Doctoral Thesis

Synthesis and characterization of poly(p-phenylene alkylene)s
Exploration of a forgotten class of polymers

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Publication Date:
1999

Permanent Link:
https://doi.org/10.3929/ethz-a-003837249

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Synthesis and Characterization of Poly(p-phenylene alkylenes) –
Exploration of a Forgotten Class of Polymers

A dissertation submitted to the
EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

for the degree of
Doctor of Natural Sciences

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Zürich 1999
Publications and Presentations in Connection with this Thesis

Journal articles:


Steiger, D.; Smith, P.; Weder, Ch. in preparation: “New Polymers by the Heck Reaction”.

Selected Presentations:

Steiger, D.; Ehrenstein, M.; Weder, Ch.; Smith, P.; Contributed lecture; ACS 1998 Spring Meeting; March 29 – April 2, 1998; Dallas, TX: “Synthesis and Properties of Poly(p-phenylene alkylene)s”.

Steiger, D.; Ehrenstein, M.; Weder, Ch.; Smith, P.; Poster presentation; Materials Day, ETH Zürich; May 29, 1998; Zürich: “Poly(p-phenylene alkylene)s – Synthesis and Properties of a Forgotten Class of Polymers”.

Steiger, D.; Weder, Ch.; Smith, P.; Invited lecture; PGS Fall Meeting; November 27, 1998; Fribourg, Switzerland: “Poly(p-phenylene alkylene)s – A Potential New Class of Engineering Plastics”.

Steiger, D.; Tervoort, T.; Weder, Ch.; Smith, P.; Invited lecture; Kolloquium für Werkstoffwissenschaften, ETH Zürich; January 20, 1999; Zürich: “Poly(p-phenylene alkylene)s – A New Family of Engineering Polymers”.

Steiger, D.; Tervoort, T.; Weder, Ch.; Smith, P.; Poster presentation; Bayreuth Polymer & Materials Research Symposium BPS’99; April 13, 1999; Bayreuth, Germany: “Structure-Property Relationships of Poly(p-phenylene alkylene)s – A Forgotten Class of Polymers”.
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List of Abbreviations, Constants, and Symbols

