds were first used as a pigment. Polypyrrolopyrroles belong to group of polycyclic pigments, which usually have weather and lightfastness, low solubility and good migration resistance. Migration means that the dissolved part of the pigment can escape to the materials that come in contact with the application. Polypyrrolopyrrole pigments are used in high grade industrial coating because of their excellent light, heat and weather durability. [32] Typical applications include plastics, inks and paints. For example diphenyl-DPP is registered as Pigment Red 254 and used in car industry due to its the good weather resistance [33].

Later, the unique properties of DPP compounds caught scientific interest. A DPP compound was used in polymerization for the first time in 1993 when Chan et al. [34] created a copolymer of phenylene, thienylene and diphenyl-DPP. First conjugated DPP polymer was synthesized by Tieke and Beyerlein in 2000 [35].

Nowadays DPP polymers are used in solar cells, OLEDs and OFETs. A patent considering he use of DPP oligomers in OPV has been published in 2011 [36]. DPPs also have applications as sensors and in the field of bioimaging. An example of the possible applications is a fluorine ion sensor used in dental health care [37]. Thanks to their good stability, DPPs have also found use in food packaging and toy materials [38].

4.2 Synthetic and structure

The succinic ester route presented by Iqbal et al. [31] is now widely used for preparing various of DPP compounds [22,39]. Succinic ester is stirred with 2 equivalents of aromatic nitrile and a strong base. The carbonitrile is selected according to the type of the target DPP monomer, for example phenyl carbonitrile gives diphenyl-DPP product. Succinic ester first reacts with one nitrile molecule to form a pyrrolinone ester, a single ring system, which further reacts with another aromatic nitrile to close the second ring. The reaction sequence for monomer prepared in this thesis is shown in Scheme 1. 2-thiophen carbonitrile **1** reacts with dimethyl succinic ester **2** to give enaminoester **3** and after ring closure pyrroline ester **4**. Repeating the stages with another nitrile gives 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione **5**. [40]
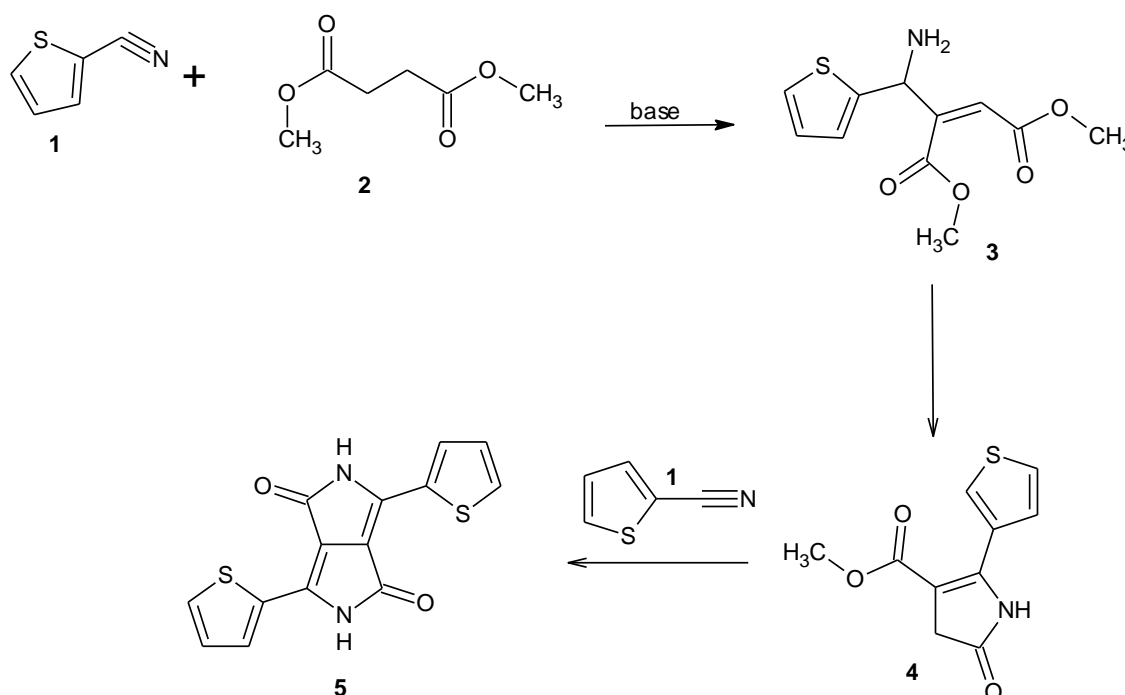
Scheme 1. *Synthesizing thiophene-DPP via succinic ester route. After* [40].

The reaction product, thiophene-DPP monomer **5**, contains two five-member γ-lactam units fused together giving in total of 8π electrons. χ-Lactam is a cyclic amide, that includes a carbonyl atom and has electron-withdrawing nature. Thus DPP acts as an

electron acceptor. [22,39] The aromatic groups originating from the nitrile take stands in ortho-position with respect to the nitrogen. Intramolecular hydrogen bonding is possible between lactam units, which makes the DPP chromophore non-soluble to almost any common solvent [41].

Solubility can be significantly improved by preventing the hydrogen bonding and thus alkylation to the nitrogen is essential to achieve a process able monomer. Variations in alkyl chains are used [22,42,43] and arylation or acylation is also possible [39]. Selection of the alkyl chain affects the packing ability of the polymer; long or bulky alkyl chains lead to non-ordered and loose packing [42]. On the other hand, alkyl chains should be long enough in order to reach good solubility and thus easy processability in monomer and most importantly in polymer form. Alkyl chains can also be asymmetrical [44,45].

The DPP body can be modified by varying the ring-group attached next to the nitrogen. This is done via selection of the corresponding nitrile during the succinic ester synthese [40]. Diphenyl-DPPs are possibly the most researched compounds followed by thiophene-DPPs. Reports of difuranyl and dithienothienyl based DPP also appeared [46]. Asymmetric DPP with two different ring structures has also been reported [47].

4.3 Properties

The properties of the DPP compounds vary depending on the aryl group used. Optical properties and solubility can be simply altered by changing the aryl groups and side chains. The DPP main unit gives all DPP compounds good chemical, mechanical and thermal stability. [48]

The color of DPP pigments range from yellow to purple depending on the ring structure, for example dithienyl-DPP is purple and difuran-DPP dark red [39,49]. Similarly, the colours of different DPP polymers cover a large scale from green to red [39]. Intensive color is due to π-π-interactions and hydrogen bonding. When a DPP powder is diluted to solvent, π-π-interactions disappear and this causes a color change, for example red diphenyl DPP turns into yellow. The UV-vis absorption maximum for diphenyl-DPP monomer is around 470 nm and photoluminescence about 530 nm in solution [35,40]. DPP compounds are also fluorescent in certain solutions [41].

All DPP compounds are almost flat and therefore strong π-π-interaction is possible between the layers of a DPP. This enables tight packing in solid form and gives DPP-compounds with good thermal stability. Thermogravimetrical analysises show that DPP-based polymers can tolerate temperatures between 300 °C and 500 °C before starting to decompose [22,39,50].

Because of their high crystallinity and fully conjugated chain, DPP polymers have good charge mobility. The structure can be tailored so that the DPP core and the aryl groups create and a push-pull system. In Hendriks' [29] study electron poor DPP core is combined with electron rich thiophene and phenylene blocks. Electrons are

pushed from the aryl groups and pulled to the DPP parts, which lowers the band gap. This kind of DPP donor gives power conversion efficiency of 8 % when combined with fullerene-acceptor. DPP-compounds can also be used both as an acceptor and as a donor in photovoltaic. As Li et al. [25] shows, an active layer based on DPP-compounds only is possible by using a DPP core and modifying the electrical properties by varying the aryl groups.

4.4 Dithienyl-DPP

Thienyl-DPPs are diketopyrrolopyrrole compounds with thiophen aryl groups, see Scheme 1. The thiophen side groups gives the compounds some specific properties. Thiophen-DPP monomer **5** has intense dark purple color, as shown by Figure 8. The solubility of the dithienyl-DPPs (Th-DPP) is even lower than that of phenyl-DPPs and thus longer alkyl chains in the monomer are needed to create soluble polymers.

Figure 8. *Color of thiophen-diketopyrrolopyrrole compound.*

The low solubility is due to the planar structure and therefore optimal π-π-interactions. According to Nielsen et al. the angle between the lactam units and the ring planes is for phenyl about 27° and for thienyl 12° [46]. The smaller angle in the case of thiophene is a consequence of the desirable interaction between the oxygen in the lac-

tam and the sulfur atom presented in the thiophene ring. Phenyl, instead, has α-proton that causes an electrical repulsion between the phenyl and lactam units and therefore causes larger twist in the chain.

Due to the favorable interaction between lactam and sulfur, dithienyl-DPPs have minor twisting in the backbone and therefore good packing in solid form. The planar nature allows the chains to be close to each other and maintain strong π-π-interactions. Therefore Th-DPPs tolerates high temperatures before decomposing. For the same reason dithienyl-DPP has good charge transfer ability [46]. Chains are close to each other, so intermolecular charge transport is possible. Furthermore, thiophene-DPPs have optimum push-pull structure and therefore they are usually low-band gap polymers. The DPP core is electron withdrawing and thiophen units are electron rich. A high hole mobility of 12 cm^2/(Vs) was reached with thiophene-DPP [51].

Because of their good charge transfer properties, Th-DPPs are applied in many electronic devices. Thienyl-DPP based Organic Field Effect Transistors (OFET) have been built by Tantiwiwat et al. [52] and Palai et al. [48] with good results. Recently, a dithienyl-DPP copolymer was patented as semiconductor composite, involving copolymer with DPP-moiety and carbon nanotube [53]. Th-DPPs are also under investigation in many groups working with OPVs [22,27,48,54].

Because of its unique properties, diketopyrrolopyrrole with thiophene aryl-groups was selected for this work. Thiophene was chosen instead of phenyl or furan to achieve a flat polymer with good π-π-interaction and tendency for self-assemble. The Th-DPP was copolymerized with electron withdrawing 1,2,4,5-tetrafluorobenzene unit in order to create a comprehensive push-pull system. The alternating push-pull structure is shown by Figure 9.
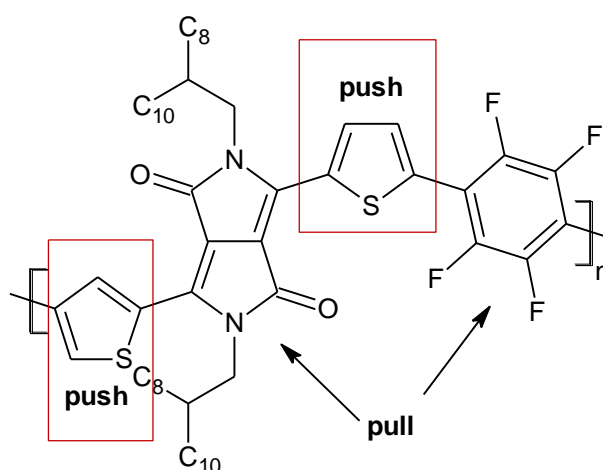
Figure 9. *Push-pull system of the synthesized copolymer. DPP core and tetrafluorobenzene are pulling and thiophene units are pushing the electrons.*

Adding an electron-withdrawing group confirms the push-pull system of the DPP polymer and further lowers the energy levels. Both LUMO and HOMO level of the co-

polymer are lower due to the electronegative fluorine atoms. In addition, the interaction between fluorine and carbon seems to improve the morphology. Fluorine is a small atom and causes no steric hindrance that would prevent the tight packing to crystals. Torsional angel between thiophene and tetrafluorobenzene ring is calculated to be only 8.5°, compared to angle of 18.4° between thiophene and unsubstituted benzene [5]. Thus the polymer chain is not twisted and intense π-π interaction is possible. These properties lead to effective packing and thus good charge transport. [5]

5 POLYMERIZATION METHODS

For the copolymerization part of the work, a fairly less studied method was chosen. The new bond between two arylic-carbons was created by direct arylation instead of traditional cross-coupling methods. In addition, a comparison between different heating methods was made. Half of the entries were made in traditional oil bath and half by using modern microwave heater.

5.1 Direct arylation

Polymerization requires constructions of new C-C-bonds by coupling reactions. Traditional and well known polymerization methods are Stille and Suzuki cross-coupling. These methods couple organoborons or organostannanes with halides. Only recently a new type of method, direct arylation (DA), has been introduced. In this approach, halide atom is attracted directly by a catalyst actived H-atom and oxidatively coupled to hydrogen, without the need for cross-coupling precursors, i.e. stannane or boron.

Examples of the Stille cross-coupling and direct arylation reaction are presented in Scheme 2. Both reactions require a transition metal catalyst and a halide or triflate leaving group. Stille reaction uses organostannane substituted aryl and acts without base. Palladium is used as a catalyst in both cross-coupling and oxidative coupling reactions, but in direct arylation cheaper variations, such as palladium acetate, are used. In some cases there is no need for ligands in direct arylation and the catalytic system can be kept simpler compared to other coupling methods [55].
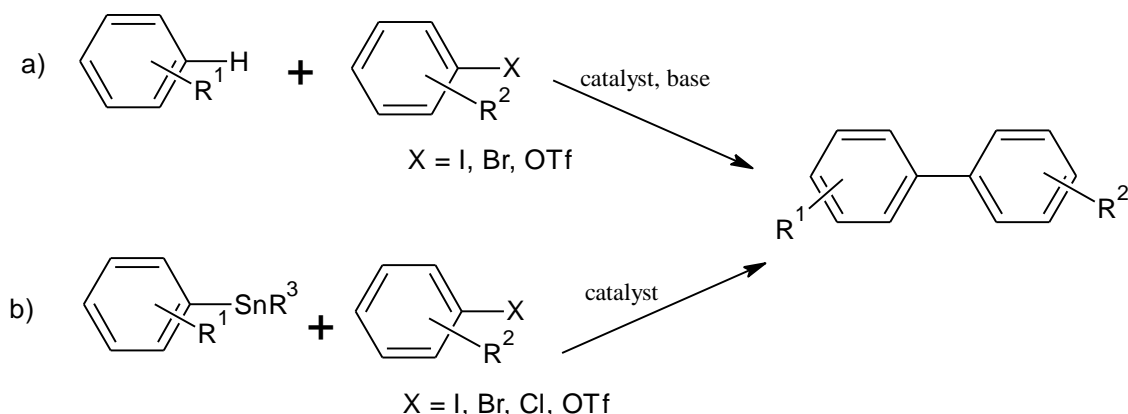
Scheme 2. *Two polymerization methods: a) direct arylation b) Stille cross-coupling. Transition metal catalyst and halide leaving group is used in both reactions. Modified from* [56].

