Developing suitable polymer semiconductors for the application in BioFETs

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Chapter 6

The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

After the results presented in the previous chapter it was decided to move away from copolymerization and to look for alternative routes to synthesize regioregular conjugated polymers. Typical homopolymerization methods are GRIM, oxidative coupling (FeCl₃), Stille homocoupling, and Yamamoto coupling. We looked at all of these methods but decided on Suzuki homocoupling with bis(pinacolato)diboron. Our results show that the large scale synthesis of the monomers and easy polymerization make this a very versatile polymerization route for a large variety of different monomers. MALDI-TOF MS analysis revealed a substantial improvement in the quality of the resulting polymers.

*Part of this work was published:

6.1 Introduction

In the previous chapter we demonstrated that the use of the standard Stille cross-coupling results in oligomers with a wide chain distribution. This wide distribution is caused by both the nature of the Stille coupling itself and the many side-reactions. Understanding these limitations is very important for the design and synthesis of conjugated polymers. The large difference in results found in the literature show that this is not always the case. Simple homo-polymers like P3HT have found their ways into industry, indicating we might have to focus on more simple systems too. We therefore decided to look toward homopolymerization in our project as well. An overview of the synthesis of regioregular polythiophenes was given by Osaka and McCullough in 2008. The routes that where discussed are represented in Figure 6.1.

![Synthetic routes for regiosymmetric polythiophenes as present bij McCullough and Osaka.](image)

Several of the routes presented there were discussed in the introduction and throughout this thesis. Methods C and E, the traditional Stille co-polymerizations, with all their problems, were discussed in the previous chapter. Although method E with equivalent monomers should give better polymerization results than Stille heterocoupling because \((XY)_nX\) is now the same as \((YX)_nY\), reducing the amount of possible chains in the obtained polymer. Method A, the oxidative polymerization, is one of the oldest methods, and although high molecular weight polymers can be obtained, they are not free of defects. Branching, in
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

particular, can prevent the formation of high quality, ordered films and therefore this method is also less suitable.

Route B is known as the Yamomoto coupling reaction and uses Ni(0) to promote a dehalogenation-condensation reaction. Unfortunately, the coupling reaction is not catalytic and because Ni(COD)$_2$ is expensive, pyrophoric, and requires storage at low temperature under inert atmosphere, it is less suitable for the synthesis of large amounts of polymer. Method D was published in 1995, but has not been used very often because of the need for the very toxic reagent hexamethylditin.$^2$

The methods which were presented by McCullough and Osaka (Figure 6.2) are specific to regiosymmetric polythiophenes, but there are other routes which might also be suitable for the synthesis of regiosymmetric polythiophenes. In Figure 6.3 we present five of these alternative routes.

![Figure 6.2 Other possible synthetic routes for regiosymmetric polythiophenes.](image)

Methods H and J are Suzuki–Miyaura co-polymerizations. The fact that the Suzuki–Miyaura cross-coupling reaction was not mentioned by Osaka and McCullough is probably related to the fact that polythiophenes are generally less suitable for polymerization by the Suzuki-Miyaura coupling method. The reason for this is the electron-rich nature of thiophenes, which slows down the oxidative addition step$^3$, resulting in an overall slower reaction and more pronounced deborylation$^4$. Deborylation is the main side reaction of the Suzuki–Miyaura coupling, resulting in low molecular weight products. For less electronegative aryl monomers like polyfluorenes, the Suzuki–Miyaura coupling is generally accepted as a better alternative than the Stille coupling, giving higher molecular weight products. A problem that
remains when using methods H and J is the fact that these are co-polymerizations and, as been shown by Janssen, have the same problems as the Stille coupling, making the methods less interesting.

Method I is also a Suzuki–Miyaura polymerization, but in this case it is also a homo-polymerization. An communication written by Yokoyama et al. in 2007 showed that by using the asymmetric 2-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as monomer in the Suzuki-Miyaura polymerization, the resulting polymer, poly(9,9′-dioctylfluorene) had a high molecular weight (17700 g/mol) and a low polydispersity (1.3) within 30 min of polymerization time. This result indicates chain growth polymerization instead of stepwise polymerization, similar to the results obtained by Yokozawa and McCullough for their optimized GRIM polymerization method. This type of polymerization proceeds via a so-called catalyst-transfer polymerization method. Analysis of the polymer by MALDI-TOF MS showed a very clean structure with having mainly chains with bromine end-groups. On paper this method has clear advantages, but in practice the application is limited. The need for monomers with two different functional groups makes the synthesis complicated and up to now only simple monomers have been polymerized. In 2008 Yokozawa published a follow-up, highlighting the development of these catalyst-transfer condensation polymerizations, and combining their results on the living Suzuki-Miyaura polymerization with that of the chain growth character of the nickel catalyzed homopolymerization (GRIM) found by Osaka and McCullough. Unfortunately, as was mentioned in paragraph 1.3.3, the use of the traditional GRIM for larger aromatic monomers is rather limited, the transmetalation reaction is inefficient for extended aromatic systems like biaryls, fluorenes, and carbazoles resulting in the formation of low molecular weight products. If this problem could be overcome, the GRIM would be a very suitable and easy method for the synthesis of regio-symmetric polymers. This is also the reason why, especially in industry, there is a big effort to activate the GRIM method, making it suitable for a larger array of different monomers.

In 2004 Knochel et al. presented results which showed that for the functionalization of aryl- and heteroaryl bromides, the magnesium-bromide exchange reaction was significantly increased when LiCl was added. This was adopted for the polymerization of poly(p-phenylene) by Yokoyama in 2006. Without LiCl only low molecular weight (~4000 g/mol) products with a large polydispersity (~2.5) where obtained, with LiCl the molecular weight was drastically increased (~13000 g/mol) and the polydispersity decreased (~1.2). Only very recently were these specific results picked-up by McCullough et al. and used to develop a more universal method. They successfully polymerized fluorene, pyrrole, and carbazole monomers, although each polymerization had to be optimized to obtain good results. The
selective halogen-metal exchange reaction of this method is the key step towards the living character of the polymerization. The organo-lithium activated nickel (OLAN) catalysis, for example, uses the more reactive and less selective n-BuLi as metal-halogen exchange reagent (no Grignard reagent) which also results in high molecular weight polymers but with a high polydispersity\textsuperscript{11}. The universal GRIM combines the advantages of easy monomer synthesis with that of the standard GRIM polymerization, making it a possible candidate for the synthesis of regiosymmetric conjugated polymers with a well-defined structure and low dispersity. This is route F in Figure 6.2.

The use of the very reactive Grignard reagent unfortunately makes it less suitable for polymers with functional groups. Remaining from Figure 6.2 is method G, a method analog to method D from Figure 6.1, with the difference that the non-toxic bis(pinacolato)diboron can be used. In 1995, Miyaura introduced bis(pinacolato)diboron as a reagent to convert aryl halides to arylboronic esters under mild conditions\textsuperscript{12}. In 2004, Bräse et al. used this Miyaura borylation to synthesize symmetrical biaryls \textit{in-situ}\textsuperscript{13}, but it was not until 2000 that this \textit{in-situ} borylation was used during a polymerization reaction. Masuda et al. published their results for the synthesis of several different poly(arylenes)s. Unfortunately their reaction conditions resulted in polymers with a low molecular weight (1870-6360 g/mol) and the article went unnoticed\textsuperscript{2}. The use of bis(pinacolato)diboron for the synthesis of biarenes was further investigated by Wu et al. They showed that after optimization of the reaction, using a stronger base (K\textsubscript{3}PO\textsubscript{4}) and a differend catalyst (Pd(dppf)Cl\textsubscript{2}), several biarenes could be obtained in good yields\textsuperscript{14}. For example, the synthesis of biphenyl from bromobenzene was done in 90% and from iodobenzene in >99%, the synthesis of bithiophene from the less reactive 2-bromothiophene was done in 93%. In, early 2007 we combined the concepts of Wu and Masuda to see if this method could be used for the synthesis of our functionalized polymer. The results will be discussed in the next paragraph.

\section*{6.2 The use of bis(pinacolato)diboron for the synthesis of regiosymmetric conjugated polymers}

\subsection*{6.2.1 Monomer synthesis and polymerizations}

To test the polymerization using bis(pinacolato)diboron we synthesized several known and a few unknown monomers, which are shown in Figure 6.3.
Figure 6.3. Monomers synthesized to test the functionality of the bis(pinacolato)diboron polymerization.

The monomers 2.10, 6.2 are relatively small bithiophene monomers. We chose alkylated bithiophenes because of the improved solubility compared to the parent bithiophenes. The synthesis of monomer 2.10 was described in Chapter 2. Monomer 6.2 was synthesized based on literature procedures. Monomer 6.2 is more sterically hindered and is likely to produce shorter polymers. Fluorene monomer 6.3 is less electronegative than the thiophene monomer 2.10 and is therefore less prone to deborylation, we therefore expected a higher molecular weight product. The synthesis was done according to literature procedures.
Figure 6.4 Synthesis of monomer 6.4 via three different pathways. i) bromohexane, KOH, TBAB, DMS, ii) Pd(PPh$_3$)$_4$, DMF/Toluene 1:1, iii) Pd(PPh$_3$)$_4$, THF, K$_2$CO$_3$, iv) Pd(dppf)Cl$_2$, v) NBS, THF.

The product of the polymerization of 6.4 is analogous to the unfunctionalized P4-1 from Chapter 4. It is possible to synthesize this monomer in several ways, including Kumada (iv), Stille (ii), and Suzuki coupling (iii) (see Figure 6.4). We found that the best results (>90%) were obtained with the Kumada coupling, but that the Suzuki coupling is also suitable (84%). The Stille coupling yielded only 59% of pure product.

