Doctoral Thesis

Synthesis of poly(m-phenylene)s by chain-growth Suzuki-polycondensation

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Synthesis of Poly\textit{(m-phenylene)s} by Chain-Growth Suzuki-Polycondensation

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for the degree of

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presented by

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Abstract

This thesis investigates the synthesis of poly(m-phenylene)s (PMP) from AB-type monomers by Suzuki-Polycondensation (SPC). Poly(m-phenylene) has a semi-flexible backbone and is expected to be more soluble and easier to process than comparable but straight rigid-rod polymers. The AB-approach was selected because it eliminates the need for precise stoichiometry of the functional groups associated with the AA/BB-approach and therefore provides better reproducibility.

First a flexible and large scale synthesis of an AB-monomer (I) with several different side-chains is described. All monomers were obtained in purity of higher than 99%, which was determined by high resolution NMR spectroscopy. The monomers were subjected to SPC to obtain poly(m-phenylene) II (Scheme I). A careful investigation of the SPC product was done in order to identify side reactions. Reaction conditions for polymerization were successfully optimized in order to suppress ligand scrambling, phosphorous incorporation and cyclization.

Scheme I: General scheme for the synthesis of poly(m-phenylene).

By addition of monofunctional compounds it could be shown that the SPC of AB-monomers does not follow the classical step-growth mechanism associated with polycondensations. Instead, a chain-growth like behavior was observed. The addition of 4-fluorobromobenzene quantitatively initiated polymerization and suppressed cyclization completely. Di-end functional polymer III was synthesized using a fluorophenyl-initiator and a methoxyphenyl-terminator.

Figure I: Structures of di-end functionalized polymers III–V.
Using sequential polymerization of different monomers block copolymer IV was synthesized. Due to contamination with homopolymers the block copolymer could not be fully isolated. However, the structure could be proven by MALDI-TOF mass spectrometry.

By exploiting the initiator-terminator method, terpyridine end-capped PMP V was synthesized. When Fe(II) and Ni(II) was added supramolecular polymers containing a metal-bis-terpyridine complex were formed. The complex formation was observed by UV/Vis spectroscopy. Complete reversibility of the formed complex was demonstrated with the addition of HEEDTA which quantitatively decomplexed the metallo polymers.
Zusammenfassung


Zuerst wird eine flexible Synthese des AB-Monomers I mit verschiedenen Seitenketten beschrieben. Alle Monomere wurden in einer Reinheit von über 99 % erhalten, was durch hochauflösende NMR Spektroskopie bestimmt wurde. Mittels SPC dieser Monomere wurde Poly(m-phenylen) II erhalten. Die erhaltenen Produkte wurden sorgfältig untersucht, um Nebenreaktionen zu identifizieren. Die Reaktionsbedingungen wurden optimiert, um Liganden Austausch, P-Inkorporation und Zyklisierung zu unterdrücken.

Schema I: Allgemeines Schema für die Synthese von Poly(m-phenylen).


Abbildung I: Strukturen der endfunktionalisierten Polymere III–V.
Mittels sequentieller Polymerisation verschiedener Monomere konnte Block-Copolymer IV erhalten werden. Verunreinigung durch Homopolymer verhinderte allerdings eine vollständige Isolierung. Durch MALDI-TOF Massenspektrometrie konnte die Struktur allerdings zweifelsfrei nachgewiesen werden.

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1 Introduction

Since the establishment of polymer chemistry, there has been significant success in the synthesis of structurally perfect polymers of different architecture and functionality. Control over the polymer structure is crucial in order to obtain polymers with desired physical properties such as mechanical and thermal properties or morphology, and chemical properties such as self-healing, stimulus-response, light emission/absorption etc. In terms of synthesis important aims are to obtain polymers with low polydispersity and controlled stereosequence as well as to obtain telechelic polymers or block copolymers.

1.1 Polyarylenes

The development of high strength and high modulus materials has been pursued since the very beginnings of synthetic polymers.[1] Staudinger already suggested that the ideal structure for fibers are rigid-rod polymers that are densely packed and perfectly aligned.[2] Poly(para-phenylene) (PPP) is the prototype form of such a polymer and Schlüter and coworkers were the first to synthesize a fully soluble PPP.[3] The direct connection of aromatic units via C-C bonds gives polyarylenes unique properties that distinguish them from flexible polymers. They are very restricted in number of conformational states as internal bond rotations do not change the chain direction. Also, they are not hydrolytically labile such as aromatic polyesters and polyamides. Like other conjugated polymers, PPP features an aromatic system along the backbone whereby interesting properties are expected aside from its mechanical strength and thermostability. The highly anisotropic,[4] electronically delocalized system leads to optical, electrochemical and electrical properties relevant for applications in electronic devices,[5-6] photovoltaics,[7] and sensors.[8]

Taking a look on the molecular structure of an unsubstituted PPP the most straightforward way to synthesize it is to polymerize benzene. Indeed, the first attempts started from benzene using Friedel-Crafts catalysts (Scheme 1).[9] Other possible reactions that have been used include Ullmann reaction,[10] Wurtz-Fittig reaction,[11] or Kumada coupling.[12] Some of these approaches suffer from regioselectivity problems and all of them have solubility problems as the unsubstituted polymers precipitated prematurely. Precipitation leads to incomplete reactions, which gives only short oligomers and various side products.
In order to circumvent the issues associated with insolubility, Rehahn et al attached solubilizing alkyl side chains to the monomer and subjected it to polycondensation using either Kumada or Suzuki-Miyura-Coupling (SMC).\textsuperscript{[13]} Kumada polycondensation only gave oligomeric products with a DP < 10 whereas Suzuki-Polycondensation (SPC) afforded PPP which remained completely soluble in organic solvents and had an average molar mass ranging from 6000 to 8000 g mol\(^{-1}\) which corresponds to a DP around 30. Although still far from being high-molar-mass material this is already long enough to offer efficient conjugation length for electro-optical applications.\textsuperscript{[14-15]} Also it marks the beginning of a development which over the years led to very high molecular weight samples, using the same methodology.

Nowadays, the surge of academic as well as industrial research confirms SPC as one of the most promising methods to synthesize polyarylenes and related polymers.\textsuperscript{[16]} The ability of the Suzuki-Miyaura reaction to tolerate many functional groups made it possible to synthesize PPP with a great range of different side chains to influence the solution or bulk properties. For example, charged substituents can be attached resulting in interesting polyelectrolytes that can be used to study solution properties.

\textbf{Scheme 1:} Different approaches to the synthesis of PPP. Not all routes ensure strict \textit{para}-connections of phenylene repeat units as the polymer structure indicates.
Introduction

Scheme 2: Two different approaches for SPC, the so-called AA/BB approach (top) and the AB-approach (bottom). The boron functional group can be either free boronic acid or a cyclic boronic ester. \( X = \text{Cl}, \text{Br}, \text{I}, \text{OTf} \).

It is natural to assume that SPC is of a step-growth type based on the Suzuki–Miyaura cross-coupling. Like other polycondensations, there are two distinctly different approaches on SPC (Scheme 2). The AA/BB route is a copolymerization of two monomers; one carrying two aryl halides and the other carrying two boron functionalities. The AB route employs a monomer which carries both functional groups on the same monomer. This small difference has extensive consequences for the execution of the polymerization as well as for the resulting polymer. The AA/BB approach in principle results in a polyarylene sequence which contains the two aromatic units in an alternating pattern. This gives rise to variability in the structure of the polymer.

From a synthetic point of view the AA/BB approach is very attractive because once the dihalide monomer is synthesized it can be copolymerized with phenyl bisboronic acid, which is commercially available. In the AB case, only one type of monomer is used, however, mixtures of different AB-type monomers can also be used. This may request additional effort in monomer synthesis since the monomer needs to be desymmetrized with two different functional groups. On the positive side though, one has to mention that the resulting polymer
chain can have chain directionality due to the head to tail connectivity that is predetermined by the AB type structure.

Even though the AA/BB approach seems to be easier in terms of monomer synthesis it suffers from one major drawback: In order to achieve high molecular weight polymer one must have a precise $1:1$ molar ratio of the two monomers, as described in Carothers’ equation (Figure 1).\cite{17} One can see that high molecular weight polymer can only be obtained if a) the conversion $p$ is close to 1 and b) the molar fraction $r$ equals 1.

Achieving perfect $1:1$ stoichiometry may sound trivial, but on the scale on which reactions are usually conducted in research laboratories even “small” differences in purity and water content as well as non-quantitative transfer of substances into the reaction vessel can lead to irreproducible results. For example Bo et al. made deliberate changes in stoichiometry in the range of 0.005 equivalents and observed dramatic changes in molecular weight of the obtained polymers.\cite{18}

On the other hand, for the AB-approach high molecular weight product is only dependent on conversion $p$ which makes results much more reproducible, as one can see from the equation for AB–type monomers (Figure 2).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Carothers equation and plot for an AA/BB-type polycondensation with $p$ = conversion.}
\end{figure}
1.2 Kinked Polyphenylenes

The preferred straight conformation of PPPs derives from the linear connection of the repeating units. Internal rotation of the connecting bonds does not change the direction of the polymer backbone. However, if at least one monomer is a \( m \)-phenylene, the obtained poly(\( m \)-phenylene)s (PMP) can adopt various conformations, ranging from helical which is the most compact form, to the most extended zig-zag form. Due to the meta-connectivity, no conjugation over the entire polymer length is possible. If the correct substituents are selected, such kinked polyphenylenes can form foldamers.\(^{[19]}\) Foldamers themselves are not new and the helical structure of oligomeric \( \beta \)-amino acids have been studied since the late seventies.\(^{[20]}\) But foldamer research has focused mainly on short oligomers, often prepared by iterative coupling reactions leading to end-to-end distances of only a few nanometers.\(^{[21-22]}\) A high molecular weight PMP however, could be the basis of a helix with a length not achievable by iterative coupling reactions. Such a helix would have a defined pore with a tunable diameter to selectively allow passage of molecules e.g. in membrane applications.\(^{[23]}\)

Not so many reports of successful syntheses of PMP exist. Most of them describe only low molecular weight product. Before the discovery of the Suzuki–Miyaura reaction Yamamoto et al. described the synthesis of an unsubstituted PMP from \( m \)-dichlorobenzene by Ni-catalyzed dehalogenation polymerization.\(^{[12]}\) No concrete molecular weight was given; X-ray analysis
however, showed broad peaks that could be caused by the simultaneous presence of *cis-trans* and *trans-trans* chains (Figure 3).

![cis-trans and trans-trans conformations](image)

**Figure 3:** Two possible conformations for PMP as described by Yamamoto *et al.*[^12]

A similar study was published by O’Mahoney and coworkers on single-crystal X-ray analysis of monodisperse oligomers with eight or ten repeating units synthesized by Ni-catalyzed coupling of *m*-dichlorobenzene[^24]. The crystal structure revealed an apparently infinite helical chain with five phenyl units for each turn (Figure 4).

![X-ray structure and crystal packing](image)

**Figure 4:** a) X-ray structure of *m*-deciphenyl, showing a single molecule within the pseudo-polymeric helical chain. b) Tetragonally packed, interleaving helical chains in the crystal of *m*-deciphenyl, viewed in perspective down the crystallographic c-direction. (Reprinted from[^24]).

Musfeldt and coworkers prepared a set of polyphenylenes with a defined sequence of *para* and *meta* repeating units (Figure 5).[^25] Polymers 1 and 2 were synthesized by
copolymerization of 1,3-bis-(trimethyl stannyl)benzene with dibromobenzene to give meta-connected biphenyl or para-terphenyl repeat units. Homopolymerization of 3,3’-dichloro-p-terphenyl gave polymer 3 which contains three para-linked phenylenes separated by a meta linkage. Polymer 4 with meta-connected quaterphenyl repeat units were synthesized from 1,3-bis(4-chloro-phenyl)-5-phenylbenzene. Polymer 5 contains an even longer quinquephenyl repeat unit and was synthesized by copolymerization of 1,3-bis-(trimethyl stannyl)benzene and 1,3-bis(4-bromophenyl)-5-phenylbenzene. In an attempt to increase solubility, a phenyl group was attached to the meta-phenylene segment of the backbone. However, the polymerizations which were performed in toluene all yielded mixtures of soluble as well as insoluble products. GPC and mass spectrometry both indicated that the soluble products were of low molecular weight in the oligomer range only. Typical molecular weights obtained by GPC calibrated against polystyrene standards went from 1000 – 1500 Da.

A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. A PMP with alkoxy side chains was reported by Reynolds and coworkers. 3,5-Dichloro phenol (6) was functionalized with dodecylbromide via classical Williamson etherification (Scheme 3). For the polymerization, a nickel-catalyzed homocoupling reaction was used to obtain 7. The synthetic route is attractive, due to the simplicity of monomer synthesis and polymerization. However, the molecular weight of the obtained polymer was rather low with \( M_n = 9700 \) Da.
Scheme 3: PMP carrying a dodecyl side chain as prepared by Reynolds et al.\textsuperscript{[26]}

A notable example for a high molecular weight polymer, synthesized by SPC, was reported by Kandre et al.\textsuperscript{[28]} This poly(\textit{m},\textit{p}-phenylene) (8) had $M_w = 83$ kDa and was obtained on a scale of several grams. Upon fractionation by precipitation a fraction with $M_w = 255$ kDa was obtained. This material was melt-compression molded into a flexible but tough film. The mechanical properties of this material were exceptional and showed tensile properties comparable to commercial polycarbonate.

In order to get a kinked polymer structure, utilizing \textit{m}-phenylene units is not the only option. In fact there are many other possibilities such as \textit{o}-phenylene (9),\textsuperscript{[29]} \textit{3,6}-phenanthrylene (10),\textsuperscript{[30-31]} and five membered rings like thiophene (11),\textsuperscript{[32-34]} However, they were not followed up in the present study because of either to demanding monomer syntheses or the low molar masses obtained.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{kinked_polymer_structures.png}
\caption{Examples of kinked polymer structures using conformationally restricted backbones.}
\end{figure}
1.3 Suzuki-Miyaura Reaction and Suzuki-Polycondensation

It is no understatement to say that metal-catalyzed cross-coupling reactions have led to a revolution in chemistry.\textsuperscript{[35]} The possibility of directly connecting sp, sp\textsuperscript{2} and most recently sp\textsuperscript{3} carbon atoms has profoundly changed the way natural products, drugs, supramolecular building blocks and polymers are synthesized.

Miyaura and Suzuki reported in 1979 the first successful Pd-catalyzed coupling of an alkenylborane with an alkenylhalide.\textsuperscript{[38]} The protocol was quickly expanded to include aromatic moieties.\textsuperscript{[39]} Several cross-coupling reactions were already known by that time, but most of them were limited in the tolerance of functional groups\textsuperscript{[40]}, utilized toxic starting materials\textsuperscript{[41]} or made the use of stoichiometric amounts of metal catalyst necessary.\textsuperscript{[42]} The versatility and ease has made SMC to a cornerstone of synthetic organic chemistry, which is reflected by the Nobel Prize in chemistry of 2010 being awarded to Akira Suzuki.

Organometallic cross-couplings are generally assumed to follow a catalytic cycle of oxidative addition – transmetallation – reductive elimination as illustrated in Figure 7. The active Pd(0)-complex (I) is usually formed from a precatalyst species. In the case of the most often used Pd(PPh\textsubscript{3})\textsubscript{4} this is achieved by dissociation of two PPh\textsubscript{3} ligands to make two coordination sites available. If a Pd(II) catalyst is used, a reduction step is necessary before the Pd(0) enters the catalytic cycle. It is assumed that the reduction takes place by the homocoupling of two arylboronic acids or by oxidation of solvent (e.g. ethanol to acetaldehyde).\textsuperscript{[43]} The Pd(0) complex I inserts into the aryl-halide bond (R\textsubscript{1}-X) by oxidative addition to afford the trans-R\textsubscript{1}-Pd(II)-X complex (II). This complex is stable and can even be isolated.\textsuperscript{[44]}

For the transmetallation, two routes are proposed. Suzuki and coworkers propose a reaction where the halide on II is first substituted by the nucleophile `OR\textsuperscript{*}. Subsequently the aryl boronic acid or its derivatives undergo transmetallation with the R\textsuperscript{1}-Pd(II)-OR\textsuperscript{*} complex (III) which gives the biaryl Pd intermediate IV. After reductive elimination of IV the catalytically active Pd(0) species I is regenerated to continue the catalytic cycle and the cross-coupled product R\textsuperscript{1}-R\textsuperscript{2} is obtained. The reaction mechanism proposed by Canary\textit{ et al.} involves a direct transmetallation from II with a previously activated boron compound that gives a trans-diarylpalladium compound (IV).\textsuperscript{[45]} After a subsequent isomerization to the \textit{cis}-isomer, which is left out for simplicity, reductive elimination takes place.
In the case of SMC, oxidative addition and reductive elimination are quite well understood. A lot of research on oxidative addition of chloroarenes has been done which are a preferred reagent for industrial applications because of cost and availability.\textsuperscript{[46]} The C-Cl bond is rather stable and therefore, metal-catalyzed cross-coupling reactions of aryl chlorides remain challenging. There are some notable examples for successful polymerizations of aryl chloride monomers using SPC. It was shown that by using a Buchwald ligand, dichloromonomers can be copolymerized with phenylene bisboronic ester monomers with obtained molar masses of $M_w = 24000$ g mol\textsuperscript{-1} and yields of 95\%.\textsuperscript{[47]} The relative reaction rate regarding halide and pseudo-halide substituents decreases in the order of $I > OTf > Br >> Cl$. Electron-poor aryl-halides are more reactive to the oxidative addition than electron-rich.\textsuperscript{[48]}

Less is known about the process of transmetallation. It is agreed upon that hydroxides and other bases have a significant accelerating effect on the reaction between $R^1$-Pd-X (X = halogen or triflate) and organoboronic acids. Boronic acid has an unoccupied $\pi$-orbital into which the hydroxyl anion can donate, therefore creating an equilibrium between free tertiary boronic acid and the negatively charged quaternary boron atom which has increased nucleophilicity of the aryl-group for arylation of $R^1$-Pd-X. No direct evidence exists that

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{smc_cycle.png}
\caption{General catalytic cycle for SMC.}
\end{figure}
hydroxyboronates (R₂-B(OH)₃⁻) undergo transmetallation with R¹-Pd-X (Scheme 4, path A). However, quaternary boronate complexes such as Ph₄BNa⁴⁹ or ArBF₃K⁵₀ readily react with R¹-Pd-X to form cross-coupled products independently of pH whereas organoboronic acids only react at basic pH₅¹ This demonstrates that quaternarization of the boronic acid is a prerequisite to transmetallation.

The alternative process that has been postulated involves transmetallation to an alkoxo⁻⁵², hydroxo- or acetoxo-palladium(II) complex that is generated in situ by ligand exchange between R¹-Pd-X and a base (R*⁻-O⁻) (path B). Such oxopalladium(II) complexes give corresponding coupling products without the aid of base."⁵³

**Scheme 4**: Transmetallation with R¹-Pd-X with R* = alkyl and R¹,R² = aromatic. X = halogen. Path A is proposed by Suzuki et al. and path B by Canary et al.