Mechanism of the direact arylation is not totally clear, but it is expected to follow the concerted metallation-deprotonation (CMD) mechanism, especially in the case of heterocycles, such as thiophene. Scheme 3 shows the mechanism of 2-phenylthiophene coupling where potassium carbonate is used as carboxylate compound and palladium as catalyst. A phosphine ligand is used to arrange the complex formation, but solvent e.g DMAc, can also take the same role in ligand-free reaction. To keep the Scheme 3 simple, thiophene and benzene are used to demonstrate the reaction mechanism. Same protocol then applies to the polymerization of dibromotetrafluorobenzene and DPP substituted thiophene. [56]
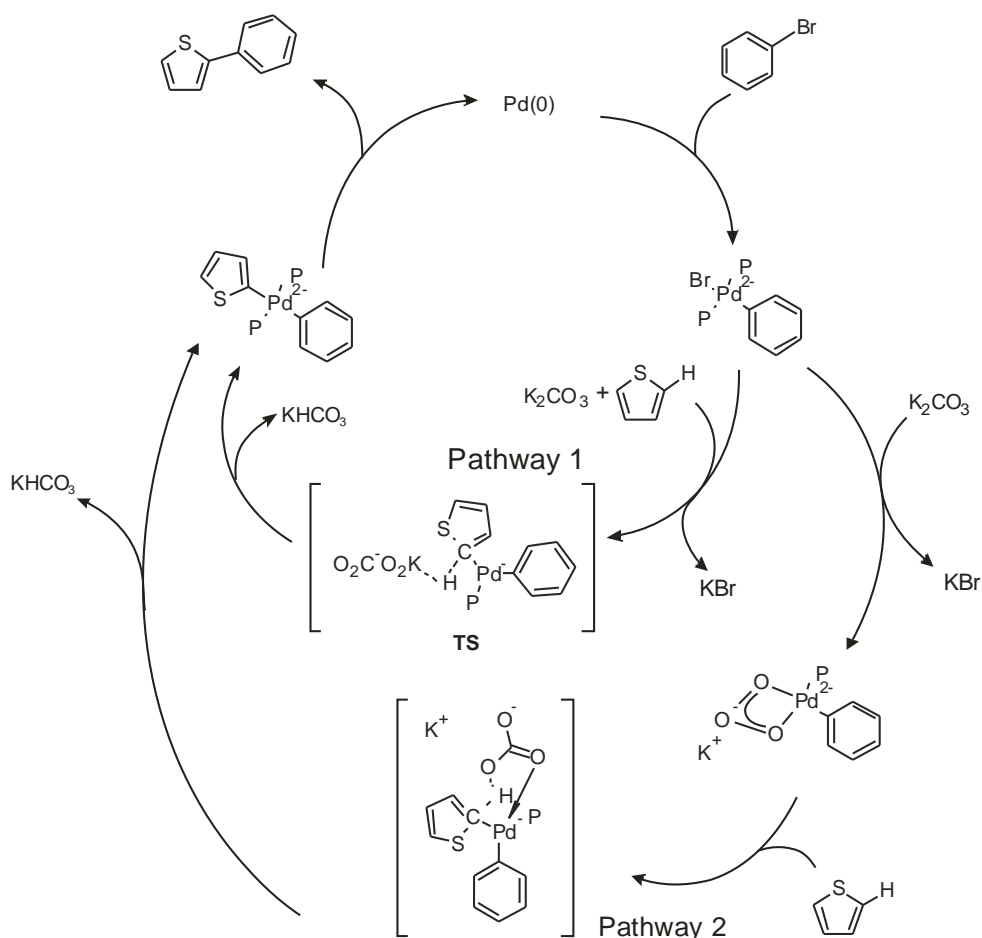
Scheme 3. *Predicted mechanism of direct arylation for example reaction of thiophene and bromobenzene. Depending of the ligand two pathways are possible. After* [56].

Two pathways are possible for metallation-deprotonation depending on ligand system. If a monodentate ligand is used, reaction can follow Pathway 1 or 2. A bidentate ligand uses the Pathway 1 only. In the Pathway 1 oxidative addition of halide-aryl is followed by C-H activation of the thiophene to lead the transition state TS. The phosphine-ligand or solvent can then reorganize the metal-center to give up the carboxylate group. The final step is the reductive elimination of expected aryl-aryl-compound. The

Pathway 2 follows the same route with the exception that the carboxylate group stays in the complex during the whole process. Activation of the C-H bond is considered to be fast and the lowest reaction step is probably the oxidative addition of the bond between carbon and bromine. [56,57]

The main benefit of the direct arylation coupling is the simplicity of the reactants. There is no need for organometallic precursors, which removes two reaction steps in monomer preparing and allows working without toxic organometallic species. This makes the process more cost and time effective and environmentally friendly. Other benefits of the method are higher atom economy and better compatibility with functional groups without lowering yield. [21],[55]

DA has been used for coupling both electron-rich and electron deficient monomers and it is widely used to couple thiophene containing monomers [58,59,60]. Currently, only few articles can be found considering the direct arylation polymerization of DPP compounds [21,50,55,61]. In these studies the results are promising; high yield and molecular weight as well as good optical and electrical properties have been achieved with direct arylation.

The problems in oxidative coupling are branching and cross-linking, if more than one proton can be activated during the reaction. To avoid these problems, arene building blocks should be selected with care. It might be necessary to block vacant sides of the arene using sterical hindrance or substitute. Substituting the active position with unreactive groups protects from cross-linking. However, even simple methanol substitutes can disturb the planarity and prevent the optimal packing. [55,56] Thiophene in the Th-DPP molecule has three protons and thus three possible C-H activation positions. Usually reaction occurs in 5-position, but 4- and 3-possitions are also possible.

The DA system is condition sensitive and reaction parameters should be optimized for each synthesis in order to reach a good quality polymer and prevent the cross-linking. Ligand, catalyst and carboxylate additive are varied depending on the monomer type. The selection of the solvent is critical since the monomers should be well soluble in the solvent and there should be a minimal possibility of side reactions caused by the solvent. For example, halide or benzene based solvents can cause chain termination when reacting with the monomer or providing an activated proton. [55]

In the literature Suzuki and Stille couplings are generally used methods for the synthesizing of DPP polymers [22,39,48]. In this work, direct arylation was chosen over other coupling methods in order to avoid organometallization and bromination steps in the monomer synthesis and to try new way to produce DPPPhF4 polymer. Park and his working group [5] have synthesized similar copolymer using Stille coupling that requires stannaneation of the monomer. With direct arylation, DPP monomer can be used right after alkylation step and dibromotetrafluorobenzene is used as received. This makes the monomer synthesis more straightforward, reaction more economical and gives better overall yield.

5.2 Microwave based heating

Microwave assisted heating offers noncontact, rapid and uniform heating of the reaction mixture. During a microwave (MW) treatment, not only temperature, but power and pressure can be adapted for given reaction. [62,63]

Microwave heating is based on the dielectric phenomenon. Temperature of the molecules increases because of their dipole moments try to align with the electromagnetic field and therefore cause spinning, colliding and friction, which produces heat. The rate and efficiency of the heating is dependent on the dielectric properties of the reaction solution. Therefore change in solvent may inflict a change in the reaction conditions [63]. When external heater, for instance oil bath, is used, inner part of the reaction mixture is heated less effectively than the outer parts near the heat source. In contrast microwaves heat up the molecules directly and equally, causing a heat flow from the core of the sample towards the reaction vessel. [64]

Specific monomodal microwave heaters are used in laboratories. These microwave ovens have small chamber size for standardized reaction vial. Reactions can be run safely and under tight control and are therefore repeatable. [62] Figure 10 presents the monomodal microwave used in this thesis. When lid is open, reaction chamber can be seen in the middle of the device. The device is computer controlled and uses compressed air to maintain desired pressure and cooling rate during the reaction.

Figure 10. *Monomodal microwave oven used in laboratories. Reaction chamber is in the middle of the picture and control panel in front.*

The main advantage using a microwave oven is the significant increase in reaction speed. This is due to the heating of the molecules themselves and thus achieving homogeneous and rapid heating. Furthermore, reaction times can be shortened even further because of the possibility to use pressurized reaction vial and thus higher reaction temperatures. In this thesis, pressurized vials were used both in thermal heating and in microwave reaction. Reaction time decreased from days to hours, when microwave irradiation was used instead of oil bath. Pressure vials also promote solubility and therefore reduces the amount of environmentally hazardous halogenated waste.

Microwave heating can also have positive effect on yield. Because the reaction conditions can be more accurately adapted for the reaction in question, the amount of side reaction can be decreased. Selectivity can be better modified by specific excitation, because microwave heating is more effective in compounds with high dipole moment. Furthermore fast heating and short reaction time gives instable product less time to decompose. [62,63]

In their review Hoogenboom and Schubert [63] claim that coupling reactions, in which metal catalyst is often used, would be especially suitable for microwave irradiation because of the specific absorption of microwave irradiation by metal ions. Microwave heating has been successfully used in transition metal catalyzed polymerizations e.g Suzuki, Yamamoto and Heck coupling and direct arylation [63,64,65].

6 METHODS FOR CHARACTERIZATION OF POLYMERS

In order to study the properties of the polymer been synthesized, different characterization methods are used. For a novel conjugated polymer it is important to determine the quality of the polymer and it's optical and thermal properties. From this information the efficiency of the preparation process and the suitability of the polymer to be used in organic solar cell can be estimated. In this chapter each characterization method is described shortly and the use of the method in the work is explained.

6.1 GPC

Gel Permeability Chromatography (GPC) is a generally used size exclusion chromatograph method and it is typically used for analyzing polymers. GPC uses a mobile phase and a stationary phase to separates molecules in terms of size. The stationary phase is column filled with a porous material. Small molecules can enter the pores and spend longer time the column while larger molecules elute quicker, i.e. they have shorter retention time. GPC measures the volume of the mobile phase needed to push the sample through the column. This data can then be transferred to the molecular weight distribution that is inversed to the spectra of elution volume. As a result, variety of molecular weights (M_n, M_w, M_z, M_y) and polydispersity index $Đ$ can be determined.

In this work, GPC had three functions. It was used to follow the polymerization rate, study purification and finally to evaluate the quality of the polymer. The measurements were run using either chloroform or tetrahydrofuran as eluent. GPC curves were measured from each raw product as well as from the pure polymer in order to check the purification process and improve it. Purification process is described more precisely in chapter 7.2.1.

GPC curves taken from pure polymers were used to determine the molecular weights. For all entries pure polymer and concentration of 0.5 mg/ml in THF was used and the curves were defined in a similar way to keep the results comparable. The shape and location of the GPC curves were also used as a tool to evaluate the product and compare the entries. Good GPC curve should be narrow and has regular shape. Changes in slope at left, the lower volume side, of the curve are called shoulders. They can be sign of faults, for example chain-chain-ending or aggregation.

Pure product was analyzed both in chloroform and in THF in order to detect the possible artifacts of the measurements. For the THF dissolved samples optimized concentration of 0.5 mg/ml was used in each case by weighting 1 mg of the polymer and

dissolving it in 2 ml of tetrahydrofuran. For chloroform samples more dilute concentration (about 0.1 mg/ml) was used. Raw product measurements were run only in THF and the concentration was monitored based on the color of the sample.

6.2 UV-vis spectrophotometer

Absorption of light is crucial to a solar cell polymer. Ultraviolet-visible spectroscopy (UV-vis) is used to examine which wavelengths a compound can absorb. The lower the band gap, which means energy difference between HOMO and LUMO, the longer the wavelength of the light absorbed.

Spectrophotometer measures the intensity change in light that takes place when light travels through a sample. The ratio of the intensities after and before the sample is called transmittance and it is related to absorbance. Absorbance describes the fraction of light absorbed for specific wavelength.

UV-vis device consists of a light source, a diffraction grating to separate the different wavelengths of light and a detector to measure the absorbance. A beam of light with increasing wavelength is directed at the sample and absorbance is measured. Results are plotted as a function of absorption intensity versus wavelength.

UV-vis was used to study the optical properties of the prepared copolymer. The measurements were run in chloroform solutions with the same cuvette. Pure chloroform was used as reference and the sample cuvette was washed with chloroform between measurements.

6.3   TGA

Thermal gravimetric analysis (TGA) measures the thermal stability of a compound by steadily increasing the temperature and measuring the weight loss originating from decomposition. Material properties can be measured either as a function of time or increasing temperature. TGA can be used for several purposes, for example to study the reaction kinetics or to characterize the material. It is especially useful for studying polymer materials.

TGA device consist of a precision scale inside a furnace, where the sample pan and an empty reference pan are placed. Temperature of the furnace is measured using a thermocouple and controlled by a closed-loop heater. Measurements can be made in air or under inert gas. The sample is continuously weighted during the heating and the result is a plot of temperature and percentage weight loss. From the results highest use temperature for polymer can be determined.

In this work TGA was used to investigate the thermal properties of the polymer product. Thus a program with constant heating rate was selected and the polymer properties were studied as a function of increasing temperature.

6.4 DSC

Differential Scanning Calorimetry (DSC) is used for measuring thermal properties of the compound. These properties include melting point (T_m), glass transition point (T_g), and crystallinity. In this work, DSC was used to investigate the melting process of the polymer.

DSC measures the heat flow required to increase the temperature of the polymer sample. The device consists of an oven that has two sample holders with precise thermo elements connected to computer. Both the actual sample and a reference sample are kept in the same temperature and the heat flow required to heat the samples at the same rate is measured. Empty sample pan is used for the reference and the baseline from the device itself is added to the heat flow. The result is the heat flow as a function of sample temperature. The melting point of the polymer can be seen as an endothermal peak in the results whereas crystallization donates energy and can be seen as drop in heat flow. The latent heat of these transitions can be calculated from the peak area. Glass transition does not create peak but a change in slope, because of the change in heat capacity.

Different programs can be used for the measurement and they can include heating, cooling and isothermal periods. Generally sample temperature is increased linearly with respect to time and heating rate is kept constant, usually 10°C/min. Heating and cooling are usually done twice. First cycle is used to remove the thermal history of the sample and second heating gives the actual thermal properties. When comparing the results, it should be noted that melting point is dependent of polymer's thermal history and molecular weight.

6.5 NMR

Nuclear Magnetic Resonance Spectroscopy is a tool to examine molecule structure, dynamics and chemical environment of the sample. The method is quite sensitive, so it can be used to monitor reaction kinetic and purity of the sample.

The NMR device contains a superconducting coil surrounded by a cooler to produce strong magnetic field, a generator to produce radio waves and a detector to receive the signals coming from sample.

Nuclei are hit by radio frequency radiation, which causes the nuclear magnets to resonate. This can then be monitored by the detector and transformed by computer program. Resulting spectrum represents peaks that correspond to certain chemical shift. The shift scale is built on tetramethylsilane standard (TMS), which is set to zero. From the chemical shifts corresponding nuclei can be identified. Splitting, coupling and area of the peak also provide useful information about the chemical environment and structure.

In this work NMR Spectroscopy was used to identify reaction products and to determine the purity of the prepared monomer. It was also used to study the structure of the copolymer. ^{1}H and ^{19}F NMR spectroscopies were used for these purposes.

7 RESULTS AND DISCUSSION

The goal of the thesis was to synthesize 2,5-dioctyldodecyl-3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione monomer and then copolymerize it with commercially available dibromotetrafluorobenzene. The second objective was to optimize monomer synthesis and polymerization process so that the monomer and the polymer could be produced with high quality and yield. Since the polymer was designed for solar cells, the overall procedure should be inexpensive and simple so that it would be suitable for commercial scale preparation.

This chapter is focused on the optimization process. Firstly, the monomer synthesis and its optimization procedure is presented. Secondly, the polymerizing protocol is introduced and the optimization process of the polymerization is presented in detail. Finally the polymer is characterized in terms of the optical and thermal properties. Detailed synthesis processes are presented in Chapter 8.

7.1 Monomer synthesis and optimization

Synthesis of Thiophene-DPP monomer requires two steps. First the DPP-core is build and then the core is alkylated in order to obtain soluble monomer. The alkylated monomer is then purified for polymerization reactions. Actual syntheses are presented in Chapter 8.

7.1.1 Thiophene-DPP

Succinic ester route was used for the synthesis of the backbone of the DPP-monomer **5**. The reaction and the conditions are shown in Scheme 4. In order to achieve thiophene-DPP monomer, 2-thiophene carbonitrile **1** was chosen as carbonitrile and heated in excess of dimethyl succinate **2**.
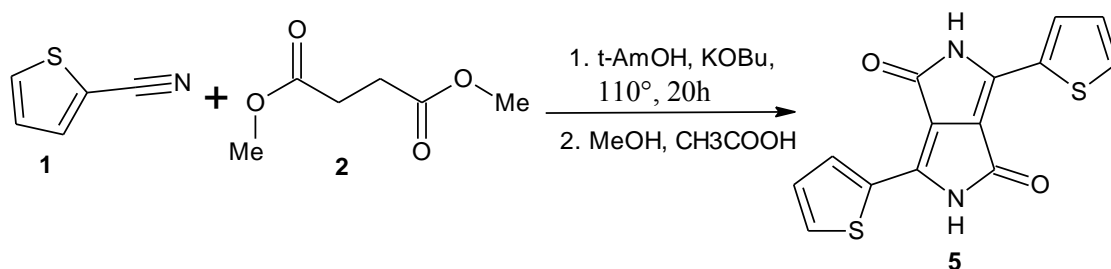
Scheme 4. *First step of the monomer synthesis.*

After the reaction the solution was neutralized with weak acid. Moving the pH of the product mixture from basic to neutral enables hydrogen-atoms to fasten the nitrogen atoms of the lactam unit. This allows the hydrogen bonding between DPP-molecules and precipitates the product so that it can then be filtered out.