Polyterthiophenes (PTTs) and polyquarterthiophenes (PQTs) are well known polymers in literature and can be seen as the conjugated analogs of the cross-conjugated P2-1 from Chapter 2. The monomers 6.5 and 6.6 can be used for the synthesis of these terthiophene and quarterthiophene polymers.

The polymerization of monomer 6.7 will result in the formation of P2-1 from Chapter 2. Monomer 6.7 has not been synthesized before and the synthesis was based on the results of monomers 6.4 – 6.6. The synthesis of 6.7 using the Kumada coupling resulted mainly in mono-coupled product. The electron rich-character of the thieno[2,3-b]thiophene probably makes it less reactive toward the oxidative addition, resulting in a slower reaction and more side-reactions. Using the milder Stille coupling we were able to obtain the product in a reasonable yield (65%).

Polymerization of the monomers was performed using the following reaction conditions: To a three-necked flask of stirring solvent were added equal molar quantities of monomer and bis(pinacolato)diboron. The solution was then sparged with dry nitrogen for 10 min before addition of 5 mol% 1,10-bis(diphenylphosphino)-ferrocenepalladium(II)dichloride dichloromethane complex (Pd(dppf)Cl$_2$) and 5 eq. of crushed K$_3$PO$_4$. An additional 10 min
of sparging was performed. The mixture was heated to 110 °C and stirred for 24 h and precipitated into methanol (except P6-1 and P6-2) before further purification by soxhlet extraction (methanol, acetone, chloroform). The final product was precipitated in methanol and dried. The obtained polymers were analyzed using ¹H-NMR, ATR-IR, GPC, and MALDI-TOF MS. The results are presented in Table 6-1. Monomers used for the polymerization are shown in Figure 6.3. Each polymer is given an number and a 'abbreviated' name which can be found in Table 6-1. Structures of the polymers can be found in the different figures presented in this chapter. From now on we will call this method the BiPi method.

Table 6-1. Polymerization of monomers 6.1 - 6.7 using bis(pinacolato)diboron

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Name</th>
<th>Monomer</th>
<th>Solvent</th>
<th>( M_n ) (g/mol)</th>
<th>( M_w ) (g/mol)</th>
<th>( M_z ) (g/mol)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6-1</td>
<td>PT2.5</td>
<td>6.1</td>
<td>DMF</td>
<td>3500</td>
<td>12400</td>
<td>71800</td>
<td>3.5</td>
</tr>
<tr>
<td>P6-2</td>
<td>PT2.3</td>
<td>6.2</td>
<td>DMF</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>P6-3</td>
<td>PFI</td>
<td>6.3</td>
<td>DMF</td>
<td>6100</td>
<td>16100</td>
<td>37100</td>
<td>2.7</td>
</tr>
<tr>
<td>P6-4</td>
<td>PficoBi</td>
<td>6.4</td>
<td>DMF</td>
<td>9500</td>
<td>25800</td>
<td>79700</td>
<td>2.3</td>
</tr>
<tr>
<td>P6-8</td>
<td>PficoBi</td>
<td>Stille</td>
<td>Tol / DMF (3:1)</td>
<td>4000</td>
<td>8800</td>
<td>15800</td>
<td>2.2</td>
</tr>
<tr>
<td>P6-5</td>
<td>PTBT</td>
<td>6.5</td>
<td>DMF</td>
<td>8900</td>
<td>22900</td>
<td>63300</td>
<td>2.6</td>
</tr>
<tr>
<td>P6-9</td>
<td>PTBT</td>
<td>Stille</td>
<td>Tol / DMF (3:1)</td>
<td>8700</td>
<td>16100</td>
<td>26000</td>
<td>1.9</td>
</tr>
<tr>
<td>P6-6</td>
<td>PQT</td>
<td>6.6</td>
<td>DMF</td>
<td>6700</td>
<td>17600</td>
<td>49200</td>
<td>2.6</td>
</tr>
<tr>
<td>P6-12</td>
<td>PQT</td>
<td>6.6</td>
<td>Tol / DMF (3:1)</td>
<td>5200</td>
<td>9600</td>
<td>17300</td>
<td>1.8</td>
</tr>
<tr>
<td>P6-10</td>
<td>PQT</td>
<td>Stille</td>
<td>Tol / DMF (3:1)</td>
<td>5900</td>
<td>9500</td>
<td>14200</td>
<td>1.6</td>
</tr>
<tr>
<td>P6-7</td>
<td>PDTT</td>
<td>6.7</td>
<td>DMF</td>
<td>5700</td>
<td>16300</td>
<td>44600</td>
<td>2.9</td>
</tr>
<tr>
<td>P6-11</td>
<td>PDTT</td>
<td>Stille</td>
<td>Tol / DMF (3:1)</td>
<td>10100</td>
<td>20200</td>
<td>33800</td>
<td>2.0</td>
</tr>
</tbody>
</table>

a) Inaccurate GPC values (low molecular weight product)

Polymers P6-1 and P6-2 are obtained as oils directly after polymerization and do not precipitate, but solidify upon standing. ¹H-NMR showed a characteristic polymer spectrum, but GPC analysis of P6-2 was unsuccessful giving molecular weights below 1000 g/mol. For low molecular weight polymers it is known that GPC can give inaccurate values²⁴. For P6-3 – P6-7 moderate molecular weights where found. The high polydispersity of these polymers indicates that the use of bis(pinacolato)diboron does not result in a catalyst-transfer type polymerization. This will be further discussed in paragraph 6.3.
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

For a fair comparison between the Stille and the BiPi method we decided to make polymer P6-4 – P6-7 via the Stille polymerization (P6-8 – P6-11) as well. We used the conditions from Chapter 5. The results are presented in table 6-1. In most cases the polymer made via the Stille coupling had a slightly lower molecular weight, but also a smaller polydispersity. For the polymers PTBT and PQT, the difference in molecular weight between the Stille en the bis(pinacolato)diboron method is neglectable, which might indicate that the solubility of the polymer limits the formation of higher molecular weight products. We decided to perform the polymerization of P6-6 in a toluene / DMF (3:1) mixture (P6-12) as well, but surprisingly this gave a reduction of the molecular weight. This is probably caused by a lower reaction speed, caused by more non-coordinating solvent (toluene), and therefore more pronounced deborylation. A larger difference between molecular weights can be found for the polymers PficoBi (9500 vs 4000 g/mol) and PDTT (5700 vs 10100 g/mol). The much higher molecular weight of PficoBi, polymerized using the BiPi method, is likely caused by the more electron-widrawing nature of fluorenes compared to thiophenes. This caused an increase in the rate of the Suzuki cycle. We found exactly the opposite for the electron-rich cross-conjugated PDTT. This means that either the Suzuki or Miyaura cycle (or both) is inhibited significantly for 6.7 (Thienothiophene is also more electron-widrawing than thiophene). We need to perform more polymerization experiments to understand this phenomenon.
6.2.2 MALDI-TOF analysis of the synthesized polymers

A MALDI-TOF spectrum was recorded for each polymer. These are presented in Figures 6.5 – 6.9. The results of P6-1 and P6-2 are presented in Figure 6.5. The molecular weight of P6-1 is higher than that of P6-2 which is not surprising because of the more reactive nature of the less sterically hindered monomer 6.1 as compared to 6.2. The lower reactivity results in more side reactions as is evident from the less clean spectrum. The main peaks in the spectra of P6-1 are X_n with H/H end-groups. Whether debromination takes place during the reaction (via borylation and then deborylation) or during work-up is unknown, but it is likely that during a later stage of the polymerization reaction (lower concentration of reactive groups) deborylation becomes competitive with the coupling reaction, terminating the polymerization. The spectrum of P6-2 shows more residual bromine groups (H/Br and Br/Br) which could indicate that steric hindrance prevents borylation in the first place, reducing the polymerization rate and molecular weight of the polymer. In the spectra of P6-1 we see, beside the main peaks, peaks that can be assigned to X_{n+0.5}. This could be caused by impurities in the monomers, double ion formation, or fragmentation of the polymer. The monomers were pure and by analysis of the polymer isotope peaks (reflectron TOF) we also concluded that these X_{n+0.5} peaks could not be assigned to double ion peaks. We did see that at higher laser intensities the ratio of X_{n+0.5} was also higher. One of requirements for a successful MALDI-TOF MS analysis is indirect ionization, it is possible that part of the light is directly absorbed by the polymer, causing partial fragmentation. The spectra of polymers P6-3 and P6-4 are presented in Figure 6.6. The more aromatic and less electron-rich polyfluorene (P6-3) has more Br/Br and Br/H end-groups than the thiophene-containing P6-4, which is in good agreement with the less pronounced deborylation that is expected for less electron-rich systems. Comparing the molecular weight values obtained from GPC with those from MALDI-TOF MS confirms the results found in literature: MALDI-TOF MS cannot be used for the accurate analysis of the molecular weight of polydisperse polymers. It does show that MALDI-TOF is a powerful tool for obtaining detailed information on the structure of the polymer and its end-groups. The spectra of polymers P6-3 and P6-4 show no significant signs of fragmentation as seen for polymer P6-1, indicating that the defect seen in P6-1 is not a defect from the BiPi method.
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Figure 6.5 MALDI-TOF MS spectra of P6-1 (top) & P6-2 (bottom), including blow-up.