### 1.4 Catalysts

In their first publication on the Suzuki cross-coupling reaction, Suzuki and Miyaura reported the use of Pd(PPh₃)₄ as catalyst.⁵⁹ The PPh₃ ligand has been one of the most popular ligands for SMC ever since, as it is simple to synthesize and fairly stable under oxygen free conditions.⁵⁴ In order to stabilize the Pd(0) species, various ligands are possible and their bulkiness and relative ratio of ligands to palladium change the reactivity towards oxidative addition, transmetallation, and reductive elimination. Phosphine ligands are the most common...
ligands used; however, their bulkiness influences the number of ligands coordinating to the metal. Therefore, palladium complexes with less than four phosphine ligands are required. This can be achieved by using weakly coordinating ligands or sterically demanding ligands. The cone angle as defined by Tolman (Figure 8) is a good measure to determine the steric effects of ligands (Table 1).\[55\]

![Figure 8: Definition of Tolman’s cone angle $\theta$ for phosphine angles. M = metal center and R = phosphine substituents.](image)

<table>
<thead>
<tr>
<th>Cone angle $\theta$</th>
<th>PEt$_3$</th>
<th>PPh$_3$</th>
<th>P(i-Pr)$_3$</th>
<th>P(o-tol)$_3$</th>
<th>P(t-Bu)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination number</td>
<td>3, 4</td>
<td>3, 4</td>
<td>2, 3</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The P(t-Bu)$_3$ ligand is exceptionally reactive not only due to its bulkiness, but also because of its strong electron donating properties.\[56\] Fu and coworkers demonstrated that P(t-Bu)$_3$ with Pd$_2$(dba)$_3$ as a source for Pd(0) gives excellent yields even for the cross-coupling of notoriously sluggish arylchlorides.\[57\] In order to accelerate the reductive elimination for coupling of alkylmetals for sp$^3$-coupling, biphosphine ligands with large phosphine-metal-phosphine angles, such as dppp, dppb and dppf have been designed. Another successful motif are the dialkylbiaryl phosphine ligands (SPhos, XPhos) developed by Buchwald and coworkers.\[58\] These monodentate, bulky and electron-rich ligands have found wide-spread application. The main reason for the accelerating effect is their ability to donate electrons to the Pd-center while dissociating easily enough to generate available coordination sites for the oxidative addition. The properties of these dialkylbiaryl phosphine ligands can be well tuned
and a veritable library of these so called “Buchwald”-ligands has been established.\textsuperscript{[59]} Very stable complexes are formed from pincer ligands such as 12 which give Pd-complexes that undergo SMC at room temperature without the exclusion of air.\textsuperscript{[60]} Recently there have been efforts to find alternatives to phosphine ligands in SMC and to date the only class to match them in terms of reactivity and stability are N-heterocyclic carbene (NHC) ligands such as 13 and 14.\textsuperscript{[61]-[62]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ligands.png}
\caption{Different ligands for palladium catalysts used in SMC.\textsuperscript{[63]-[64]}}
\end{figure}

\subsection*{1.4.1 Precatalysts}

Many catalysts are generated in situ from a suitable ligand and an additional palladium source. This is a convenient option if the catalytically active species is difficult to obtain in pure form or unstable. There are many possible sources available and the key factor for selection is the efficiency for formation of the catalytically active, coordinative unsaturated Pd(0) complex. Pd(II) salts such as Pd(OAc)\textsubscript{2} are popular because they are stable towards oxidation. However, they need to be reduced to Pd(0) before entering the catalytic cycle. This can be achieved by reduction of solvent molecules\textsuperscript{[43]}, homocoupling of arylboronic acids (see 1.5.1), or the deliberate addition of a reducing agent, such as a tertiary amine.\textsuperscript{[65]-[66]} Recently a new set of precatalysts for Buchwald-type ligands has been developed (16 and 17) (Figure 10).\textsuperscript{[67]-[68]} They convert to the active Pd(0) species by reductive elimination of indoline or carbazole. While there are many different Pd(II) sources, only few Pd(0) sources are utilized.
The most widely used is Pd(dba)$_2$ (18). It is fairly air stable and has no competing phosphine ligands to stabilize its oxidation state,\cite{69} which is beneficial for the prevention of ligand scrambling (see 1.5.2). Pd(dba)$_2$ is an equimolar mixture of Pd(dba)$_3$ and Pd$_2$(dba)$_3$ and after recrystallization Pd$_2$(dba)$_3$ can be obtained as a solvent adduct.\cite{70}

![Figure 10: Precatalysts used for SMC.](image)

The catalyst loading generally used for SPC is between 1 – 3 mol\%. However, much smaller concentrations are necessary if one wants to avoid traces of remaining catalyst in the polymeric product.\cite{28} Buchwald and coworkers have shown, that for SMC catalyst concentrations of as low as 0.0005 mol\% can still give reproducible results.\cite{71} In another study it was reported that even the “homeopathic” amounts of palladium contaminating commercially available sodium carbonate (down to 50 ppb) can catalyze cross-coupling reactions using microwave heating in water at 150 °C.\cite{72}

### 1.4.2 Catalyst Removal

Removal of catalyst residue is an ongoing issue in SPC, as metal and ligand residues can severely decrease the electrical conductivity and operation time of optoelectronic devices such as OLED. For industrial applications great care is taken to remove these residues and palladium contents of around 1 ppm are achieved. Typical methods for removal of palladium residues are column chromatography,\cite{73-74} soxhlet extraction,\cite{75} water washing,\cite{76} repeated precipitation\cite{77} and scavenger extraction.\cite{78} Scavenger extraction is especially effective for reduction of the palladium content. Treatment with aqueous NaCN is very simple and effective for removal of residual palladium.\cite{79} Another approach is to use water soluble phosphine ligands such as 19a and 19b, which reduce the palladium content in the organic phase of biphasic reactions. Krebs and coworkers reported the very efficient azothioformamide 20 which forms a complex with Pd(0) which has a strong UV absorption at
around 800 nm (Figure 11).\textsuperscript{[80]} Since this wavelength region is normally not covered by conjugated polymers, the palladium content can be conveniently determined by UV/Vis spectroscopy with a detection limit in the sub ppm range. Because the prevalent ligands for SPC are phosphine based, and due to the fact that they undergo ligand scrambling (see 1.5.2) and oxidation, it is desirable to either avoid, or to be able to remove them. One promising possibility for this are solid-phase supported catalysts, which facilitate purification of the products and can also be reused.\textsuperscript{[81-82]}

![Figure 11: Metal complexing scavengers for palladium removal.](image)

1.5 Side Reactions

1.5.1 Homocoupling

The coupling of two arylboronic compounds is called homocoupling (Scheme 5) and has been already reported by Suzuki and coworkers to occur under anhydrous conditions using Pd(OAc)\textsubscript{2} and PPh\textsubscript{3}.\textsuperscript{[83]} This has not been further investigated until Smith and coworkers reported the synthesis of symmetrical biaryls from palladium catalized homocoupling of arylboronic acids with addition of oxygen, which turned the undesired side reaction into a useful synthetic method.\textsuperscript{[84]} Song and Wong similarly described the synthesis of furan-3,4-diyl oligomers by Pd-catalyzed homocoupling\textsuperscript{[43]}

A mechanistic study was carried out by Moreno-Mañas and coworkers in which a double transmetallation is postulated, followed by reductive elimination of the biaryl.\textsuperscript{[85]} A significant acceleration of homocoupling was observed when the reaction was done under oxygen atmosphere. Electron-drawing substituents such as –CF\textsubscript{3} gave lower yields than electron donating substituents (e.g. –OMe).
Scheme 5: Homocoupling of phenylboronic acid to biphenyl.

Table 2: Biphenyl yield by homocoupling of phenyl boronic acid under different atmospheres.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Biphenyl yield [%]</th>
<th>Reaction time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>23</td>
<td>5</td>
</tr>
<tr>
<td>Air</td>
<td>64</td>
<td>5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>66</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Full disclosure of the homocoupling mechanism in the presence of oxygen was achieved by Amatore and Jutand in 2006.\[^{86}\] The key intermediate in the catalytic cycle is the peroxo complex ($\eta^2$-O\textsubscript{2})Pd(PPh\textsubscript{3})\textsubscript{2} (Scheme 6) which is known to be generated from Pd(PPh\textsubscript{3})\textsubscript{4} in the presence of dioxygen.

For polymer synthesis the stoichiometric mismatch generated by homocoupling is detrimental to achieve high molar masses.\[^{87}\] It is important to note that structural defects derived from homocoupling cannot be healed and it is therefore essential to perform reactions under rigorous exclusion of air.
1.5.2 **Ligand Scrambling**

Phosphine based ligands are still the vast majority of catalyst systems employed in SPC. The possibility of aryl exchange between aryl phosphine ligands and the growing polyarylene chain has been reported early on.[88-89] Electron-rich aryls and electron-rich phosphine substituents are more prone to ligand scrambling[90] which can lead to phosphine- or aryl-terminated polymer chains and phosphorous incorporation into the polymer backbone (Scheme 7).

The use of sterically more demanding phosphine ligands such as P(ρ-tol)₃ or P(σ-tol)₃ leads to reduced phosphorous incorporation. The degree of phosphorous incorporation has been quantified for an exemplary PPP and was considered to be of negligible importance.[91] However, phosphorous acts as a kink or a branching point and can significantly hamper with the otherwise linear rigid-rod like structure of PPP. The search for phosphorous-free ligands is therefore still an ongoing issue.

**Scheme 6:** Mechanism of the Palladium-catalyzed homocoupling of arylboronic acids in the presence of dioxygen.
1.5.3 Deboronation

Cleavage of the C-B bond by hydrolysis (protodeboronation) is an undesired side reaction which however, is quite common for SMC (Scheme 8). For small molecule couplings this can be compensated by adding the boron component in excess, an option that is not possible for polymerization where stoichiometry is of key importance. Substituents at the ortho-position increase the protodeboronation rate as well as adjacent aryl heteroatoms. Electron withdrawing substituents also accelerate B-C bond cleavage. The process is pH dependent and weak bases such as aqueous KHCO₃ slow down the rate of deboronation.
1.5.4 Dehalogenation

Dehalogenation of organic halides is a quite common side-reaction in cross-coupling reactions even though it is not often discussed. It is known that reactions with arylboronic esters lead to alcohols via ester hydrolysis, which in turn can act as hydride donors for dehalogenation. The hydride derives from $\beta$-hydride elimination from Ar-Pd-OCH$_2$R, giving Ar-Pd-H and RCHO (Figure 12). [52, 94]

![Scheme 8: Proposed mechanism for the hydrolytic C-B bond cleavage (protodeboronation).](image)

Figure 12: Dehalogenation by $\beta$-hydride elimination in SMC.

Aryl boronic esters formed from tertiary alcohols such as pinacol prevent such eliminations. DMF can also act as a hydride donor when used in presence of a base and it is therefore beneficial to replace it with N,N-dimethylacetamide (DMA). [95] Steric crowding also seems to increase dehalogenation as the coupling of arylboronic esters to hexabromobenzene only yields penta-substituted product. [96]

1.6 Analysis of Polymers by Mass Spectrometry

In order to fully understand the relation of macro- and microscopic properties of polymers and their chemical structure it is necessary to be able to fully analyze and characterize the
polymeric material. Polymer analysis is crucial for investigating the polymerization process in order to optimize reaction conditions as well as for quality control of polymeric products.

A wide variety of analytical methods are available for polymer analysis such as gel permeation chromatography (GPC),\(^{[97-98]}\) UV/Vis spectroscopy,\(^{[99]}\) nuclear magnetic resonance (NMR),\(^{[100]}\) X-ray crystallography,\(^{[101]}\) and mass spectrometry (MS).\(^{[102-104]}\) Each of them has its strengths and weaknesses and more than often they are combined to give a detailed analysis of the system investigated. But MS can provide quantitative absolute molecular mass and molecular mass distribution. Due to its sensitivity minor polymer components or impurities can be detected and identified.

Most of the MS methods that have been developed so far have been tried for the analysis of polymers. However, not all of them were equally successful. Traditional ionization methods such as electron ionization (EI) or chemical ionization (CI) are still used for structure or composition elucidation, but they are very limited in terms of molar mass range. Except for certain favorable polymer systems such as poly(ethylene glycol) (PEG)\(^{[105]}\) only low-molar mass polymers or their precursors (monomers, oligomers) can be ionized with such techniques.

Matrix-Assisted Laser Desorption / Ionization (MALDI) has dramatically increased the possibilities of polymer analysis by MS and has become a widely used method to analyze mainly biopolymers such as peptides or DNA and synthetic polymers. For both applications molecular ions of 100’000 Da and higher could be generated without fragmentation. MALDI is usually coupled with a time-of-flight detector (TOF), which offers a large mass range (Figure 13).
Figure 13: Scheme of a MALDI-TOF MS with the TOF in reflectron mode.

MALDI is based on the co-crystallization of analyte and matrix, with a 100 to 100,000 fold excess of matrix molecules. There is a wide variety of matrices and preparation techniques and so far only rules of thumb can be applied to their selection. Some of the most common matrix materials are 2,5-dihydroxybenzoic acid (DHB), sinapinic acid (SA) or dithranol. The sample is usually prepared by the dried droplet method,\[106\] or in the case of insoluble analytes by solvent free preparation techniques.\[107\] The sample preparation is crucial and should serve three purposes: a) co-crystallization with the analyte without cluster formation, b) strong absorption of the laser energy and transfer to the analyte, c) ionization of the analyte.

The sample is irradiated with laser pulses of a few nanoseconds. Typically nitrogen lasers (377 nm) or Nd:YAG lasers (355 or 266 nm) are used. The desorption / ionization step is, although investigated in detail,\[108\] still not entirely understood. It is generally accepted that the excitation by the laser energy leads to ablation of the surface layer of the analyte / matrix co-crystal. A compressed gas plume is formed in which the charge transfer reactions from the matrix molecules to the analyte can take place (proton or metal ion cationization). The ionization of synthetic polymers usually takes place by cationization as opposed to biopolymers, which usually are protonated. Polymers with polar functional groups might form sodium or potassium adducts, even when this salts are not intentionally added.\[109\] These cations are present as impurities in glassware, solvents, reagents etc. Low concentrations in the MALDI sample are already sufficient for polymers with high affinity to cations. Most heteroatom-containing polymers (polyethers, polyacrylates, polyesters, polyamides etc.) will cationize after the addition of sodium or potassium salts. Apolar polymers without
heteroatoms (polyphenylene, polystyrene, polybutadiene, and polyisoprene) can be cationized with the addition of silver or copper salts in the +1 oxidation state, which interact with the double bonds of the polymer.\textsuperscript{110}

The analysis of mass to charge \( m/z \) is done by a TOF analyzer. The ions produced by the laser ablation are accelerated through a potential \( V \) (Eq. 1) and travel a certain distance \( d \) through a vacuum tube and reach a detector after a certain time \( t \) (Eq. 2). The flight time is dependent on the velocity \( v \) which is dependent on \( m/z \) (Eq. 3). Therefore larger ions and thus larger masses take longer to reach the detector.

\[
zeV = \frac{m v^2}{2} \rightarrow v = \sqrt{\frac{2zeV}{m}} \quad \text{(Eq. 1)}
\]

\[
t = \frac{d}{v} \quad \text{(Eq. 2)}
\]

\[
t = \sqrt{\frac{m}{z}} \frac{d}{\sqrt{2zeV}} \quad \text{(Eq. 3)}
\]

The TOF analyzer suffers from poor resolution if operated in linear mode. Ions of the same mass can have different velocities upon generation, which leads to different kinetic energies after acceleration. Also ions generated at slightly different locations on the sample have different distances to travel. The distribution of kinetic energy and distance can be equalized by using a reflectron. The reflectron is an electric field acting as an ion mirror which slows the incoming ions down and eventually reflects them. Faster ions with higher kinetic energy penetrate deeper into the electric field until they are reflected and therefore reach the detector at the same time as slower ions which are reflected quicker. This refocusing effect greatly enhances the resolution of the TOF analyzer.

The theoretically unlimited mass range, combined with the enhanced resolution when employing reflectron and time-lag focusing and the soft ionization of MALDI make the TOF analyzer an ideal set-up for the analysis of biological and synthetic macromolecules.\textsuperscript{111}

MALDI-TOF MS has proven to be an ideal analytic tool to elucidate the complex mechanism of SPC and the many possible side reactions. The possibility to directly analyze the different end-groups of a polymer after SPC has given much insight into the termination reactions of thiophenebisboronic derivatives and diiodobenzenes polymerized by SPC (Figure 14).\textsuperscript{112}
Figure 14: Different end group patterns after SPC and MALDI-TOF mass spectra of SPC under various conditions (Matrix: α-cyano-4-hydroxycinnamic acid). (Reprinted from [112]).
A very nice example of end-group analysis in SPC of an AA/BB system is provided by Sangvikar et al.\textsuperscript{[113]} The MALDI-TOF mass spectrum displays all possible combinations of monomers with the intact reactive functional groups. From this it was concluded that the reaction mechanism must be of a step-growth nature. One must note though, that the molar mass of the used sample is low.

\[
\text{MALDI-TOF mass spectrum of the SPC product (Matrix: trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) with AgOTf) (X = 2,5-dihexyloxy-1,4-phenylene, Y = 1,8-anthrylene, B(pin) = boron pinacolate, OTf = triflate). (Reprinted from\textsuperscript{[113]}.)}
\]
2 Aim of the Work

The aim of the presented work is to synthesize high molecular weight poly(m-phenylene) by SPC. A great number of poly(para-phenylene)s and polymers containing meta-repeating units have been synthesized so far. However, no true high molecular weight poly(meta-phenylene) with an all-meta backbone has been synthesized yet. In order to achieve this, a simple monomer synthesis needs to be established. The synthesis needs to be flexible to allow for easy introduction of a wide array of side-chains and boronic acid derivatives. The synthetic route to obtain the monomer has to be suited for large-scale synthesis. Once the monomer is obtained in high purity, efficient conditions for polymerization need to be found. The underlying mechanistic details for SPC of an AB-type monomer have to be studied for further optimization of the reaction conditions. In order to achieve a controlled and high yielding polymerization, the most important questions that need to be answered are:

- Clarity whether SPC of AB-type monomers follows a step-growth or a chain-growth mechanism.
- The identification of terminating side reactions by end-group analysis and how to prevent them.

Further goals include:

- Controlled introduction of desired end-groups in order to synthesize asymmetric polymer chains.
- Analysis of secondary structure formation of the polymers in solution.
3 Monomer Synthesis and Polymerization

Synthesis of high molecular weight polymers by SPC is not trivial. No generally established SPC protocol exists and the SPC conditions need to be optimization for each set of monomers. In order to exclude all issues related to stoichiometry that come along with an AA/BB approach (see 1.1) an AB type monomer was chosen for the present study. Due to the kinked nature of PMPs the meta connectivity of the halogen and boron functional group was predetermined. An important aspect of the monomer design was the introduction of various side chains, preferably at a late stage of monomer synthesis. To find optimal SPC conditions a screening process was necessary, for which a cheap and easy synthesis was desirable which would allow for a large-scale production of the monomer.