Ac Acetyl
ADMET Acyclic Diene Metathesis
9-BBN 9-Borabicyclo[3.3.1]nonane
BCB Benzocyclobutane
bpy Bipyridine
Bu Butyl
COSY Correlation Spectroscopy
CRT Cooling to Room Temperature
CVD Chemical Vapor Deposition
Cy Cyclohexyl
DCB Dichlorobenzene
DMAc N,N-Dimethylacetamide
DMSO Dimethyl Sulfoxide
DP Degree of Polymerization
Dec Decomposition
dmpe Dimethylphosphinoethane
dppf Diphenylphosphinoferrocene
dppp Diphenylphosphinopropane
DSC Differential Scanning Calorimetry
DVS-BCB Divinylsiloxanebenzocyclobutane
$\varepsilon_r$ Relative Permittivity
Et Ethyl
exp Experimental
$\gamma$ $T_g/T_m$
GPC Gel Permeation Chromatography
$\Delta H_m$ Enthalpy of Fusion
$\Delta H_{mi}$ Group Contribution Increments to the Enthalpy of Fusion
HMPA Hexamethylphosphoramide
HT-GPC High-temperature Gel Permeation Chromatography
$k_a$ Coefficient of Molecular Packing for the Amorphous Polymer
$k_{cr}$ Coefficient of Molecular Packing for the Ideal Crystal
$M$ Molecular Weight of the Polymer Repeat Unit
$M_n$ Number-Average Molecular Weight
$M_w$ Weight-Average Molecular Weight
Me Methyl
Ms Mesyl
MEM 2-Methoxy-ethoxymethyl
NMR Nuclear Magnetic Resonance
$n_f$ Number of Flexible Segments per Repeat Unit
$n_r$ Number of Rigid Segments per Repeat Unit
$p$ Turnover
PE Polyethylene
PET Polyethylene Terephthalate
Ph Phenyl
POM Polyoxymethylene
PP  Polypropylene
α-PP  Atactic Polypropylene
i-PP  Isotactic Polypropylene
s-PP  syndiotactic Polypropylene
PPE  Poly(p-phenylene ethynylene)
PPP  Poly(p-phenylene)
PPPB  Poly(p-phenylene butylene)
PPPH  Poly(p-phenylene hexylene)
PPPO  Poly(p-phenylene octylene)
PPPr  Poly(p-phenylene propylene)
PPV  Poly(p-phenylene vinylene)
PPX  Poly(p-xylene)
PTC  Phase Transfer Catalysis, Phase Transfer Catalyst
PTFE  Polytetrafluoroethylene
PS  Polystyrene
α-PS  Atactic Polystyrene
i-PS  Isotactic Polystyrene
s-PS  Syndiotactic Polystyrene
PX  p-Xylylene
ROMP  Ring-Opening Metathesis Polymerization
RRF  Ratio of Rigid and Flexible Segments per Repeat Unit
RT  Room Temperature
ΔSm  Entropy of Fusion
ΔSm group  Group Contribution Increments to the Entropy of Fusion
Tc  Crystallization Temperature
Tg  Glass Transition Temperature
TBAH  Tetrabutylammonium Hydrogen Sulfate
TCB  Trichlorobenzene
Tf  Triflate
TGA  Thermogravimetric Analysis
Tm  Melting Temperature
Tm  Equilibrium Melting Temperature
Tm'  Melting Temperature of the Flexible Homopolymer
TLC  Thin Layer Chromatography
THF  Tetrahydrofuran
VPO  Vapor Pressure Osmometry
VK  Van Krevelen
WAXD  Wide-Angle X-ray Diffraction
v/v  Volume per Volume
w/w  Weight per Weight
n  Number-Average Degree of Polymerization
Ym  Additive Molar Melt Transition Contribution Function
Ym'  Additive Molar Melt Transition Contribution Function Increment
Abstract

In the present work, a series of new representatives of a novel class of hydrophobic hydrocarbon polymers has been synthesized and characterized. With the objective to produce crystalline polymeric materials that combine the outstanding processability of polyethylene and the remarkable materials properties of poly(p-xylylene), the primary goal of this thesis was to explore the family of poly(p-phenylene alkylene)s.

The discussion of various synthetic tools, which might be useful for the synthesis of the target polymers, clearly reveals that the synthesis of these target polymers is, despite their rather simple chemical structure, not a trivial, straightforward task. Among the synthetic tools experimentally investigated in this thesis, the Suzuki cross-coupling reaction and acyclic diene metathesis polymerization were found to be the most suitable methods for the preparation of poly(p-phenylene alkylene)s. In the course of this work, four new representatives of the respective family, namely poly(p-phenylene octylene) (PPPO), poly(p-phenylene hexylene) (PPPH), poly(p-phenylene butylene) (PPPB) and poly(p-phenylene propylene) (PPPPr) with weight-average molecular weights of up to 25,000 were synthesized. The properties of the latter, in particular the melting temperatures, were found to strongly depend on the number of methylene groups in the repeat unit, separating the aromatic rings from each other. The polymer properties are, as expected, governed by the nature of the backbone. Whereas PPPO (90 °C), PPPH (120 °C) and PPPPr (110-130 °C) have surprisingly low melting temperatures, the highly crystalline PPPB, melting between 200 and 225 °C, is the only polymer of the studied series that exhibits a melting temperature which is significantly higher than that of polyethylene. The thermal properties of PPPB perfectly fall into the envisioned regime, in which thermoplastic processing without decomposition is possible. Hence, the high-melting PPPB meets many of the requirements that are essential for a novel, hydrophobic, processable, engineering polymer. Indeed, PPPB represents a thermoplastic polymer, which might be of interest as a processable PPX-substitute and that also could be of use in applications typically covered by polymers such as polyethylene, polypropylene or polystyrene.