The spectra of polymers P6-6 and P6-12 are presented in Figure 6.8 and are very similar to the previously presented spectra. P6-6 made in DMF and P6-12 made in toluene / DMF are not significantly different. The distribution of chains for P6-12 seems to slightly shifted to the low molecular weight products compared to P6-6; this was also observed by GPC. P6-6 contains more polymer chains with Br/Br and Br/H end-groups, which could indicate less side reactions. This partially confirms the hypothesis that the molecular weight is likely limited by the deborylation reaction.
The spectrum of P6-5 is given in Figure 6.7. Also in this spectrum the main peaks correspond to chains with H/H end-groups. According GPC, the $M_n$ is almost 9000 g/mol, while in the MALDI-TOF spectra the main peak has a mass of 2113 amu. This difference is caused by the dispersity of the sample and the fact that small chains reach the detector more readily, causing discrimination of the longer chains. This effect is enhanced by the fact that the detector becomes less sensitive after being bombarded with the small chains. By using the low mass gate (LMG)$^{25}$ of the machine it is possible to increase the sensitivity. The low mass gate blocks the sensor for the lower molecular weight molecules. The effect can
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be seen in the middle spectrum of Figure 6.7. Before using the LMG, peaks up to n=8 were clearly visible, but this was increased to n=14 after using a LMG of 4000. Zooming in showed peaks even up to n=27 (14200 amu). The bottom spectrum of Figure 6.7 is a close-up and shows that in addition to $X_n$, $X_n$Br, $X_n - 223$ amu can be identified. The mass of 223 amu corresponds with a 3-decylthiophene unit and is indication that part of the polymer is defragmented by the laser, similar to P6-1 (although on a smaller scale).

Figure 6.7 MALDI-TOF MS spectra of P6-5, with (middle) and without (top) LMG. Including blow-up (bottom).
The first spectrum in Figure 6.9 shows the spectrum of **P6-7** measured in a terthiophene matrix. We expected to see a similar spectrum as observed for our other polymers, but beside the expected $X_n$, $X_n\text{Br}$ and $\text{Br}X_n\text{Br}$ three other repeating peaks where found. Measuring the monomer (inset spectra 1) showed almost no mass of the monomer and only that of two by-products, the mass of these products were 167 and 334 amu higher than the mass of the monomer. NMR spectra of the monomer had already proven that the monomer was pure, indicating that these higher masses where an artefact in the MALDI-TOF. Focussing on the oligomers part of the P7 spectra showed also these peaks of $+167 \text{ m/z}$ and $+334 \text{ m/z}$, and a third extra mass of $+88 \text{ m/z}$ as well. As we expected MALDI-TOF to be the cause of these peaks we measured the polymer without matrix. These results can be also be found in Figure 6.9c. Without matrix the polymer is more difficult to ionize and the resulting spectrum contains more noise and only low molecular weight product is detected. Still the spectrum does confirm our suspicion since only the expected peaks are found. Changing to dithranol as the matrix (Figure 6.9d) solved our problems, which resulted in a nice spectrum (Figure 6.11d). Compared to **P6-6**, or our other thiophene polymers, **P6-7**
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers contains more functional groups, which means less pronounced deborylation; the broken conjugation might be the cause for that.

The byproducts were only visible when using terthiophene as a matrix, which indicated that they where likely originating from a reaction with the matrix. Because of the high absorption of the P6-7 in the UV-range, it is likely that (part) of the polymer is directly ionized.

Figure 6.9 MALDI-TOF MS spectra of P6-7. (a) Spectrum of P6-7 (terthiophene matrix) (b) Spectrum of 6.7 (monomer, terthiophene matrix) (c) Close-up of P6-7 (terthiophene matrix) (d) Spectrum of P6-7 (no matrix) (e) Spectrum of P6-7 (dithranol matrix).
While under normal circumstances the sample becomes ionized (forming a radical-cation) via charge transfer from the matrix, direct absorption could cause the formation of radicals via a cleavage of the C-Br bond.

These radicals then react with the matrix forming terthiophene end-caped oligomers. In theory, mono- and bis-functionalization of the monomer would result in extra mass peaks with +168 amu and +335 amu. These were the exact values found in the spectra. The extra mass of +89 amu, which is only found in the polymer spectrum, originates from mono terthiophene-functionalized product with H/H end-groups. The fact that this product is only found in the polymer sample and not the monomer indicates that debromination occurs during the polymerization reaction or work-up procedure and not during the MALDI-TOF MS experiment. The exact mechanism and details on the role of the matrix and polymer need to be further investigated for a better understanding.

![Figure 6.10 Schematic representation of the possible side-product occurring in the ionization using terthiophene as matrix.](image)

Although the individual results show that the BiPi method is a very suitable method for the synthesis of regiosymmetric monomers, without comparison with MALDI-TOF MS spectra of polymers made via the traditional Stille coupling it is not possible to conclude that the method is also better. The MALDI-TOF spectra of P6-4 to P6-11 are presented in Figure 6.11. The clear advantage of the use of the BiPi method is also visible from these spectra. Although this method results in polymers with the same repeat unit, one has to remember that the actual polymers are not completely the same as the ones produced via the Stille polymerization. The different end-groups makes it truly a different polymer, this is also visible in Figure 6.11.

In general, one can conclude that the BiPi method is very reproducible and suitable for a wide variety of monomers.
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

Figure 6.11 A comparison of the MALDI-TOF spectra for polymers prepared using the BiPi and Stille method.
6.3 Discussion on the mechanism

![Diagram of the proposed mechanism for the bis(pinacolato)diboron coupling reaction of aryl halides.](Figure 6.12)

*Figure 6.12 The proposed mechanism for the bis(pinacolato)diboron coupling reaction of aryl halides.*
We showed that after modifying the BiPi polymerization method based on the results presented by Wu\textsuperscript{14} it became a suitable method for the synthesis of short regiosymmetric polymers. The modified method produces very clean polymers with minimized side products. The mild reaction conditions make the polymerization method very versatile and suitable for a wide variety of monomers. Understanding the reaction mechanism is very important to further improve the polymerization results.

The proposed reaction mechanism of the synthesis of biaryls with bis(pinacolato)diboron was presented by Wu and is given in Figure 6.12. The coupling mechanism proceeds via two catalytic cycles. In the first cycle (bottom) the aryl halide is \textit{in-situ} borylated via oxidative addition, transmetalation, and reductive elimination. This borylated intermediate then enters the more traditional second coupling cycle involving the same oxidative addition, transmetalation, and reductive eliminations steps. The first cycle is called the Miyaura borylation and can also be applied individually to synthesize borate monomers from mono- or dihaloaryls. The functionalization via the Miyaura borylation method proceeds in over 90\% yield\textsuperscript{26}. A schematic representation of two possible polymerization mechanisms is given in Figure 6.13. In the ideal case and under optimized conditions, all bis-functional monomers are converted into a monomer with one halide and one borate group which then leads to catalyst-transfer polymerization. This would result in polymers with a low polydispersity and well-defined structures. Unfortunately the broad polydispersity of the polymer samples indicates that the real polymerization proceeds via a stepwise mechanism. It is likely that during borylation non-, mono-, and bisborylated monomers are formed which block the catalyst-transfer process and the catalyst has to dissociate from the growing chain, this is presented in Figure 6.13 on the right.

The first polymerization tests showed that although polymerization is successful, the polymers have a moderate molecular weight and broad polydispersity. This is mainly caused by the stepwise polymerization mechanism. Changing the polymerization mechanism to the catalyst-transfer mechanism would give better results; unfortunately the Miyaura borylation has a low selectivity and should be replaced with a more selective method if one wants to change the mechanism. The current method can be improved by reducing the deborylation reaction which is still dominant as been shown by MALDI-TOF MS. It is possible that by speeding up the coupling reaction with, for example additives such as LiCl or CsF, or changing the Pd catalyst, deborylation is reduced and higher molecular weight products are obtained. During the final stages of our research Reynolds et al. published their results on the polymerization of different fluorenes with bis(pinacolato)diboron\textsuperscript{27}. Their system involves the use of a tricyclohexylphosphonium tetrafluoroborate ligand, CsF and TBAB in toluene.
This base-free system produced poly(dioctylfluorene) in 98% yield with a molecular weight of 30000 g/mol. Unfortunately no MALDI-TOF spectra was provided.

Both our results as well as the results presented by Reynolds show that the use of bis(pinacolato)diboron for the synthesis of regiosymmetric conjugated polymers with moderate molecular weights and a defined structures is very successful. There is still a lot of improvement possible and more research is needed.

Figure 6.13 Proposed reaction scheme for the ideal and the ‘real’ polymerization route using bis(pinacolato)diboron. (a) Miyaura borylation (b) oxidative addition (c) transmetalation, reductive elimination, and catalyst-transfer (d) transmetalation, reductive elimination (e) dissociation of the catalyst.
6.4 Synthesis of functional polymers with bis(pinacolato)diboron

![Image](image.png)

Figure 6.14. Monomer used for the synthesis of functionalized conjugated polymers.

After the positive results of the polymerization of the non-functionalized monomers we synthesized a functionalized analog to test if the BiPi method is also usable for the synthesis of functional polymers. We decided to polymerize a protected monomer, followed by deprotection to obtain our bromine-functionalized polymer. The monomer 6.8 is shown in Figure 6.14. The synthesis of the functionalized quarterthiophene 6.8 is derived from the synthesis of the functionalized bithiophene 3.8, combined with literature procedures. The complete synthesis is given in Figure 6.15. The synthesis of bithiophene 6.11 was carried out by standard bromination with NBS of bithiophene. The synthesis of 3.7 can be found in Chapter 3. Compound 6.9 was obtained in 25% by performing a Kumada coupling between compounds 6.10 and 6.11. Bromination of 6.9 using NBS in THF resulted in the formation of monomer 6.8. Because of the low solubility of the monomer in DMF the polymerization was performed in DMF / toluene (1:3) using the conditions and work-up presented in section 6.2. The polymer P6-13 (see Figure 6.17 for the structure) was obtained as an orange powder in 73% yield. GPC analysis of the polymer showed a $M_n$ of 7400 with PDI of 1.9. This result is very similar to the non-functionalized polymer P6-12. The higher molecular weight is partially caused by the heavier monomer. Dividing $M_n$ by the weight of the monomers in both cases resulted in an average length of around 8.5 units (8.5 vs. 8.7). The MALDI-TOF spectrum of P6-13 is presented in Figure 6.16 and looks similar to the spectra presented in paragraph 6.2. The main peaks are again $\text{HX}_n\text{H}$. Applying a LMG of 5000 shows that $n$ can be as large as 17, equivalent to 68 thiophene units. The deprotection was performed using the newly developed method presented in Chapter 3, with BBr$_3$ in dichloromethane.
The amount of recovered product was low which could indicate the occurrence of side reactions. The product P6-14 was analyzed with GPC and MALDI-TOF MS. GPC showed a decrease in molecular weight to 4200 ($M_n$) and a dispersity of 1.4. Deprotection should reduce the molecular weight, but not as much as presented here. A schematic representation of the deprotection step is given in Figure 6.17.