According to the reported synthesis the commercially available aminobenzoate was brominated to afford the dibromide (Scheme 9). The deamination step to furnish was slightly modified since it proved to give unreliable yields (25 – 69%). At a temperature of 75 °C phenols and diazo coupled side products were observed. In order to avoid these side reactions the reaction was performed with hypophosphoric acid (H₃PO₂) at 5 °C, which resulted in improved and more reliable yields from 65 – 83%. Reduction of the ethyl ester afforded the important building block. The convenience of this synthesis scheme lies in the simple purification of each intermediate by crystallization allowing reactions on large scale (>100 g).

Scheme 9: Synthesis of building block. The amounts and yields are from three independent runs.

3.1 Monomers with Various Side Chains

Benzylic alcohol offers great versatility for the introduction of solubilizing side chains. From the “hairy-rod” concept applied to rigid-rod polymers it is known that flexible side
chains are required to achieve solubility.\textsuperscript{[116]} Since PMP comprises kinked \textit{m}-phenylene units, it was expected that relatively short side chains already mediate solubility sufficiently. A butyl side chain was thus introduced to the monomer by standard Williamson etherification. The butylated dibromide 25 could be easily purified by fractional distillation under reduced pressure. Column chromatography was used to obtain its dodecyl analog 26. Note that etherification with 1-bromododecane proceeded very slowly and even after 24 h product could only be isolated in 30\% yield, the rest being starting material. 1-Iodododecane was used instead but gave no product at all, presumably due to its decomposition by base-catalyzed elimination.\textsuperscript{[117]} Fortunately, by using 1-bromododecane with a catalytic amount of imidazole the product yield could be improved to 73\%.

![Scheme 10: Synthesis of monomers 10a and 10b.](image)

The replacement of one bromide of 25 with a boronic acid was performed by lithiation and subsequent borylation with triisopropylborate to furnish the AB-monomer 27. In order to ensure solubility and investigate the effects of the side chain length for SPC, monomer 28 which carries dodecyl side chains was also synthesized according to similar procedures. For details see Experimental Section.

The monomer needed to be purified carefully in order to remove starting material and side products which disturb the stoichiometric balance for SPC. Possible side product include doubly-borylated 29 and monofunctional products 30 and 31 (Figure 16).

![Figure 16: Possible undesired side products after lithiation and borylation of 9.](image)
Boronic acid 27 could be recrystallized from boiling water and suitable crystals for single crystal X-ray analysis were obtained. This is significant because it proves that purification to a very high degree and on a large scale is possible. The single crystal structure shows no H$_2$O molecules included in the crystal lattice, nor self-condensation of the boronic acids (Figure 17). Both hydrogens of the boronic acid are involved in hydrogen bonding. One is coordinating with the ether oxygen and the other with another boronic acid oxygen.

**Figure 17:** X-Ray single crystal structure of monomer 27 crystallized from water. Note that there is no water in the crystal structure. Hydrogen bonds are marked with dashed green lines.

**Scheme 11:** Synthesis of THP-protected monomer 16.

Besides monomers 27 and 28 which carry alkyl side chains also monomer 33 was synthesized. It carries 2-tetrahydropanyl (THP) a base-stable alcohol protecting group, which can be easily removed by acid hydrolysis after polymerization. The protecting group acts also as a solubilizing side chain. After lithiation of dibromide 32 with $n$-BuLi and
subsequent borylation with isopropyl pinacolyl borate, pinacol ester 33 was obtained (Scheme 11). Monomer 33 was purified by consecutive recrystallization in petrolether and acetonitrile. Analysis by high resolution $^1$H-NMR revealed that a small impurity at 7.20 ppm was still present. The exact nature of the impurity is not clarified; presumably it is a phenol derivative. Assuming that the signal at 7.20 ppm corresponds to one proton, the purity of the product was determined to be > 99.8 % by comparing the $^1$H-NMR signal intensity of the impurities with the intensity of the $^{13}$C satellite signals of the product (Figure 18).

![Figure 18: $^1$H-NMR spectrum (700 MHz) of monomer 33 in CDCl$_3$. Marked with asterisks (*) are the $^{13}$C-satellite peaks of the product. The impurity at 7.20 ppm is suspected to be from a phenolic derivative.](image)

### 3.2 Derivatization of Arylboronic Acid

It is well known that phenyl boronic acid can self-condensate to form cyclic triphenyl boroxine (Scheme 12). However, the boroxine is usually at equilibrium with the free boronic acid, making it difficult to calculate the true amount of monomer for SPC.
Boroxine formation from phenylboronic acid.

Additionally, boronic acids are prone to undergo C-B bond cleavage at elevated temperature and in basic aqueous solutions, which are the conditions necessary for SPC. Therefore it was decided to convert the boronic acid into the more stable and easier to handle boronic ester (Scheme 13). First boronic acids 27 and 28 were esterified using 1,3-propanediol in toluene with azeotropic removal of water. However, the resulting esters 34 and 35 turned out to be not stable enough against acidic silica gel and significant losses during chromatographic purification were observed. Dodecyl side chain carrying 35 could be crystallized without the need of purification by column chromatography. To overcome this problem, boronic acids 27 and 28 were esterified with pinacol to give ester 36 and 37. Gratifyingly, they were found to be much more stable, which facilitated purification. Another benefit of pinacol compared to 1,3-propanediol is the lack of α-protons. It is assumed that migration of the α-proton to the palladium atom can cause dehalogenation. Model studies with Me₂CDOH as solvent have been reported which quantitatively gave deuterated compounds. This side reaction is detrimental to SPC and can be circumvented by using pinacol esters (see 1.5.3).

Esterification of boronic acids 10a and 10b with 1,3-propanediol and pinacol.

Esterification of boronic acids generally is a quantitative reaction and NMR proved complete conversion of the crude product of monomers 17a - d. However, upon purification by column chromatography significant losses were observed. Thin layer chromatography (TLC) studies showed partial decomposition of the product due to hydrolysis by the acidic silica gel. Even with the addition of 1% triethyl amine to the eluent this could not be prevented. In order to
achieve the necessary high degree of purity, multiple purifications by column chromatography were sometimes necessary, aggravating the losses.

Several protecting groups for boronic acids with improved stability have been reported.\textsuperscript{[120-122]} \(N\)-methyliminodiacetic acid (MIDA) boronates are stable under silica gel column chromatography conditions and are inactive towards transmetallation. Under the right conditions MIDA boronates can hydrolyze back to the boronic acid during SMC.\textsuperscript{[123]} This slow hydrolysis has the advantage that the concentration of the active boronic acid is kept at a minimum throughout the polymerization which reduces protodeboronation.

The boronic acid of 27 was esterified with MIDA in toluene with azeotropic removal of water (Scheme 14). The obtained product 38 could be easily purified by column chromatography. However, SPC of 38 with Pd[\(P(p\text{-Tol})_3\)]\(_3\) as catalyst in THF/water yielded only very low molecular weight product with a lot of deboronated monomer. The rate of hydrolysis seems to be to slow and leads to prolonged reaction times. The use of MIDA boronates for SPC was thus discarded. Monomers with cyclic triolborates were also synthesized. The C-B bond of the tetracoordinated ate-complex is intramolecularly activated and does not need additional base. Good solubility in organic solvents, stability towards air and a high propensity to crystallize make them attractive for use in SPC. Esterification of 27 with 1,1,1-tris(hydroxymethyl)ethane and potassium hydroxide furnished triolborate 39 which was purified by column chromatography, since 39 could not be crystallized. SPC of the triolborate was done with Pd[\(P(p\text{-Tol})_3\)]\(_3\) without additional base in THF. After 72 h at reflux temperature less than 50% of the monomer was converted and the product was of very low molecular weight in the oligomer range.

\textbf{Scheme 14:} Synthesis of MIDA-borionate 38 and triolborate 39 from boronic acid 27.
3.3 Optimization of SPC Conditions

In contrast to other polymerization techniques (e.g. controlled radical polymerization) there are still no general reaction conditions for SPC that universally yield high molecular weight polymers. In fact, each class of monomers usually requires a certain degree of optimization of the reaction conditions. Many factors are involved such as Pd source, catalyst ligands, base, solvents, reaction temperature and nature of the boron moiety. Due to the many parameters involved and the still unclear dependencies to each other the optimization process is very iterative. The different reaction conditions mainly used in this study are presented in Table 3. Condition i) derives from a previously reported synthesis of PMPP which achieved high molecular weight.\cite{28} Due to the structural similarity of the used monomers, condition i) was selected as the starting point for optimization.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Base</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>i)</td>
<td>Pd[P(p-tol)$_3$]$_3$</td>
<td>NaHCO$_3$</td>
</tr>
<tr>
<td>ii)</td>
<td>Pd[P(p-tol)$_3$]$_3$</td>
<td>Cs$_2$CO$_3$</td>
</tr>
<tr>
<td>iii)</td>
<td>Pd[P(p-tol)$_3$]$_3$</td>
<td>Bu$_4$NOH·30 H$_2$O</td>
</tr>
<tr>
<td>iv)</td>
<td>Pd(dba)$_2$ / SPhos</td>
<td>NaHCO$_3$</td>
</tr>
</tbody>
</table>

Table 3: Different reaction conditions for SPC. The reaction temperature was always 70° C.

3.3.1 SPC Using Monomers with Different Boron Groups

The influence of different boron functional groups on SPC was investigated with monomers 27, 34 and 36 under the previously reported condition i): Pd[P(p-Tol)$_3$]$_3$, NaHCO$_3$, in THF / water (3:1), 70 °C for 3d under nitrogen (Scheme 15).

Scheme 15: SPC of monomers 27, 34 and 36 with different boron groups.
Chapter 3

Analysis of the SPC product 41 by gel permeation chromatography (GPC) showed a bimodal distribution with a less intense peak of higher molar mass ($P_H$) and a more intense peak of lower molar mass ($P_L$) (Figure 19). The peak maxima of $P_H$ and $P_L$ correspond to the degrees of polymerization (DP) of around 50 and 10 respectively. The DP values were calculated from the molar masses estimated by GPC relative to polystyrene standards.

There were only little differences of the retention volumes of $P_H$ and $P_L$ while their relative peak intensity slightly varied depending on the boron functional group. From these results, the least propensity for side reactions (see chapter 3.2) and ease of purification it was decided to continue with pinacol protected monomers 33 and 36 in the following SPC studies.

![Figure 19: GPC elution curves of SPC product 41 from monomers 27, 34 and 36.](image)

### 3.3.2 SPC Using Monomers with Different Side Chains

In order to determine the influence of different side chains on SPC monomers 33, 36 and 37 were polymerized under the same conditions as above (Scheme 16). The SPC products 40 - 42 were analyzed by gel permeation chromatography (GPC) and were found to be of low molar mass. The elution curves showed the same bimodal distribution as above with a less intense $P_H$ and a more intense $P_L$ (Figure 20). $P_L$ corresponds to a peak molecular weight $M_p = 1500$ Da and $P_H$ corresponds to a molecular weight of 8000 – 9000 Da. For the dodecylated...
polymer 42 $P_H$ is shifted towards lower retention volumes, which is to be expected due to the significantly higher molar mass of the repeat units.

The bimodal feature was also observed on GPC curves of the other SPC products and is thus considered to be a common feature for poly($m$-phenylene)s under the current SPC conditions irrespective of the side chains of the monomer. There is no significant difference concerning molecular weight between polymer 40 and 41. It was therefore decided to utilize the THP protected monomer 33 since its synthesis is much easier and possible on larger scale due to the ability to crystallize (see 3.1).

Scheme 16: SPC of monomers 33, 36 and 37 with different side chains.

Figure 20: GPC elution curves for polymerizations of monomers 40 - 42 (top to bottom) using condition i): Pd[P(p-Tol)$_3$]$_3$ (0.01 eq), NaHCO$_3$ (8 eq), THF / H$_2$O (3:1).
3.3.3 SPC with Different Bases

It is known that transmetallation is often a rate-determining step in SMC (see 1.3). The rate of activation of the boronic acid functionality towards transmetallation can be significantly influenced by the base that is selected. NaHCO$_3$ lacks enough solubility in organic solvents, making the addition of a large amount of water necessary. Therefore bases with better solubility in organic solvents and different amounts of water were tested using monomer 16: (ii) Pd[P(p-Tol)$_3$]$_3$ (0.01 eq), CsCO$_3$ (1.5 eq), water (5 eq) in THF and (iii) Pd[P(p-Tol)$_3$]$_3$ (0.01 eq), Bu$_4$NOH·30H$_2$O (1.6 eq), in THF (Table 3).

Conditions (ii) and (iii) also yielded bimodal products but with being $P_H$ being more intense. From conditions (iii) $P_H$ was shifted towards higher molar mass (10 kDa) compared to those from conditions (i) and (ii) (Figure 21), while $P_L$ always remained at around 1.5 kDa.

![Figure 21: GPC elution curves of SPC products from monomer 16 under various reaction conditions.](image)

These results exemplify that the molecular weights of SPC products can be improved by the choice of base. However the choice of base is not independent of the choice of catalyst and other conditions for overall optimization of SPC such as solvents, reaction temperature, or monomer concentration (see below). Thus, the overall optimization is a delicate issue which requires a portion of intuition.
3.4 Structural Analysis of SPC Products

In order to get more information on the nature of the two peaks $P_H$ and $P_L$, as well as on the termination reactions responsible for the low molar masses, THP protected polymer obtained under condition (ii) was subjected to preparative GPC. Two fractions I and II were separated at the saddle point of $P_H$ and $P_L$ and subjected to matrix-assisted laser desorption / ionization – time of flight mass spectrometry (MALDI-TOF MS). The mass spectra revealed that $P_H$ consists of open linear chains with various end-group patterns (Figure 23) and $P_L$ of cyclic product (Figure 24). Since $P_H$ and $P_L$ partially overlap, the mass spectrum of fraction I contains also cyclic product however, only in the lower mass region. Neither bromo nor boron terminated chains could be observed, indicating that chain-growth has come to a complete halt by either cyclization or side reactions such as cyclization, ligand scrambling, hydration and hydroxylation (Figure 22). Note that no sign of P-incorporation into the backbone of the chain was detected. All detected species except cycles suffered from side reactions at least at one end, which indicates that the loss of end-groups is a major issue that needs to be addressed in order to achieve high molar mass products.

Figure 22: End-groups as detected by MALDI-TOF mass spectrometry.
Figure 23: MALDI-TOF mass spectrum of the higher molar mass fraction I of polymer 40. The enlarged part shows all detected end-group patterns with an assignment.

Fraction II consists of cyclic oligomers with the hexamer being the smallest one (n = 6–25). According to the peak intensity of the mass spectrum the formation of smaller cycles is preferred (Figure 24). This can be intuitively understood with the lower probability for intramolecular chain-end collision when the chain length increases. Fraction II was further separated by preparative GPC with the intent to isolate the individual oligomers. Cycles (n = 6–14) could be separated but not fully isolated in pure form. The larger oligomers were contaminated with oligomers of similar ring size, due to the difference in hydrodynamic volume which gets smaller with larger ring size. The cyclic hexamer was the most abundant presumably due to its preferred formation caused by the least ring strain. This assumption is further supported by comparing the 1H-NMR spectra of the individual cycles. It is assumed that its planar conformation leads to intermolecular stacking which causes a downfield shift of the aromatic protons. The inner aromatic protons (H₆) of the cyclic hexamer experience a significantly stronger deshielding effect compared to the outer protons (H₈) (Figure 25). This
suggests that the macrocycle assumes a planar conformation. It should be noted that the meta connectivity of the macrocycles prevents ring currents through the entire cycle.\cite{124} With increasing ring size the deshielding effect for H$_a$ decreases, reaching a minimum at $n = 9$ whereas it increases asymptotically to the chemical shift of the open chains.

![MALDI-TOF mass spectrum](image)

**Figure 24:** MALDI-TOF mass spectrum of the lower molar mass fraction II showing only cyclic product.
Figure 25: $^1$H-NMR spectra of cyclic oligomers $40_{cyc}$ with $n = 6 - 14$ in CDCl$_3$.

3.5 Suppression of Cyclization and Other Side Reactions towards High Molar Mass

MALDI-TOF mass spectrometry gave evidence that one of the main reasons for the early halt of growth is ligand scrambling (Figure 14). Ligand scrambling is a side reaction that is enhanced with slow turnover catalysts. Therefore, an alternative catalyst system was considered. Buchwald reported that biphenyl phosphine ligands such as SPhos serve for high turnover catalysis.$^{[64]}$ Monomer 33 thus was subjected to SPC using a new catalyst system: Pd(dba)$_2$ (0.01 eq), SPhos (0.02 eq), NaHCO$_3$ (8 eq), in THF/water (3:1), 70 °C under N$_2$. The progress of the reaction was monitored by GPC and as expected the polymerization was
accelerated and completed within 24 h. The GPC elution curve shows the same bimodal characteristics with an open-chain peak ($P_H$) and a cycle peak ($P_L$) as with the previous reaction conditions (Figure 26). The position of $P_L$ remained at around 1.5 kDa, but the peak maximum of $P_H$ was remarkably shifted to much higher molar masses of about 40 kDa.

![Retention Volume (mL)](image)

Figure 26: GPC elution curves obtained from SPC with improved catalyst system: Pd(dba)$_2$ (0.01 eq), SPhos (0.02 eq), NaHCO$_3$ (8 eq) in THF-water (3:1).

Aside from ligand scrambling, hydration (protodeboronation) and hydroxylation are side reactions which presumably occur at the boron terminus. The inherent instability of the C-B bond towards the basic aqueous reaction conditions of SPC needed to be addressed. Due to the long reaction times during SPC the boronate esters are exposed to the adverse conditions for prolonged time. This needed to be counteracted; therefore, a monomer solution was added slowly over a period of 10 h to the reaction mixture. The effect of monomer slow addition on the distribution of cycles versus open chain polymer is striking. $P_L$ was strongly suppressed in relation to $P_H$ while keeping the maxima of both peaks at the same retention volumes.

These results indicate that slow addition suppresses cyclization of the chain and promotes linear chain extension. In order to gain further insight and to optimize the reaction conditions several different reaction parameters were tested.
3.6 Monomer Addition Rate

The effects of different monomer addition rates on molecular weight were also investigated. Polymerizations were conducted with the addition of 500 mg monomer 33 in THF (5 mL) over a period of 6.5 h (190 μmol/h), 10 h (120 μmol/h) and 66 h (20 μmol/h). Analysis by GPC reveals that the optimal addition rate is around 120 μmol/h (Table 4). If the addition was faster, a slight decrease of the open chain molecular weight was observed and significantly more cycles were obtained. At a slower addition rate the molecular weight was even more significantly decreased and the open chain peak PH suffers from strong tailing such that it overlaps completely with the cyclic peak PL (Figure 27).