Huo's et al. [22] protocol was followed with the exception of increased reaction time. Furthermore, methanol was not distilled of during the reactions, because it was noted that no methanol had been formed after one hour reaction time. Figure 11 presents the reaction arrangement for the monomer synthesis.


Figure 11. *Reaction arrangement for the monomer synthesis.*

The reaction product is purified only by washing the filter cake. There is no need for further purification because the product is directly used in the next reaction step, i.e. alkylating. NMR measurements were not made from the product because it is not soluble in any common NMR solvents.
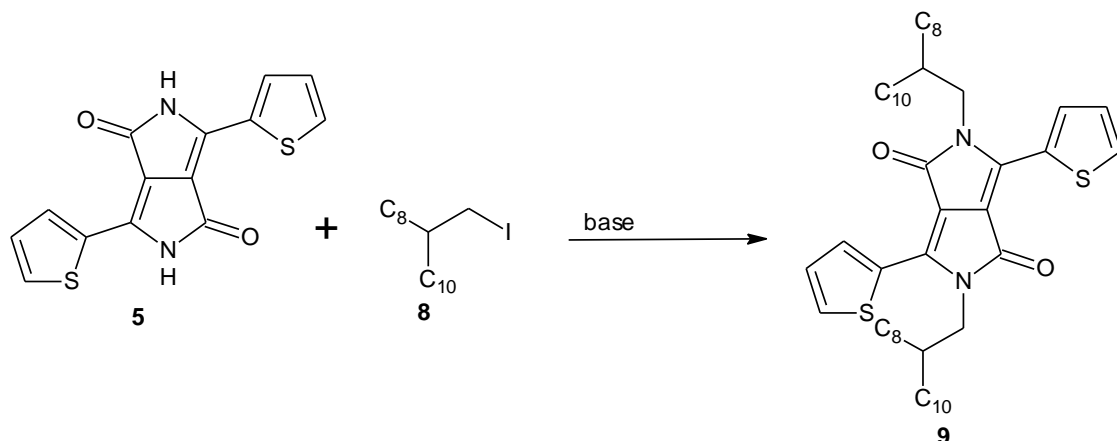
7.1.2 Alkylation

DPP monomer is not soluble in common solvents without the presence of a base and thus it needs to be alkylated. Adding the long alkyl chains improve the solubility and thus improves processability. The alkyl chains need to be long enough so that monomer dilutes properly and can therefore polymerize effectively. Finally, the actual polymer should be soluble in order to prepare the solar cell.

Octyldodecyl chains were chosen as alkyl chains for thiophene-DPP. These chains are long enough to guarantee enough solubility but not too bulky. The selection of the side chains influences not only the solubility of the polymer but other properties too. It has been proved by Mallari et al. that alkyl chains affect photophysical and electronic properties and morphology. Long chains take more space and change solid state packing and structural order compared to branched chains [42]. Thus, morphology affects the absorbed wavelength of light and hence has an impact on the usability in a solar cell. Halogenated octyldodecyl alkyl chains are not commercially available so they needed to be synthesized before alkylating step. Iodine was selected as a halide part to avoid working with bromine and because iodine is usually slightly more reactive than other halides. Iodination was done by following Letizia et al [66] and is shown in Scheme 5. Iodine **7** is added to octyldodecyl **6** in the excess of imidazole and triphenylphosphine to give octyldodecyliodine **8**.
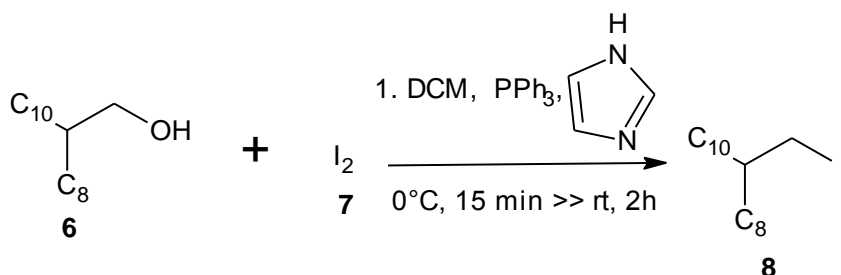
Scheme 5. *Synthesis of the alkyl chain used for alkylating the monomer.*

Alkylation reaction (Scheme 6) was the most critical step in the optimization of the monomer synthesis. Alkylation was initially expected to be straightforward, but introducing iodinated alkyl chain **8** to monomer **5** turned out to be challenging. The product, octyl-dodecyl-alkylated DPP **9**, was difficult to handle and purify and the yield was poor.

Scheme *6. *Second step of the monomer synthesis: alkylation.*

The first alkylation was run as described by Matthews et al [67]. Monomer and base were preheated for several hours to ensure that the base is removing the proton from nitrogen and giving space to alkyl chain. Then octyldodecyliodine was added and reaction was further refluxed.

However, working up process did not yield proper solid, not even when the product was poured into 1:1 mixture with methanol and water instead of water only. Next, the method introduced by Lee et al. [43] was tried, which resulted a proper solid product. Nevertheless, in order to avoid the time consuming column purification and the use of isohexane-toluene eluent mixture, a different work up was tried. The alkylated monomer product was dissolved in dichloromethane (DCM) and washed with excess water in order to remove dimethylformamide (DMF). Some material was noted to adhere to the bottom line of a thin-layer chromatography (TLC) plate. For the removal of these impurities, DCM solution was run through a short silica phase. Water was removed with magnesium sulfate and the solvent was evaporated. In order to remove the rest of the DMF the product was let to dry in 50°C under vacuum over 50h. An oily layer appeared on top of the product, because the excess 1-iodo-2-octyldodecane has high boiling point and could not be removed with these treatments. Recrystallization with ethanol was done two times in order to remove all of iodine and other impurities.

The yield of the alkylation process was very low, around 30%. However, low yield in alkylating reactions can also be noted in the literature [43,68]. Quite few articles have been published regarding the alkylating DPP monomers with octyldodecyl. It seems that with shorter alkyl chains the yield increases [22]. The insoluble monomer is hard to purify and likely contains impurities that affect the next reaction step, thus attenuating the alkylation process. There are some side reactions too, that can be seen in the TLC.

The optimization of the alkylating process was tried also in terms yield: reaction was let to run longer. However, based on the TCL-samples no progress could be seen between 15 h and 72 h. The reaction was run at three different temperatures: 110°C, 120°C and 130°C, but increasing the temperature did not increase the yield. Lower reaction temperature should decrease the amount of by-products, so different reaction condi-

tions used by Zhu [40] were tried. The reaction was run at 60°C and with potassium t-butoxide in 1-Methyl-2-pyrrolidone (NMP) solvent, but without any improvement in yield. Most likely the low temperature decreases not only the side reaction but the main reaction rate too.

Alkylation entries are in listed in Table 1. Because of the alkyl-chain residuals and purification with recrystallization, entries were not directly compared in term of yield. The yields of the alkylation entries were impossible to compare because the alkyl chain rest could not be removed by evaporation. After the recrystallization the yield is dependent not only on the success of the alkylation process and work up but also on the crystal grow and isolation. Therefore the results of each entry are described verbally.

Table 1. Optimizing the monomer alkylation.

Entry	Reaction conditions	Work up	Comments
1	130°C, 15h, 4 eq K_2CO_3, 0.2M DMF, 3 eq iodine	Filtered from ice-water, washed H_2O with and MeOH	Product sticky, no proper solid
2	110°C, 18h, 4 eq K_2CO_3, 0.23M DMF, 3 eq iodine dropped	Filtered from MeOH:H_2O	Dried in 90°C for 72h, no proper solid
3	130°C, 18h, 4 eq K_2CO_3, 0.2M DMF, 3 eq iodine added slowly	Filtered from ice-water, washed with $CHCl_3$, column with i-Hexane-toluene	Not perfectly diluted to chloroform, product dark solid
4	130°C, 20h, 4 eq K_2CO_3, 0.27M DMF, 3 eq iodine added slowly	Diluted to DCM, filtered, washed with H_2O, short silica plug	Product dark solid, yield seems good but lot of alkyl rests
5	130°C, 72h, 4 eq K_2CO_3, 0.27M DMF, 3 eq iodine dropped in 2 portions	Equal to entry 3	Similar to entry 3
6	120°C, 18h, 4 eq K_2CO_3, 0.27M DMF, 3 eq iodine dropped in 2 portions	Equal to entry 3	Product dark solid, yield better than in entries 3 and 4
7	60°C, 16h, 4 eq KOBu, 0.27M NMP, 3 eq iodine dropped in 2 portions	Equal to entry 3	Only one spot in TLC, lot of alkyl rests, remains liquid

Adding 1-iodo-2-octyldodecane in two portions seems to slightly increase the yield but using a dry solvent does not notably improve the reaction. Heeney et al. [69] have tried cesium carbonate (Cs_2CO_3) as a base and 18-crown-6 as a ligand, but the yield still remained low.

Apart from the low yield, NMR spectrum (Appendix 3) of the product 9 shows some unidentified peaks at the aromatic region. These may be signs of partial alkylation of the DPP monomer. This can be also seen on the TLC plate. Two product spots can be seen, but these plots are so close to each other that they are very difficult and ineffective to separate by column chromatography. Intensity of these peaks is, however, low and the monomer is considered to be pure enough. The problem of low yield stays unresolved, but based on the trials the best possible conditions were found in entry 6.

7.2 Polymerization

In this work two kind of copolymerization were performed. The main interest was in optimizing the copolymerization of above mentioned DPP-monomer **9** and 1,4-dibromotetrafluorobenzene **10** which is commercially available. Reaction product is dithiophen-diketopyrrolopyrrole/tetrafluorobenzene (DPPPhF$_4$) copolymer **11**. Because of the steric hindrance, C-H activation is believed to occur only at the 5,5´-positions of the thiophene. Long and branched alkyl groups should give steric hindrance and protect from cross-linking. Scheme *7* depicts the reaction equation, while the color of both monomers and prepared polymer are presented by Figure 12.

Figure 12. *Colors of the dibromotetrafluoro monomer (left), DPP monomer and polymer product (right). All solutions are in tetrahydrofuran.*
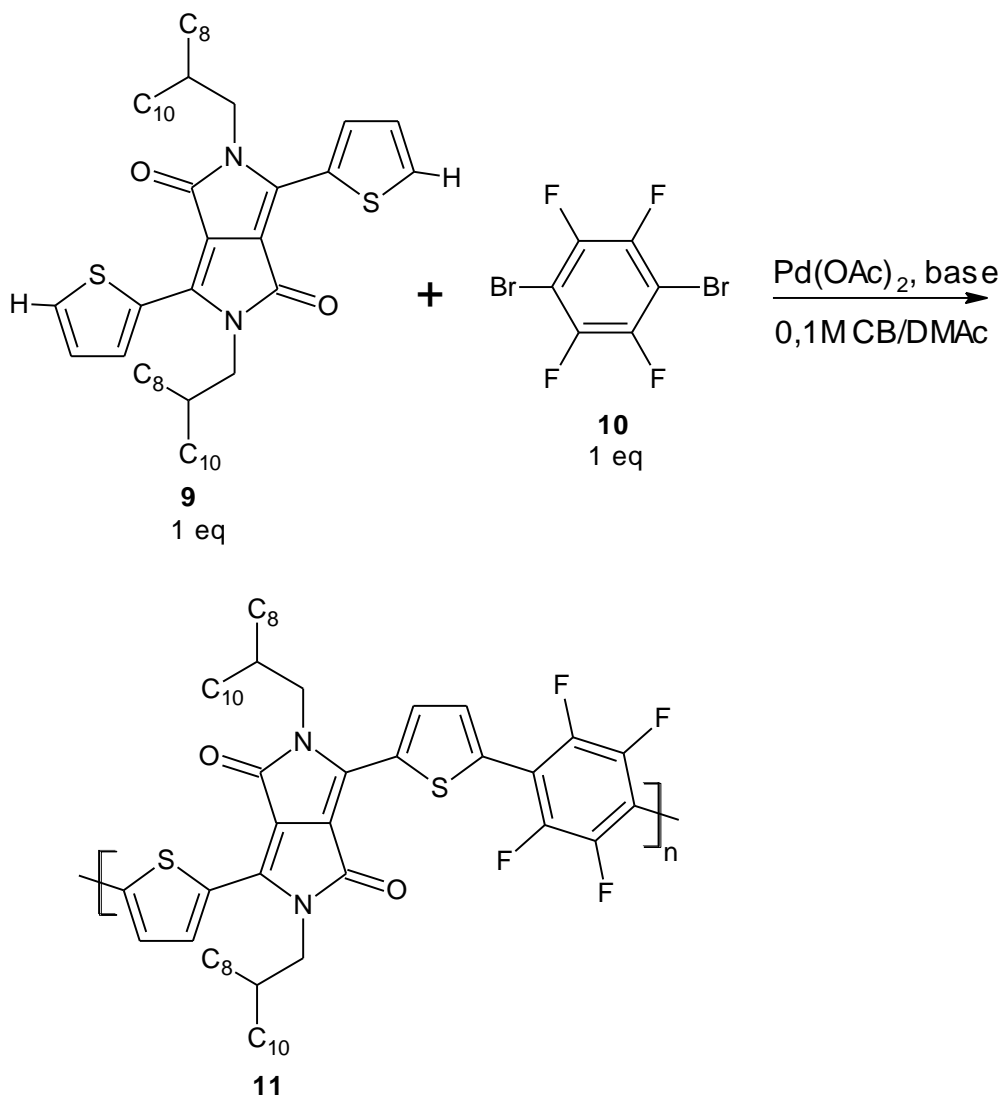
Scheme 7. *Polymerization of diketopyrrolopyrrole/tetrafluorobenzene copolymer via direct arylation.*

The polymerizations were done with direct arylation, which couples electron withdrawing carbon of the DPP-monomer to the bromine containing carbon of the fluorine-monomer. The target of the optimization process of the DPPPhF$_4$ polymer was to accomplish a polymer that is high in molecular mass and consists of polymer chains equal in length. The optimization process can be divided into early trials, finding the correct temperature, progress into the microwave reactions and actual optimization by varying reaction temperature, catalyst loading, reaction time and microwave power. The reaction was also tested in terms of ligands and best acid-base system. The solvent, the concentration and the palladium acetate as a catalyst were not changed during the optimization. Entries were compared in terms of yield and molecular mass. Furthermore, GPC curves were used as a tool to compare entries by monitoring shoulders and other signs of defects.

In the following subchapters polymer syntheses are described, starting from the general assumptions and followed by reaction preparations and purification of the accomplished polymer. The main reaction presented by Scheme *7* was optimized in terms of heating method, reaction time, temperature, ligand, base-acid-system, catalyst loading and power. Microwave assisted polymerization was used for the parameter screening. In addition to speed up the optimizing process, incoming microwave heating could be compared to conventional thermal heating.

7.2.1 Preparation of polymers and work-up

The polymerizations were performed by following a constant protocol during the whole series to keep them comparable. Because of the sticky nature of the pure DPP-polymer, accurate weighting was challenging. Some monomer particles tended to adhere to the weighting paper and thus it was difficult to place all the monomer in the reaction vessel. The weighting paper was flushed with reaction solvent to extract all the monomer. Degasing times were kept constant and reaction vials were moved to oil bath or microwave chamber without waiting at room temperature. In the oil bath, reaction temperature and stirring rate were kept as identical as possible. In the case of microwave reactions, the same stirring and cooling rates were used in all reactions if not otherwise noted and the reaction time was counted from the moment the reaction vial achieved the desired reaction temperature.