The MALDI-TOF spectra of both the protected and deprotected polymers are presented in Figure 6.18. After deprotection the chain with $n=1$ is missing, the reason for this is unclear. The deprotection is not complete and the amount of deprotected groups increases with increasing chain length. At $n=2$ the polymer has four functional groups and the main fraction is not deprotected. Going to $n=3$ the fraction of deprotected groups is already larger, around 50% of the total amount of groups. For $n=4$ the balance is shifted, and the fraction of deprotected side-chains in polymer is larger compared to the protected ones. Around $n=5$ all detail is lost and it is difficult to draw conclusions about the exact degree of deprotection.
At $n=5$ the mass difference between completely protected and completely deprotected polymer chain is as large as 435 amu, resulting in a broad distribution as seen in the spectra. Although it is clear that from $n=5$ a large fraction of the chains are deprotected. The fact that a larger fraction of longer chains is more deprotected is strange and cannot be explained without further investigation. It is possible that the shorter deprotected chains are consumed in a side reaction. From these results we concluded that although the polymerization of methoxyphenol-functionalized monomers was a success, deprotection was unsuccessful. A more labile protective group, like tetrahydropyranyl (THP), or no protective group might be the solution for this problem.
In Chapter 4 we synthesized 2,7-dibromo-9,9-bis(bromohexyl)-9H-fluorene (4.7) and we decided to test if direct polymerization was possible. Using the exact reaction conditions as presented in chapter 6.2 we obtained mainly insoluble material. In literature several examples of successful Suzuki copolymerizations with monomer 4.7 can be found. In most cases more milder conditions are used. We therefore tested the polymerization with K₂CO₃ which resulted in more-soluble material, unfortunately ¹H-NMR showed a large fraction of elimination product. A base-free system as presented by Reynolds could solve this problem.
6.5 Conclusion

We have shown that the updated BiPi method is very useful for the synthesis of regiosymmetric polymers. The polymers have a moderate molecular weight and a well-defined structure. We have showed that the method can be applied for thiophenes or fluorenes. From MALDI-TOF we concluded that the main end group of these polymers are H/H with a small fraction of H/Br end-groups. Borylated end-groups were not found. Both results indicate that deborylation is the most dominant side reaction. Reducing the deborylation side reaction might result in an improvement in molecular weight. The polymerization mechanism is a step-wise polymerization process which limits the use for applications where a living-type polymerization process is required. It also means that the dispersity of the polymer is broad. This method leaves room for improvement.

The versatility of the polymerization method was further proven by the polymerization of the methoxyphenol functionalized quarterthiophene monomer 6.8. Unfortunately deprotection was incomplete. The use of a milder protective group might be the solution to this problem.
6.6 Experimental

Measurements
NMRs were measured using a Varian VXR-300 (300 MHz) or a Varian Gemini-200 (200 MHz) instrument at 25 °C. FT-IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer. Solids were measured in KBr using a Smart Collector DRIFT setup. ATR-IR spectra were recorded on a Bruker IFS88. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5µ mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in chloroform at a concentration of 1 mg / ml. MALDI-TOF measurements were performed on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (terthiophene or dithranol, 20 mg / ml in CHCl₃) and the sample (1 mg / 5 mL in CHCl₃) in a 1:1 ratio. All the samples were measured in negative ion mode.

Materials and Methods
All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise indicated. Kumada, Stille and Suzuki coupling reactions were performed under dry conditions and nitrogen atmosphere. The synthesis of 2,5-bis(trimethyltin)thieno[2,3-b]thiophene (2.5), 2-bromo-3-hexythiophene, 2-bromo-3-decythiophene and 5,5'-dibromo-4,4'-didecyl-2,2'-bithiophene (2.12) can be found in Chapter 2. The synthesis 2-bromo-3-[10-(4-methoxyphenoxy)decyl]thiophene (3.7) can be found in Chapter 3. The synthesis of 5,5'-di(trimethyltin) bithiophene (4.6) can be found in Chapter 4.
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2-hexylthiophene [-]

This compound was made according to literature procedure. The reaction was performed under dry conditions and nitrogen atmospheres. To a cooled mixture (-70°C) of 6.7 gram (84 mmol) of thiophene in 70 ml THF was added dropwise a solution of 33 ml 2.5 M (88 mmol) n-Buli in hexane. The cooling was removed and the mixture was allowed to warm to RT and stirred for an additional 2 hrs. The mixture was then cooled to -20 °C and 13.87 grams (84 mmol) of 1-bromohexane was added in a continuous flow. The cooling was removed and the mixture was allowed to warm to RT and left to react overnight (16 h). Water (100 ml) was added to quench the reaction and the mixture was extracted with ether (150 ml) The organic layers where combined and dried with MgSO₄ and the solvent was removed in vacuo. The product was purified by vacuum distillation (70-75 °C, 9 Torr). After distillation 11.2 gram (66 mmol, 79%) of colourless oil was obtained.

1H NMR (200 MHz, CDCl₃) δ 7.10 (dd, J= 5.1, 1.1 Hz, 1H), 6.91 (dd, J= 5.1, 3.4 Hz, 1H), 6.84 – 6.71 (m, 1H), 2.82 (t, J= 7.6, 7.6 Hz, 2H), 1.68 (p, J= 7.3, 2H), 1.49 – 1.21 (m, 2H), 0.97 – 0.81 (t, J= 6.5 Hz, 2H)

13C-NMR (50 MHz, CDCl₃) δ: 145.88, 126.60, 123.87, 122.68, 31.78, 31.57, 29.93, 28.80, 22.58, 14.08. IR (neat) cm⁻¹: 3107, 2929, 2854, 1651, 1534, 1511, 1460, 1411, 1374, 1338, 1304, 1283, 1227, 1146, 1117, 1089, 1047, 1002, 889, 873, 824, 798, 731, 590, 481

2-bromo-5-hexylthiophene [-]

This compound was made according to literature procedure. The reaction was performed under exclusion of light and under a nitrogen atmosphere. To a cooled (0°C) mixture of 4.0 gr. (22 mmol) 2-hexylthiophene in 40 ml THF was added portion wise 3.78 gram (22 mmol) of n-bromosuccinimide over 30 minutes. The mixture allowed to warm up to RT overnight. The mixture was poured into water and extracted with ether. The organic layer was washed with 0.1 M HCl and brine. Dried on Na₂SO₄ and the solvent was removed in vacuo. Residual succinimide was removed by flash column chromatography, yielding 4.4 gram (18 mmol, 83%) of off-white transparent oil. The product was used without further purification.

1H-NMR (300 MHz, CDCl₃) δ: 6.84 (d, J= 3.6 Hz, 1H), 6.53 (d, J= 3.7 Hz, 1H), 2.74 (t, J= 7.6, Hz, 2H), 1.61 (q, J= 8.0 Hz, 2H), 1.45 – 1.18 (m, 6H), 0.90 (t, J = 6.4 Hz, 3H).

IR (neat) cm⁻¹: 3079, 3052, 2928, 2855, 1725, 1581, 1542, 1447, 1378, 1255, 1215, 1183, 1154, 1047, 962, 850, 790, 725, 692, 630, 609
5,5'-dihexyl-2,2'-bithiophene [ - ]

The reaction was performed under dry conditions and nitrogen atmosphere. To a suspension of 0.39 gr. (16 mmol) Magnesium in 20 ml of anhydrous ether a solution of 4 gr. (16 mmol) 2-bromo-5-hexylthiophene in 5 ml anhydrous ether was added dropwise. The solution was refluxed for 2 hrs and cooled to room temperature. The solution was then transferred dropwise thru a cannula to a second solution (0°C) containing 2 gram (8 mmol) 2-bromo-5-hexylthiophene with 28 mg Ni(dppp)Cl2 in 30 ml anhydrous ether. The mixture was left to react overnight. The reaction was then quenched by dropwise addition of saturated NH4Cl solution. The product was extracted with ether and the organic layer was washed with water and dried on Na2SO4. The solvent was removed in vacuo. The crude product was further purified by column chromatography (silica) using hexane and then recrystallized from ethanol yielding 1.7 gram (5 mmol, 65%) of white powder.

$^1$H-NMR (300 MHz, CDCl3) $\delta$: 7.31 (d, J= 5.7 Hz, 2H), 7.09 (d, J= 5.6 Hz, 2H), 2.54 (t, J= 8.3 Hz, 2H), 1.69 – 1.49 (m, 1H), 1.39 – 1.18 (m, 12H), 0.88 (t, J = 6.7 Hz, 6H) $^13$C-NMR (50 MHz, CDCl3) $\delta$: 144.67, 135.29, 124.52, 122.56, 31.57, 30.14, 28.74, 22.58, 14.08. IR (KBr) cm$^{-1}$: 3706, 2951, 2923, 2852, 1726, 1583, 1536, 1466, 1426, 1370, 1328, 1282, 1206, 1165, 1114, 1047, 997, 871, 793, 779, 729, 594, 539, 493

5,5'-dihexyl-3,3'-dibromo-2,2'-bithiophene [6.2]

This compound was made according to literature procedure.29 The reaction was performed under exclusion of light. 580 mg (1.75 mmol) of 5,5'-dihexyl-2,2'-bithiophene was dissolved in 20 ml DMF and cooled to 0 °C. 680 mg (3.84 mmol) of NBS was dissolved in 10 ml of DMF and added dropwise over 1 hour. The solution stirred overnight and allowed to warm-up to RT. The mixture was poured into water and extracted with ether. The organic layer was washed with 0.1 M HCl and brine. Dried on Na2SO4 and the solvent was removed in vacuo. The raw product was purified by column chromatography (silica) using hexane and recrystallized from ethanol. This yielded 524 mg (63% of pure product).