Monomer addition speed is considered crucial for the present polymerization. The existence of an optimal monomer addition rate can be explained as follows. If the addition rate is too high an excess of monomer builds up in the reaction mixture which promotes chain-transfer to the monomer. Therefore, many short chains are formed which increases the probability of cyclization. In contrast, an addition rate which is slower than the reaction rate causes a shortage of monomer. Chain transfer is increased because the idle catalyst dissociates from the chain leading to chain-transfer and a very broad molecular weight distribution.

Table 4: Yields and molecular weights obtained by GPC calibrated against polystyrene standards at different addition rates. Obtained from GPC calibrated against polystyrene standards.

<table>
<thead>
<tr>
<th>Addition rate</th>
<th>Isolated Yield</th>
<th>M_n</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>[h]</td>
<td>[%]</td>
<td>[kDa]</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>88</td>
<td>20.1</td>
<td>1.59</td>
</tr>
<tr>
<td>10</td>
<td>86</td>
<td>21.2</td>
<td>1.83</td>
</tr>
<tr>
<td>66</td>
<td>85</td>
<td>14.0</td>
<td>1.76</td>
</tr>
</tbody>
</table>

It is reasonable to assume that continually increasing addition rates is shifting the ratio between open chain and cyclic product towards the cyclic product. The end-point of this process would be the situation of the batch reaction which equals a reaction with where all monomer is present in the reaction from the beginning.
The reaction temperature has a strong influence on reaction rates and product distribution. Polymerization reactions were performed at heating bath temperatures of 30 °C, 70 °C and 90 °C. At 30 °C the temperature was not high enough to dissolve all of the NaHCO₃. Since it is used in 8-fold excess and since a saturated solution at room temperature already contains more than one equivalent NaHCO₃ the solid NaHCO₃ was considered negligible. The reaction was monitored by submitting small aliquots to GPC. At 30 °C the reaction was considerably slowed down compared to the standard reaction temperature. It took 4 days until no further progress was monitored, whereas at 70 °C and above the reaction was finished after 20 h or less. Water and THF form an azeotrope with a boiling point of 64 °C.[125] Therefore the reaction at 90° C was done in a sealed reaction vessel.

The highest molecular weight was achieved at 70 °C with the highest ratio of \( P_H \) versus \( P_L \). At 90 °C more cyclic product was formed. Cyclization is an intramolecular reaction and as such entropically favorable over intermolecular chain extension. This corresponds with the significantly lower molecular weights of the open chain products. At lower temperature the open chain products suffered a slight decrease in molar mass but polydispersity was increased.

---

**Figure 27**: GPC elution curves of polymerizations with monomer addition over a) 6.5 h, b) 10 h and c) 66 h.
Table 5: Molecular weights after polymerizations at different temperatures. Obtained from GPC calibrated against polystyrene standards.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Yield [%]</th>
<th>$M_n$ [kDa]</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>77</td>
<td>20.4</td>
<td>2.23</td>
</tr>
<tr>
<td>70</td>
<td>86</td>
<td>21.0</td>
<td>1.74</td>
</tr>
<tr>
<td>90</td>
<td>84</td>
<td>16.4</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Figure 28: GPC elution curves of polymerizations performed at temperatures of a) 90 °C, b) 70 °C and c) 30 °C.

3.8 Catalyst Concentration

The results from the experiments with different addition rates suggest that the relative amount of monomer and catalyst concentration is crucial. It is generally desirable for SPC to reduce the metal loading as much as possible. Thus, a polymerization with 0.1 mol-% Pd relative to the monomer, ten times less the usual catalyst loading was set up. The product displayed the same molecular weights for the open chain and the cyclic fraction as with the 1 mol-% catalyst loading. However, the ratio was shifted towards the cyclic product. This is in
agreement with the previous observations at elevated addition rates. The monomer to Pd ratio is increased in both cases.

![Figure 29: GPC elution curves of polymerizations with a) 1 mol-% Pd and b) 0.1 mol-% Pd.](image)

### 3.9 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis method in which the change of weight of a specific sample is recorded as a function of increasing temperature (constant heating rate) or as a function of time (constant temperature). It provides information about physical and chemical processes such as vaporization, sublimation, oxidation and decomposition.

TGA of polymer 40 was done under a N₂ atmosphere with stepwise isothermal heating. The thermogram indicated a significant weight loss of 44 % after 170 °C (Figure 30). This can be attributed to the cleavage of the THP protecting group which accounts for 45 % of the repeat unit’s total mass. A second transition occurs at around 380 °C. The thermogram of the deprotected polymer 43 shows no substantial weight loss until 360 °C.
Figure 30: TGA thermograms of a) THP protected polymer 40 and b) deprotected polymer 43.

A thermostatic experiment at a temperature of 180 °C shows a weight loss of 43 % after 120 min (Figure 31). The colorless residue was insoluble in THF or chloroform and could only be slowly dissolved in DMSO. $^1$H-NMR spectroscopy of the residue confirms cleavage of the THP protecting group as can be seen in Figure 32.

Figure 31: TGA thermogram of THP protected polymer 40 with isothermal heating over 120 min.
Figure 32: $^1$H-NMR spectrum of polymer 43 obtained from polymer 40 by heating at 180 °C for 120 min. The THP side chain is completely cleaved.

The thermograms of butylated polymer 41 show rapid loss at a temperature above 275 °C (Figure 30). The first transition occurs between 275 and 360 °C and accounts for a weight loss of 42%, which is assumed to be due to the cleavage of the ether bond and elimination of the butoxy side-chain. Similar cleavage of ether bonds have been observed by Vahlenkamp and Wegner on alkoxy substituted PPPs. The butoxy side chains accounts for 45% of the repeat unit’s total mass. For polymer 42 carrying a dodecyl side-chain a similar behavior was observed with the onset of weight loss at 240 °C and 72% of the mass being lost, which also corresponds to the calculated value of 68% for a dodecyloxy side chain. Upon heating over 180 °C discoloration could be observed, presumably due to small amounts of impurities still present in the sample.

Reddinger and Reynolds have measured TGA of dodecyloxy-functionalized PMPs and observed similar decomposition behavior.
Figure 33: TGA thermograms of a) butylated polymer 41 and b) dodecylated polymer 42.

3.10 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the difference of energy that is required to increase the temperature of a sample and reference is measured as a function of temperature. In this study the DSC analysis of the synthesized polymers with different side-chains are presented in Figure 34. The thermograms show distinct side-chain dependent glass transitions which are listed in Table 6.

The large differences in $T_g$ are a direct effect of the different side-chains of the investigated polymers. The long and flexible dodecyl side chain creates a lot of free volume, therefore reducing the glass transition temperature drastically. On the other hand the THP group is more rigid and bulkier and leads to a higher $T_g$. For all polymers no other exothermic or endothermic processes could be observed.

Table 6: Glass transition temperatures $T_g$ for PMP with different side chains.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain</th>
<th>$M_w$ [kg/mol]</th>
<th>DP</th>
<th>$T_g$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-THP</td>
<td>44.0</td>
<td>124</td>
<td>49</td>
</tr>
<tr>
<td>41</td>
<td>$-C_4H_9$</td>
<td>31.0</td>
<td>129</td>
<td>25</td>
</tr>
<tr>
<td>42</td>
<td>$-C_{12}H_{25}$</td>
<td>48.2</td>
<td>94</td>
<td>-48</td>
</tr>
</tbody>
</table>
Figure 34: DSC thermogram of polymers 40, 41 and 42 with different side-chains revealing different glass transition temperatures.

3.11 Optical Spectroscopy Measurement

The photo-physical properties of conjugated polymers are of great interest. Blue emission has been observed for poly(phenylene vinylene),\textsuperscript{127} poly(alkylfluorene)\textsuperscript{128} and poly(p-phenylene).\textsuperscript{129} Such electroluminescence has found widespread use in polymer based LED-applications.\textsuperscript{130} Photoluminescence is a prerequisite of electroluminescence; therefore the measurement of photoluminescence is an easy process for the screening of potential electroluminescent light emitters. In contrast to the fully conjugated PPP, the conjugation length of PMP is interrupted with each meta-repeat unit, giving very discrete emitter centers.

Solution UV/Vis spectrometry of polymer 40 was measured in two different solvents, dichloromethane and THF (Figure 35a and Figure 35b). The absorption maximum $\lambda_{\text{max}}$ was measured at $\lambda = 255$ nm in both solvents. Note that measurements below $\lambda = 240$ nm were not possible for dichloromethane due to the strong UV absorption of the solvent. The absorbance at $\lambda_{\text{max}}$ of polymer 40 increased linearly for both solvents (Figure 35c).

PMP is only conjugated over two repeating units, which means that the absorption of 255 nm corresponds to the absorption maximum of biphenyl at 248 nm. Extending the conjugation
length by a phenylene unit, to give poly\((m-p\)-phenylene) increases the absorption maximum to 293 nm.\[^{131}\] The fully conjugated PPP has reported UV/Vis absorption maxima between 335 and 348 nm depending on the substituents.\[^{131-132}\]

**Figure 35:** UV/Vis spectra of polymer 40 dissolved in a) THF and b) dichloromethane measured at different concentrations. The concentration dependent absorbance at \(\lambda_{\text{max}} = 255\) nm is plotted for THF and for dichloromethane (c). \(T = 25^\circ\) C, path length \(l = 1\) cm.

### 3.12 Fluorescence Measurements

The fluorescence properties of polymer 40 in solution were measured. The excitation-emission plot in THF is shown in Figure 36a. For fluorescence measurement the sample was irradiated at 255 nm and the wavelength of maximum emission was found to be 348 nm with slight shoulders at 339 nm and 369 nm. The excitation spectrum was recorded at 348 nm. The majority of the fluorescent emission lies in the UV region and the faint blue emission, visible under a UV lamp is due to the tailing into the visible spectrum. This finding corresponds with
the results of Reddinger et al. who reported an emission maximum of 346 nm for alkoxy functionalized PMPs.\[^{26}\]

The fluorescence emission was recorded at different concentrations. The signal intensity decreased proportionally with the concentration and no change of peak maximum or shape was observed (Figure 36b and Figure 36c). This is an indicator that no self-absorption takes place. A Stoke shift of 8718 cm\(^{-1}\) was observed.

![Fluorescence excitation-emission spectrum of polymer 40 in THF](image)

**Figure 36:** Fluorescence excitation-emission spectrum of polymer 40 in THF (a). The emission spectrum was recorded with an excitation wavelength of \(\lambda = 255\) nm and the excitation spectrum at a wavelength of \(\lambda = 348\) nm. The emission spectrum was recorded at different concentrations (b). The intensity of the emission maximum decreased linearly with concentration (c).

### 3.13 Mechanistic Investigations

Having established the conditions under which high molar mass linear polymers with reduced amounts of cyclic byproduct can be synthesized reproducibly, the SPC was investigated from...
a mechanistic point of view. It is widely accepted that SPC of an AA/BB monomer follows a step-growth mechanism. This means that the bi-functional monomers first form dimers, then trimers, longer oligomers and finally polymers with a long chain. For the AB approach this has also been the widely believed mechanism until 2004, when McCullough and Yokozawa both independently reported the Ni-catalyzed synthesis of poly(3-hexylthiophene) (P3HT) by a chain-growth mechanism.\[133-134\] The proposed mechanism of the polymerization involves a \( \text{Ni}^0 \)-arene \( \pi \)-complex as the key intermediate, which is generated after reductive elimination.\[135-137\] Subsequently, indicators for a similar chain-growth mechanism of SPC with AB-monomers were observed.\[138\] Chain-growth polymerization of conjugated polymers by SPC offers some distinct advantages over step-growth polymerization such as controlled molecular weights, narrow molecular weight distribution and defined microstructures (e.g. end-group control).\[139\] Whereas methods exist for controlled Ni-catalyzed polymerization in solution\[140-142\] as well as on surfaces,\[143-145\] there is very limited knowledge about the circumstances under which SPC follows a step-growth mechanism. In 2010 Yokozawa and coworkers reported the synthesis of block copolymers from AB-monomers by SPC.\[146\]

A SPC with slow addition of the THP protected monomer 33 was set up and small samples of the reaction mixture were taken at regular intervals, precipitated into methanol-water, freeze-dried and subjected to GPC analyses. It was observed that \( \text{P}_1 \) appeared at around 40 kDa from a very early stage of the polymerization on, when the conversion was still very low.

If one assumes SPC to follow a step-growth mechanism, like other polycondensations, then a significant decrease of molar mass of the products should be observed, if the mole ratio between the two functional groups A and B is misbalanced. Because monomer 33 is an AB-type monomer with built-in 1:1 ratio (see 1.1), monofunctional products were externally added to disturb the stoichiometry on purpose.

\[
\begin{align*}
\text{F} & \quad \text{Br} \\
\begin{array}{c}
44 \\
45
\end{array}
\end{align*}
\]

\textbf{Figure 37}: Structure of monofunctional 4-fluorophenyl bromide (44) and 4-fluorophenyl boronic acid (45).

After slow addition of 10% of the monomer solution an excess amount of either bromide 44 or boronic acid 45 was added, and thereafter the monomer addition was continued to completion. Time profiles of the two reactions were monitored by GPC (Figure 38). The
addition of a large excess of 44 did not seem to disturb the SPC significantly and afforded only slightly decreased molecular weights after 18h ($M_n$ around 20 kDa). In contrast, the addition of one equivalent of 45 caused SPC to come to an immediate halt giving only short oligomeric product ($M_n < 1$ kDa). These results are in clear contradiction to the Carothers equation and support a chain-growth-like mechanism, where the chain extension is occurring at the bromo terminus because capping it with 45 stops the polymerization, whereas capping of the boron terminus with 44 does not hinder chain extension.

![Figure 38: GPC elution curves of SPCs with 33 and monofunctional compounds 44 and 45. After slow addition of 10% of the monomer over 1h, either 44 (5 eq) or 45 (1 eq) was added and then monomer addition was continued.](image)

### 3.14 Initiated Polymerization

To gain further evidence of the chain-growth mechanism the following end-capping experiment was designed. 4-Fluorobromobenzene (44) (0.25 eq) was added to the catalyst mixture before slowly adding monomer 33 (Scheme 17). The GPC elution curve of the resulting products shows a decrease of the overall molecular weight ($M_n = 18$ kDa) and complete absence of cyclic product ($P_L$) compared to the SPC without 44 (Figure 39). Additionally, analysis by MALDI-TOF MS shows two signal series both having a fluorophenyl group as one of the end-groups. The dominating series is terminated with dicyclohexyl phosphine, suggesting P-incorporation; the minor series is terminated by ligand
scrambling and carries a cyclohexyl end-group. This proves that most of the polymer chains have reacted with 44 at their boron terminus while the bromo terminus underwent ligand scrambling (Figure 40).

**Figure 39:** GPC elution curves obtained from SPCs (a) without the presence of 44 prior to the slow addition of monomer 33 and (b) in the presence of it.

This result suggests that the chain growth is initiated with 44 and terminated by ligand scrambling. Both the suppression of cyclization and the decreased average molar masses observed by GPC can be easily explained by the end-capped boron terminus which prevents both cyclization and chain-chain coupling. Once initiated, the chain can only grow at the bromo terminus by addition of monomers, which are the only species present carrying boron functionalities. Slow addition of the monomer is still necessary with initiated SPC, because if monomer was added at once, significant formation of cycles ($P_L$) and a slight shift of $P_H$ to higher molar mass were observed (Figure 41). This is an indicator that initiation of polymerization with 44 only works with low monomer concentration relative to the initiator; otherwise the monomer itself can also act as an initiator.
**Scheme 17:** SPC using initiator 44 and subsequent slow addition of monomer 33.

![MALDI-TOF mass spectrum](image)

**Figure 40:** MALDI-TOF mass spectrum from SPC using initiator 44 (0.25.eq) and subsequent slow addition of monomer 33.

![GPC elution curves](image)

**Figure 41:** GPC elution curves of obtained from SPCs using initiator 44 and addition of monomer 33 in one batch or slowly over 10h.

Ni-catalyzed polymerizations of Grignard-type AB monomers by Tamao-Kumada coupling reactions have been reported to proceed in a chain-growth manner.\(^{133}\) The nickel catalyst is
intramolecularly transferred and is active at the end of the growing chain.\textsuperscript{[135]} Yokozawa and coworkers have previously proposed a similar mechanism for SPC for the synthesis of polyfluorenes and poly($p$-phenylene)s using AB monomers.\textsuperscript{[138, 146]} The palladium catalyst migrates after oxidative addition towards the bromo terminus. This accounts for the present SPC mechanism as shown in Scheme 18.

Scheme 18: The present SPC can be explained by the “catalyst-transfer” mechanism for SPC as proposed by Yokozawa \textit{et al}.

### 3.15 Initiator Concentration

The concentration of the initiator 44 at the beginning of the polymerization has a direct influence on the molecular weight of the product polymer. SPC with slow addition of monomer 33 to reaction mixtures with different initiator concentrations were performed. The molecular weight of the polymer plotted against the feed ratio of monomer 33 to initiator 44 shows a proportional increase while the polydispersity remains narrow (Figure 42). This implies that the polymerization proceeds through a living chain-growth mechanism. However, a monomer vs. initiator ratio of 10 would then give a molecular weight of 1900 g/mol instead of 35000 g/mol.
Figure 42: Plot of molecular weight $M_n$ and polydispersity $M_w/M_n$ against the feed ratio of monomer 33 and initiator 44.

3.16 Di-Endfunctionalized Polymers

The MALDI-TOF mass spectrum of initiated polymer 46 showed that the polymer chain carry end-groups that derive from the ligand scrambling side-reaction. It is assumed that the termination reaction caused by ligand scrambling is a slow reaction compared to polymer propagation. This means that the active bromo termini are still active right after completion of monomer addition. Therefore, the active chain-end could still react with an end-capping reagent to furnish an endfunctionalized polymer.

To end-cap the initiated polymer, 4-methoxyphenylboronic pinacolate (47) was added right after monomer addition was completed (Scheme 19). GPC analysis showed no change of the elution curve before and after 47 (1 eq) was added. The MALDI-TOF mass spectrum clearly showed that the resulting products indeed were largely end-capped at the bromo terminus. This shows that chain growth was initiated from 44 and terminated by 47 proving that SPC with efficient end-functionalization with different functional moieties at both the bromo and boron termini is possible.
Scheme 19: SPC of di-end-functionalized polymer with slow addition of monomer 33 using initiator 44, and terminator 47.

Figure 43: MALDI-TOF mass spectrum from SPC with slow addition of monomer 33. Monofunctional compounds 44 (0.25 eq) and 47 (1 eq) were added before and after the monomer addition.

3.17 Investigation of Chain Directionality

Side reactions such as ligand scrambling, hydration or hydroxylation can in principle occur on either bromo or boron terminus. To assign the original chemical structure of the chain termini is therefore often difficult once they have suffered from such side reactions. Using the
presently developed end-capping protocol, the original bromo and boron end groups can be distinguished by selectively converting them with bromide 44 and boronic ester 47 respectively. With this tool, one can investigate directly whether the chain directionality is retained, as it is expected from the AB monomer structure used for SPC.