Solvent, concentration and catalyst were always the same in all entries. Both monomers were used in equal amounts, 1 mole diphenyl-DPP and 1 mole dibromotetrafluorobenzene while monomer concentration was 0.1 M. Chlorobenzene (CB) and dimethylacetamide (DMAc) were chosen in equal amounts as a solvent mixture. This solvent mixture is not commonly used in literature, but it has worked well in similar direct arylation polymerization done by other member of the current research group. DMAc is similar in structure with respect to DMF used for the alkylation and it is known to dissolve DPP monomer well. Solvents were mixed directly in the reaction vessel. 3 eq potassium salt of pivalic acid (PivOK) was used to regulate the pH of the reaction mixture. PivOK is a 1:1 mixture of potassium carbonate and pivalic acid and it has yielded good results in earlier polymerizations carried out at the Institute for Macromoleculare Chemistry.

The polymer products were purified with soxhlet treatment and after the purification polymer should be free from monomer and catalyst residuals as well as oligomer free. The polymer particles formed in the methanol solution were filtered with filter paper or extraction thimble. Extraction thimbles were chosen instead of filter paper if the polymer particles were large and therefore needed extended purification. In those cases the extracted particles were mixed with spatula inside the thimble in order to break down larger aggregates and remove all impurities between the particles. Afterwards the product was let to further purify in soxhlet. The use of cellulose thimbles makes it possible to mix the product without breaking the paper and losing the product.

The extraction thimble or the filter paper with the product was put into soxhlet and the soxhlet was placed between the solvent flask and the cooler (Figure 13). In the process the solvent was heated to 100°C so that it becomes gas, travels up to the cooler and condenses again to drop into the soxhlet chamber. In this way the product can be effectively flushed with pure, hot solvent.
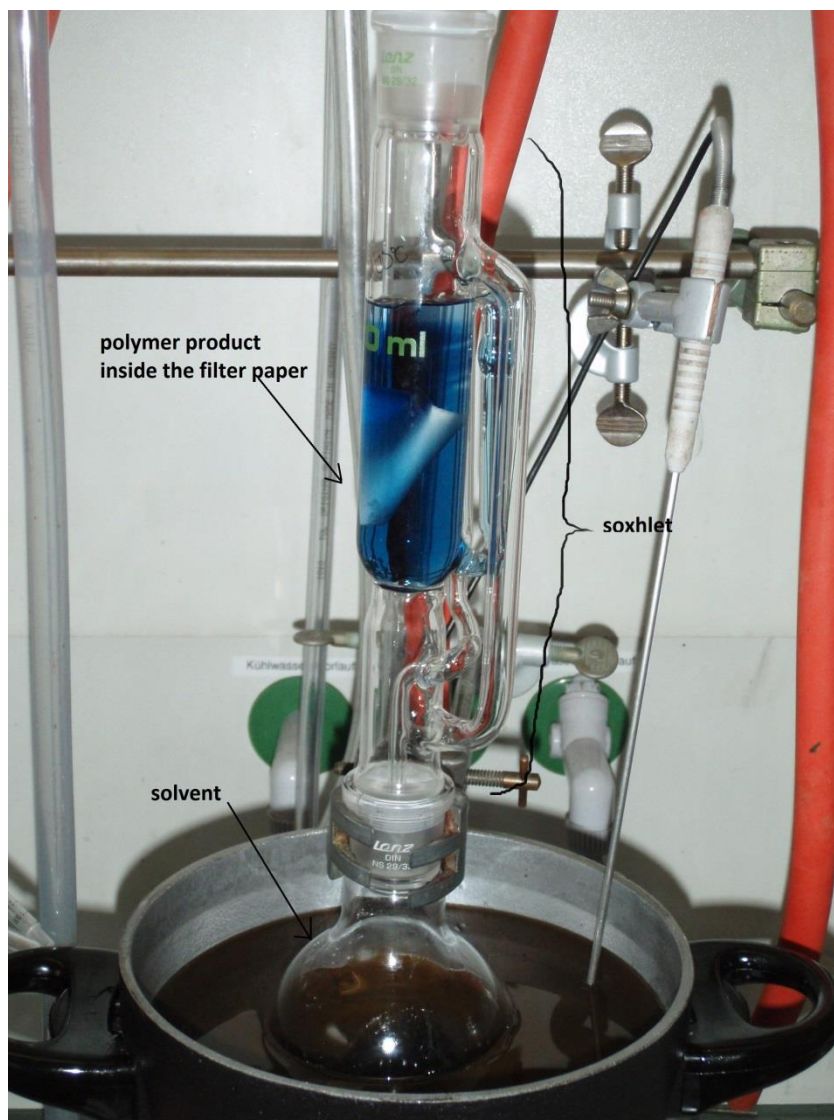
Figure 13. *Reaction arrangement in the extraction treatment. Polymer product is inside the filter paper.*

Methanol was used as the first solvent in order to remove base and salts. The second solvent was then used to remove unwanted oligomers. Acetone was used as a second solvent for Entries 1 to 3. The purification result achieved with acetone can be seen in Figure 14. There are still some oligomers left after purification with methanol and acetone. In order to improve the purification process the choice of the solvent was reconsidered.
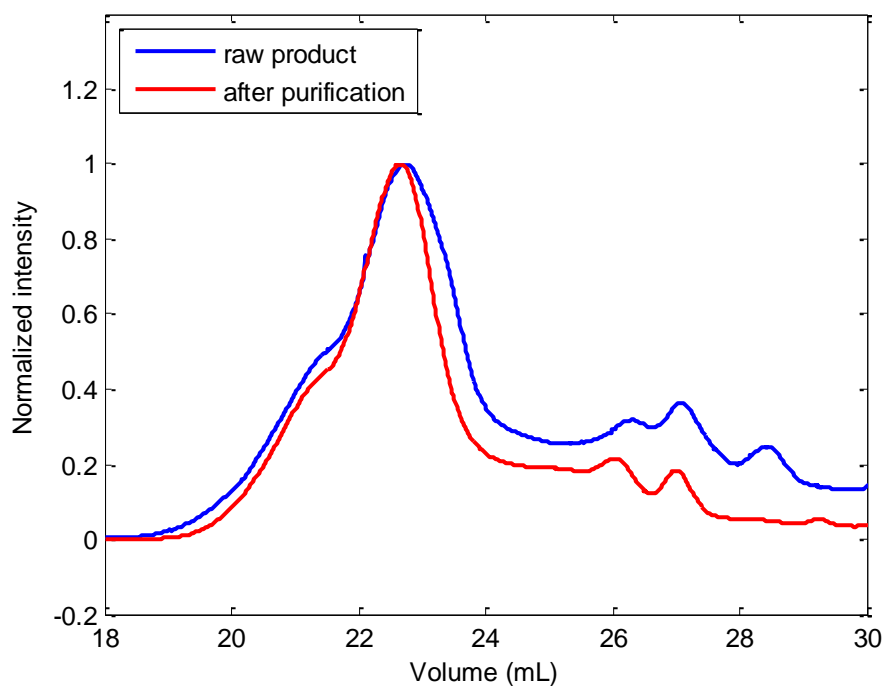
Figure 14. *The GPC curve of a polymer purified with acetone shows slightly less oligomers than the raw product.*

In order to find a suitable solvent, polymer samples were tested with acetone and isohexane. 1 mg of polymer sample was diluted to 1 ml acetone or 1 ml isohexane and shaken. Isohexane solution becomes immediately colored, which means that it dissolves too well and is likely to remove the actual polymer instead of only the oligomers. The solution with ethyl acetate remains unchanged after shaking and becomes slightly colored after warming the test tube. It thus appears that ethyl acetate is a suitable solvent for the purification process.
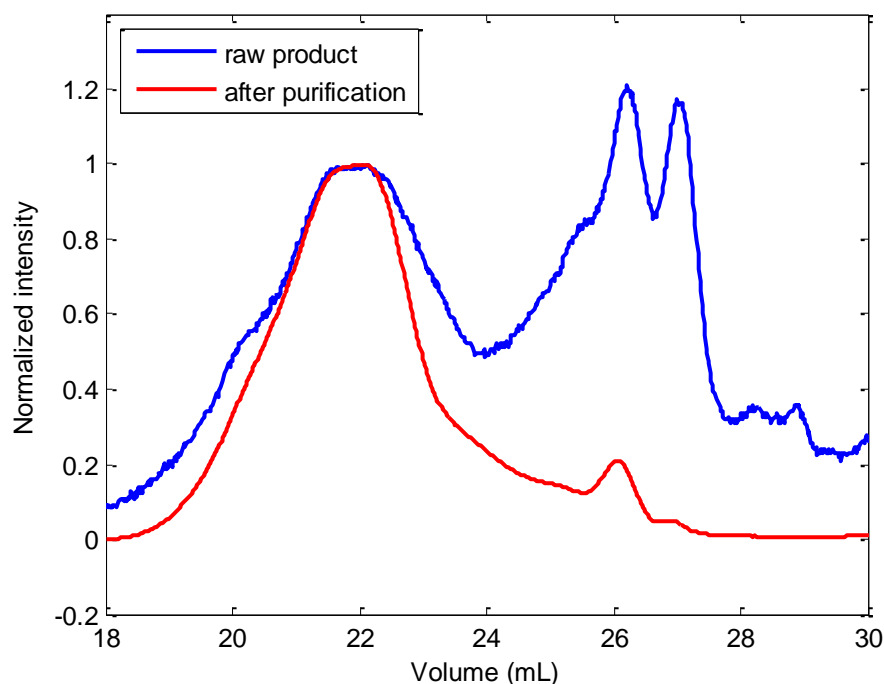
Figure 15. *The GPC curve of a polymer purified with ethyl acetate shows notably less oligomers compared to the raw product.*

Entry 4 was successfully purified with methanol and ethyl acetate. Ethyl acetate was noted to remove oligomers better than acetone but not to remove too much of the polymer, which could be noted from the GPC curves taken before and after the purification (Figure 15). Therefore the purification process was decided to be continued with methanol and ethyl acetate. This treatment was used for all the future entries.

The polymers produced with thermal heating were made in pressure vial under nitrogen. Monomers, base-acid system and both solvents were measured and closed in a vial. The solvents were added and the mixture was degased through a rubbery cap via needles. The catalyst was added and the rubber cap was replaced with cap including a Teflon disc. The new cap was flushed carefully with nitrogen gas and the vial was closed tightly. The hole free and Teflon insulated cap maintains pressurized conditions. Reaction vessel was put into an oil bath, stirred and let to boil.

The preparation was almost identical when polymerization was done with the microwave instead of the oil bath. Reagents were loaded to a glass vessel suitable for microwave treatment. The vessel was closed with rubbery cap equipped with Teflon disc and degased as noted above. In this case there was no need to change the vial cap after piercing it with the degasing needle, since for safety reasons it is important not to have gastight cap in the microwave oven. The reaction vial was placed in the reaction chamber of the microwave heater where pressure is adjusted automatically. Reaction time, temperature, power and pressure were set and the desired program was started. The actual reaction time was counted from the moment the reaction vial achieved target temperature. During the ramping period the temperature of the reaction vial is increased

towards the right reaction temperature and the input power is modified if needed. As soon as stable conditions are reached, the actual polymerization period begins.

After the reaction polymer mixture was cracked out in methanol, solid polymer particles were filtered and the first GPC sample was taken from the raw material. The particles were filtered with filter paper or with extraction thimbles. The polymer was put through the soxhlet treatment described above. After the purification the polymer was diluted to chloroform and put through a short silica layer. Then the chloroform was evaporated. The blue polymer film was released from the flask with methanol, filtered and dried.

7.2.2 GPC measurements

GPC measurements were used for the comparison of the entries and for the calculation of molecular weights. Hence GPC conditions were optimized in order to obtain as reliable results as possible. Four solutions with accurate concentration of 0.5 mg/ml, 0.25 mg/ml, 0.125 mg/ml and 0.05 mg/ml were prepared from the same polymer diluted to THF. Based on the GPC curves, most concentrated solution of 0.5 mg/ml gives the clearest curve with best baseline. Decrease in the concentration clearly increases the artifacts originating from the measurement itself. If the peaks indicated as artifacts would be from the sample, they would increase with increasing concentration. Molecular weights were calculated from the GPC curves of the pure polymer diluted to THF in optimized concentration.

7.2.3 Time dependence in oil bath

Optimization process was started with the first try on, entry 1. In the literature [21,55,59] 100 °C is quite common reaction temperature for the direct arylation of DPP monomer and it was hence selected as initial value. The first entry was wanted to keep simple and thus no ligands were added. The amount of catalyst, 4 mol-% palladium acetate, and the reaction time were kept low in order to avoid aggregation.

The first entry was promising and no aggregation could be seen, i.e. the mixture had low viscosity after 24 hours of reaction. The second entry was run with identical conditions with the exception of extended reaction time. This reaction was monitored regularly to see any signs of viscosity increase. After 72 h the solution still had low viscosity. The results are presented in Table 2 and Figure 16.

Table 2. *The yields and molecular weights obtained with starting conditions.*

Entry	Reaction time (h)	Other reaction conditions	Yield (%)	M_n (g/mol)
1	24	100 °C, PivOK , Pd(Oac)$_2$	78	15 971
2	72	100 °C, PivOK , Pd(Oac)$_2$	96	16 528
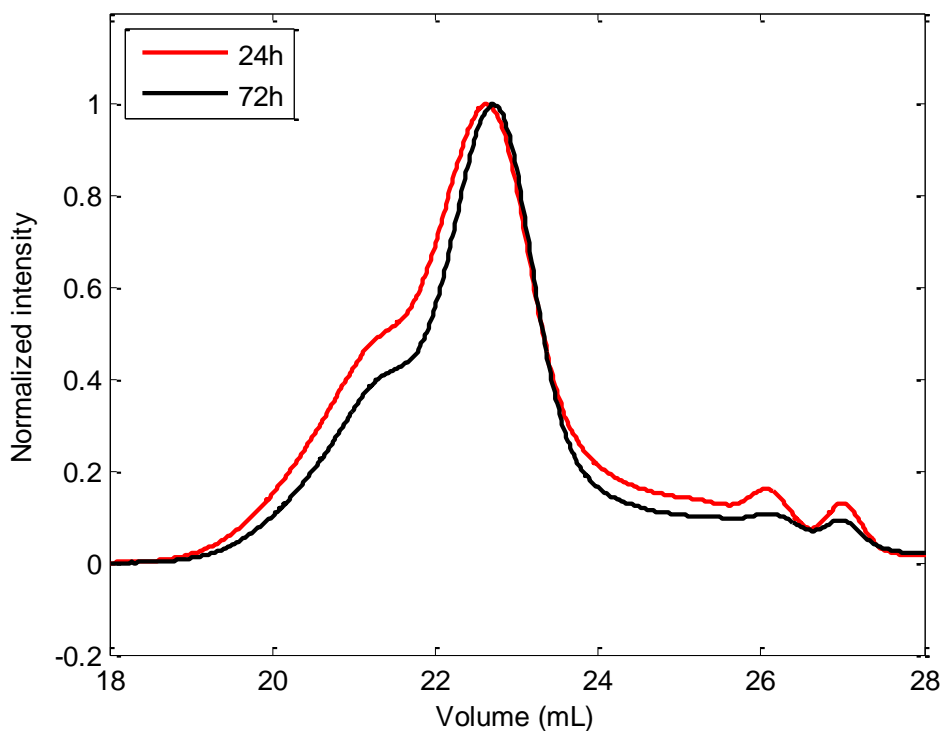
Figure 16. *GPC curves from entries 1 and 2 with different reaction time.*

Entry 2 with longer reaction time produced better yield and slightly higher molecular weight compared to entry 1. GPC curves look similar; a shoulder can be seen in both entries. Shape of the peak is narrower in the entry 2 with longer reaction time and indicates a more equal chain length that has smaller polydispersity index. Thus 72 hours was used in all the following entries.

7.2.4 Temperature screening

Temperature screening in oil bath was done with initially determined reagents and amounts. The solvent was CB/DMAc, catalyst 4 mol-% palladium acetate and pH was controlled with 3 eq PivOK. Relatively large batches of DPP-monomer (200 mg) were used to ensure the comparability of the reaction series. The reaction time was 72 hours in all reactions and temperature was varied from 80 °C to 120 °C. Since there appeared to be a decreasing trend in both yield and molecular weight outside these values (see Table 3 and Figure 17) they were set as limits.