Within the synthetic investigations of the present work, the thermal application window of different ADMET catalysts was systematically explored, and the respective
application limits were evaluated. As a result, the scope of these highly sensitive catalysts – in connection with ADMET polymerizations – could significantly be extended to a higher temperature regime. The optimized high-temperature reaction conditions have not only enabled the synthesis of some of the alkarotic polymers investigated in this thesis, but may also be of importance for the ADMET polymerization of other polymers that are only soluble at elevated temperatures. Experiments in connection with the Heck reaction have further demonstrated, the general viability of the palladium-catalyzed coupling of a terminal, aliphatic acetylene function (i.e. a terminal acetylene that is adjacent to at least one methylene group) to an aromatic halide. With the synthesis of several corresponding polymers we have shown that this, to the best of our knowledge, new synthetic variant of the Heck polymerization indeed represents a versatile tool in polymer chemistry.

In connection with the above described efforts to tailor the melting temperature of alkarotic polymers, a simple, semi-empirical methodology to estimate melting temperatures of unknown representatives of homologous series of polymers was developed and verified. By means of the so-called RRF-approach (Ratio of Rigid and Flexible segments in the polymer backbone), which is conceptually based on Van Krevelen’s group contribution theory, the melting temperatures of PPPH and PPPB could be predicted with a remarkable accuracy. In addition, it was shown that the application range of the RRF-approach is not restricted to the present alkarotic polymers, but it seems to have a rather broad applicability as evidenced by the successful application to numerous other polymer series, including various liquid crystalline hydrocarbon polymers and different polyamides.
Zusammenfassung


Innerhalb der synthetischen Untersuchungen dieser Arbeit wurde der thermische Anwendungsbereich von verschiedenen ADMET Katalysatoren systematisch untersucht.

Experimente in Zusammenhang mit der Heck Reaktion haben im weiteren die generelle Realisierbarkeit einer Palladium-katalysierten Kupplung einer terminalen, aliphatischen Acetylen-Funktion (d.h. einer terminalen Acetylenfunktion benachbart zu mindestens einer Methylengruppe) mit einem aromatischen Halogenid aufgezeigt. Mit der Synthese von mehreren jeweiligen Polymeren wurde gezeigt, dass diese gemäss unserem Wissen neue Variante der Heck Polymerisation eine vielseitig verwendbare Methode für die Polymersynthese ist.

Im Zusammenhang mit den oben beschriebenen Bemühungen, die Schmelztemperaturen von Poly(p-phenylen alkylen)en masszuschneiden, wurde eine einfache, semi-empirische Methode entwickelt und verifiziert, die es ermöglicht, Schmelztemperaturen von unbekannten Vertretern aus homologen Polymer-Serien abzuschätzen. Mit Hilfe dieser neuen Methode, welche vom Konzept her auf Van Krevelen’s Gruppen-Beitrags-Theorie beruht, konnten die Schmelztemperaturen von PPPH und PPPB mit einer bemerkenswerten Genauigkeit vorhergesagt werden. Zusätzlich konnte gezeigt werden, dass das Anwendungsspektrum dieses Verfahrens nicht nur auf die vorliegenden Poly(p-phenylen alkylen)e beschränkt ist, sondern dass diese Methode auch erfolgreich bei vielen anderen Polymer-Serien angewandt werden kann, z.B. bei diversen flüssig-kristallinen Kohlenwasserstoff-Polymeren und verschiedenen Polyamiden.
Chapter 1
Introduction

1.1 General Considerations

Hydrocarbon polymers, including polyolefins (e.g. polyethylene, polypropylene, polystyrene, polybutadiene), polyalkenes, poly(p-xylylene), polycycloolefins and many conjugated polymers (e.g. poly(p-phenylene), poly(p-phenylene vinylene), poly(p-phenylene ethynylene) (Figure 1.1) represent very important classes of polymers that exhibit very different materials properties.