Figure 44: MALDI-TOF mass spectra of end-capped SPC using a) 1 mol-% Pd(dba)$_2$, b) 1 mol-% Pd(OAc)$_2$ and c) 10 mol-% Pd(OAc)$_2$.

Moore and coworkers reported the synthesis of a hyperbranched PMP using a catalyst system composed of Pd(OAc)$_2$ and SPhos.\textsuperscript{[147]} The catalyst systems seemed to be very active as it yielded high molecular weight product within minutes at room temperature and 0 °C. The same conditions were also applied to the present SPC using monomer 33 and produced high molecular weight product within hours at room temperature in 91% yield. Analyzing the end-capped polymers synthesized with Pd(OAc)$_2$ / SPhos by MALDI-TOF MS, one can clearly assign signals to chains which originally were terminated with two bromides. The signals became significantly enlarged when the amount of Pd(OAc)$_2$ was increased. A rough estimation based on the MS signal intensity suggests a bi-directionality of 1% when using 1%
Pd(OAc)$_2$ and increases tenfold when 10% catalyst were used. This is in contrast to the polymers prepared with Pd(dba)$_2$ / SPhos, which largely retain their chain directionality. The occurrence of dibromo terminated species is a clear indicator of homocoupling reactions of boron termini, which can happen when Pd(II) is reduced to Pd(0). The small amount of homocoupling present with Pd(dba)$_2$ presumably occurred from oxygen invasion which generated Pd(II).

Homocoupling leads to a bifunctional initiator from which the chain can grow in two directions, thus giving a longer chain. This is supported by GPC data which gives a higher molecular weight for the SPC with Pd(OAc)$_2$ ($M_w = 57$ kDa) compared to Pd(dba)$_2$ ($M_w = 44$ kDa) (Figure 45).

![Figure 45: GPC elution curves obtained from SPC using a) Pd(OAc)$_2$ / SPhos and b) Pd(dba)$_2$ / SPhos.](image)

### 3.18 Conclusions

A large scale synthesis for AB-monomers was established. The synthesis is very versatile and allows a great degree of flexibility concerning different side chains and boronic esters. Monomers with different side chains and boronic acid derivatives were synthesized and subjected to SPC. Bimodal molecular weight distributions were observed for all monomers and reaction conditions. The THP protected PMP is very well suited for MALDI-TOF MS analysis and after fractionation, the structural analysis by MS revealed a series of side
reactions namely, cyclization, ligand scrambling and deboronation and dehalogenation. Cyclization in particular seems to have the largest negative effect on molecular weight. The use of bases which are more soluble in organic solvents such as Bu$_4$NOH can promote open chain growth. Further investigation of the cyclic fraction could provide insights into the conformational structure of such macrocycles and their bulk properties such as viscosity compared to open cyclic chains.

TGA analysis demonstrated that the THP protecting group can be thermally cleaved. The alkylated polymers are thermally stable until 280 °C but suffer from discoloration upon heating over 180 °C. DSC of the polymers showed glass transition temperatures $T_g$ between -48 and 50 °C depending on the side chains. Polymers 41 and 43 could be cast into films by the solvent evaporation technique. However, the obtained films were too brittle to be tested for mechanical properties.

The SPhos ligand together with Pd(dba)$_2$ is a very efficient catalyst which significantly increased the molecular weight of the SPC products from 10 to 40 kDa. The amount of cyclic byproduct was reduced by slow addition of the monomer. The use of a monofunctional initiator completely suppressed the formation of cycles and proved that the SPC does not follow a classical step-growth mechanism as expected from a polycondensation reaction but rather a chain-growth-like mechanism. End-capping of the polymer chain after SPC gave a di-endfunctionalized PMP. The quantitative formation of these PMP was confirmed by MALDI-TOF MS. By using this end-capping method it was further confirmed that the use of Pd(II) catalyst precursors leads to homocoupling of monomer at the boron terminus leading to a loss of chain directionality.
4 Block Copolymerization

The feasibility of capping the chain ends with a monofunctional compound proved that the chain ends are still active after polymerization. This led to the question whether it was possible to replace the end-capping reagent with another monomer to continue polymerization leading to block copolymers.

4.1 Sequential Polymerization

Using initiator 44, monomer 33 was slowly added to the reaction mixture over a period of 3.3 h. After completion of the first monomer addition a solution of the second monomer 36 was added over 2.5 h. The reaction was then quenched with 47 (Scheme 20) to obtain block copolymer 49. The entire reaction was monitored by taking samples for GPC measurement out of the reaction mixture and freeze-drying them (Figure 47). Due to the overlapping peaks, especially in the beginning of the reaction (Figure 46), an accurate determination of $M_w$ and $M_n$ was difficult and therefore the peak molecular weight $M_p$ was measured.

![Scheme 20: Sequential polymerization using THP protected monomer 33 and butylated monomer 36.](image)

One can see a monotonous increase of $M_p$ until the end of the addition of the first monomer. Once the addition was finished there was no further increase of $M_p$. However, if it was followed by adding another monomer, the molecular weight continued to increase with a decreased rate. The order of monomer addition can be reversed by adding butylated monomer 36 first, and THP protected monomer 33 second (Scheme 21).
Figure 46: Overlay of GPC elugrams for the sequential polymerization of polymer 49.

Figure 47: Plot of $M_p$ versus time. The first monomer 33 was added over 200 min after which the addition was stopped (red circles) or continued with the second monomer 36 over another 200 min (black squares).
Scheme 21: Sequential polymerization using butylated monomer 36 and THP protected monomer 33.

Figure 48: Plot of $M_p$ versus time. Monomer 36 was added until 200 min after which the addition was stopped (red circles) or continued with monomer 33 until 400 min (black squares).

4.2 Structural Analysis

Structural analysis of block copolymers is difficult, especially if the block copolymers are possibly contaminated by homopolymers. The obtained product was thus first subjected to acidic hydrolytic conditions to cleave the THP protecting groups. The deprotected polymer
with its benzyl alcohol side chains exhibited very poor solubility in apolar organic solvents. Only very polar aprotic solvents such as DMF or dimethyl sulfoxide (DMSO) were suitable.

Once deprotected, the polymer was subjected to Soxhlet-extraction. Extraction with chloroform separated the apolar butylated homopolymer followed by extraction with cold N,N-dimethylformamide (DMF) to separate the polar benzyl alcohol homopolymer. The remaining residue was dissolved in boiling DMF and since it was not fully soluble in DMSO it was acetylated with acetic anhydride to increase solubility in chloroform. Each fraction was analyzed by $^1$H-NMR. The spectra show that in the chloroform and DMF fraction aside from solvent impurities only the homopolymers are contained.

![Figure 49: $^1$H-NMR spectra of individual fractions after Soxhlet extraction. a) DMF soluble fraction in $d_6$-DMSO, b) chloroform soluble fraction in CDCl$_3$ and c) acetylated remaining fraction in CDCl$_3$. Impurities: (#) toluenesulfonic acid, (*) DMF, (+) H$_2$O.](image)

Analysis of the individual fractions by MALDI-TOF MS supported the assumed structures of the chloroform and DMF fractions. The mass spectrum of the acetylated fraction indicated that still some homopolymer was present. However, signals could be assigned to polymers that contain the initiator and both repeating units (Figure 50).
Figure 50: MALDI-TOF mass spectrum of the acetylated fraction after extraction with chloroform and DMF. The arrows indicate signals that correspond to block copolymers.

In a second experiment, instead of acylation, the deprotected benzylic alcohols were reprotected with THP after extraction with chloroform and DMF (Scheme 22). The same was done with the DMF soluble homopolymer. This was advantageous because it was known that the THP group contributed to the good ionization of the polymer. The GPC elution curves of the individual fractions could also be compared after reprotection, showing monomodal distributions (Figure 51). The determined molar masses were $M_n = 11$ kDa before deprotection and $M_n = 12$ kDa for the reprotected extracted fraction.
Scheme 22: Separation of the contaminating homopolymer and re-protection with THP.

Figure 51: GPC elution curves of the crude product after sequential polymerization (a), the chloroform soluble part (b), the DMF soluble part after re-protection with THP (c), the remaining fraction after re-protection with THP (d).
The MALDI-TOF MS of the last fraction shows that still a major part is remaining homopolymer (Figure 52). However, the minor peaks can be nicely attributed to structures containing both the butylated and the THP-protected repeating unit. It is possible to find for every combination of block-length a corresponding peak in the spectrum.

**Figure 52:** a) MALDI-TOF mass spectrum of reprotected fraction after chloroform and DMF extraction. The arrows indicate signals that correspond to an exemplary series of blockcopolymers. b) Measured (black) and calculated (red) isotope pattern for n = 10, m = 3. c) Measured (black) and calculated (red) isotope pattern for n = 11, m = 3
4.3 Conclusions

The results in this chapter support the view that SPC of AB-type monomers does not follow the classical step-growth like mechanism. The linear increase of the molecular weight rather supports a chain-growth mechanism. The fact that the molecular weight increases after addition of a second monomer proves that the growing chain remains active after monomer addition has stopped. The optimal sequence of monomer addition relative to their reactivity still needs to be determined. The control of the polymerization is still insufficient as can be seen by the significant amounts of homopolymers that are formed. Partial removal of these components is possible and the molecular weight average obtained is $M_n = 12$ kDa. It is expected that lower reaction temperatures prevent chain transfer and therefore homopolymerization, but they also lower reaction rates and give rise to other side reactions. A more reactive catalyst system still needs to be found. Nevertheless there is unambiguous proof of the block copolymer structure by MALDI-TOF mass spectrometry.
5 Endfunctionalization with Terpyridinyl Units

Polymers combining the features of repeating units that are conventionally linked by covalent bonds with those that are linked by bisterpyridine metal-complexes are getting increased interest in recent years. Such supramolecular polymer architectures are characterized by the reversibility of the terpyridine-metal complex, which can be tuned by changing the metal ion.\cite{148} This property is essential for the development of smart and switchable materials such as smart glues and self-repairing coatings.\cite{149-150} The synthesis of the supramolecular block copolymers based on PMP was done along the same procedures as described in chapter 3.15. Three different approaches are possible: 1) Initiation of the polymerization from a compound containing a terpyridinyl unit and an arylbromide (51), 2) termination of the polymerization with a compound containing a terpyridinyl unit and an arylboronic acid (52) and 3) both. Approaches 1) and 2) give polymers 53 and 54 with controlled functional end groups (telomers), approach 3) gives a macromonomer 55, ready to form a metallo-polymer.

![Figure 53](image)

**Figure 53:** Terpyridine carrying initiator 51 and terminator 52 used to synthesize terpyridine functionalized polymers 53, 54 and 55.
5.1 Synthesis of Polymers Carrying a Terpyridine Unit

Syntheses of 4'-substituted 2,2':6,2'' terpyridine derivatives are well known in literature and are traditionally done by ring condensation reactions or, more recently, by transition metal mediated cross coupling procedures.\[151]\ Due to the simplicity of the central ring assembly approach, in the present work, a modified Kröhnke reaction was used by treating 2 equivalents of 2-acetylpyridine (56) with 4-bromobenzaldehyde (57) and aqueous ammonia under basic conditions to afford initiator 51 (Scheme 23).\[152-153]\ Substitution of the phenylbromide with pinacol boronic ester by Miyaura borylation reaction using bis(pinacolato)diboron (58) afforded terminator 52 (Scheme 24).

Scheme 23: Synthesis of initiator 51 by modified Kröhnke reaction from 2-acetylpyridine (56) and 4-bromobenzaldehyde (57).

Scheme 24: Synthesis of terminator 52 by Miyaura borylation reaction.

According to the established procedure, 0.25 equivalents of 51 were added to the catalyst solution before slowly adding monomer 33 over 3 h (Scheme 25). The polymerization was quenched with the addition of one equivalent of terminator 52. The reaction mixture was worked up by stirring with an aqueous NaCN solution and washing with water. GPC analysis of the crude product before work-up revealed a large amount of methoxy biphenylyl terpyridine (59). This cross-coupling product of the polymerization initiator 51 and terminator

Figure 54: MALDI-TOF mass spectrum of terpyridine-functionalized polymer 30. The H / PCy₂ series derives from uninitiated, “wild” polymerization.
47 needed to be effectively removed as it disturbs the ligand stoichiometry of the subsequent metal-complexation. Separation was done by fractional precipitation and preparative GPC. Analysis of the obtained polymer by MALDI-TOF mass spectrometry revealed that the polymer chains were only partially initiated from the terpyridine initiator and a significant amount of uncontrolled polymerization has occurred (Figure 54). The terpyridinyl substituent of initiator 51 is much less electron withdrawing compared to 4-bromofluoro benzene and oxidative addition is therefore much slower.

To circumvent the problem of incomplete initiation of polymerization, the terpyridine ligand was introduced after polymerization as a terminator (Scheme 26). Thus, after polymerization, the terminator 52 was added in an excess amount, enhancing the end-capping yield. Purification of the polymer by preparative GPC gave the terpyridine end-capped polymer 54.

Scheme 26: Synthesis of terpyridine functionalized polymer 33 using terminator 52.

The end-capped polymer was analyzed by MALDI-TOF MS and indicated that, though low in intensity, only peaks corresponding to the end-capped species were present (Figure 55). This result proved that near quantitative end-capping with terpyridine derived terminators is possible.
Endfunctionalization with Terpyridinyl Units

5.2 Supramolecular Polymers Containing Metal Bis-Terpyridine Complexes

Metal bis-terpyridine complexes $[\text{M(tpy)}_2]^{2+}$ form via their corresponding mono-complex $[\text{M(tpy)}]^2+$. The binding strength of the metal ion to the ligand have a great influence on the equilibrium constant. The stability of the mono and the bis-complex can be described as follows:\[154\]

$$
\text{M} + \text{tpy} \leftrightarrow \text{M(tpy)} \quad \text{therefore} \quad K_1 = \frac{[\text{M(tpy)}]}{[\text{M}][\text{tpy}]}
$$

$$
\text{M(tpy)} + \text{tpy} \leftrightarrow \text{M(tpy)}_2 \quad \text{therefore} \quad K_2 = \frac{[\text{M(tpy)}_2]}{[\text{M(tpy)}][\text{tpy}]} = \frac{[\text{M(tpy)}_2]}{K_1[M][\text{tpy}]^2}
$$

$[\text{M}]$, $[\text{tpy}]$, $[\text{M(tpy)}]$ and $[\text{M(tpy)}_2]$ correspond to the equilibrium constants of the metal, ligand mono, and bis-complex, respectively.

The Fe$^{2+}$ ion has a good binding strength with terpyridine (log $K_1 = 7.1$, log $K_2 = 13.8$ in water)\[155\] and was selected because of the strong metal-to-ligand-charge-transfer (MLCT) absorption in the range of 580 nm which makes monitoring of the complexation reaction simple. A solution of polymer 54 with a molecular weight of $M_n = 18.4$ kDa in THF (0.01 mM) was titrated with a THF solution of Fe(BF$_4$)$_2$ (0.052 mM) and the UV/Vis spectrum was
recorded. From the spectra shown in Figure 56 one can see the increase of the absorption at λ = 575 nm which is characteristic for the [Fe(tpy)₂]²⁺ complex. The absorbance increases linearly until saturation is reached at 80 μl which corresponds to 0.5 equivalents of Fe(II). It is important to note that the absorbance does not decrease if more than 0.5 equivalents are added. This means that the bis-complex remains stable even if an excess of Fe(II) is added.

Figure 56: a) UV/Vis spectrum of terpyridine-functionalized polymer 54 in CHCl₃ titrated with Fe(BF₄)₂ in THF. b) Absorption of terpyridine-functionalized polymer 54 at absorption maximum of 575 nm.

GPC measurement of the metallo-supramolecular Fe(II) bis-terpyridine PMP showed no increase of molecular weight. It is assumed that breakage of the complex occurred due to shear forces and interaction with the column material. Schubert and coworkers have done extensive studies on the behavior of ruthenium bis-terpyridine containing poly(ethylene oxide) in GPC.¹⁵⁶-¹⁵⁷ Because of this observation it was decided to use Ni(II) which has higher equilibrium constants for complex formation (log K₁ = 10.7 and log K₂ = 11.1 in water).¹⁵⁵ Because the second equilibrium constant K₂ is slightly higher than K₁ it was assumed that the equilibrium is still shifted entirely to the bis-complexed form.

A solution of polymer 54 in THF was treated with a methanolic solution of 0.5 equivalents Ni(OAc)₂ and heated to reflux for 14 h. After ion exchange with NH₄PF₆ a colorless solid was obtained. The UV/Vis spectrum confirmed complex formation, characterized by the absorption band at at λ = 343 nm (Figure 56). GPC measurement of the bis-complex showed a shift to lower retention times and thus an increase of molecular weight to Mₙ = 39.0 kDa (Figure 58).
Endfunctionalization with Terpyridinyl Units

Figure 57: UV/Vis spectrum of polymer 54 before and after complexation with Ni(II).

Figure 58: GPC elution curves of terpyridine end-capped monomer 54 a) before complexation (Mn = 18.4 kDa),
b) after complexation with Ni(OAc)$_2$ (Mn = 39.0 kDa) and c) after decomplexation with HEEDTA (Mn = 19.2 kDa).

One of the main reasons for the interest in supramolecular polymers lies in the reversibility of their connecting interactions.$^{158}$ Terpyridine containing polymers can form complexes with transition metal ions which can be decomplexed if the metal ion is offered a stronger ligand. In order to study the reversibility of complex formation the Ni(II) bis-terpyridine containing PMP, 54 was treated with hydroxyethyl ethylenediaminetriacetic acid (HEEDTA) which is a
strong chelating ligand for transition metals and can even break Ru(II) bis-terpyridine complexes. A solution of polymer 54 in chloroform was stirred with aqueous HEEDTA and subsequently washed with water. UV/Vis spectroscopy showed that the Ni(II) complex was completely dissociated. Measurement by GPC confirmed that the completely uncomplexed polymer with a molecular weight of $M_n = 19.2$ kDa was obtained (Figure 58).

5.3 Conclusions

Conjugated metallopolymers exhibit very interesting photophysical and electrochemical properties, due to the possibility of charge carrier formation. The reversible redox processes of the metal or ligands are beneficial for applications in OLED or polymer solar cells. Additionally the characteristic MLCT transition of some metallopolymers extends the materials absorption range.

Quantitative end-capping of PMPs allows introduction of functionality at the polymer chain-end. With terpyridine end-functionalized PMP it is thus possible to obtain supramolecular polymers by metal ion complexation. Functionalization of both chain-ends of the PMP is desirable in order to achieve a metallo-supramolecular polymer with metal-terpyridine complexes in the backbone. However, the terpyridine containing initiator needs to be improved in reactivity to achieve quantitative polymer initiation.