Table 3. *The yields and molecular weights obtained with various reaction temperatures.*

Entry	T (°C)	Other reaction conditions	Yield (%)	M_n (g/mol)
3	80	72h, PivOK , Pd(Oac)$_2$	90	15 006
4	90	72h, PivOK , Pd(Oac)$_2$	78	23 968
5	110	72h, PivOK , Pd(Oac)$_2$	4	4 896
6	120	72h, PivOK , Pd(Oac)$_2$	44	4 546

The largest molecular weight was achieved at 90°C (entry 4) with good yield; although entry 3 with 80°C gives even higher yield. It should be noted that the purification procedure was changed during temperature screening. Entry 3 was purified only in soxhlet with methanol and acetone. In contrast, entry 4 was additionally washed with ethyl acetate. The purification process was then optimized and entries 5 and 6 were purified with methanol and ethyl acetone. Thus the lower yield of entry 4 can be due to better purification. Both M_n and yield decrease at lower (80°C) or higher (110°C) temperatures (Figure 17).
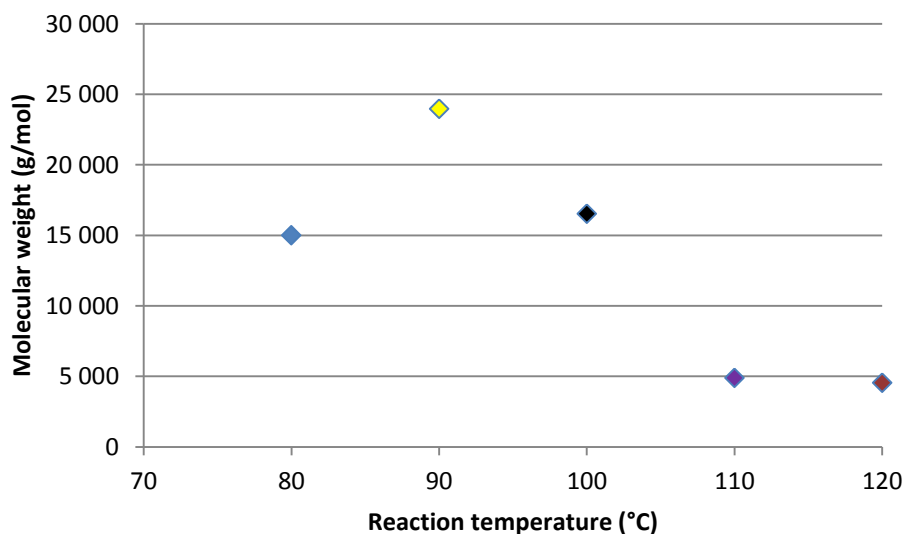
Figure 17. *Effect of reaction temperature on the molecular weight.*

Temperatures higher than 100 °C provide clearly weaker results. All entries were prepared in an identical manner so very low yield in entry 5 appears to be an experimental error, perhaps due to poor stirring. However, same trend of low molecular weight and low yield can be seen also in entry 6. Thus the reaction did not seem to tolerate higher temperatures. Rising the temperature gives more energy for the reaction to form the transition state. However, the limiting step in the reaction is the oxidative addi-

tion of C-Br bond. Higher temperature may speed up the activated addition of the chlo-robenzene molecule instead of the desired dibromotetrafluorobenzene.

When compared with entry 2 it can be seen that entry 4 produces less product but of higher quality in terms of molecular weight. Thus the optimum reaction tempera-ture seems to lie somewhere between 90 and 100°C. Polymerizations were also attempt-ed at 87°C and 93°C, but unfortunately the results were not comparable because of rea-gent impurity. It was later revealed that the PivOK used for these entries was contami-nated by moisture due to its hydroscopic nature. Presence of water interrupts the reac-tion and these entries were therefore left out of the comparison.

### 7.2.5 Effects of the ligand and the base

The effect of tricyclohexylphosphine-ligand was tested in entries 7 and 8. PCy_3 is bulky monodentate ligand that has high basicity [70]. It is widely used in DPP polymeriza-tions [50,61]. The acid-base system was also studied by using 3 eq potassium carbonate (K_2CO_3) as the base and 1 eq pivalic acid (PivOH) as the acid instead of the normally used PivOK. The results of the systems with ligands are presented in Table 4.

Table 4. *The yields and molecular weights obtained with ligands.*

Entry	Ligand	Base	Other reaction conditions	Yield (%)	M_n (g/mol)
7	PCy_3	PivOK	100 °C, $Pd(Oac)_2$	33	12 934
8	PCy_3	PivOH+ K_2CO_3	100 °C, $Pd(Oac)_2$	2	6 867

Using PivOK and K_2CO_3 separately gives poor results compared to the integrat-ed system of PivOK. In literature similar system with 1 eq PivOK and 2,5eq K_2CO_3 has been used and reported to give at least average results [50,65]. Potassium carbonate serves as carboxylate compound in the reaction cycle and pivalic acid is found to be crucial in the CMD mechanism [61]. In the case of this polymer, it appears that mixing the base and acid in equal amounts in advance makes an improvement, when compared to the case that acid and base are mixed and reacted in the solution.
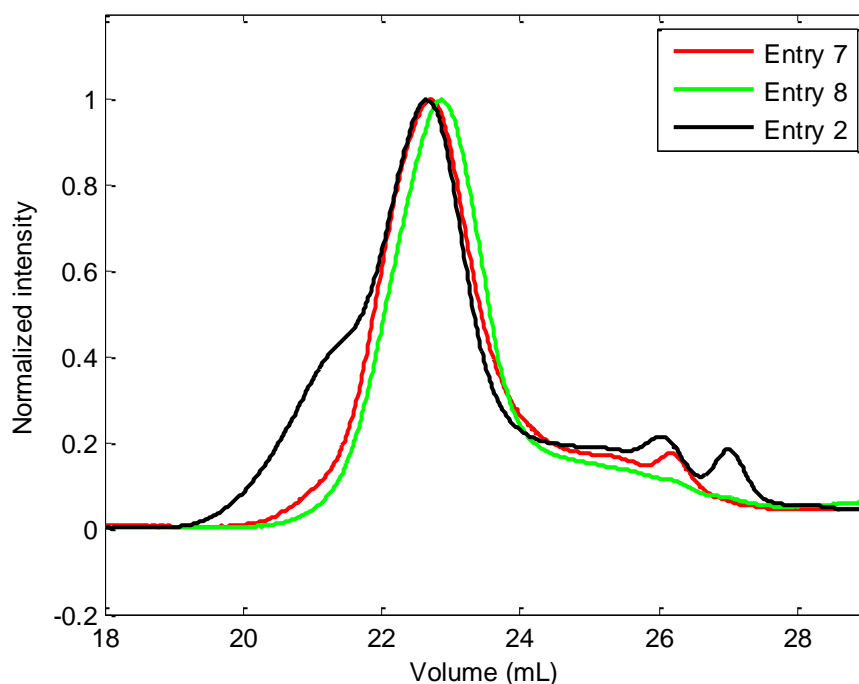
Figure 18. *GPC curves of ligand containing (entries 7 and 8) and ligand free (entry 2) systems.*

The results obtained with the ligand were also not promising. Comparison of the GPC curves is presented by Figure 18. Entries 2 and 7 were made in equal conditions except of the addition of ligand in entry 7. Both yield and M_n were better with ligand free system (entry 2). PCy_3 is monodentate ligand so both pathways 1 and 2 are possible (see Scheme 3) similar to the ligand free system. In ligand free system the solvent takes the role of the ligand and the smaller DMAc might work better than PCy3 that causes larger steric hindrance. It is interesting to note that the shoulder that can be seen in ligand free systems (for example in entry 2) disappears when Pcy_3-ligand is added. The same shoulder appears in all concentration so it cannot be due to cross-linking and thus it might be caused by some side reaction. However, based on the better yield and the molecular weight further entries were carried out without the ligand and with the integrated PivOK system.

7.2.6 Microwave assisted polymerization

After early tests in the oil bath the polymerization was tried with microwave based heating. The same reaction conditions were kept as in entry 1, i.e. one mole of both monomers and 3 eq PivOK were dissolved to DMAc/CB mixture and 4 mol-% $Pd(OAc)_2$ was added. Stirring was set to a high level and the cooling was in maximum level. The first microwave assisted reaction (entry 9) was let to run at 100°C and 60 W power for 4 hours. Initial results seemed promising and thus additional tests were run at different temperatures (Table 5).

Table 5. *The yields and molecular weights obtained at various reaction temperatures by using the microwave heating.*

Entry	T (°C)	Other reaction conditions	Yield (%)	M_n (g/mol)
9	100	4h, 64W, Pd(Oac)$_2$	38	14 871
10	90	4h, 61W, Pd(Oac)$_2$	58	20 385
11	110	4h, 89W, Pd(Oac)$_2$	40	14 858

Based on molecular weight and yield, the temperature of 90°C gives the best results also in microwave. The same molecular weight of about 20 000 g/mol can be achieved with both oil bath and microwave. It should also be noted that the shoulder that is clearly seen in the entries made with thermal heating, has disappeared. However, the GPC curves presented in the Figure 19 indicate some smaller shoulders at 90°C and 110°C. At 110°C (blue curve) the peak is wider, which can be a sign of side reactions. The small peak at 26 mL is related to the amount of oligomers and is clearly smallest at 100°C. Since it is not related to monomer peaks, the larger amount of oligomers at 90°C and 110°C may be related to early chain termination.
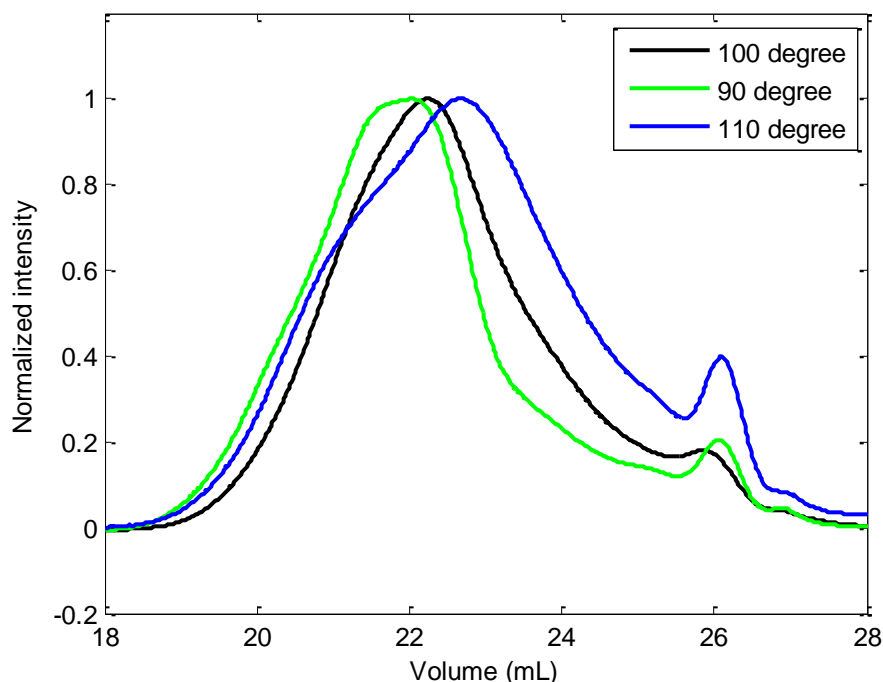
Figure 19. *The effect of temperature on molecular mass and molecular weight distribution indicated by GPC curves.*

Four hours of microwave heating at 90°C (Entry 10) gives almost the same result than 72 h of thermal heating (Entry 4) although the yield is 20 percentage points better with thermal heating (78%) compared to microwave heating (58%). Additionally,

microwave also seems to produce a polymer with equal quality. Compared to the polymer produced by thermal heating, the product mixtures made with microwave are more viscous and form bigger particles in methanol. Therefore they are easily filtered before and after the purification process.

7.2.7 Effect of reaction time

The effect of time in the microwave reactions was studied with 2 h and 8 h entries. The so far optimal reaction temperature of 90°C was used for the 8 hour reaction. A higher temperature of 100°C was used for entry 12 in an attempt to optimize the usage of short reaction time. The results are presented in Table 6.

Table 6. *The yields and molecular weights obtained with various reaction times using the microwave*

Entry	Reaction time (h)	Other reaction conditions	Yield (%)	M_n (g/mol)
12	2	100 °C, PivOK, Pd(Oac)$_2$	19	11 350
13	8	90°C, PivOK , Pd(Oac)$_2$	44	13 365

Based on the comparison with Table 5, the original reaction time of 4 hours seems to give the best results. Lower reaction time (entry 12) leaves the reaction unfinished and gives only a little polymer product and plenty of unreacted monomer. Doubling the reaction time has virtually no impact and results in entries 9 and 12 are almost identical.
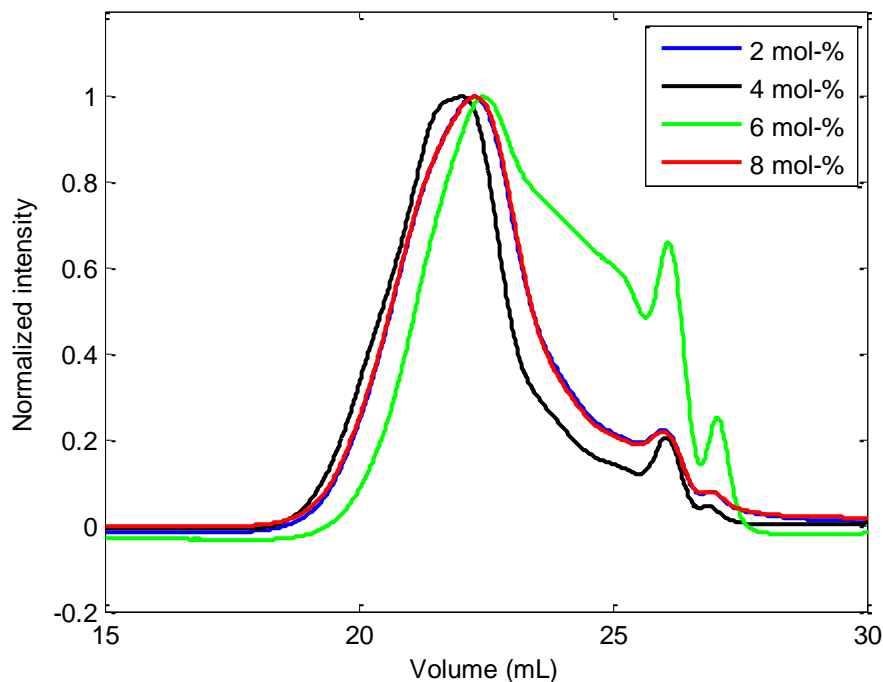
7.2.8 Effect of the catalyst loading

Based on the results presented above, 4 h reaction time was used for the optimization of the amount of the catalyst. Temperature was 100°C in each case and the amount of Pd(OAc)$_2$ was varied between 2 mol-% and 8 mol-%. For the lowest amount of catalyst, 2 mol-%, the reaction time was increased to 8 h in order to fully utilize the catalyst. The results are listed in Table 7.

Table 7. *The yield and molecular weight (M_n) obtained with various amounts of catalyst.*

Entry	Catalyst (mol-%)	Other reaction conditions	Yield (%)	M_n (g/mol)
14	2	100°C, 76W, 8h, PivOK	26	16 036
15	6	100°C, 76W, 4h, PivOK	74	9 563
16	8	100°C, 61W, 4h, PivOK	36	17 171

Unfortunately, low catalyst load gives low yield despite of the prolonged reaction time. 6 mol-% of catalyst (entry 15) gives good yield, but causes side reactions and lower molecular mass. This can be seen as a broad and unsymmetrical GPC curve in Figure 20.

Figure 20. Effect of catalyst loading on the GPC curve; increasing the catalyst load results in broad and unsymmetrical curves.