$^1$H-NMR (300 MHz, CDCl3) $\delta$: 6.47 (s, 2H), 2.77 (t, 4H, J= 7.8), 1.68 (m, 4H), 1.35 (m, 12H), 0.90 (t, 6H, J= 6.60). $^13$C-NMR (50 MHz, CDCl3) $\delta$: 147.52, 127.53, 110.99, 104.76, 31.48, 31.03, 30.21, 28.73, 22.53, 14.05. IR (KBr) cm$^{-1}$: 3107, 2929, 2854, 1651, 1534, 1411, 1282, 1206, 1165, 1114, 1047, 997, 871, 793, 779, 729, 594, 539, 493
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1374, 1338, 1283, 1227, 1146, 1117, 1089, 1047, 1002, 889, 873, 824, 798, 731, 590, 481

2,7-dibromo-9,9-dihexyl-9H-fluorene [6.3]

This compound was made according to literature procedure. A mixture of 4.9 gram (15 mmol) of 2,7-dibromofluorene and catalytic amounts of the phase catalyst tetrabutylammonium chloride (0.3 g, 1 mmol) in 25 ml of DMSO was stirred for 30 min at room temperature. 7.5 ml of 50% aqueous KOH solution was added to the mixture and the mixture was heated to 60 °C. The colour changes from colourless to dark red. Then 5.8 gram (35 mmol) of 1-bromohexane was added in one portion and the mixture was stirred over night at 60 °C. The reaction mixture was then poured into 300 ml of ice water and extracted with ether. The organic layers were combined and neutralized with hydrochloric acid, which resulted in a color change to yellow. The organic layer was dried with Na₂SO₄ and the solvents removed in vacuo. The crude product was purified by column chromatography (silica) using petroleum ether and recrystallized from hexane. Yield 11.1 gram (11.4 mmol, 76%) of white crystals. mp 68-74 °C (lit. 67-71 °C);

¹H-NMR (300 MHz, CDCl₃) δ 7.51 (dd, 4H, J= 8.4 Hz, J 13.2 Hz), 7.44 (s, 2H), 1.92 (m, 4H), 1.14 (m, 12H), 0.78 (t, 6H, J= 6.6 Hz), 0.59 (t, 4H, J= 6.6 Hz); ¹³C-NMR (50 MHz, CDCl₃) δ 152.75, 139.26, 130.35, 126.37, 121.66, 121.34, 55.89, 40.42, 31.67, 29.79, 23.85, 22.79, 14.22.

2,7-dithien-2-yl-9,9'-dihexyl-9H-fluorene; Kumada [-]

This compound was made according to literature procedure. The reaction was performed under dry conditions and nitrogen atmosphere. To 400 mg (17 mmol) of activated Magnesium turnings was added 10 ml of dry THF. To this mixture was added dropwise (keeping a constant reflux) a solution of 2.4 gram (15 mmol) of 2-bromothiophene in 20ml of dry THF. After addition the mixture was refluxed for an additional 3h. The mixture was cooled to RT and transferred via cannula to a second flask containing 2.46 gram (5 mmol) 6.3, 20 mg Pd(dppf)Cl₂ in degassed and 20 ml dry THF. After complete addition of the Grignard reagents the mixture was refluxed over night. The reaction cooled to room temperature and was quenched with NH₄Cl. The mixture was extracted with dichloromememethane (DCM) and the organic layer was washed with brine
followed by drying over Na$_2$SO$_4$. The solvent removed in vacuo and the crude product purified by column chromatography (silica) using petroleum ether/DCM (10:1) as the eluent. Pure product was obtained by recrystallization from isopropanol/methanol (3:1) as green crystals (2.26 gram, 91%)

mp 125-133 °C (lit. 122 °C); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.56 (s, 2H), 7.39 (d, J = 3.5 Hz, 2H), 7.30 (d, J = 4.9 Hz, 2H), 7.12 (t, J = 3.6 Hz, 2H), 2.12 – 1.83 (m, 4H), 1.21 – 0.90 (m, 12H), 0.83 – 0.53 (m, 10H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 151.66, 145.14, 140.17, 133.23, 128.04, 124.95, 124.51, 122.87, 120.11, 120.06, 55.26, 40.42, 31.44, 29.65, 23.70, 22.56, 13.99.

2,7-dithien-2-yl-9,9'-dihexyl-9H-fluorene; Stille [ - ]

The reaction was performed under dry conditions and nitrogen atmosphere. 2.5 gram (5 mmol) of 6.3, 3.7 gram (10 mmol) 2-tributylstannylthiophene and 30 mg of Pd(PPh$_3$)$_4$ were added to 100ml of a mixture of dry DMF/toluene (1:1). The reaction mixture was heated under stirring at 85 °C over night in the absence of light. The mixture was cooled to room temperature and poured into ice water and extracted with DCM. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$ followed by removal of the solvent in vacuo. The crude product was purified by a short column with silica gel and petroleum ether/DCM as the eluent. Pure product was obtained by recrystallization from hexane as green crystals (1.48 gram, 59%)

mp 118-125 °C (lit. 122 °C); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.56 (s, 2H), 7.39 (d, J = 3.5 Hz, 2H), 7.30 (d, J = 4.9 Hz, 2H), 7.12 (t, J = 3.6 Hz, 2H), 2.12 – 1.83 (m, 4H), 1.21 – 0.90 (m, 12H), 0.83 – 0.53 (m, 10H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 151.66, 145.14, 140.17, 133.23, 128.04, 124.95, 124.51, 122.87, 120.11, 120.06, 55.26, 40.42, 31.44, 29.65, 23.70, 22.56, 13.99.

2,7-dithien-2-yl-9,9'-dihexyl-9H-fluorene; Suzuki [ - ]

This compound was made according to literature procedure.$^{32}$ The reaction was performed under dry conditions and nitrogen atmosphere. 2.5 gram (5 mmol) of 6.3 and 1.29 gram (10 mmol) 2-thiopheneboronic acid were dissolved in 40ml of dry DMF. 2.14 gram (10 mmol) of Crushed and dried K$_3$PO$_4$ was
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added to the solution resulting in a white suspension. The mixture was degassed three times, followed by the addition of 23mg Pd(pph$_3$)$_4$ catalyst. After addition the solution was degassed again. The reaction mixture was stitted at 110 °C over night in the absence of light. Cooled down to room temperature and poured into ice water followed by extraction with DCM and the combined organic layers washed with brine and dried over Na$_2$SO$_4$. The solvent was removed in vacuo and the crude product was purified by short column chromatography (silica) using petroleum ether/DCM (10:1) as the eluent. Pure product was obtained by recrystallization from isopropanol/methanol (4:1) as green crystals (2.0 gram, 84%)

mp 125-130 °C (lit. 122 °C); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 (d, J= 7.9 Hz, 2H), 7.60 (d, J= 7.9 Hz, 2H), 7.56 (s, 2H), 7.39 (d, J= 3.5 Hz, 2H), 7.30 (d, J= 4.9 Hz, 2H), 7.12 (t, J= 3.6 Hz, 2H), 2.12 – 1.83 (m, 4H), 1.21 – 0.90 (m, 12H), 0.83 – 0.53 (m, 10H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 151.66, 145.14, 140.17, 133.23, 128.04, 124.95, 124.51, 122.87, 120.11, 120.06, 55.26, 40.42, 31.44, 29.65, 23.70, 22.56, 13.99. HRMS (APCI) calculated for [M+H]+ 499.2488, found 499.2479.

2,7-bis(5-bromo-2-thienyl)-9,9'-dihexyl-9H-fluorene [6.4]

The reaction was performed under exclusion of light. To a mixture of 900mg (1.8 mmol) 2,7-dithien-2-yl-9,9'-dihexyl-9H-fluorene in 50 ml THF was added dropwise a solution of 705 mg (4.0 mmol) N-bromosuccinimide in 15 ml THF dropwise over 1h. After complete addition the reaction mixture was stirred over night resulting in a color change from green to yellow. The mixture was poured into ice water and extracted with DCM and the combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product (orange oil) purified by a short column (silica) using heptane as eluent. Pure product was obtained by recrystallization from isopropanol/methanol (3:1) as yellow, slightly green crystals (1.72 gram, 88%).

mp 100-110 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.67 (d, J= 7.9 Hz, 2H), 7.50 (d, J= 7.9 Hz, 2H), 7.45 (s, 2H), 7.12 (d, J= 3.8 Hz, 2H), 7.06 (d, J= 3.7 Hz, 2H), 2.11 – 1.86 (m, 4H), 1.21 – 0.92 (m, 12H), 0.76 (t, J= 6.5 Hz, 6H), 0.72 – 0.52 (m, 4H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 151.82, 146.50, 140.39, 132.61, 130.85, 124.67, 123.04, 120.28, 119.79, 111.11, 73.72, 55.32, 40.35, 31.43, 29.62, 23.70, 22.55, 13.99. HRMS (APCI) calculated for [M+H]+ 657.0678, found 657.0685.
Chapter 6

5,5'-dibromo-2,2'-bithiophene [6.11]

The reaction was performed under exclusion of light. To a cooled (0 °C) mixture of 5 gram (30 mmol) of bithiophene in 50 ml of DMF was added dropwise a solution of 11.7 gram (66 mmol) NBS in 100 ml of DMF. The resulting mixture allowed to warm up to RT overnight and poured into 800 ml of 0.1 M HCl followed by extraction with DCM. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by a short column (silica) using hexanes, followed by recrystallization from isopropanol/methanol (3:1). 7.6 gram (23 mmol, 78%) of pure product was obtained.