Different metal cations can be used according to the desired strength and reversibility of the resulting metal-terpyridine complex. Complex formation was observed by UV/Vis spectroscopy. The Fe(II) complex could not be analyzed by GPC, since the complex dissociated on the column, presumably due to high shear forces. The Ni(II) complex however, was stable enough to elute as a peak at twice the molecular weight as the starting polymer. The complex formation is reversible and upon addition of a stronger ligand such as HEEDTA, the metal bis-terpyridine complex can be decomplexed.
6 Preliminary Investigations of Secondary Structure Formation of PMPs

6.1 Foldamers

In biology only three basic polymeric structures exist: proteins, ribonucleic acids and polysaccharides. Many of the functions carried out by these biomacromolecules such as molecular recognition, information storage and catalysis derive from their structurally stable and yet soluble “shape”. This “shape” is defined by the more or less fixed conformation of the backbone polymer which deviates only little from its equilibrium coordinates. In order to understand how biomacromolecules function and to obtain synthetic macromolecules with new functions one must study the formation of secondary structure of synthetic polymers.

A foldamer is an oligomer which assumes a conformationally ordered state that is stabilized by non-covalent interactions. Many driving forces, often in combination, have been utilized to achieve folding of polymers such as hydrogen bonding, steric interaction, metal-coordination, aromatic stacking and solvophobic interaction. Kinked aromatic polymers are ideal candidates for foldamers stabilized by aromatic stacking and solvophobic effects. Poly(meta-phenylene ethynylene) (PMPE) (Figure 60) can collapse into foldamers when the CHCl$_3$/MeCN mixture is polar enough to promote solvophobic interaction. PMP with attached optically active oligo(ethylene oxide) side chains can be dissolved in CHCl$_3$ and upon addition of methanol form a chiral helix as indicated by circular dichroism (CD) spectroscopy and NMR.

![Figure 59: A space filling model of a poly(m-phenylene) with 15 repeating units. Molecular mechanics calculation using a MM2 force field.](image-url)
6.2 Deprotected PMP for Foldamer Formation

Upon acidic hydrolysis of the THP protecting group of polymer 40 the benzylic alcohols of 43 act as a hydrophilic shell for the aromatic backbone of the PMP. It is assumed that in a polar environment the backbone assumes a helical conformation due to the solvophobic effect.

The deprotected polymer 43 is soluble only in very polar aprotic solvents such as N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Dynamic light scattering (DLS) measurements of a 0.5 mg/ml solution in pure DMF revealed a negligible amount of very small particles indicating full dissolution of the polymer. Upon addition of water, formation of particles with sizes between 10 to 30 nm occurred. At water contents of above 10 vol% much larger particles in the micrometer range formed, until precipitation could be visibly observed at water contents above 30 vol%.

The conformational structure of polymer 43 in a DMF-d7/D2O mixed solvent system was investigated by 1H-NMR spectroscopy. A solution of 43 in DMF-d7 (0.67 mg/mL) was titrated with D2O and the chemical shifts of the aromatic protons were recorded. The addition of D2O produced a downfield shift of the aromatic signals of 43 until around 12 vol% D2O (Figure 62). Upon further addition of D2O the signals shifted upfield until the polymer starts to precipitate at around 30 vol%. Yashima et al. reported similar behavior of PMP carrying
Preliminary Investigations of Secondary Structure Formation of PMPs

optically active side chains.\textsuperscript{162} The downfield shift can be rationalized with the increased deshielding effect of the aromatic units being stacked in a helix conformation.

Further insights could be gained by UV/Vis spectroscopy because the aromatic stacking interactions produce a bathochromic shift. However, the absorption of the polymer is entirely superimposed by the UV absorption of the solvent. Unfortunately, no alternatives to DMF and DMSO could be found.

![Chemical shifts of aromatic protons of polymer 43 in DMF-d7 titrated with D2O.](image)

**Figure 62:** Chemical shifts of aromatic protons of polymer 43 in DMF-d7 titrated with D2O.

![Volume distribution plot of H2O titration measured by DLS.](image)

**Figure 63:** Volume distribution plot of H2O titration measured by DLS.
6.3 Conclusions

The presented data gives only circumstantial evidence for foldamer formation of PMP. However the results correspond well with previously reported work. Similar changes of chemical shifts were observed for oligo($m$-phenylene)s carrying chiral side chains and for oligoresorcinols.\(^{[162-163]}\) Further experiments to determine the structure of PMP in solvents with varying polarity are necessary. In order to get deeper insight into the conformation of the polymer backbone of PMP, NMR exploiting the Nuclear-Overhauser-Effect (NOE) can be measured. A helical secondary structure of the PMP requires a \textit{cis} arrangement of all phenylene units. In a \textit{trans} arrangement the protons $H^1$ and $H^2$ are located closely together within 4.6 Å, whereas in the \textit{cis} case the proton in a distance of 8.4 Å (Figure 64). Since the NOE effect is measurable within a distance of approximately 5.5 Å, the \textit{cis} conformation gives an observable NOE signal whereas in the \textit{trans} case there is none.

The ability to selectively introduce end-groups allows helicity induction from the chain-end.\(^{[164]}\) By end-capping with a chiral terminator, one-handed helix formation can be promoted which then can be measured by circular dichroism (CD) spectroscopy.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure64.png}
\caption{NOE interactions depending on \textit{cis} or \textit{trans} conformation of the PMP backbone.}
\end{figure}
7 Conclusions and Outlook

7.1 Summary and Conclusions

In this thesis the synthesis of high molecular weight poly(m-phenylene) by SPC from an AB-type monomer was studied. It was expected that the all-meta structure greatly improves the solubility of the obtained polymer. The AB approach was selected to achieve a high reproducibility.

A simple synthetic route to an AB monomer which offers great flexibility concerning side chains and allows a multi-gram scale was established. The THP protecting group was selected as a side chain because it can be deprotected after polymerization and allows for post-polymerization modification.

In a first phase, SPC was performed with Pd[P(p-tolyl)₃]₃ as catalyst. Only low molar mass polymer was obtained. Fractionation and analysis of the individual fractions by NMR and MALDI-TOF MS revealed the side reactions that were preventing chain growth: cyclization, ligand scrambling and loss of functional groups.

In order to overcome these limiting side reactions, the Pd(dba)₂ / SPhos catalyst system was used. This highly reactive catalyst could greatly decrease the amount of ligand scrambling and high molar mass polymer with $M_p = 40$ kDa was obtained. Cyclization could be significantly reduced with slow addition of the monomer.

Mechanistic insights were gained when monofunctional compounds with only one bromide or boronic acid functional group were added to the SPC. The reaction only continued in the bromide case whereas chain growth came to an immediate halt when additional boronic acid was added. From this, it was concluded that SPC of AB-type monomers does not follow the classical step-growth mechanism, but that the polymerization is more of a chain-growth nature.

In order to completely suppress cyclization, the polymerization was initiated from a monofunctional compound. In a second step the growing polymer chain was end-capped with a monofunctional terminator. MALDI-TOF MS proved that di-end functionalized polymers could be quantitatively obtained.
By sequential polymerization with two different monomers, block-copolymers could be synthesized. The control over the polymerization is still insufficient as the product still contained homopolymers that were difficult to remove completely.

With a terpyridine carrying terminator a PMP could be synthesized that is able to form a supramolecular metallopolymer by forming a metal-bisterpyridine complex. The complex formation with Fe$^{2+}$ was observed with UV/Vis spectroscopy, the complex however, was not stable enough to be measured by GPC. The more stable Ni$^{2+}$ complex formed a metallopolymer with a molecular weight increased by a factor of two respective to the precursor. The complex formation is reversible as was shown by decomplexation with HEEDTA.

Many results show that SPC of AB-monomers follows a chain-growth mechanism. However, further investigation is necessary. This allows for the possibility to control the molecular weight, polydispersity, and end-group of polyarylenes. The ability to synthesize \( \pi \)-conjugated block copolymers allows to combine two distinct semiconductors with different charge transport properties and energy bandgaps. This greatly enhances the performance of organic photovoltaics or light emitting devices due to self-assembly into regular nanostructures.\[165\]

### 7.2 Outlook

Possible future working areas are outlined in the following:

- Better control of the polymerization reaction. Improving control results in less chain-transfer. This can be achieved by finding even more reactive catalyst systems that allow reactions at lower temperature without extending reaction times. One might also consider a monomer carrying the more reactive iodide as the halide component.
- Synthesis of block copolymers will be facilitated with improved control over the polymerization.
- Improvement of molecular weight for material application. It has been demonstrated with poly(\textit{para-meta}\textendash phenylene)s that kinked polyphenylenes exhibit great mechanical strength.\[28\] Should the presented chain-growth AB approach prove to be inferior in terms of molecular weight a comparison with the AA/BB approach would be worthwhile.
- Synthesis of terpyridine end-capped PMP was successfully achieved. To obtain PMP carrying terpyridine on both chain-ends, it is necessary to have an efficient terpyridine
derived initiator. The initiator needs to be electronically optimized for fast oxidative addition in order to initiate the growing chain quantitatively.

- Synthesis of a supramolecular metallopolymers from terpyridine end-capped PMP. Linear metallopolymers are attractive materials because they can exhibit mechanical strength, yet due to their reversible and dynamic formation can be easily processed as low molecular compounds.\[^{166}\]

- Further investigation on helix formation in solution. Introduction of chiral side chains or end-groups leads to single-handed helices, which can be analyzed by CD spectroscopy. NOESY experiments can give additional information on secondary structure formation of PMPs in solution.
8 Materials and Methods

8.1 General

8.1.1 Reagents
All the reagents were purchased from commercial sources and were used without further purification unless noted. Solvents were dried using a SP-105 solvent purification system from LC Technology Solutions Inc. Degassing was performed by at least three consecutive freeze-pump-thaw cycles. \( \text{Pd}[(\rho\text{-tol})_3]_{167} \), \( \text{Pd(dba)}_2[69] \) and \( \text{Pd}_2(\text{dba})_3(\text{CHCl}_3)_{70} \) were prepared according to literature procedures. SPhos was purchased from Sigma-Aldrich.

8.1.2 Column Chromatography
Column chromatography was performed by using Merck silica gel Si60 (particle size 40-63 \( \mu \)m). Predestilled technical grade solvents were used.

8.1.3 NMR
NMR was recorded with a Bruker AVANCE (\(^1\text{H}: 200\) MHz, \(300\) MHz or \(700\) MHz, \(^{13}\text{C}: 75.5\) MHz) at room temperature. The solvent signal was used as internal standard of chemical shift (CDCl\(_3\): \(^1\text{H}: \delta = 7.24\) ppm, \(^{13}\text{C}: \delta = 77.00\) ppm; DMSO: \(^1\text{H}: \delta = 2.50\) ppm, \(^{13}\text{C}: \delta = 39.52\) ppm).

8.1.4 Mass Spectrometry
High-resolution mass spectrometry (HRMS) analyses were performed by the MS-service in the laboratory of organic chemistry at ETH Zurich using an electrospray-ionization (ESI) MS spectrometer with a Quadrupole-Time-of-flight tandem mass analyzer (Q-TOF) (Bruker Daltonics maXis) or electron-impact-ionization (EI) (Micromass AutoSpec-Ultima). MALDI-TOF mass spectra were recorded using a Bruker UltraFlex II MALDI-TOF mass spectrometer (Bremen, Germany) equipped with a \(\text{N}_2\) smartbeam laser (\(\lambda = 337\) nm, \(150\) \(\mu\)J, 3 ns) operating at a pulse rate of 100 Hz. For MALDI-TOF MS analyses, the ions were accelerated with pulsed ion extraction (PIE) by a voltage of 25 kV. The analyzer was operated in reflection mode unless otherwise stated, and the ions were detected using a microchannel plate detector. A total of 500-1000 shots were accumulated for each mass spectrum. As matrix material \(\text{trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)}\) with NaOTf or AgOTf was used.
8.1.5 Analytical GPC
Analytical GPC measurements were performed using a Viscotek GPC-system (Malvern Instruments Ltd., UK) with chloroform eluent, equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 ml/min), a detector module (Viscotek 302 TDA) and three columns (1 × PLGel Mix-B and 1 × PLGel Mix-C, 7.5 × 300 mm for each). Universal calibration was performed with polystyrene standards (Polymer Laboratories) in the range of \( M_p \) 1480 to 4340000. Prior to injection, the sample solution was filtered through a sintered stainless steel filter (pore size 2 \( \mu \)m).

8.1.6 Preparative GPC
Preparative recycling GPC separation was done on a LC-9101 system (Japan Analytical Industry Co., Ltd. (JAI)) with two columns (1 × JAIGEL-2H and 1 × JAIGEL-2.5H, 20 × 600 mm each) using chloroform as eluent. The JAI 3702 UV detector was set to a wavelength of 285 nm.

8.1.7 UV/Vis Spectrometry
UV/Vis spectra were recorded on a Specord S600 spectrophotometer (Analytik Jena AG, Germany) at room temperature using a Hellma SUPRASIL quartz cell with a path length of 1 cm.

8.1.8 Fluorescence Spectrometry
Fluorescence spectra were measured on a Spex Fluorolog 2 Series spectrofluorometer (Spex Industries Inc., USA) using a Hellma Fluorescence Macrocell 101-QS, \( V = 3.5 \) mL, \( l = 1 \) cm.

8.1.9 CD spectroscopy
CD spectra were recorded on a Malvern Zetasizer Nano (Malvern Instruments Ltd., UK) using a Hellma SUPRASIL quartz cell with a path length of 1 cm.

8.1.10 Single Crystal X-Ray Crystallography
Crystallographic data was collected by the X-ray analysis service group at the laboratory organic chemistry ETH Zürich.

8.1.11 Melting Points
Melting points were measured on a Melting Point B-540 apparatus (BUCHI Labortechnik AG, Switzerland) with open glass capillaries.
8.1.12 Thermogravimetric Analysis
TGA was measured on a TGA Q500 instrument (TA Instruments, USA) under N$_2$ atmosphere in a platinum pan. The thermograms were recorded in stepwise isothermal mode with a heating rate of 10 °C/min and an isothermal entering threshold of 0.5 °C and exit threshold of 0.05 °C. The sample size was between 2 mg and 5 mg.

8.1.13 Differential Scanning Calorimetry
DSC was measured on a DSC Q1000 instrument (TA Instruments, USA) in N$_2$ atmosphere aluminum pans using a scan rate of 10 °C/min. All samples were heated up to 200 °C and then cooled down to the starting temperature at a rate of 10 °C/min prior to recording the thermograms presented. The sample size was between 2 mg and 4 mg.

8.1.14 Slow Addition
For slow addition an AL-1000 syringe pump (World Precision Instruments, USA) or a Orion Sage M361 syringe pump (Thermo Scientific, USA) with a 1000 Series gastight syringe (Hamilton Bonaduz AG., Switzerland) was used. The reactions were performed in a Schlenk flask under nitrogen atmosphere. The monomer solution was fed through PTFE tube with 21 AWG (0.723 mm diameter).

Figure 65: Experimental setup for polymerization with slow addition of monomer.
8.2 Procedures for Monomer Synthesis

Ethyl 4-amino-3,5-dibromobenzoate (22)\(^{114}\)

![Chemical Structure](attachment:structure.png)

To a vigorously stirred solution of ethyl 4-aminobenzoate (186 g, 1.13 mol) in AcOH (2500 mL) at 0 °C was added dropwise a solution of Br\(_2\) (120 mL, 2.34 mol) in AcOH (300 mL). After additional stirring for 1.5 h at room temperature the reaction mixture was poured onto ice, filtered and washed with water. The remaining white solid was recrystallized from MeOH to give 22 (358.84 g, 99%) as white needles.

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 8.10\ (d, J = 1.2\ \text{Hz}, 2\ \text{H}, \text{Ar-H}); 7.84\ (t, J = 1.5\ \text{Hz}, 1\ \text{H}, \text{Ar-H}); 4.38\ (q, J = 7.2\ \text{Hz}, 2\ \text{H}, \text{CH}_2); 1.4\ (t, J = 7.2\ \text{Hz}, 3\ \text{H}, -\text{CH}_3).\) \(^{13}\)C-NMR (75 MHz) \(\delta/\text{ppm}: 164.5, 145.6, 133.3, 121.2, 107.4, 61.1, 14.3.\)

Ethyl 3,5-dibromobenzoate (23)

![Chemical Structure](attachment:structure.png)

\(
\begin{align*}
\text{H}_2\text{SO}_4 \ (1430\ \text{mL}) & \text{ was slowly added to ice water (700 mL) with occasional addition of dry ice to cool the solution. The solution was cooled to } -10\ \text{°C and NaNO}_2 \ (53.5\ \text{g}, \ 0.77\ \text{mol}) \text{ was added in small portions. Precooled hypophosphorous acid (272 mL, 2.76 mol) was added while the temperature was maintained at } -5\ \text{°C. A solution of ethyl 4-amino-3,5-dibromobenzoate (22) (91.2 g, 0.28 mol) in AcOH (1400 mL) was added dropwise. The solution was stirred at 5 \text{°C for 1.5 h and then put into a refrigerator at 6 } \text{°C overnight. Excess NaNO}_2 \text{ was quenched with aqueous urea and the solution was extracted with CHCl}_3 \ (3 \times 500\ \text{mL}). The organic phases were combined, dried over MgSO}_4 \text{ and evaporated. Recrystallization in MeOH yielded 23 (59.7 g, 69 %) as colorless needles.}\n\end{align*}
\)

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 7.58\ (s, 1\ \text{H}, \text{Ar-H}); 7.45\ (s, 2\ \text{H}, \text{Ar-H}); 4.66\ (s, 2\ \text{H}, \text{CH}_2); 1.82(s, 1\ \text{H}, -\text{OH}).\) \(^{13}\)C-NMR (75 MHz) \(\delta/\text{ppm}: 164.0, 138.1, 133.7, 131.3, 123.0, 61.8, 14.2.\)
Lithium aluminium hydride (17.53 g, 0.46 mol) was suspended in 400 ml Et₂O and cooled to 0 °C under nitrogen atmosphere. 23 (110 g, 0.35 mol) was dissolved in Et₂O (600 ml) and added dropwise over 3 h. Upon completion the solution was stirred overnight at room temperature. The mixture was cooled to 0 °C and water (17 mL) was added slowly, followed by the addition of aqueous NaOH (17 mL, 1 M). Thereafter water (50 mL) was added, the cooling bath was removed and the solution was dried over MgSO₄. Solids were removed by filtration and the solvent was evaporated. The product was recrystallized from a mixture of hexane and EtOAc (6:1) to furnish of 24 as white needles (77.12 g, 83 %).

¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.58 (s, 1 H, Ar-H); 7.45 (s, 2 H, Ar-H); 4.66 (s, 2 H, CH₂); 1.82(s, 1 H, -OH). ¹³C-NMR (75 MHz) δ/ppm: 144.8, 133.2, 128.5, 123.2, 63.6.
1,3-dibromo-5-(butoxymethyl)benzene (25):

In an oven dried Schlenk flask 6.1 g NaH (254 mmol) was suspended in dry THF (200 mL) and kept under a N₂ atmosphere. A solution of 45 g (3,5-dibromophenyl)methanol (24) (169 mmol) in dry THF (130 mL) was slowly added. The mixture was heated to reflux whereby the solution turned orange. After 45 min 54.8 mL 1-bromobutane (508 mmol) was added in one portion. After 18 h the slightly yellow suspension was cooled to room temperature and excess NaH was quenched by adding water (300 mL). The two clear phases were separated and the aqueous phase was extracted with Et₂O (3 x 150 mL). The organic phases were combined, dried over MgSO₄, filtered and evaporated to give an orange oil. Vacuum distillation (0.2 mbar, 125 °C) yielded 25 (47.9 g, 88 %) as a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.59 (s, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 4.46 (s, 2H, Ar-CH₂-), 3.50 (t, J = 6.5 Hz, 2H, -O-CH₂-CH₂-), 1.64 (m, 2H, O-CH₂-CH₂-), 1.43 (m 2H, CH₂-CH₃), 0.96 (t, J = 7.3 Hz, 3H, -CH₃). ¹³C-NMR (75 MHz) δ/ppm: 142.9; 132.9; 129.0; 122.9; 71.2; 70.7; 31.7; 13.3; 13.9. HRMS (EI): m/z calculated for C₇H₆Br₂ [M]⁺ 319.9411, found 319.9396, calculated for C₇H₅Br₂O [M-C₄H₉]⁺ 262.8707, found 262.8703, calculated for C₃H₅Br₂ [M-C₄H₉O]⁺ 246.8758, found 246.8760.
1,3-dibromo-5-(dodecyloxyethyl)benzene (26):

To a stirred mixture of 20.70 g (3,5-dibromophenyl)methanol (24) (75.5 mmol) and 320 mg imidazole (4.7 mmol) in dry THF (200 mL) in a Schlenk tube under N₂ was added 5.39 g NaH (224.7 mmol). After stirring for 2 h, 72.0 mL dodecyloxymethylbromide (297.6 mmol) was added and the solution was stirred for 4 d at 40 °C. Then the reaction mixture was quenched with water (100 mL), the phases were separated and the aqueous phase was extracted with Et₂O (3 x 70 mL). The combined organic phase was washed with brine (70 mL), dried over MgSO₄ and the solvent was evaporated. From the remaining yellow oil the excess dodecyloxymethylbromide was distilled off under reduced pressure (0.6 mbar, 92 °C). A yellowish solid precipitated overnight and was washed with an ice-cold mixture of ethanol/isopropanol (1:1) to give 26 (23.92 g, 73%) as a white solid.

mp: 31 – 32 °C. ¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.57 (s, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 4.43 (s, 2H, Ar-CH₂-), 3.46 (t, J = 6.4 Hz, 2H, -O-CH₂-CH₂), 1.62 (quint, J = 5.1 Hz, 2H, -O-CH₂-CH₂-), 1.26 (s, 18H, -(C₆H₄)_3CH₃), 0.8 (t, J = 6.5 Hz, 3H, -CH₃). ¹³C-NMR (75 MHz) δ/ppm: 142.9; 132.9; 129.0; 122.9; 71.2; 71.0; 31.91; 29.654; 29.636; 29.629; 29.599; 29.580; 29.43; 29.34; 26.12; 22.68; 14.11. HRMS (EI): m/z calculated for C₇H₆Br₂ [M-C₁₂H₂₅O]+ 246.8758, found 246.8752, calculated for C₇H₆Br [M-C₁₂H₂₅BrO]+ 246.8758, found 246.8752.
(3-bromo-5-(butoxymethyl)phenyl)boronic acid (27)

A stirred solution of dibromide 25 (6 g, 18.6 mmol) in dry THF (50 mL) and dry Et₂O (50 mL) under nitrogen atmosphere was cooled to -72 °C and n-BuLi (12.8 mL, 1.6 M in hexane, 20.5 mmol) was dropwise added. The deep red solution was stirred for 1 h and triisopropyl borate (5.2 mL, 22.4 mmol) was added in one portion. Stirring was continued overnight and the solution was allowed to warm to room temperature. Water (50 mL) was added until all solids were dissolved. Aqueous HCl (6 M) was added until the solution was acidic. The phases were separated and the aqueous phase was extracted with Et₂O (2 x 200 mL). The organic phases were combined, washed with water (2 x 200 mL), dried over MgSO₄, filtrated and evaporated. The crude product was purified by column chromatography (SiO₂, Hex/EtOAc, 6:1 → 0:1) to give 27 (2.79 g, 52 %).

1H-NMR (300 MHz, CDCl₃) δ/ppm: 7.92 (s, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 7.60 (s, 1H, Ar-H), 4.52 (s, 1H, Ar-CH₂-), 3.51 (t, J = 6.5 Hz, 2H, -O-CH₂-CH₂-), 1.65 – 1.56 (m, 2H, -CH₂-CH₂-CH₃), 1.48 – 1.36 (m, 2H, -CH₂-CH₂-CH₃), 0.93, (t, J = 7.2 Hz, 3H, -CH₂-CH₃).
(3-bromo-5-((dodecyloxy)methyl)phenyl)boronic acid (28)

To a stirred solution of dibromide 26 (10.06 g, 23.2 mmol) in THF (250 mL) under nitrogen atmosphere at -78 °C was added n-BuLi (16.5 mL, 1.6 M in hexane 26.4 mmol). After stirring for 45 min triisopropyl borate (6.50 mL, 28.1 mmol) was added and the mixture was warmed up to room temperature over night. The solvent was evaporated, the remaining oil was dissolved in Et₂O (80 mL) and acidified with 1M HCl (22 mL), the phases were separated, the aqueous phase was extracted with Et₂O (2 x 50 mL). The combined organic phase was washed with water (60 mL) and brine (60 mL), dried over MgSO₄ and evaporated. The crude yellow solid crystallized upon standing overnight and was washed with ice-cold n-pentane to give 28 (5.56 g, 60 %) as white solid.

¹H-NMR (200 MHz, (CD₃)₂CO) δ/ppm: 7.88 (s, 1H, Ar-H), 7.77 (s, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 4.49 (s, 2H, Ar-CH₂), 3.47 (t, J = 6.4 Hz, 2H, -O-CH₂-CH₂-), 1.62 – 1.53 (m, 2H, -O-CH₂-CH₂-), 1.27 (s, 18H) 0.86 (t, J = 6.6 Hz, 3H, -CH₃).
A stirred solution of 10 g (38 mmol) (3,5-dibromophenyl)methanol (24) in CH$_2$Cl$_2$ was cooled to 0 °C. 5.2 mL (56 mmol) 3,4-dihydropyran and 71 mg (0.38 mmol) 4-methylbenzensulfonic acid monohydrate was added. The mixture was allowed to warm up to room temperature overnight. The dark brown solution was quenched with NEt$_3$ (10 mL) upon which the color changed to orange. The solvent was evaporated and the crude product was purified using medium pressure liquid chromatography (SiO$_2$, dichloromethane/hexane, 1:1) to give (12.19 g, 93%) of 32 as a colorless liquid.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm: 7.57 (s, 1 H, Ar-H); 7.44 (s, 2H, Ar-H); 4.75 – 4.62 (m, 2 H, benzyl and THP); 4.43 (d, $J = 12.7$ Hz, 1H, benzyl); 3.94 – 3.77 (m, 1H, THP); 3.61 – 3.46 (m, 1H, THP); 1.91 – 1.48 (m, 6H, THP). $^{13}$C-NMR (75 MHz) δ/ppm: 142.4; 132.9; 129.1; 122.8; 98.0; 67.2; 62.1; 30.4; 25.3; 19.2. ESI-MS: $m/z$ calculated for C$_{12}$H$_{14}$Br$_2$NaO$_2$ [M+Na]$^+$ 370.9253, found 370.9257.
2-(3-bromo-5-((tetrahydropyranoxy)methyl)phenyl)pinacol borane (33):

A stirred solution of (3,5-Dibromobenzylxy)tetrahydropyran (32) (19.5 g, 55.7 mmol) in dry Et₂O (300 mL) under nitrogen atmosphere was cooled to -78 °C and n-BuLi (38.3 mL, 1.6 M in hexane, 61.3 mmol) was added dropwise over 45 min. After stirring the yellow mixture for 3 h, isopropyl pinacol borate (13.6 mL, 66.8 mmol) was added. The mixture was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight saturated NH₄Cl aq. (150 mL) was added to the white suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 100 mL). The ether phases were combined, dried over MgSO₄ and evaporated at 0.1 mbar to give a yellow oil. The residue was recrystallized in petrol ether (b.p.: 80 – 110 °C) and again recrystallized in acetonitrile to give 16.03 g 33 (72 %) as a white crystalline solid.

m.p.: 68 – 70 °C. ¹H-NMR (700 MHz, CDCl₃) δ/ppm: 7.84 (s, 1H, Ar-H); 7.66 (s, 1H, Ar-H); 7.64 (s, 1H, Ar-H); 4.74 (d, J = 12.2 Hz, 1H, CH₂); 4.69 (t, J = 3.5 Hz, 1H, THP), 4.45 (d, J = 12.2 Hz, 2H, Ar-CH₂); 3.91 – 3.88 (m, 1H, THP); 3.56 – 3.53 (m, 1H, THP); 1.89 – 1.84 (m, 1H, THP); 1.76 – 1.72 (m, 1H, THP); 1.68 – 1.53 (m, 4H, THP); 1.34 (s, 12 H, -CH₃). ¹³C-NMR (75 MHz) δ/ppm: 140.0; 136.5; 133.4; 132.4; 122.5; 97.9; 54.1; 68.0; 62.1; 30.4; 25.4; 24.8; 19.2 (Carbon attached to boron was not observed due to quadrupolar relaxation). HRMS (ESI): m/z calculated for C₁₈H₃₀BBrNO₄ [M+NH₄]⁺: 414.1446, found: 414.1448.
2-(3-bromo-5-(butoxymethyl)phenyl)-1,3,2-dioxaborinane (34)

A stirred solution of boronic acid 27 (2.0 g, 7.0 mmol) and 1,3-propanediol (530 mg, 7.0 mmol) in toluene (70 ml) was heated to reflux for 16 h, with azeotropic removal of water using a Dean-Stark trap. The solvent was evaporated to give 34 as colorless yellow oil (2.29 g, quantitative).

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$/ppm: 7.79 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 4.45 (s, 2H, Ar-CH$_2$), 4.15 (t, $J$ = 5.5 Hz, 4H, dioxaborinane), 3.45 (t, $J$ = 6.5 Hz, 2H, -O-CH$_2$), 2.05 (quint, $J$ = 5.3 Hz, 2H, dioxaborinane), 1.62-1.56 (m, 2H, -O-CH$_2$-CH$_2$-), 1.43-1.35 (m, 2H, -CH$_2$-CH$_3$), 0.93 (t, $J$ = 7.3 Hz, 3H, -CH$_3$). $^{13}$C-NMR (75 MHz) $\delta$/ppm: 140.3, 136.4, 133.5, 132.2, 122.5, 72.14, 70.6, 62.1, 31.9, 27.2, 19.3, 13.9 (Carbon attached to boron was not observed due to quadrupolar relaxation).

2-(3-bromo-5-(dodecyloxy)methyl)phenyl)-1,3,2-dioxaborinane (35)

A stirred solution of boronic acid 28 (5.56 g, 13.9 mmol) and 1,3-propanediol (1.12 ml, 15.5 mmol) in toluene (35 ml) was heated to reflux for 18 h, with azeotropic removal of water using a Dean-Stark trap. The solvent was evaporated to give a pale yellow oil which crystallised overnight and was washed with ice-cold acetonitrile to give 35 (4.80 g, 78%) as white crystals.

mp: 44 - 45 °C. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm: 7.78 (s, 1H, Ar-H), 7.60 (s, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 4.45 (s, 2H, Ar-CH$_2$), 4.15 (t, $J$ = 5.4 Hz, 4H, dioxaborinane), 3.44 (t, $J$ = 6.6 Hz, 2H, -O-CH$_2$), 2.05 (quint, $J$ = 5.4 Hz, 2H, dioxaborinane), 1.26 (s, 18 H), 0.88 (t, $J$ = 6.6, 3H, -CH$_3$). $^{13}$C-NMR (75 MHz) $\delta$/ppm: 140.20, 135.63, 132.61, 131.27, 122.48, 72.14, 70.67, 62.03, 31.91, 29.71, 29.60, 29.47, 29.34, 27.36, 26.16, 22.67, 14.10 (Carbon attached to boron was not observed due to quadrupolar relaxation).
2-(3-bromo-5-(butoxymethyl)phenyl)pinacol borane (36):

A stirred solution of dibromide 25 (8.15 g, 25.3 mmol) in dry diethyl ether (140 mL) under nitrogen atmosphere was cooled to -78 °C and n-BuLi (16.6 mL, 1.6 M in hexane, 26.6 mmol) was added dropwise over 20 min. After stirring the yellow mixture for 3 h, isopropyl pinacol borate (6.2 mL, 30.4 mmol) was added. The mixture was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight saturated NH₄Cl aq. (100 mL) was added to the white suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 100 mL). The ether phases were combined, dried over MgSO₄ and evaporated. The resulting oil was purified by medium pressure liquid chromatography (SiO₂, hexane/ethyl acetate, 95:5) to give 3.4 g 36 (35 %) as a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.84 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 4.45 (s, 2H, Ar-CH₂), 3.46 (t, J = 6.6 Hz, 2H, -O-CH₂-CH₂), 1.65-1.53 (m, 2H, -O-CH₂-CH₂), 1.45-1.34 (m, 2H, -CH₂-CH₃), 1.34 (s, 12H, pinacol), 0.92 (t, J = 7.3 Hz, 3H, -CH₃).

¹³C-NMR (75 MHz) δ/ppm: 140.4; 136.5; 133.3; 132.2; 122.5; 84.1; 70.5; 72.0; 31.8; 24.8; 19.3; 13.9 (Carbon attached to boron was not observed due to quadrupolar relaxation). HRMS (EI): m/z calculated for C₁₇H₂₆BBrO₃ [M]⁺ 368.1158, found 368.1157, calculated for C₁₆H₂₃BBrO₃ [M-CH₃]⁺ 353.0924, found 353.0922, calculated for C₁₃H₁₇BBrO₂ [M-C₄H₉O]⁺ 295.0505, found 295.0515.
2-(3-bromo-5-(dodecyloxymethyl)phenyl)pinacol borane (37):

A stirred solution of (2.0 g, 4.61 mmol) dibromide (26) in THF (50 mL) under nitrogen atmosphere was cooled to -50 °C and n-BuLi (3.0 mL, 1.6 M in hexane, 4.84 mmol) was added dropwise over 10 min. After stirring the deep red solution for 45 min, isopropyl pinacol borate (1.4 mL, 6.91 mmol) was added. The yellow/orange solution was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight water (50 mL) was added to the yellow suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The ether phases were combined, dried over MgSO₄ and evaporated. The resulting oil was purified by column chromatography (SiO₂, hexane/ethyl acetate, 5:1) to give 0.71 g 37 (32 %) as a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.84 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 4.46 (s, 2H, Ar-CH₂-), 3.45 (t, J = 6.6 Hz, 2H, -O-CH₂-CH₂-), 1.61 (t, J = 7.2 Hz, 2H, -O-CH₂-CH₂-), 1.34 (s, 12H, pinacol), 1.26 (s, 18H, -(CH₂)₉-CH₃), 0.88 (t, J = 6.6 Hz, 3H, -CH₂-CH₃). ¹³C-NMR (75 MHz) δ/ppm: 140.4; 136.5; 133.3; 132.2; 122.5; 84.1; 72.0; 70.8; 31.9; 29.68; 29.65; 29.61; 29.589, 29.580, 29.46; 29.33; 26.1; 24.8; 22.7; 14.1 (Carbon attached to boron was not observed due to quadrupolar relaxation). HRMS (EI): m/z calculated for C₂₅H₃₉BBrO₃ [M-CH₃]+ 465.2176, found 465.2169, calculated for C₁₃H₁₇BBrO₃ [M-C₁₂H₂₅]⁺ 311.0454, found 311.0463.
(3-bromo-5-(butoxymethyl)phenyl)boronic acid MIDA ester (38)

Boronic acid 27 (4.10 g 14.3 mmol) and N-methyliminodiacetic acid (2.84 g, 19.29 mmol) were dissolved in toluene (200 mL) and DMSO (25 mL) and heated to reflux with azeotropic removal of water using a Dean-Stark trap. After 14 h the solvent was evaporated and the crude product was adsorbed on silica gel and eluted with Et₂O → Et₂O/CH₃CN (2:1) to furnish 38 (5.02 g, 89 %) as a colorless solid.

¹H-NMR (200 MHz, CD₃CN) δ/ppm: 7.54 (s, 2H, Ar-H), 7.38 (s, 1H, Ar-H), 4.46 (s, 2H, Ar-CH₂-), 4.09 (d, J = 17.2 Hz, 2H), 3.90 (d, J = 17.2 Hz, 2H), 3.45 (t, J = 6.5 Hz, 2H, -OCH₂-CH₂-), 2.53 (s, 3H, N-CH₃), 1.64 – 1.49 (m, 2H, -CH₂-CH₂-CH₃), 1.46 – 1.28 (m, 2H, -CH₂-CH₂-CH₃), 0.90 (t, J = 7.2 Hz, 3H, CH₂-CH₃). ¹³C-NMR (75 MHz) δ/ppm: 169.4, 142.40, 134.97, 131.95, 131.19, 123.23, 72.30, 70.88, 62.91, 48.59, 32.47, 32.47, 20.04, 14.15 (Carbon attached to boron was not observed due to quadrupolar relaxation). HRMS (ESI): m/z calculated for C₁₆H₂₂BBrNO₅ [M+H]⁺ 398.0774, found 396.0768.
Potassium 1-(3-bromo-5-(butoxymethyl)phenyl)-4-methyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-ui (39)

Boronic acid 27 (950 mg, 3.31 mmol) and 1,1,1-tris(hydroxymethyl)ethane (398 mg, 3.31 mmol) were dissolved in toluene (50 mL) and heated to reflux for 4 h with azeotropic removal of water using a Dean-Stark trap. Potassium hydroxide (177 mg, 3.15 mmol) was added and azeotropic distillation was continued overnight. The solvent was evaporated and the crude product was purified by medium pressure liquid chromatography (SiO₂, CH₂Cl₂/CH₃CN, 10:1) to give 0.58 g 39 (43 %) as a colorless oil.