![Polyethylene]
\[ \text{CH}_2=\text{CH}_2 \]

Polyethylene

![Polypropylene]
\[ \text{CH}_3 \text{CH}_2=\text{CH}_2 \]

Polypropylene

![Polystyrene]
\[ \text{CH}_2=\text{CH} \text{CH}_2 \]

Polystyrene

![Poly(p-xylylene)]
\[ \text{Ph} \text{CHCHPh} \]

Poly(p-xylylene)

![Poly(cycloolefins), e.g. Polynorbornene]
\[ \text{Cyclic structure} \]

Poly(cycloolefins), e.g. Polynorbornene

![Conjugated polymers, e.g. Poly(p-phenylene)]
\[ \text{Ph} \text{Ph} \]

Conjugated polymers, e.g. Poly(p-phenylene)

Figure 1.1: Selected examples of hydrocarbon polymers.
One obvious feature that these polymers have in common is their water-repulsive, hydrophobic character, which makes them interesting for protecting applications (coatings, packaging). All other characteristics of this entire family of polymers, such as solvent-resistance (solubility), degree of crystallinity, mechanical, thermal and many other properties, even electrical, depend on the chemical structure of the macromolecule. In industry, commerce and household the by far largest volume of polymers with an entire (saturated) hydrocarbon backbone is represented by the group of polyolefins, emphasizing the importance of this class of polymers. In Section 1.2, a brief description of the most important hydrocarbon polymers used in the field of packaging, coatings and high-strength fibers is given, focusing on the aspects that are of relevance to the present work. A succinct overview of another current research area, namely low-dielectric-constant materials, in which hydrocarbon polymers play an important part, is given in Section 1.3. In view of the wealth of hydrocarbon polymers and the readily available, comprehensive reviews thereon, the following overview is restricted to certain representatives that are of particular interest in the context of this thesis.

1.2 Hydrocarbon Polymers

1.2.1 Polyethylene

Since its accidental discovery in 1898 by Von Pechmann and the first patent application in 1937 by ICI, polyethylene (PE) has become the classical, most common packaging, coating and engineering polymer, which has abundant applications in both daily life and technology, ranging from plastic bags to bulletproof vests. Due to its most simple chemical structure, polyethylene allows to form perfect crystal packing and an optimal orientation of the polymer chains upon uniaxial drawing, resulting in fibers or films with outstanding mechanical properties. The melting temperature of 135 °C readily enables conventional melt- and solution-processing. However, despite its reasonable stability, the low melting temperature limits the application window of polyethylene to temperatures below approximately 100 °C. The limited thermal operation range is a serious disadvantage of this otherwise extremely attractive polymer.
1.2.2 Polypropylene

The stereospecific polymerization of propylene by Natta and Ziegler in 1954 was a scientific breakthrough with immediate industrial significance. This achievement was recognized by the award of the 1963 Novel prize in chemistry. Currently, polypropylene (PP) is one of the most important commercial thermoplastics; the global polypropylene annual growth rates typically reach 6 to 7%. The properties and applications of crystalline polypropylene resemble to a significant extent those of polyethylene. However, due to its higher melting temperature, crystalline PP exhibits a higher thermomechanical stability and is more solvent-resistant than PE. The introduction of a methyl group in the repeat unit entails the main difference between PE and PP, namely the occurrence of tacticity (Figure 1.2). Because of its irregular structure, atactic PP (α-PP) comprises zero or a very low degree of crystallinity and, as a consequence, is a soft, wax-like amorphous material, which has no use in mechanical applications. By contrast, the crystalline weight-fraction of isotactic PP (i-PP) can reach up to 65% (Figure 1.2), yielding a thermoplastic material with excellent materials properties.