³H NMR (300 MHz, CDCl₃) δ = 6.94 (d, J=3.8, 2H), 6.83 (d, J=3.8, 2H); ¹³C NMR (50 MHz, CDCl₃) δ = 137.99, 130.87, 124.36, 111.74.

3,3''-didecyl-2,2':5',2'':5'',2'''-quaterthiophene [-]

This compound was made according to literature procedure.³³ The reaction was performed under dry conditions and nitrogen atmosphere. 4.0 gram (13 mmol) of 2-bromo-3-decyl thiophene was dissolved in 15 ml of dry THF. The solution was added dropwise to 380 mg (15 mmol) of activated magnesium, keeping a constant reflux. After complete addition the mixture was refluxed for an additional 5 h. The mixture was cooled to RT and added via a cannula to a second flask containing 1.5 gram (5 mmol) of 6.11, 46 mg of Ni(dppp)Cl₂ and 40 ml of dry THF / Toluene (4:3) mixture. After complete addition of the Grignard reagents the mixture was refluxed overnight. The reaction was cooled to room temperature and quenched with saturated NH₄Cl solution. The mixture was extracted with dichloromethane (DCM) and the organic layer was washed with brine followed by drying over Na₂SO₄. The solvent removed in vacuo and the crude product purified by two times column chromatography (silica) using hexanes as the eluent. The product was recrystallized from isopropanol/methanol (3:1) yielding 1.87 gram (3 mmol, 60%) of fluorescent yellow product.

¹H NMR (300 MHz, CDCl₃) δ = 7.16 (d, J=5.2, 2H), 7.11 (d, J=3.7, 2H), 7.00 (d, J=3.8, 2H), 6.92 (d, J=5.2, 2H), 2.85 – 2.67 (m, 4H), 1.62 (d, J=7.6, 4H), 1.24 (s, 28H), 0.85 (t, J=6.6, 6H); ¹³C NMR (50 MHz, CDCl₃) δ = 140.08, 136.99, 135.50, 130.51, 130.30, 126.72, 124.06, 124.02, 32.14, 30.89, 29.85, 29.83, 29.75, 29.68, 29.57, 29.48, 22.92, 14.36. HRMS (APCI) calculated for [M+H]+ 611.2868, found 611.2866.
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5,5''-dibromo-3,3''-didecyl-2,2':5',2''-quaterthiophene [6.6]

The reaction was performed under exclusion of light. To a cooled (0 °C) mixture of 1.0 gram (1.6 mmol) 3,3''-didecyl-2,2':5',2''-quaterthiophene in 50 ml of THF was added dropwise a solution of 637 mg (3.6 mmol) NBS in 15 ml of THF. The resulting mixture was allowed to warm up to RT overnight and poured into 200 ml of 0.1 M HCl followed by extraction with DCM. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by a short column (silica) using hexanes, followed by recrystallization from isopropanol/methanol (3:1). 1.1 gram (1.4 mmol, 88%) of pure product was obtained.

\[^{1}H\text{ NMR (200 MHz, CDCl}_{3}\] \(\delta = 7.08 \text{ (d, J}=3.7, 2H), 6.94 \text{ (d, J}=3.8, 2H), 6.88 \text{ (s, 2H), 2.69 (t, J}=7.9, 4H), 1.53 \text{ (s, 6H), 1.24 (s, 28H), 0.84 (t, J}=6.5, 6H);}^{13}C\text{ NMR (50 MHz, CDCl}_{3}\] \(\delta = 140.74, 137.25, 134.26, 132.92, 131.89, 127.17, 124.20, 110.87, 32.13, 30.74, 29.83, 29.78, 29.62, 29.56, 29.41, 22.91, 14.36.} \text{ HRMS (APCI) calculated for [M+H]^{+} 769.1057, found 769.1058.}

3,3''-didecyl-2,2':5',2''-terthiophene [-]

The reaction was performed under dry conditions and nitrogen atmosphere. To a mixture of 120 ml dry toluene and 40 ml of dry DMF was added 1.7 gram (4.1 mmol) of 2,5-bis(trimethyltin)thiophene, 2.5 gram (8.1 mmol) of 2-bromo-3-decylthiophene and 150 mg of Pd(PPh₃)₄. The mixture was degassed several times and heated to 110 °C for 16 h. The mixture was then cooled to RT and poured into ice water and extracted with chloroform. The combined organic layers were washed with 2 M HCl solution, brine, and dried over Na₂SO₄ followed by removal of the solvent in vacuo. The crude product was purified by column chromatography (silica) with petroleum ether as the eluent followed by recrystallization from isopropanol/methanol (3:1). 1.4 gram (2.7 mmol, 65%) of a yellow oil was obtained.

\[^{1}H\text{ NMR (300 MHz, CDCl}_{3}\] \(\delta = 7.15 \text{ (d, J}=5.2, 2H), 7.03 \text{ (s, 2H), 6.92 \text{ (d, J}=5.2, 2H), 2.76 \text{ (t, J}=7.6, 4H), 1.71 – 1.56 (m, 4H), 1.24 (s, 28H), 0.85 (t, J}=6.6, 6H);}^{13}C\text{ NMR (50 MHz, CDCl}_{3}\] \(\delta = 139.92, 136.26, 130.61, 130.29, 126.25, 123.93, 32.14, 30.99, 29.86, 29.80, 29.73, 29.58, 29.52, 22.92, 14.36.}
5,5''-dibromo-3,3''-didecyl-2,2':5',2''-terthiophene [6.5]

The reaction was performed under exclusion of light. To a cooled (0 °C) mixture of 1.0 gram (1.9 mmol) 3,3''-didecyl-2,2':5',2''-terthiophene in 20 ml of THF was added dropwise a solution of 707 mg (3.9 mmol) NBS in 30 ml of THF. The resulting mixture allowed to warm up to RT overnight and poured into 200 ml of 0.1 M HCl followed by extraction with DCM. The combined organic layers where washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from isopropanol/methanol (3:1) yielding 940 mg (1.4 mmol, 74%) of light yellow powder.

\[ ^1H \text{NMR (200 MHz, C}_2\text{D}_2\text{Cl}_4) \delta = 6.96 \text{ (s, 2H), 6.88 \text{ (s, 2H), 2.78 \text{ – 2.52 (m, 4H), 1.71 \text{ – 1.41 (m, 4H), 1.41 \text{ – 1.03 (s, 28H, 0.82 (t, J=6.7, 6H); } ^13C \text{NMR (50 MHz, C}_2\text{D}_2\text{Cl}_4) \delta = 140.42, 134.88, 132.81, 131.46, 126.31, 110.41, 31.82, 30.46, 29.55, 29.51, 29.36, 29.35, 29.27, 29.19, 29.11, 22.65, 14.18. HRMS (APCI) calculated for [M+H]⁺ 687.1181, found 687.1180.} \]

2,5-bis(3-decylthiophen-2-yl)thieno[2,3-b]thiophene [ - ]

The reaction was performed under dry conditions and nitrogen atmosphere. To a mixture of 120 ml dry toluene and 40ml of dry DMF was added 1.9 gram (4.1 mmol) of 2.5, 2.5 gram (8.1 mmol) of 2-bromo-3-decylthiophene and 150 mg of Pd(PPh₃)₄. The mixture was degassed several times and heated to 110 °C for 17 h. The mixture was then cooled to RT and poured into ice water and extracted with chloroform. The combined organic layers were washed with 2 M HCl solution, brine, and dried over Na₂SO₄ followed by removal of the solvent in vacuo. The crude product was purified by column chromatography (silica) with petroleum ether as the eluent followed by recrystallization from isopropanol/methanol (3:1). 1.3 gram (2.2 mmol, 51%) of a white powder was obtained.

\[ ^1H \text{NMR (300 MHz, CDCl₃) } \delta = 7.20 \text{ (d, J=6.1, 4H), 6.94 (d, J=5.2, 2H), 2.85 \text{ – 2.66 (m, 4H), 1.63 (s, 4H), 1.24 (s, 28H), 0.85 (t, J=6.6, 6H); } ^13C \text{NMR (50 MHz, ccdc₃) } \delta = 146.54, 140.64, 138.67, 130.75, 130.70, 130.70, 130.08, 124.60, 119.21, 32.13, 31.12, 29.83, 29.76, 29.70, 29.57, 29.36, 22.92, 14.36. HRMS (APCI) calculated for [M+H]⁺ 585.2712, found 585.2712. \]

Calc. for C₃₄H₄₈S₄: C, 69.81; H, 8.27; S, 21.92. Found: C, 69.52; H, 8.26; S, 22.22.
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

2,5-bis(5-bromo-3-decylthiophen-2-yl)thieno[2,3-b]thiophene [6.7]

The reaction was performed under exclusion of light. To a cooled (0 °C) mixture of 1.0 gram (1.7 mmol) 2,5-bis(3-decylthiophen-2-yl)thieno[2,3-b]thiophene in 20 ml of THF was added dropwise a solution of 640 mg (3.6 mmol) NBS in 20 ml of THF. The resulting mixture allowed to warm up to RT overnight and poured into 200 ml of 0.1 M HCl followed by extraction with DCM. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from isopropanol/methanol (3:1) yielding 807 mg (1.1 mmol, 65%) of an off-white powder.