¹H-NMR (300 MHz, CDCl₃) δ/ppm: 7.81 (s, 1H, Ar-H), 7.63 (s, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 4.45 (s, 2H, Ar-CH₂-), 4.00 (b, 2H, B-O-CH₂-), 3.82 (b, 2H, B-O-CH₂-), 3.60 (b, 2H, B-O-CH₂-), 3.46 (t, J = 6.6 Hz, 2H, -O-CH₂-CH₂-), 1.62 – 1.54 (m, 2H, -CH₂-CH₂-CH₃), 1.43 – 1.35 (m, 2H, -CH₂-CH₂-CH₃), 0.98 (s, 1H, C-CH₃), 0.92 (t, J = 7.2 Hz, 3H, -CH₂-CH₃). ¹³C-NMR (75 MHz) δ/ppm: 140.21, 135.81, 132.81, 131.47, 122.49, 72.12, 70.43, 36.89, 31.77, 19.32, 17.34, 13.90 (Carbon attached to boron was not observed due to quadrupolar relaxation). HRMS (ESI): m/z calculated for C₁₆H₂₃BBBrO₄ [M-K] 369.0873, found 369.0871.
2-(4-methoxyphenyl)-pinacol borane (44)

A stirred solution of bromoanisole (3 g, 16.0 mmol) in dry THF (30 mL) under nitrogen atmosphere was cooled to −72°C and n-BuLi (12.03 mL, 1.60 M in hexane, 19.3 mmol) was added dropwise. After stirring the solution for 30 min isopropyl pinacol borate (3.6 mL, 17.6 mmol) was added. The solution was slowly warmed to room temperature and stirred overnight. Saturated aqueous NH₄Cl (30 mL) and diethyl ether (30 mL) were added to the white suspension. The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 20 mL). The ether phases were combined, dried over MgSO₄, filtrated and evaporated. The resulting colorless liquid was purified by column chromatography (SiO₂, hexane/ethyl acetate, 10:1) to yield 2.29 g of 44 (61 %) as a colorless liquid which solidified upon standing for a prolonged time.

\[ ^1H-NMR \ (300 \text{ MHz, CDCl}_3) \delta/\text{ppm}: 7.75 \ (d, J = 8.4 \text{ Hz, 2H, Ar-H}), 6.90 \ (d, J = 8.7 \text{ Hz, 2H, Ar-H}), 3.83 \ (s, 3H, -O-CH₃), 1.33 \ (s, 12H, -CH₃). \]

\[ ^{13}C-NMR \ (75 \text{ MHz}) \delta/\text{ppm} : 162.2, 136.5, 113.3, 83.5, 55.1, 24.95. \]

4'(4-Bromophenyl)-2,2':6',2''-terpyridine (51)[153]

To a stirred solution of 4-bromobenzaldehyde (15.3 g, 82.6 mmol) in ethanol (400 mL) was added 2-acetylpyridine (20.0 g, 165.0 mmol), aqueous ammonia (25%, 200 mL) and KOH (9.3 g, 165 mmol). After 4 d the suspension was filtered and the filtrate was washed with cold ethanol to yield 13.6 g of 51 (42%) as white solid.

\[ ^1H-NMR \ (300 \text{ MHz, CDCl}_3) \delta/\text{ppm}: 8.74 \ (d, J = 4.8, 1.7, 0.8 \text{ Hz}), 8.70 \ (s, 2H), 8.67 \ (d, J = 8.0 \text{ Hz, 2H}), 7.88 \ (td, J = 7.7, 1.8 \text{ Hz, 2H}), 7.80 \sim 7.75 \ (m, 2H), 7.66 \sim 7.6 \ (m, 2H), 7.36 \ (ddd, J = 7.5, 4.8, 1.1 \text{ Hz, 2H}), ^{13}C-NMR \ (75 \text{ MHz}) \delta/\text{ppm} : 156.07 \sim 156.02, 149.14, 149.00, 137.4, 136.9, 132.1, 128.9, 123.9, 123.5, 121.4, 118.5. \]
4’(4-Pinacolatoboronphenyl)-2,2’:6’,2”-terpyridine (52)[168]

A mixture of bromide 51 (1.0 g, 2.58 mmol), bis(pinacolato)diboron (1.96 g, 7.74 mmol) and potassium acetate (0.76 g, 7.74 mmol) in DMSO (15 mL) was degassed and [Pd(dppf)Cl₂] (63 mg, 0.08 mmol) was added. After stirring for 60 h at 80 °C the solvent was evaporated and the crude was extracted with chloroform. Recrystallization from methanol gave 0.68 g 52 (61%) as a grey solid.

1H-NMR (300 MHz, CDCl₃) δ/ppm: 8.79 – 8.76 (m, 4H), 8.70 (d, J = 8.0 Hz, 2H), 8.00 – 7.96 (m, 4H), 7.91 (td, J = 7.7, 1.8 Hz, 2H), 7.39 (ddd, J = 7.5, 4.8, 1.1 Hz, 2H), 1.41 (s, 12H). 13C- NMR (75 MHz) δ/ppm: 156.3, 156.0, 150.1, 149.1, 141.0, 136.7, 135.3, 126.6, 123.7, 121.4, 118.7, 84.0, 24.9.

Dibenzylideneacetone

A solution of benzaldehyde (11.04 mL, 109.0 mmol) and acetone (4 mL, 54.5 mmol) was prepared and the first half was added to a stirred solution of NaOH (10.99 g, 275 mmol) in water (110 mL) and ethanol (87 mL). After 3 min a yellow precipitate formed and after 15 min the rest of the solution was added. The suspension was filtered after 1.5 h and washed with water (3 x 50 mL), dried under vacuum. Recrystallization from ethyl acetate (25 mL) furnished 9.56 g dibenzylideneacetone (75 %) as yellow needles.

m.p. 112 – 113 °C. 1H-NMR (300 MHz, CDCl₃) δ/ppm: 7.75 (d, J = 15.9 Hz, 2H, ph-CH=CH-), 7.64 – 7.60 (m, 4H, ph), 7.44 – 7.39 (m, 6H, ph), 7.09 (d, J = 16.2 Hz, -CH=CH-CO-). 13C- NMR (75 MHz) δ/ppm: 188.8, 143.1, 134.7, 130.5, 128.9, 128.3, 125.4.
Materials and Methods

8.3 Procedures for Suzuki-Polycondensation

Procedure for Suzuki-Polycondensation in batch:
A Schlenk flask was charged with 750 mg monomer (1.89 mmol) and 1.05 g Cs₂CO₃ (3.21 mmol). The flask was evacuated and back-filled with N₂ for three times. In a glove box, 38 mg Pd[P(₃-tol)₃]₂ (2 mol%) was weighed, dissolved in degassed THF (1 mL) and added by syringe. The mixture was degassed and vigorously stirred at 70 °C under an N₂ atmosphere. After 3 d THF was evaporated and dichloromethane (30 mL) was added. The organic phase was washed with water (3 x 50 mL), dried over MgSO₄, filtered and evaporated to give the product as grey solid (320 mg, 89 %).

Procedure for Suzuki-Polycondensation with slow addition of monomer:
A Schlenk flask was charged with Pd(dba)₂ (7.2 mg, 0.013 mmol), SPhos (10.3 mg, 0.025 mmol), and NaHCO₃ (845 mg, 10.1 mmol). The flask was evacuated and back-filled with N₂ for three times. Degassed THF (10 mL) and water (10 mL) was added, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of monomer (500 mg, 1.26 mmol) in THF (10 mL), was added by syringe pump at a rate of 0.74 mL/h. After the addition, stirring and heating was continued for 1 d. After cooling to room temperature, water (25 mL) and chloroform (25 mL) were added and the heterogeneous solution was stirred with NaCN (50 mg) for at least 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 25 mL). The organic phases were combined, dried over MgSO₄, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into 50 mL methanol at -15 °C. The precipitate was collected by filtration or centrifugation and dried in vacuo to afford the product (210 mg, 88 %) as an colorless powder.

Procedure for sequential polymerization:
A Schlenk flask was charged with Pd(dba)₂ (3.6 mg, 6.26 μmol), SPhos (5.2 mg, 12.7 μmol), NaHCO₃ (430 mg, 5.12 mmol) and 4-fluorobromobenzene (34 μL, 0.311 mmol). The flask was evacuated and back-filled with N₂ for three times. Degassed THF (2.5 mL) and water (2.5 mL) was added, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of butylated monomer XX (123 mg, 0.333 mmol) in THF (2.5 mL) was added by syringe pump at a rate of 0.74 mL/h after addition was finished, a degassed solution of THP protected monomer XX (132 mg, 0.333 mmol) in THF (2.5 mL) was added at a rate of 0.74
Chapter 8

ml/h. Stirring and heating was continued for 1d. After cooling to room temperature, water (25 mL) and chloroform (25 mL) was added and the mixture was stirred with NaCN (50 mg) for 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 25 mL). The organic phases were combined, dried over MgSO₄, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into 50 mL methanol at -15 °C. The precipitate was collected by filtration or centrifugation and dried in vacuo to furnish a grey solid (52 mg).

Deprotection and extraction after sequential polymerization:
The crude polymer (40 mg) and p-toluenesulfonic acid hydrate (8.6 mg, 45 μmol) was dissolved in THF (10 mL) and water (0.5 mL) and stirred for 16 h at reflux. Water (10 mL) was added and the solution was freeze-dried. The white solid was extracted overnight with chloroform using a Soxhlet apparatus followed by extraction with DMF (room temperature). The solid remains were dissolved in boiling DMF and furnished a brown solid (19 mg).

Procedure for Suzuki-Polycondensation giving di-end functionalized polymer:
A Schlenk flask was charged with Pd(dba)₂ (3.6 mg, 6 μmol), SPhos (5.2 mg, 13 μmol) and NaHCO₃ (423 mg, 5.0 mmol). The flask was evacuated and back-filled with N₂ for three times. Degassed THF (10 mL), water (10 mL) and 4-bromofluorobenzene (27.5 mg, 0.157 mmol) was added. Then, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of monomer 16 (250 mg, 0.63 mmol) in THF (5 mL), was added by syringe pump at a rate of 1 mL/h. After the addition, a solution of 4-anisylpinacolborane in degassed THF (2 mL) was added. Stirring and heating was continued for 1 d. After cooling to room temperature, water (25 mL) and chloroform (25 mL) were added and the heterogeneous solution was stirred with NaCN (25 mg) for at least 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 20 mL). The organic phases were combined, dried over MgSO₄, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into methanol (30 mL) at -15 °C. The precipitate was collected by filtration or centrifugation and dried in vacuo to afford the product (99 mg, 83 %) as a colorless powder.

Procedure for Suzuki-Polycondensation giving terpyridine functionalized polymer:
A Schlenk flask was charged with Pd(dba)$_2$ (3.6 mg, 6 μmol), SPhos (5.2 mg, 13 μmol) and NaHCO$_3$ (423 mg, 5.0 mmol). The flask was evacuated and back-filled with N$_2$ for three times. Degassed THF (10 mL), water (10 mL) and 4-bromofluorobenzene (27.5 mg, 0.157 mmol) was added. Then, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of monomer 16 (250 mg, 0.63 mmol) in THF (5 mL), was added by syringe pump at a rate of 1 mL/h. After the addition was finished, a degassed solution of terpyridine derivative 29 (137 mg, 0.31 mmol) in THF (1.5 mL) was added. Stirring and heating was continued for 14 h. After cooling to room temperature, water (25 mL) and chloroform (25 mL) were added and the heterogeneous solution was stirred with NaCN (25 mg) for at least 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 20 mL). The organic phases were combined, dried over MgSO$_4$, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into 25 mL methanol at -15 °C. The precipitate was collected by filtration or centrifugation and dried in vacuo to afford the product (83 mg, 70 %) as a colorless powder.

**Poly(1,3-(5-((tetrahydropyranyloxy)methyl)phenylene) (40)**

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm: 7.83 (s, 1H, Ar-H); 7.66 (s, 2H, Ar-H), 4.94 (d, J = 12.0 Hz, 1H, Ar-CH$_2$); 4.79 (t, J = 3.3 Hz, 1H, THP), 4.65 (d, J = 12.0 Hz, 1H, Ar-CH$_2$); 3.95 (t, J = 7.8 Hz, 1H, THP); 3.56 (t, J = 5.4 Hz, 1H, THP); 1.88 – 1.52 (m, 6H, THP). $^{13}$C-NMR (75 MHz) δ/ppm: 141.9, 139.5, 126.1, 125.7, 98.0, 68.8, 62.2, 30.6, 25.4, 19.4.

**Poly(1,3-(5-butoxy)phenylene) (41)**

$^1$H-NMR (300 MHz, CD$_2$Cl) δ/ppm: 7.83 (s, 1H, Ar-H), 7.64 (s, 2H, Ar-H), 4.65 (s, 2H, Ar-CH$_2$), 3.55 (t, J = 6.5 Hz, 2H, O-CH$_2$-CH$_2$), 1.64 – 1.60 (m, 2H, O-CH$_2$-CH$_2$), 1.42 – 1.39 (m, 2H, CH$_2$-CH$_3$), 0.90 (t, J = 7.4 Hz, 3H, -CH$_3$). $^{13}$C-NMR (75 MHz) δ/ppm: 141.9, 139.9, 125.8, 125.6, 72.6, 70.5, 31.8, 19.4, 13.9.
Poly(1,3-(5-dodecyloxy)phenylene) (42)

\[ \text{OC}_{12}H_{25} \]

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm: 7.85 (s, 1H, Ar-H), 7.65 (s, 2H, Ar-H), 4.66 (s, 2H, Ar-CH$_2$), 3.55 (t, $J$ = 6.9 Hz, 2H, O-CH$_2$-CH$_2$), 1.65 – 1.62 (m, 2H, O-CH$_2$-CH$_2$), 1.30 – 1.34 (m, 2H, CH$_2$-CH$_3$), 1.24 (s, 18H), 1.28 (s, 18H), 1.18 (t, $J$ = 7.0 Hz, 3H, CH$_2$-CH$_3$). $^{13}$C-NMR (75 MHz) $\delta$/ppm: 141.88, 139.89, 125.90, 125.61, 72.87, 70.84, 66.26, 31.89, 29.78, 29.624, 29.619, 29.52, 29.33, 26.22, 22.66, 14.09 (one carbon of the dodecyl chain was not observed due to overlap).

Deprotected poly(3-hydroxymethyl phenylene) (43)

A solution of THP-protected polymer 40 (40 mg, 2.1 mmol) and p-toluenesulfonic acid monohydrate (8 mg) in THF (10 mL) and water (0.5 mL) was stirred and heated to reflux for 15 h. The white precipitate was separated by centrifugation, redispersed in THF and centrifuged again to obtain deprotected polymer 43 (19 mg, 86 %) as a white solid.

$^1$H-NMR (300 MHz, DMSO-$d_6$) $\delta$/ppm: 7.91 (s, 1H, Ar-H), 7.72 (s, 2H, Ar-H), 5.34 (t, $J$ = 5.6 Hz, 1H, -OH), 4.68 (d, $J$ = 5.1 Hz, 2H, Ar-CH$_2$). $^{13}$C-NMR (75 MHz) $\delta$/ppm: 144.04, 141.03, 124.52, 124.37, 62.92.
9 Appendix

9.1 Abbreviations and Symbols

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</tr>
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<td>CD</td>
<td>circular dichroism</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
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<td>dimethyl sulfoxide</td>
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<td>EI</td>
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<td>equivalents</td>
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<td>HEEDTA</td>
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<tr>
<td>$J$</td>
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</tr>
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</tr>
<tr>
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</tr>
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<td>mole</td>
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9.2 Crystallographic Data of compound 27

Crystals were obtained from boiling H$_2$O.

C$_{11}$H$_{16}$BBrO$_3$

M$_r$ = 286.966

Orthorhombic

Pna$_2_1$

a = 9.6484 (3)Å

b = 9.5487 (3)Å

c = 14.1280 (5)Å

$\alpha$ = 90.00°

$\beta$ = 90.00°

$\gamma$ = 90.00°

V = 1301.61 (7)Å$^3$

Z = 4

F(000) =

D$_x$ = 1.464 Mg m$^{-3}$

Density measured by: not measured

fine-focus sealed tube

Mo Kα radiation $\lambda$ = 0.71073

Cell parameters from 6806 refl.

$\theta$ = 2.425—27.485 °

$\mu$ = 3.147 mm$^{-1}$

T = 173 K

Cube

0.21 x 0.06 x 0.02 mm

Colourless

Crystal source: MatS ETH Zurich

Data collection

KappaCCD CCD diffractometer

Absorption correction: integration

$T_{	ext{min}}$ = 0.690 , $T_{	ext{max}}$ = 0.915

10021 measured reflections

2831 independent reflections

2522 observed reflections

Criterion: >2sigma(I)

Refinement

Refinement on $F^2$

fullmatrix least squares refinement

$R$(all) = 0.0434

$R$($gt$) = 0.0365

wr($R$($gt$)) = 0.1133

wr($R$($gt$)) = 0.1029

$S$(ref) = 0.834

2831 reflections

154 parameters

2 restraints

H-atom refinement mixed

Calculated weights 1/[σ$^2$(I$_o$)+(I$_c$+I$_e$)/2]/900]

$\Delta$/$\sigma_{\text{max}}$ = 0.003

$\Delta$ρ$_{\text{max}}$ = 0.254eÅ$^3$

$\Delta$ρ$_{\text{min}}$ = -0.795eÅ$^3$

Extinction correction: none

Atomic scattering factors from International Tables

Vol C Tables 4.2.6.8 and 6.1.1.4

Flack parameter = -0.016 (13)


Data collection: KappaCCD

Cell refinement: HKL Scalepack (Otwinowski & Minor 1997)

Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997)

Program(s) used to solve structure: SIR97(Altomare et al., J. Appl. Cryst.,1999)

Program(s) used to refine structure: SHELXL-97 (Sheldrick, 1997)
Table 7. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\AA^2$)

$U_{eq} = \frac{1}{3} \sum \sum \ U_{ij} a_i^* a_j^* a_i a_j$.

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<th>y</th>
<th>z</th>
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Table 8. Anisotropic displacement parameters ($\AA^2$)

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10 References


References


[96] T. Bauer, Eidgenössische Technische Hochschule (Zürich), **2012**.


References


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Publications

Part of this work has been published.

Peer-reviewed journals:


*Suzuki Polycondensation toward High Molecular Weight Poly(m-phenylene)s: Mechanistic Insights and End-Functionalization.*

Oral presentations:


*Synthesis of poly(m-phenylene)s by Suzuki-Polycondensation using an AB-Monomer.*

Poster presentations:


*Suzuki Polycondensation to Linear and Cyclic Poly(m-phenylene)s*

B. Hohl, A. D. Schlüter, J. Sakamoto, 3rd EuCheMS Chemistry Congress, 2010, EuCheMS, Nuremberg, Germany.

*Cyclic and Linear Poly(meta-phenylene) by Suzuki Polycondensation*

B. Hohl, A. D. Schlüter, J. Sakamoto, Fall Meeting, 2010, SCS, Zurich, Switzerland.

*Synthesis of Kinked Poly(m-phenylene) and Poly(m-p-phenylene) by Suzuki Polycondensation*

B. Hohl, A. D. Schlüter, J. Sakamoto, Fall Meeting, 2009, SCS, Zurich, Switzerland.

*Synthesis of Novel Kinked Poly(m-phenylene)s by Suzuki-Polycondensation*