![Figure 1.2: Different stereochemical forms of polypropylene.](image)

The tacticity and the less simple structure compared to polyethylene gives rise to a complex melting behavior and morphology. Syndiotactic PP (s-PP) melts at 138 °C, whereas the melting temperature of i-PP ranges from 162 °C (40 % isotactic) to 171 °C (100 % isotactic). As mentioned above, a substantial degree of crystallinity is often required in order to obtain good mechanical properties. One of the major drawbacks of PP compared to PE is its relatively slow rate of crystallization. The maximum crystal growth rate of i-PP (typically of the order of 1 μm/sec) is at least more than two orders of magnitude lower than that of polyethylene, causing an expensive
prolongation of the thermoplastic processing cycles, e.g. with injection moulding, and often requiring the use of nucleating agents. The organization of the chains within the crystal unit cell is of predominant importance for a number of solid-state properties, including the crystal modulus, which ultimately determines the maximum mechanical properties of polymers. The conformation that causes the maximum crystal modulus along the chain axis for a flexible polymer is the planar-zigzag form. Polymers that can exhibit this conformation, such as polyethylene (320 GPa\(^8\)), polyvinylalcohol (287 GPa\(^8\)) and nylon-6 (\(\alpha\)) (312 GPa\(^8\)) distinguish themselves by the highest moduli of all flexible, organic polymers. Polymers which adopt a helical crystal conformation, including isotactic PP (45 GPa\(^8\)), polyoxymethylene (109 GPa\(^8\)) and nylon-6 (\(\gamma\)) (54 GPa\(^8\)) exhibit substantially inferior mechanical properties.\(^21\)

Summarizing the features of polypropylene, the introduction of a methyl group in the polyethylene repeat unit causes some stiffening of the polymer backbone leading to a desired, enhanced melting temperature, which is expanding the thermal application window. Disadvantageous is the resulting slow rate of crystallization and the changed crystalline structure that is detrimental to the axial mechanical properties.

1.2.3 Polystyrene

As described above for polypropylene, the aspect of tacticity also determines to a large extent the morphology, properties, and, consequently the applications of polystyrene (PS). Among all constitutional isomers of polystyrene, atactic polystyrene (\(\alpha\)-PS) is the most widely used type of this thermoplastic material, mainly due to its transparent appearance and its low production costs. Because of its completely amorphous nature and a \(T_g\) of around 90 °C, atactic polystyrene is rather brittle at room temperature and has only fair mechanical properties. Consequently, the use of this material is limited to temperatures below approximately 70 °C and to applications, for which mechanical strength has not a high priority, for example in coffee cups, videocassettes, transparent containers, compact disc jackets, etc.

\(^{21}\) Calculated values
Although crystallization is not expected and has never been observed in atactic polystyrene, both isotactic and syndiotactic polystyrene (Figure 1.3) can be crystallized. Whereas only few thermal property data for crystalline syndiotactic polystyrene have been reported,22-25 the properties of crystalline isotactic polystyrene have been extensively reviewed.26,27 Although amorphous, isotactic polystyrene has been found to have the same $T_g$ as atactic polystyrene,28 there are different opinions on the effect of crystallinity on $T_g$, with some data suggesting that $T_g$ decreases with increasing crystallinity 29 and other data suggesting it increases with increasing crystallinity.30 The crystalline weight-fraction of annealed isotactic polystyrene was reported to be up to around 40 %.27

![Figure 1.3: Different stereochemical forms of polystyrene.](image)