The results were compared to entry 9 where the usual amount of 4 mol-% catalyst was used. Both adding and reducing the amount of catalyst gives lower molecular mass compared to entry 9. The smallest possible amount of catalyst is preferred in order to keep the product clean and purification process easier. However, catalyst loading of 2 mol-% (entry 14) gives poor yield and adding the catalyst up to 4 mol-% is more economical. Unfortunately power was not equal in all entries, which can affect the results. Even when this aspect is taken into account, 4 mol-% of catalyst seems to give best results and it was used also in the subsequent entries.

7.2.9 Effects of power and cooling rate

Finally, the effect of the power levels used in the microwave was studied. Temperature was kept constant, at 100°C and the power was halved from 61 W to 31 W. For all the other microwave reactions cooling rate was maximized but in the entry 17 minimal cooling was imposed in order to reach the 100 °C temperature with the lower power

level. Table 8 compares the results obtained at low power with those obtained at normal power setting.

**Table 8**. *The yields and molecular weights (M_n) obtained by lowering the power.*

Entry	Power (W)	Other reaction conditions	Yield (%)	M_n (g/mol)
17	31	100 °C, 4 h, PivOK, Pd(Oac)$_2$	2	7 826
9	61	100°C, 4h, PivOK , Pd(Oac)$_2$	38	14 871

The results are unambiguous, yield and molecular weight decrease drastically with decreasing power. Based on earlier entries, this result is expected.

7.3 Comparison of the heating methods

The microwave polymerizations did not produce as good results as the oil bath. Microwave entry 10 gave a copolymer with 58% yield and 20 385 g/mol molecular weight. Yield is clearly lower than in the best polymerization made in oil bath, entry 4 has 78% yield and slightly higher molecular weight of 23 968 g/mol. Thermal heating reached the yield of 96%, while the best microwave yield was 78%. It should be taken into consideration that comparison is not straightforward because of the different batch sizes. Due to limited supply of the monomer, the size of the reaction batch was smaller for microwave entries (100 mg) than for thermal entries (200 mg). Using the bigger batch size in all entries would make the comparison of GPC curves, yields and molecular weights more trustful. With small monomer amount even smallest inaccuracies can cause an error of several percent. This may explain the lower yield in microwave entries.

The GPC curve of the microwave assisted polymerization (entry 10) was compared to the thermal heated reaction (entry 3), presented in Figure 21. Reactions were made with identical reaction conditions: in 90 °C, 4-mol-% catalyst and with PivOK and same solvent system. Microwaves give broad peak and small shoulder at 21.5 mL. Reaction in oil bath gives narrower peak with distinct shoulder. The larger amount of oligomers in entry 3 is due to the weaker purification result with acetone. Microwave assisted entry 10 has been purified with ethyl acetate to reach better results and clearer GPC curve.
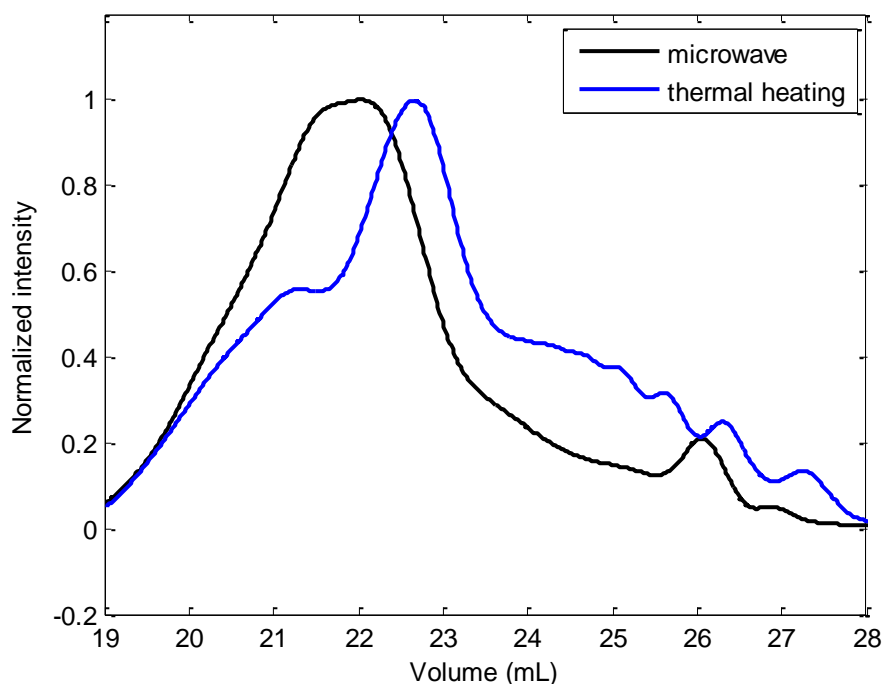
Figure 21. *GPC curves of the entries made with microwaves or thermal heating.*

In spite of the overall lower molecular weight, microwave seemed to produce more easily handleable product. In most cases, microwave assisted products formed bigger particles and more colorless solution when cracked to methanol after reaction. Moreover, filtering the particles is easier and after purification the pure product breaks off the flask walls more easily than in the case of thermally produced copolymers. Additionally, with microwave constant quality was maintained: reasonable yields and molecular weight was obtained throughout the whole series, with only few exceptions. This may be due to more stable heat flow through the sample compared to the oil bath where the temperature can vary several degrees during the 72h reaction time. Constant pressure and stirring conditions are also more easily reached in microwave chamber than during thermal heating.

7.4 Polymer characterization

The result of the polymerization was thiophen-diketopyrrolopyrrole/tetrafluorobenzene copolymer. Properties of the product were studied with several characterization methods. DSC and TGA were run from the batches that had highest molecular weights. NMR and UV-vis were measured from a collection of samples. GPC measurements showed a number average molecular mass of 23 984 g/m and polydispersity index (*Đ)* of 3.7 for the best entry made with thermal heating. Corresponding parameters for the best monomer assisted entry are M_n= 20 385 g/mol and *Đ* 2.4.

From the ^{1}H NMR spectrum of the copolymer (Appendix 3) chain length could be estimated to be approximately 13 units, which means that relatively long polymer chains have been achieved. Because tetrafluorobenzene contains no hydrogen, polymer spectrum is similar to monomer spectrum (Appendix 2). Hydrogens attached to the thiophene ring placed on the polymer chain give signals at 8.99 ppm and 7.90 ppm. Signals at 7.88 ppm and 8.88 ppm are assigned to the hydrogens of the thiophen unit just before the end group. The end group of thiophene gives signals at 8.78 ppm, 7.68 ppm and 7.32 ppm. The signal at 7.12 is related to the hydrogen at the very end of the tetrafluorobenzene end group. Signals at 4.14 ppm and 2.07-0.90 ppm are assigning to the alkyl chains. Deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$) solvent gives a peak at 6 ppm and peaks 3.7 – 2.3 ppm originate from DMAc reaction solvent. Peaks at 7.6-7.31 ppm are possibly due to the CB reaction solvent.

In order to examine the end groups, ^{19}F NMR was run from the copolymer. The spectrum is shown in Appendix 4. The fluorides in the polymer chain gives signal at -138.9 ppm and the fluorides before the last DPP unit at -138.9 ppm. Signals at -132.9 ppm and -137.7 ppm are from the bromine substituted tetrafluorobenzene end group. The minor peak at -138.45 ppm originates from the fluorines at the hydrogen substituted tetrafluorobenzene end group. Because the intensity of the end group signals is small compared to the signals originating from the fluorides inside the polymer chain, chain ending is rarely due to tetrafluorobenzene. That is, polymer chain is mostly ended with a thiophene unit.

Diketopyrrolopyrroles are usually hole conductors and therefore p-type semiconductors. However, DPPPhF4 has so low LUMO level, that it is considered to show n-type semiconducting properties. It carries electrons better than holes and can therefore be used as acceptor material. Park et al. have a measured good electron mobility of 2.36 $cm^2V^{-1}s^{-1}$ for the thiophene-DPP/tetrafluorobenzene copolymer [5].

The copolymer has metallic shining maroon color in solid form. When dissolved in solvent, color turns to greenish-blue as seen in Figure 22. The blue color relates to adsorption in the red range of the electromagnetic spectra, near UV-area. This indicates a low band gap polymer and thus the polymer appears to be suitable for donor material.

Figure 22*. Color of the diketopyrrolopyrrole/tetrafluorobenzene copolymer in isohexane.*

In order to examine the adsorption band more quantitatively, UV-vis spectroscopy was used. Results of the measurement of entry 2 are presented in Figure 23.
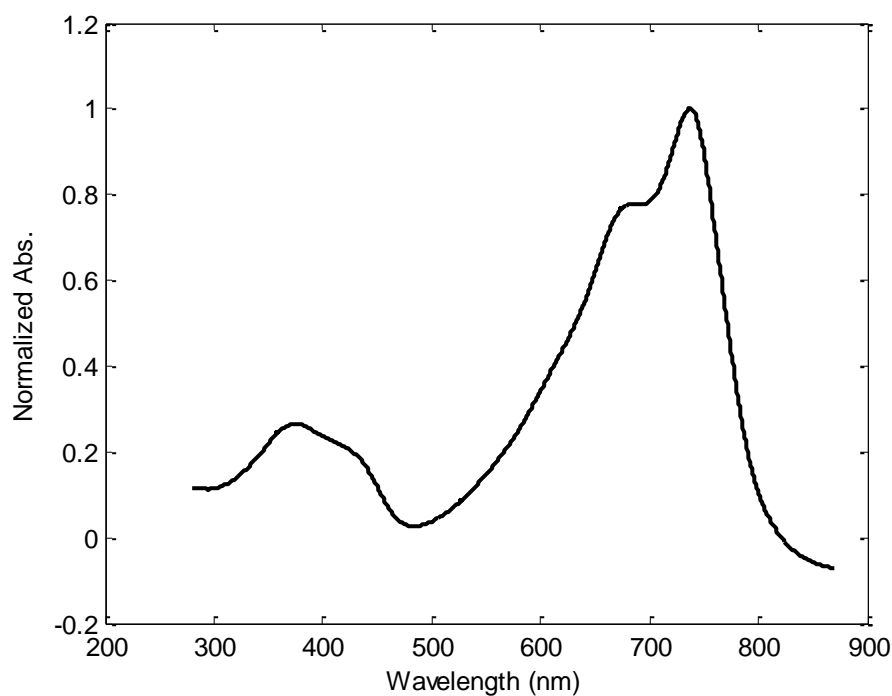

Figure 23*. UV-vis spectroscopy shows the adsorption band of the copolymer.*

The absorption area is broad and consists of two bands. The peak in the longer wavelengths is due to charge transfer in the DPP core and the smaller peak at the shorter wavelength region is due to the π-π* transition of electrons in the conjugated chain [22,52]. The absorption maximum is at 731 nm and has a shoulder, which indicates the strong polarity of the lactam groups. The absorption region is located in long wave-

length which indicates low band gap and good absorption of photons. Furthermore, polymers that absorb light in the near-infrared area usually show good aggregation and π-stacking in the solid form. All these properties are beneficial for the active layer material. Results are in accordance with spectra taken from similar DPP polymers [5,22,40,71].

The effect of molecular weight on the adsorption band was studied by measuring the UV-vis spectrum from three entries with different molecular weight. The results of normalized absorption peaks are presented in Figure 24.
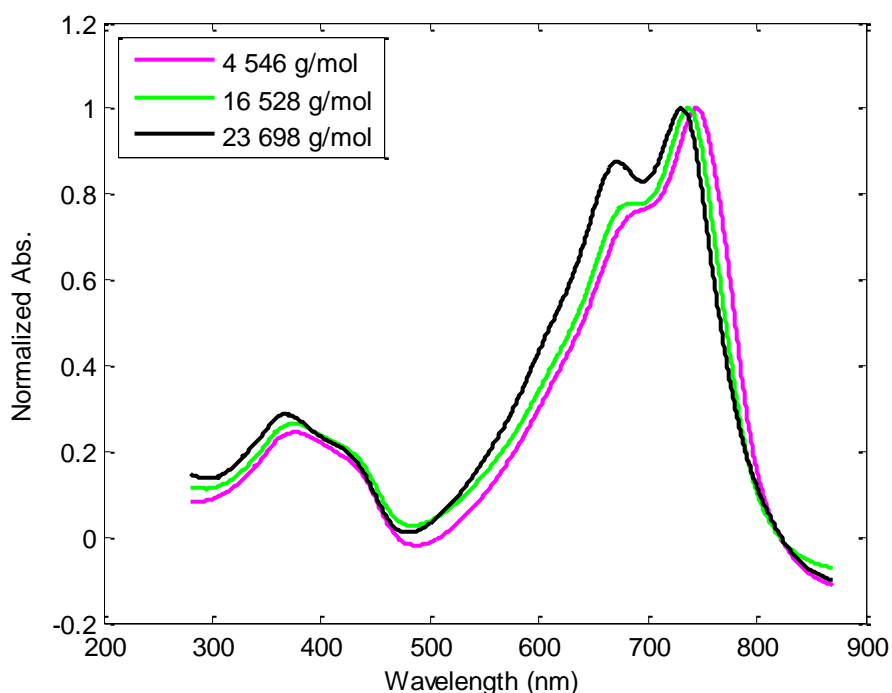
Figure 24. *The absorption band at different molecular weight.*

With higher molecular weight the absorption intensity is raised as expected, the trend can be seen especially at wavelengths 360 nm and 640 nm. Higher molecular weight and thus longer molecule chain extend the π-π-conjugation of the molecule and increases the absorption intensity. Higher molecular weight seems also be causing blue shift of the adsorption band, even though usually reversed behavior is expected [72].

The effect of the ligand used during polymerization on the quality of the product was also studied with UV-vis. Ligand-free entry 2 is compared to an equal entry 7 in which Pcy$_3$-ligand was used. The reaction conditions were equal except for the presence of the ligand. Spectra are presented by Figure 25.
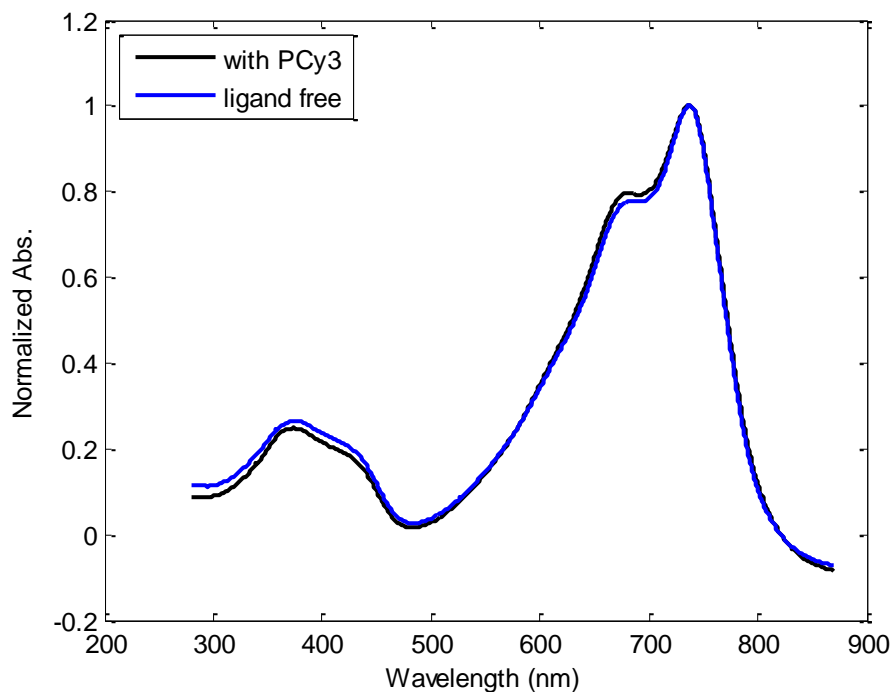
Figure 25. *Using the ligand has no effect on the the adsorption band.*

Both entries give almost identical spectrum. The ligand-free system (blue curve in Figure 25) has slightly higher intensity, but this can be also explained with the higher molecular mass compared to ligand containing entry 7.