¹H NMR (200 MHz, CDCl₃) δ = 7.13 (s, 2H), 6.91 (s, 2H), 2.64 (t, J=7.7, 4H), 1.76 – 1.42 (m, 4H), 1.42 – 1.00 (m, 28H), 0.83 (t, J=6.6, 6H); ¹³C NMR (50 MHz, CDCl₃) δ = 146.02, 141.17, 137.14, 132.58 (2x), 131.59, 119.32, 111.03, 31.82, 30.62, 29.52, 29.47, 29.33, 29.25, 29.01, 22.65, 14.18. HRMS (APCI) calculated for [M+H]+ 743.0901, found 743.0898. Calc. for C₃₄H₄₆Br₂S₄: C, 54.98; H, 6.24; S, 17.27. Found: C, 54.49; H, 6.23; S, 17.39.

3,3''-bis[10-(4-methoxyphenoxy)decyl]-2,2':5',2''-quaterthiophene [6.9]

This compound was made according to a modified literature procedure.³³ The reaction was performed under dry conditions and nitrogen atmosphere. 5.6 gram (13 mmol) of 3.7 was dissolved in 15ml of dry THF. The solution was added dropwise to 380 mg (15 mmol) of activated magnesium, keeping a constant reflux. After complete addition the mixture was refluxed for an additional 5 h. The mixture was cooled to RT and added via a cannula to a second flask containing 1.5 gram (5 mmol) of 6.11, 46 mg of Ni(dpdp)Cl₂ and 40ml of dry THF / Toluene (4:3) mixture After complete addition of the Grignard reagents the mixture was refluxed over night. The reaction was cooled to room temperature and quenched with saturated NH₄Cl solution. The mixture was extracted with dichloromethane (DCM) and the organic layer was washed with brine followed by drying over Na₂SO₄. The solvent removed in vacuo and the crude product purified by two times column chromatography (silica) using hexanes as the eluent. The product was recrystallized from isopropanol/methanol (3:1) yielding 1.03 gram (1.2 mmol, 25%) of fluorescent orange product.
Chapter 6

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.16$ (d, J=5.2, 2H), 7.10 (d, J=3.7, 2H), 7.00 (d, J=3.8, 2H), 6.92 (d, J=5.2, 2H), 6.80 (s, 8H), 3.86 (t, J=6.6, 2H), 3.74 (s, 6H), 2.77 (t, J=7.7, 2H), 1.71 (m, 4H), 1.62 (m, 4H), 1.28 (s, 24H). $^{13}$C NMR: No spectra (insufficient solubility).

5,5'''-dibromo-3,3'''-bis(10-(4-methoxyphenoxy)decyl)-2,2':5',2''':5'',2''''-quaterthiophene

[6.8]

The reaction was performed under exclusion of light.

To a cooled (0 °C) mixture of 900 mg (1.1 mmol) 6.9 in 20 ml of THF was added dropwise a solution of 409 mg (2.3 mmol) NBS in 20 ml of THF. The resulting mixture allowed to warm up to RT overnight and poured into 200 ml of 0.1 M HCl followed by extraction with DCM. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from isopropanol/methanol (3:1) yielding 848 mg (0.84 mmol, 80%) of a dark orange powder.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.08$ (d, J=3.8, 2H), 6.94 (d, J=3.8, 2H), 6.87 (s, 2H), 6.80 (s, 4H), 3.86 (t, J=6.5, 2H), 2.75 – 2.60 (m, 2H), 2.67 (t, J=7.9, 4H), 1.64 – 1.47 (m, 4H), 1.48 – 1.17 (m, 24H). $^{13}$C NMR: No spectra (insufficient solubility).
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

General Polymerization procedure using bispinacolato diboron (BiPi method).

All reactions were performed under anhydrous conditions under a nitrogen atmosphere. To a three-necked flask of stirring solvent were added equal molar quantities of monomer and bis(pinacolato)diboron. The solution was then sparged with dry nitrogen for 10 min before addition of 5 mol% 1,10-bis(diphenylphosphino)-ferrocenepalladium(II)dichloride dichloromethane complex (Pd(dppf)Cl2) and 5 eq. of crushed K3PO4. An additional 10 min of sparging was performed. The mixture was heated to 110 °C and stirred for 24 h, cooled to RT, and the solvent was removed by rotary evaporation. The remaining residue was dissolved in a minimal amount of CHCl3 and precipitated by pouring slowly into 1 L of CH3OH. To facilitate the precipitation, 1 mL of concentrated HCl was then added. The resulting slurry was stirred for an hour and the precipitate collected by centrifugation at 4000 rpm for 10 min and dried in vacuo. The crude polymer was then purified in a soxhlet extractor using CH3OH, acetone, and CHCl3, in which the purified polymer dissolved before being re-precipitated into cold CH3OH and dried in vacuo.

Poly(4,4′-dihexyl-2,2′-bithiophene) [P6-1]

1.08 gr. (5.08 mmol) K3PO4, 0.5 gr. (1.02 mmol) 2.10, 10.2 mg of Pd(dppf)Cl2 and 260 mg. (1.02 mmol) bis(pinacolato)diboron were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded a sticky brown/orange gum. No accurate yield could be determined.

1H NMR (300 MHz, CDCl3) δ = 7.17 – 6.32 (m, 2H), 2.88 – 2.46 (m, 4H), 1.81 – 1.46 (m, 4H), 1.46 – 1.11 (m, 12H), 1.05 – 0.67 (m, 6H); ATR-IR (cm⁻¹): 3058, 2953, 2922, 2852, 1703, 1659, 1532, 1455, 1436, 1376, 1259, 1230, 1160, 1114, 1084, 1039, 926, 884, 832, 792, 749, 723; GPC: 3500 g/mol (Mn), 12400 g/mol (Mw), 71800 g/mol (Mz), 3.5 (PDI)

Poly(5,5′-dihexyl-2,2′-bithiophene) [P6-2]

431 mg (2.03 mmol) K3PO4, 200 mg (0.41 mmol) of 6.2, 4 mg of Pd(dppf)Cl2 and 103 mg (0.406 mmol) bis(pinacolato)diboron were reacted in 20 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded a sticky brown/orange gum. No accurate yield could be determined.

1H-NMR (300 MHz, CDCl3) δ = 7.01 – 5.95 (b, 2H), 3.04 – 2.25 (b, 4H), 1.93 – 1.45 (b, 4H), 1.45 – 0.98 (b, 12H), 0.98 – 0.56 (b, 6H). ATR-IR (cm⁻¹): 3058, 2952,
Poly(9,9'-dihexylfluorene) [P6-3]

500mg (1.03 mmol) 6.3, 1.06 gram (5 mmol) of K₃PO₄, 25 mg of Pd(dppf)Cl₂ and 258 mg (1.02 mmol) bis(pinacolato)diboron were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded 220 mg of a light brown solid (66%).

$^1$H-NMR (300 MHz, CDCl₃) δ = 8.26 – 6.81 (b, 10H), 2.71 – 1.62 (b, 4H), 1.55 – 0.99 (b, 12H), 0.99 – 0.26 (b, 10H); ATR-IR (cm⁻¹): 3058, 2924, 2852, 1723, 1605, 1455, 1402, 1376, 1249, 1093, 99, 883, 811, 756, 740, 722; GPC: 6053 g/mol (Mₙ), 16105 g/mol (Mₘ), 37074 g/mol (Mₚ), 2.7 (PDI)

Poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] [P6-4]

806 mg K₃PO₄ (3.8 mmol), 500mg (0.76 mmol) 6.4, 193 mg (0.75 mmol) bis(pinacolato)diboron and 14 mg Pd(dppf)Cl₂ were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded 279 mg (74%) of a yellow/green powder.

$^1$H-NMR (300 MHz, CD₂Cl₂) δ = 8.02-7.47 (b, 6H), 7.47-6.98 (b, 4H), 2.38-1.74 (b, 4H), 1.40-0.91 (b, 12H), 0.91-0.45 (b, 10H); ATR-IR (cm⁻¹): 3064, 2922, 2850, 1888, 1748, 1606, 1464, 1416, 1375, 1257, 1196, 1134, 1065, 1005, 878, 815, 788, 742, 722; GPC: 9500 g/mol (Mₙ), 25800 g/mol (Mₘ), 79700 g/mol (Mₚ), 2.7 (PDI)

Poly(3,3′-didecyl-terthiophene) [P6-5]

223 mg K₃PO₄ (2.60), 150 mg 6.5 (0.22 mmol), 56 mg (0.22 mmol) bis(pinacolato)diboron, 5 mg Pd(dppf)Cl₂ were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded 56 mg (48%) of a dark red polymer.