Even though the melting temperatures of crystalline polystyrene (isotactic polystyrene: 228 °C; syndiotactic polystyrene: 270 °C) would make these polymers attractive candidates for high temperature applications, commercial use of these materials has not developed because of its slow rate of crystallization, which, as mentioned in Section 1.2.2, entails expensive, long residence times during thermoplastic processing. For example, the crystal growth rate of isotactic polystyrene was observed to be in the range of a few nm/s.20 This is a value that is 100 times lower than that of isotactic polypropylene and even 25,000 times lower than typical crystal growth rates of polyethylene. The crystallization rate of syndiotactic polystyrene is significantly faster than that of isotactic polystyrene. It is only about 10 times lower than the rate of high density polyethylene.25 In an attempt to produce a more usable form of crystalline polystyrene, some studies have been devoted to the crystallization of blends of atactic and isotactic31 and syndiotactic22 polystyrene. The maximum rate of crystallization for
each of the blends (atactic/isotactic polystyrene) was observed at a temperature corresponding closely to 8/9 of the equilibrium melting temperature.\textsuperscript{31}

1.2.4 Cycloolefinpolymers

Polynorbornene produced via ring-opening metathesis polymerization (ROMP) (Figure 1.1 and Figure 1.4 (left)) is a polyalkenamer that is commercially produced in large amounts.\textsuperscript{32} Special features of this material are a thermoplastic behavior with melting points varying between 170 and 205 °C and the ability to take up unusually high amounts of extender or plasticizer oils. Polynorbornenes can be processed into rubbers and find applications in the automotive and construction industry.

A structurally different polynorbornene with the structure depicted in Figure 1.4 (right) is produced via a vinylic polymerization mechanism which is catalyzed by transition metals.\textsuperscript{33} The catalysts employed can control the polymerization of bulky, side-chain derivatized monomers to form saturated polymers with high glass transition temperatures. The polymerization mechanism enables a high degree of control over stereoselectivity and molecular weight. This new family of polymers has been commercialized and is known under the trademark AVATREL\textsuperscript{®}, specifically designed for use as interlevel dielectrics (Section 1.3.2.2).

\begin{figure}[h]
\begin{center}
\includegraphics[width=0.8\textwidth]{structure.png}
\end{center}
\caption{Chemical structure of polynorbornenes polymerized via ring opening metathesis polymerization (left) and through a vinylic mechanism (right).}
\end{figure}

A further interesting cycloolefincopolymer is produced under the trademark ®TOPAS by Ticona GmbH (Figure 1.5).\textsuperscript{34} ®TOPAS (Thermoplastic Olefin Polymer with Amorphous Structure) is an amorphous copolymer of linear and cyclic olefins. Depending on the choice and ratio of the comonomers, copolymers are obtained featuring characteristics such as a low density (1.02 g/cm\textsuperscript{3}), good processability, high transparency, low birefringence, very low moisture uptake (< 0.01 %), brilliant barrier function, and good dielectric properties (\(\varepsilon_r = 2.35\)). This material is biocompatible and
is temperature-resistant up to 170 °C. Ticona offers five different types of TOPAS copolymers, especially tailored for the application as packaging material for moisture sensitive goods, in medical uses, and for optical applications (e.g. lenses).

![Figure 1.5: Chemical structure of the copolymer TOPAS of Ticona.](image)

1.2.5 Poly(p-xylylene) (PPX)

Poly(p-xylylene) (PPX) (Figure 1.6), usually formed upon chemical vapor deposition (CVD) polymerization, offers a unique matrix of excellent properties that has attracted significant interest in both, academic and industrial environment. PPX exhibits outstanding thermal and mechanical properties, good solvent resistance, high crystallinity and bulk barrier properties which are among the best of organic polymeric coatings. Thus, PPX-coatings have proven to be attractive materials for use in electronics, medical applications or optical devices. Although there is ample evidence that several industrial groups had research interest focused on the manufacturing of PPX and derivatives during the 1950s, industrial exploitation was stifled by the obstacle PPX presents to conventional processing technologies. Because PPX is not soluble in most common solvents, even at elevated temperatures, it cannot be used for solvent-based coating processes; neither can it be cast into films nor spun into fibers from solution. In addition, the high crystalline melting point (424 °C, close to the degradation temperature) also prevents melt-processing of PPX.