TGA measurement was made for 10.38 mg of DPP-copolymer with molar mass ~ 16 000 g/mol (Entry 2). The measurement was run in air by increasing the temperature from 50°C to 650°C with a heating rate of 10°C/min. As shown by Figure 26, this polymer sustains high temperatures und decomposes at around 400°C.
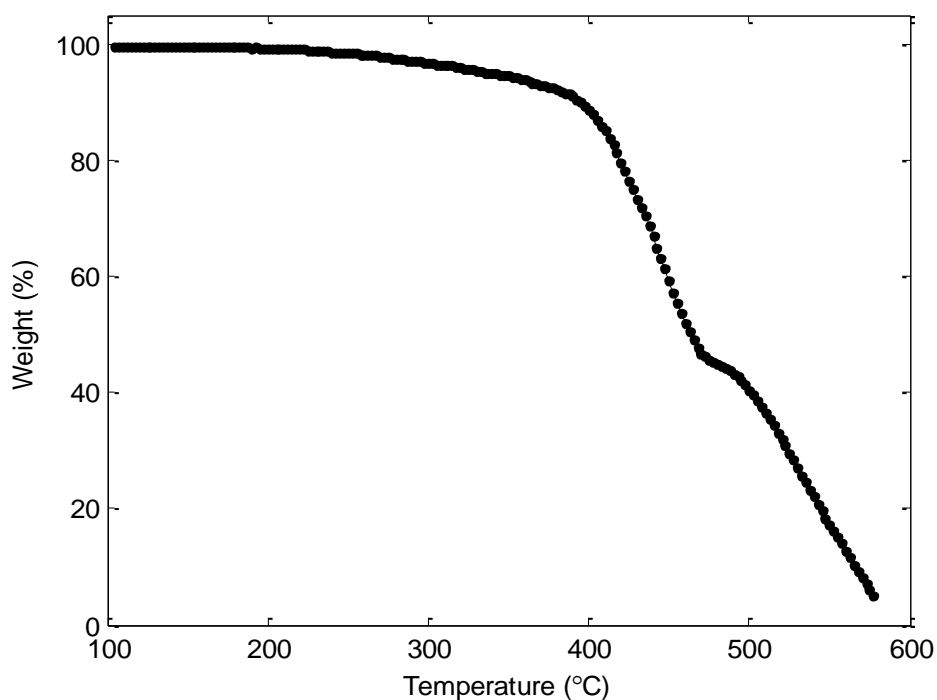
Figure 26. *TGA shows onset-value of 410°C.*

The onset value was 410°C and after 2 minute period at 600°C 1.46% of the sample was still remaining. This indicates that the polymer has very good thermal stability in air. This property is important, since in the industry solar cell fabrication is preferably made in air and stability against oxygen also increases the device of the lifetime [22]. Similar TGA results have been published for other diphenyl-DPP [50].

DSC measurement was done in order to determine the melting point of DPP-PhF$_4$. The measurement was run three times for the same polymer (Entry 4). In each case the cover of the sample pan was punctured in order to release the pressure. Heating and cooling rate of 10°C/min was used except for the baseline, which was determined at a higher rate (30°C/min). Initially a common sample amount of 5 mg was used but it turned out to be too excessive. Polymer melt flowed out of the sample pan and the measurement could not be considered trustworthy. In the second attempt smaller sample of 3.13 mg was used and successfully heated from 25°C to 380 °C and then cooled back to room temperature. Finally a third sample of 3.3 mg was also measured by heating and cooling two times between 40°C to 390°C. The obtained DSC curve is presented by Figure 27.
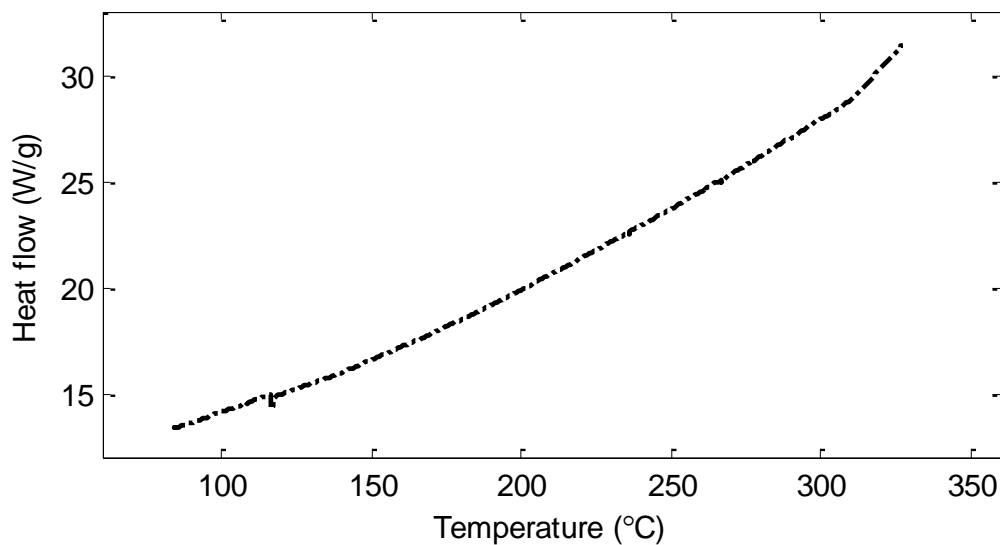
Figure 27. *DSC measurement for DPPPhF4 copolymer.*

Only minor and broad melting peak can be seen at 310°C and no sign of glass transition appears. The DSC measurement was repeated several times with similar result. In the literature very few articles give information about the DSC behavior of DPP polymers and direct reference curve taken from DPPPhF$_4$ is not available. Beyerlein et al. report similar peakless behavior for phenylene containing DPP [35]. In comparison, thiophene-DPP copolymerized with thiophene units shows notable melting peaks and clearly lower melting point around 100°C [27,52,73].

8 CONCLUSIONS

In this work, diketopyrrolopyrrole/tetrafluorobenzene copolymer was successfully synthesized and its properties were studied. DPPPhF$_4$ shows wide absorption band in the near infrared area and evidently has low band gap and highly conjugated system. It has thermal resistance up to 410 °C and good stability in air. Based on the characterization results, the copolymer can be considered as potential material for organic solar cells.

Optimal reaction conditions were searched for the monomer synthesis and the work up protocol was improved. Due to the direct arylation, the monomer synthesis contains two reaction steps fewer than the previously reported polymerization using Stille cross-coupling [5]. The direct arylation method results in a comparable yield and quality of the copolymer. A number average molecular mass around 20 000 g/mol was reached in several entries, while similar DPPPhF$_4$ copolymer prepared with Stille cross-coupling has a M$_n$ of around 16 000 g/mol [5]. A higher yield of 90% was achieved with direct arylation compared to the 63% yield in Stille method [5]. The produced copolymer is well soluble in common solvents and there is no sign of crosslinking in the NMR spectrum.

The polymerization process was optimized and best result were achieved by thermal heating at 90 °C, 72 h reaction time, 0.1 M solvent mixture of dimethylacetamide and chlorobenzene, 3 eq PivOK and 4 mol-% palladium acetate. The yield was somewhat lower than at 100°C but molecular weight was highest at 23 000 g/mol. The polymerizations were also done with microwave assisted heating. The thermal heating produces slightly better results but microwave can still be considered a good way to speed up the optimization process and to produce polymer of uniform quality.

The solvent system was not included in the optimizing process although it would be useful to further study the effects of different solvents. It appears that chlorobenzene is not the best solvent choice because it may interrupt the reaction prematurely. Benzene-ring in chlorobenzene reacts with DPP-monomer and ends the chain growth, which can be the reason for the relative low molecular mass in all entries. A molecular weight of 24 000 g/mol was the best result obtained here, while other research groups have reported a M$_n$ up to 47 000 g/mol with the same thiophene-DPP-monomer [37]. DMAc is commonly used solvent for direct arylation, although Mercier et al. also reported problems with DMAc [56]. Thus changing the reaction mixture partly or fully might be justifiable. Good results have been obtained for example with toluene, DMAc and DMAc/THF mixture [37,50].

In the microwave assisted polymerizations higher power input together with moderate temperature and time are recommended. Lower reaction temperature sup-

presses side reactions while high power input combined with high cooling rate provides enough energy for an effective reaction rate. For example 90° with 70 W could be tried for 4 hours. In literature high power input has already been used in microwave heating, but usually at high temperatures over 160°C [5,65]. Part of the catalyst loading series could also be repeated at 90°C reaction temperature since it seems to work well with 4 mol-% catalyst.

In order to fully elucidate the effects of structure and molecular weight on the absorption band, the UV-vis measurement should be repeated with a larger amount of the sample. Measurements on polymer films would more clearly indicate the dependency of the absorption on the molecular mass, since the solution based method used here may mask the effect of the conjugation length on the absorption band. In addition, structure characterization, for example NMR measurements, could be used to analyze the possible dependence between the polymer structure and the shift of the absorption peak.

9 EXPERIMENTAL PART

9.1 Materials and methods

Technical solvents were purchased from Sigma Aldrich Chemical Co. and pure solvents and reagents from VWR. Soxhlet and other glasswares as well as extraction thimbles were supplied by VWR as well. TLC plates were Silica gel 60 layered aluminium sheet and for column chromatography and silica plugs Silicagel with 40-63μm pores were used. Both silica products and molecular sieves of size 4 Å were purchased from Merck. pH-indicator paper was from Sigma Aldrich. All the reagents were used as received, except for N,N-dimethylformamide, chlorobenzene and dimethylacetamide which were dried before use.

The gel permeation chromatography curves and ^{1}H nuclear magnetic spectroscopy of 1-iodo-2-octyldodecane were measured at the Institute of Macromolecular Chemistry, University Freiburg. Alfred Hasenhindl measured the NMR samples with Bruker ARX 300 Spectrometer. Solvent was CHCl$_3$-d and standard TMS. Frequency of 300 MHz was used for room temperature measurements. GPC were measured by Marina Hagios in THF or CHCl$_3$ solutions against polystyrene standard. Flow rate of the mobile phase was 1.0 mL/min and UV-detector at 254 nm was used for detection.

^{1}H and ^{19}F NMR spectra of the polymer product were measured in Leibnitz Institut für Polymerforschung e.V, Dresden by Hartmut Komber. The spectrometer was Bruker Avance 500 and frequency of 500 MHz was used for ^{1}H spectrum and 470 MHz for ^{19}F-spectrums. Measurements were done at 120 °C and deuterated 1,1,2,2-tetrachloroethane (C$_2$D$_2$Cl$_4$) was used as a solvent and tetramethylsilane (TMS) as a standard. All the chemical shifts are given in ppm and the spectra were interpreted based on the method by Gottlieb et al. [74].

Thermogravimetric analysis was done at Freiburg Material Research Center. Netzsch STA 409 device with 75 mL oven volume was used. Measurements were run in air from 50°C to 650°C.

Differential Scanning Calorimetry was measured with Perkin Elmer Pyris 1 device. Heating rate was 10°C/min and indium calibration was used.

UV-vis spectra were measured with Shimadzu UV-1800 Series spectrometer which was controlled by UVProbe 2.30 program. Cuvettes were made of quartz and solvent was pure CHCl$_3$. Exitation wavelength ranged from 200 nm to 900 nm. Concentration of the samples was 0.01 mg/ml.

Microwave oven CEM Discover-SP was used for polymerization. The oven was controlled by CEM Synergy program.

9.2 Synthesis procedures

Detailed synthesis procedures and reaction conditions are presented in this chapter. Furthermore, general aspects are described considering the monomer syntheses. The reaction products are identified with NMR spectroscopy and spectra are presented in the Appendice.

9.2.1 General aspects

N,N-dimethylformamide was used as a solvent in the alkylating step and it was dried before use. Distill system was prepared and molecular sieves were placed to both flasks. The whole system was put under vacuum and heated with heater to remove all possible moisture. DMF was poured over the molecular sieves and a large stirring bar was added into distillation flask. The system was put under nitrogen atmosphere and DMF was let to stir with molecular sieves overnight. In the morning the brownish mixture was heated to 153 °C and DMF was distilled over the pure molecular sieves and then stored with them.

Purification of the alkylated monomer was done by recrystallization. Several solvents were tested for this purpose. Three 5 mg samples of the monomer were weighted and added to 0.5 ml of three different solvents: acetone, methanol and ethanol. Each sample was heated in evaporator and then slowly cooled. After 12 hours rate of crystallization was inspected. Acetone and methanol solutions remained dissolved but in the ethanol solution small amount of solid could be seen at the bottom of the flask. In order to distinguish between a real solid and dregs, the separation of the phases was analyzed with TLC. Sample from the liquid phase was placed at the TLC plate as such and let to dry completely. The solid phase was quickly washed with acetone, let to dry and then diluted to isohexane and applied to TLC plate. Eluent was a 2:1 mixture of DCM and isohexane. Separation of the phases could be seen and the solid phase did not leave marks at the bottom line in contrast to the behavior of the liquid phase. Based on to these results ethanol was selected as recrystallization solvent.

Recrystallization was done by adding 35 ml pure ethanol to 2 g of monomer. Mixture was heated almost until boil (75°C) in evaporator. When necessary, ethanol was added with Pasteur pipette until all monomer was dissolved. The overall concentration was about 18 ml/mg. Because of the intense purple color of the solution, the point when all the monomer was dissolved was not easy to notice. Solution was slowly cooled first to room temperature and then to 8°C. It was let to crystallize at least 24h and then TLC was run to see if the recrystallization had taken place. The liquid phase was applied as such and the solid phase was again dissolved to isohexane. Spots were let to ascend in the DCM eluent. Much less impurities could be seen in solid phase than in liquid phase but some identical spots could still be seen in both samples. NMR measurements also showed the presence of some impurities and thus the recrystallization was repeated.

The crystals obtained from the first recrystallization were filtered in vacuum and washed with a small portion (about 20 ml) of cold ethanol. Ethanol was cooled in liquid nitrogen and the washing was repeated until the washing solution was almost colorless (overall consumption of ethanol about 500 ml). Finally, the product was washed once with cold methanol for faster drying. Then the recrystallization procedure was repeated as described above.

The NMR sample was taken from two times recrystallized, filtered and dried monomer and it indicated that the alkylated monomer was pure. The double recrystallization process was done for all monomer batches and the purification was verified with NMR in each case.

9.2.2 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5)
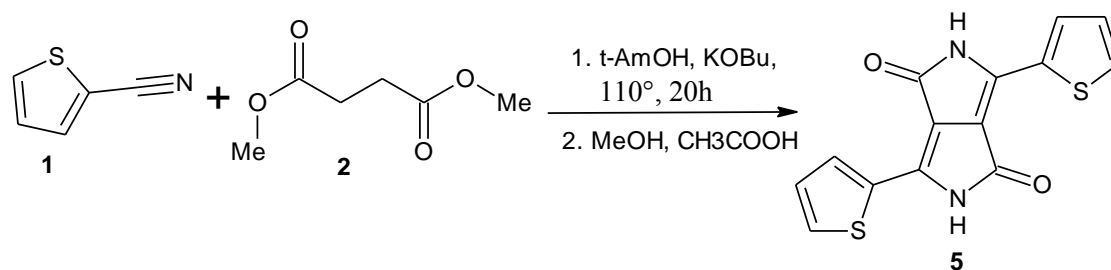
Scheme 8. *Synthesization of the thiophene-DPP-monomer **5**. (Reprint of scheme 4)*

100 ml 3-neck flask was flushed with nitrogen and loaded with the base, i.e. potassium tert-butoxide (7.0 g, 62.4 mmol). 2-thiophenecarbonitrile **1** (6.087 g, 55.767 mmol, 2.5 eq) was diluted to amyl alcohol (2-metyyli-2-butanol, 30 ml), degased and injected in to the reaction flask. The base and nitrile were stirred thoroughly and the mixture was heated to 110°C. Dimethyl succinate **2** (3.136 g, 22.3 mmol, 1.0 eq) was diluted to 10 ml of amyl alcohol, degased and slowly inserted to the reaction mixture via dripping funnel. After all succinate was added, the reaction was let to run overnight. It was then let to cool to the boiling point of methanol, 65°C. Dark purple and quite viscous reaction mixture was diluted to methanol and neutralized with 100% acetic acid. Neutralizing reaction was monitored with pH-paper and afterwards the mixture was refluxed for 10 minutes. Then it was filtered and washed twice with boiling hot methanol (50°C) and once with room temperature water. Black filter cake was then let dry in vacuum. Yield: 82%. NMR measurement was not run because product has very low solubility in common solvents.