$^1$H-NMR (300 MHz, CD₂Cl₂) δ = 7.45-6.70 (b, 4H), 3.04-2.56(b, 4H), 1.89-1.52 (b, 4H), 1.51-1.11 (b, 28H), 1.04-0.73 (b, 6H); ATR-IR (cm⁻¹): 3062, 2952, 2918, 2849, 1497, 1456, 1376, 1187, 1065, 821, 782, 720; GPC: 8900 g/mol (Mₙ), 22900 g/mol (Mₘ), 63300 g/mol (Mₚ), 2.6 (PDI)
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

**Poly(3,3′-didecyl-quaterthiophene) (DMF) [P6-6]**

552 mg K$_3$PO$_4$ (2.60), 400mg 6.6 (0.52 mmol), 132 mg (0.52 mmol) bis(pinacolato)diboron and 7 mg Pd(dppf)Cl$_2$ were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded 128 mg (37%) of a dark red powder.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.45-6.73 (b, 6H), 2.98-2.60 (b, 4H), 1.93-1.52 (b, 4H), 1.52-1.03 (b, 28H), 1.03-0.72 (b, 6H); ATR-IR (cm$^{-1}$): 3062, 2951, 2918, 2848, 1495, 1455, 1375, 1260, 1065, 821, 780, 720; GPC: 6700 g/mol (M$_n$), 17600 g/mol (M$_w$), 49200 g/mol (M$_z$), 2.6 (PDI)

**Poly(3,3′-didecyl-quaterthiophene) (Tol/DMF) [P6-12]**

550 mg K$_3$PO$_4$ (2.60 mmol), 400mg 6.6 (0.52 mmol), 132 mg (0.52 mmol) bis(pinacolato)diboron and 7 mg Pd(dppf)Cl$_2$ were reacted in a mixture of 8 ml of dry DMF and 17 ml of dry toluene according to the general BiPi polymerization procedure. Precipitation in methanol yielded 268 mg (77%) of a dark red powder.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.35-6.85 (b, 6H), 2.97-2.56 (b, 4H), 1.87-1.53 (b, 4H), 1.53-1.05 (b, 28H), 1.01-0.72 (b, 6H); ATR-IR (cm$^{-1}$): 3062, 2918, 2849, 1495, 1456, 1375, 1189, 1067, 821, 780, 720; GPC: 5200 g/mol (M$_n$), 9600 g/mol (M$_w$), 17300 g/mol (M$_z$), 1.8 (PDI)

**Poly(2,5-bis(3-decylthiophen-2-yl)thieno[2,3-b]thiophene) [P6-7]**

551 mg K$_3$PO$_4$ (2.60), 400mg (0.53) 2,5-bis(5-bromo-3-decylthiophen-2-yl)thieno[2,3-b]thiophene, 134 mg (0.53 mmol) bis(pinacolato)diboron and 7 mg Pd(dppf)Cl$_2$ were reacted in 25 ml of dry DMF according to the general BiPi polymerization procedure. Precipitation in methanol yielded 208 mg (67%) of a red powder.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.31-7.12 (b, 2H), 7.12-6.87 (b, 2H), 2.96- 2.52 (b, 4H), 1.87-1.52 (b, 4H), 1.52-0.98 (b, 28H), 0.98-0.68 (b, 6H); ATR-IR (cm$^{-1}$): 3062, 2918, 2849, 1495, 1456, 1375, 1189, 1067, 821, 780, 720; GPC: 5700 g/mol (M$_n$), 16300 g/mol (M$_w$), 44600 g/mol (M$_z$), 2.9 (PDI)
Poly(3,3’-(4-methoxyphenoxy)decyl-2-yl)-quaterthiophene) [P6-13]

350 mg (0.35 mmol) 6.8, 97 mg (0.38 mmol) bis(pinacolato)diboron, 417 mg (2.0 mmol) K$_3$PO$_4$ and 7 mg Pd(dppf)Cl$_2$ were reacted in a mixture of 8 ml dry DMF and 24 ml of dry Toluene according to the general BiPi polymerization procedure. Precipitation in methanol yielded 253 mg (73%) of a red powder.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.33-6.92 (b, 6H), 6.88-6.71 (b, 8H), 4.02-3.78 (b, 4H), 3.78-3.64 (b, 6H), 3.00-2.56 (b, 4H), 1.89-1.52 (b, 8H), 1.52-1.09 (b, 24H); ATR-IR (cm$^{-1}$): 3059, 2918, 2848, 1505, 1462, 1436, 1389, 1289, 1179, 1102, 1069, 1037, 821, 785, 719; GPC: 7400 g/mol (M$_n$), 13800 g/mol (M$_w$), 41800 g/mol (M$_z$), 1.9 (PDI)

Deprotection of P6-13 [P6-14]

100 mg of P6-13 was dissolved into 15 ml of dry CH$_2$Cl$_2$. After the polymer was completely dissolved 250 µL of 1 M BBr$_3$ in CH$_2$Cl$_2$ was added at once. The mixture was stirred at RT for 30 min and then refluxed for 90 min. The mixture cooled and hydrolyzed by slow addition of methanol. After quenching the reaction mixture was poured into 500 ml of methanol and the precipitate was collected by centrifugation. 42 mg of a red powder was obtained. Because of the incomplete deprotection no accurate yield can be calculated. According to $^1$H-NMR 50% of the functional groups is deprotected.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.37-6.90 (b, 6H), 6.90-6.64 (b, 4H), 4.03-3.76 (b, 2H), 3.76-3.63 (b, 2H), 3.51-3.28 (b, 2H), 2.99-2.49 (b, 4H), 2.01-1.54 (b, 8H), 1.54-1.07 (b, 24H).

ATR-IR (cm$^{-1}$): 3059, 2918, 2848, 1505, 1462, 1436, 1389, 1289, 1227, 1179, 1102, 1069, 1037, 821, 785, 719; GPC: 4200 g/mol (M$_n$), 5900 g/mol (M$_w$), 8200 g/mol (M$_z$), 1.4 (PDI)
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

**General Polymerization procedure using Stille polymerization**

All reactions were performed under anhydrous conditions under a nitrogen atmosphere. To a three-necked flask of stirring solvent were added equal molar quantities of both monomers. The solution was then sparged with dry nitrogen for 10 min before the addition of 5 mol% Pd(PPh₃)₄ and an additional 10 min of sparging. The mixture was heated to reflux and stirred for 24 h, cooled to RT, and the solvent removed by rotary evaporation. The remaining residue was dissolved in a minimal amount of CHCl₃ and precipitated by pouring slowly into 1 L of CH₃OH. To facilitate the precipitation, 1 ml of concentrated HCl was then added. The resulting slurry was stirred for an hour and the precipitate collected by centrifugation at 4000 rpm for 10 min and dried in vacuo. The crude polymer was then purified in a Soxhlet extractor using CH₃OH, acetone, and CHCl₃, in which the purified polymer dissolved before being re-precipitated into cold CH₃OH and dried in vacuo.

**Poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] (Stille) [P6-8]**

![Polymer structure](image)

491 mg (1.0 mmol) **4.6**, 492 mg (1.0 mmol) **6.3** and 58 mg Pd(PPh₃)₄ were reacted in a mixture of 17 ml dry DMF and 83 ml of dry toluene according to the general Stille polymerization procedure. Precipitation in methanol yielded 356 mg (71%) of a orange powder.

$^1$H-NMR (300 MHz, CDCl₃) δ = 8.29-6.62 (b, 10H), 3.31-2.60 (b, 2H), 2.63-1.78 (b, 2H), 1.49-0.93 (b, 12H), 0.93-0.21 (b, 10H); ATR-IR (cm⁻¹): 3064, 2922, 2850, 1888, 1748, 1602, 1455, 1375, 1256, 1195, 1134, 1066, 1005, 979, 877, 816, 788, 752; GPC: 4000 g/mol (Mₙ), 8800 g/mol (Mₘ), 15800 g/mol (Mₚ), 2.2 (PDI)

**Poly(3,3′-didecyl-tertthiophene) [P6-9]**

410 mg (1.0 mmol) **2.12** and 59 mg Pd(PPh₃)₄ were reacted in a mixture of 16 ml dry DMF and 80 ml of dry toluene according to the general Stille polymerization procedure. Precipitation in methanol yielded 160 mg (30%) of a dark red powder.

$^1$H-NMR (300 MHz, CDCl₃) δ = 6.68-6.15 (b, 4H), 2.42-1.61 (b, 4H), 1.20-0.84 (b, 4H), 0.84-0.33 (b, 28H), 0.33-0.02 (b, 6H); ATR-IR (cm⁻¹):3061, 2951, 2916, 2848, 1497, 1456, 1434, 1375, 1260, 1183, 1066, 817, 776, 719; GPC: 8700 g/mol (Mₙ), 16100 g/mol (Mₘ), 26000 g/mol (Mₚ), 1.9 (PDI)
Poly(3,3′-didecyl-quaterthiophene) [P6-10]

492 mg (1.0 mmol) \(4.6\), 605 mg (1.0 mmol) \(2.12\) and 58 mg Pd(PPh\(_3\))\(_4\) were reacted in a mixture of 17 ml dry DMF and 80 ml of dry toluene according to the general Stille polymerization procedure. Precipitation in methanol yielded 552 mg (90%) of a dark red powder.

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.85-6.61\) (b, 6H), 3.18-2.31 (b, 4H), 1.91-1.52 (b, 4H), 1.52-1.04 (b, 28H), 1.00-0.72 (b, 6H); ATR-IR (cm\(^{-1}\)): 3061, 2951, 2917, 2848, 1493, 1455, 1435, 1375, 1309, 1158, 1120, 820, 779, 722; GPC: 5900 g/mol (M\(_n\)), 9500 g/mol (M\(_w\)), 14200 g/mol (M\(_z\)), 1.6 (PDI)

Poly(2,5-bis(3-decylthiophen-2-yl)thieno[2,3-b]thiophene) [P6-11]

600 mg (1.0 mmol) \(2.5\), 774 mg (1.0 mmol) \(2.12\) and 75 mg Pd(PPh\(_3\))\(_4\) were reacted in a mixture of 17 ml dry DMF and 80 ml of dry toluene according to the general Stille polymerization procedure. Precipitation in methanol yielded 659 mg (87%) of a dark orange powder.

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.42-7.14\) (b, 2H), 7.14-6.91 (b, 2H), 3.01-2.41 (b, 4H), 1.98-1.52 (b, 4H), 1.52-1.13 (b, 28H), 1.05-0.73 (b, 6H); ATR-IR (cm\(^{-1}\)): 3068, 2918, 2849, 1648, 1536, 1456, 1375, 1302, 1159, 1100, 1063, 963, 898, 818, 720; GPC: 10100 g/mol (M\(_n\)), 20200 g/mol (M\(_w\)), 33800 g/mol (M\(_z\)), 2.0 (PDI)
The use of bis(pinacolato)diboron for the synthesis of regioregular homopolymers

6.7 References