9.2.3 1-iodo-2-octyldodecane (8)
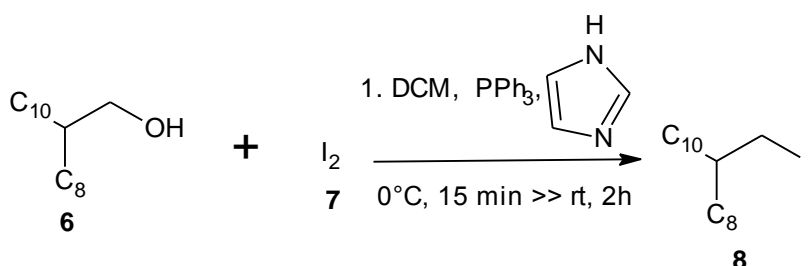
Scheme 9. *Iodination of the 2-octyl-1-dodecanol. (Reprint of scheme 5)*

9,56 g imidazole, 37,0 g triphenylphosphine and 35 g 2-octyl-1-dodecanol **6** were diluted to 225 ml dichloromethane, degased with nitrogen and stirred in ice bath. Iodine **7** was added in small portions, to avoid the mixture to overreact and boil. Adding iodine warms up the mixture and turns it to bright yellow. When all the iodine was added, reaction was let to stir in ice for 15 minutes, until warming up stopped and reaction stabilized. Then the ice bath was removed and the mixture was let to cool down to room temperature. After 2 hours 28 ml of saturated Na_2SO_3-solution was added and the color turned to citron yellow and oily-like. Organic phase was separated and concentrated in evaporator. Organics were then poured into 1000 ml beaker and isohexane was added until the beaker was full. White precipitate was filtered out and the reaction solution was washed three times with water and once with saturated NaCl. Organic phase was put through a short silica phase (about 5 cm), dried with $MgSO_4$ and isohexane was evaporated. The product is colorless light oil. Yield: 89%.

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 3.20 (d, J=4,55 Hz, 2H); 1.49 (m, 1H); 1.40-1.20 (m, 32H); 0.78-0.83 (m, 6H) ppm. NMR in accordance with literature [66]. Appendix 1.

9.2.4 2,5-dioctyldodecyl-3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (9)
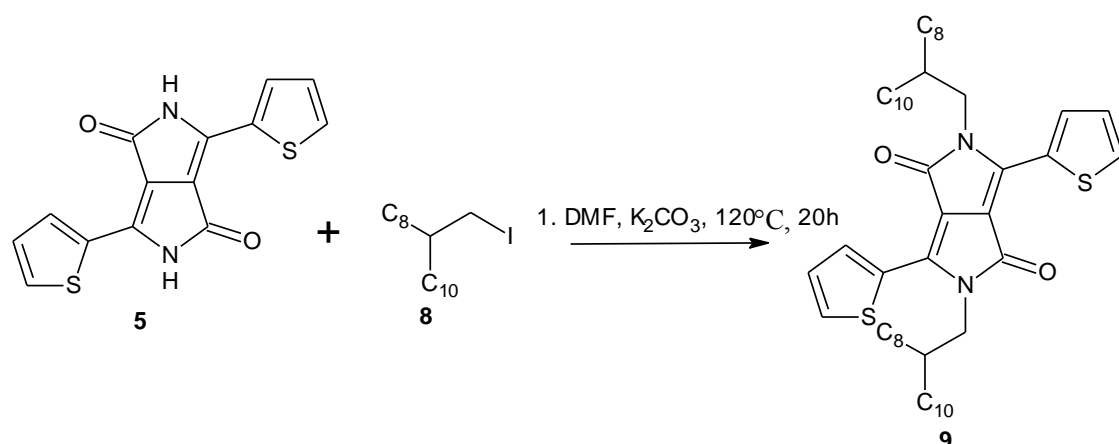
Scheme 10. *Alkylation of the monomer.*

DPP-monomer **5** (2.0 g, 6.66 mmol, 1.0 eq) and potassium carbonate (3.67 g, 26.56 mmol, 4 eq) were diluted to 25 ml of dry N,N-dimethylformamide. Mixture was degased and stirred in 120°C for 4 hours. Then octyldodecyliodine **8** (8.0 g, 19.90 mmol, 3 eq) was slowly added via syringe, in two portions. Reaction was let to run 20 h. Then it was diluted to dichloromethane and washed two times with excess water. Organic phase was put through a short silica plug, dried with magnesium sulfate and DCM was evaporated. Purple sticky product was let to dry at 50°C in vacuum overnight. The product was recrystallized two times with ethanol. Dark purple crystals were filtered in vacuum and washed with plenty of cold ethanol and once with cold methanol. Product was dried in vacuum to yield dark purple alkylated monomer. Yield: 30%.

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 8.8 (d, 2H), 7.5 (d, 2H), 7.2 (m, 2H), 4.0 (d, 4H), 1.5 (s, 2H), 1.3-1.0 (m, 32H), 0.84-0.75 (m, 6H) ppm. NMR result is in accordance with literature [22]. Appendix 2.

9.2.5 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione /tetrafluorobenzene copolymer (11) with thermal heating

Pure DPP-monomer **9** (200.0 mg, 0.2322 mmol, 1.0 eq) and 1,4-dibromotetrafluorobenzene **10** (71.48 mg, 0.2322 mmol, 1.0 eq) and PivOK (97.87 mg, 0.6965 mmol, 3 eq) (or PivOH (23.71 mg, 0.2322 mmol, 1.0 eq) and K$_2$CO$_3$ (96.26 mg, 0.6965 mmol, 3.0 eq) for entry 8 was placed into 10 ml pressure vial. The solids were diluted to chlorobenzene (2.3 ml, 0.05 M) and dimethylacetamide (2.3 ml, 0.05M). The mixture was stirred and degased via rubbery cap about 20 min. Then palladium acetate (2.09 mg, 0.0093 mmol, 4 mol-%) was added and rubbery cap was replaced with Teflon-included cap. The new cap was flushed carefully with nitrogen and the vial was closed tightly. Reaction vessel was put into an oil bath, stirred and let to boil for 24h or 72h.

^{1}H-NMR (300 MHz, C$_2$D$_2$Cl$_4$): δ = 8.9 (d, 2H), 8.78 (d, 2H), 7.9 (d, 2H), 7.68 (d, 2H, endgroup), 7.32 (t, 2H, endgroup), 7.12 (m, 1H, endgroup), 4.14 (d, 4H), 2.0 (s, 2H), 1.3-1.0 (m, 32H), 0.84-0.75 (m, 6H) ppm. Appendix 3.

^{19}F-NMR (300 MHz, C$_2$D$_2$Cl$_4$): δ = -132.9 (m, 2F), -137.7 (m, 2F), -138.5 (m, 2F), -138.8 – -138.9 (d, 2F) ppm. Appendix 4.

9.2.6 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione /tetrafluorobenzene copolymer (11) with microwave

Pure DPP-monomer **9** (100.0 mg, 0.1161 mmol, 1.0 eq) and 1,4-dibromotetrafluorobenzene **10** (35.74 mg, 0.1161 mmol, 1.0 eq) and PivOK (48.9 mg, 0.0046 mmol, 3 eq) was placed into 10 ml microwave reaction vial. Solids were diluted to chlorobenzene (1.15 ml, 0.05 M) and dimethylacetamide (1.15 ml, 0.05M). The mixture was mixed and degased via rubbery cap for 20 min. Then palladium acetate

(0.52 mg – 2.09 mg, 2 to 8 mol-% depending on the entry) was added and mixture was further degased for 2 minutes and then placed into the reaction chamber of the microwave heater. ^{1}H-NMR and ^{19}F-NMR, see above.

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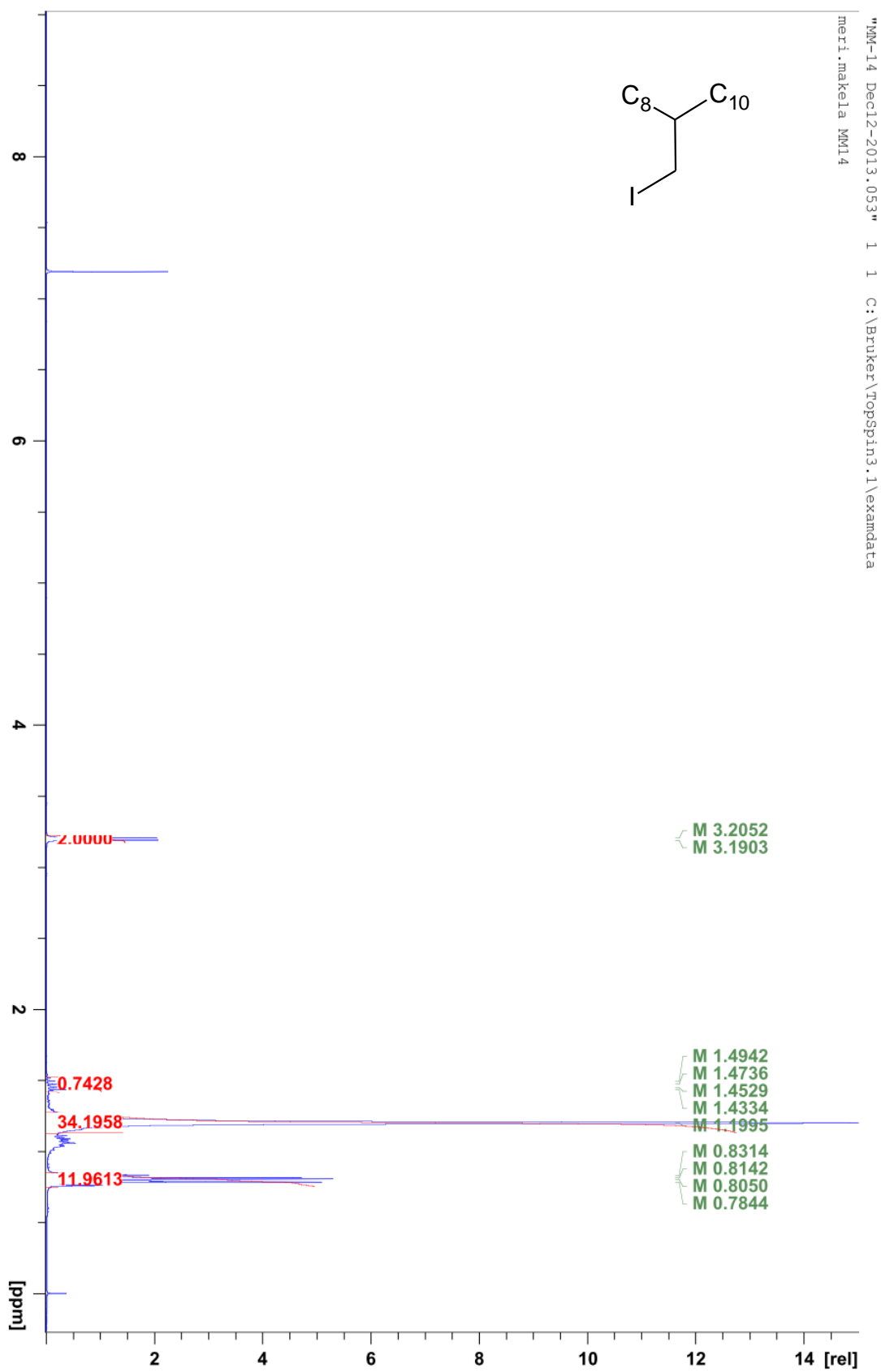
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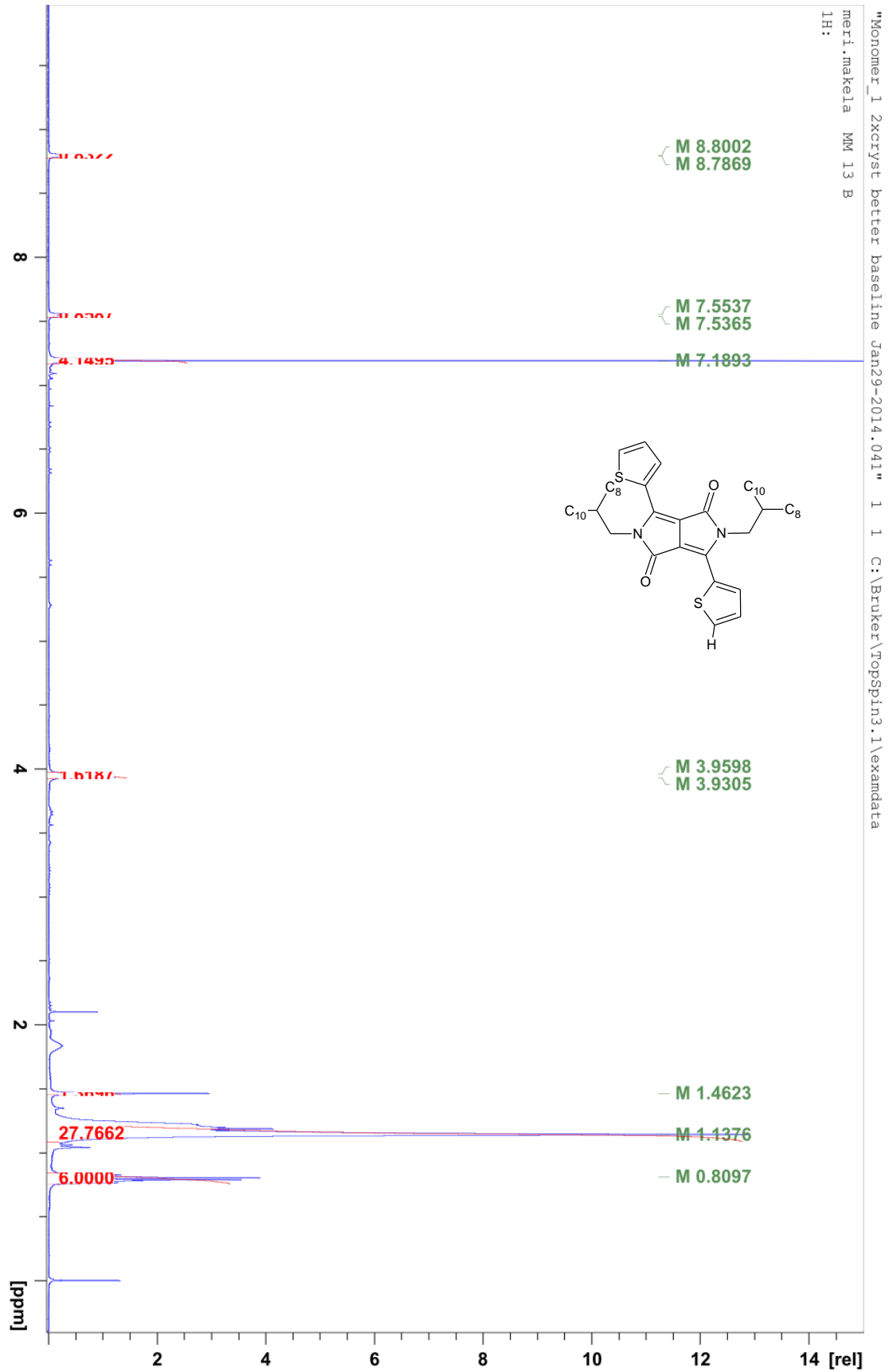
APPENDICES

Appendix 1.

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Appendix 2.

1H:
meri.makela MM 13 B
"Monomer_1 2xcryst better baseline Jan29-2014.041" 1 1 C:\Bruker\TopSpin3.1\examdata

M 8.8002
M 8.7869

M 7.5537
M 7.5365

M 7.1893

M 3.9598
M 3.9305

M 1.4623

27.7662   M 1.1376

6.0000   M 0.8097

Appendix 3.

Appendix 4.