![Figure 1.6: Chemical structure of poly(p-xylylene) PPX.](image)
The chemical structure of PPX displays some very attractive features. Due to the absence of side-groups, no tacticity issues occur and a favorable crystal packing is possible. The simple chemical structure enables the formation of a dense molecular packing and a crystalline conformation that is beneficial to a favorable crystal modulus. The lack of side-groups causes a small cross-sectional area per chain. This is a crucial requirement for materials designed for high-modulus applications. Thus, PPX displays many advantageous polymer characteristics, but, unfortunately, poor processing properties.

1.2.6 Other Hydrocarbon Polymers

Kantor et al. investigated some other related all-hydrocarbon (liquid-crystalline) polymers having various numbers of methylene spacers and biphenylene units in the polymer backbone (Figure 1.7). The polymers with even numbers of methylene spacers were completely insoluble in common organic solvents and their isotropization temperatures were in the range of 150-270 °C. By contrast, the polymers with odd numbers of methylene spacers were soluble in CHCl₃ at room temperature and showed lower isotropization temperatures than polymers comprising an even number of methylene groups. Similar results were obtained with a polymer containing a tolan moiety in the polymer backbone (Figure 1.7).

![Chemical structure of main-chain liquid crystalline polymers based on a biphenyl (left) and a tolan mesogen (right).](image)

Discussions of further, non-conjugated, pure hydrocarbon polymers, synthesized by Cramer et al., Brown et al. (Section 4.1 and 4.2.2), Brown et al. (Section 4.1) and Wright et al. (Section 3.6.3) are given elsewhere in this thesis.
1.3 Low-Dielectric-Constant Materials

Within the microelectronics industry, an ongoing trend toward miniaturization coupled with higher performance can be observed (Table 1.1). The scaling of transistors toward smaller dimensions, higher speeds, and lower power has resulted in an urgent need for low dielectric constant (also known as relative permittivity) interlevel insulators\(^5\) featuring additionally high solvent resistance, high glass transition temperature, good mechanical performance and good adhesive properties to a variety of metals, particularly copper, and metal oxides. Although a variety of inorganic materials may be used in low-\(\varepsilon_r\) applications, which are usually featuring an O-Si-O backbone\(^5\), the focus of the present summary of potential materials, is on organic compounds. Polymers have the ability to planarize the topography to a much greater degree than inorganic materials and often have lower dielectric constants.

<table>
<thead>
<tr>
<th>Year</th>
<th>Feature Size / (\mu\text{m})</th>
<th>Metal Levels</th>
<th>Device Frequency / MHz</th>
<th>Relative permittivity (\varepsilon_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>0.35</td>
<td>4-5</td>
<td>200</td>
<td>4.0</td>
</tr>
<tr>
<td>1998</td>
<td>0.25</td>
<td>5</td>
<td>350</td>
<td>2.9</td>
</tr>
<tr>
<td>2001*</td>
<td>0.18</td>
<td>5-6</td>
<td>500</td>
<td>2.3</td>
</tr>
<tr>
<td>2004*</td>
<td>0.13</td>
<td>6-7</td>
<td>750</td>
<td>~2</td>
</tr>
<tr>
<td>2007*</td>
<td>0.10</td>
<td>7-8</td>
<td>1,000</td>
<td>2-1</td>
</tr>
</tbody>
</table>

*Table 1.1: Technology trends and the need for materials with low-dielectric constant (*desired)\(^5\)*

Materials with a low dielectric constant are usually processed by two common routes: vapor deposition, including plasma-enhanced chemical vapor deposition, and spin-coating. Numerous polymers are reported to exhibit low-dielectric constants. However, most of these materials do not have the mechanical or thermal properties required for use in low-\(\varepsilon_r\) integrated circuit applications. For example, Teflon\(^\text{®}\) has a relative permittivity of below 2.0 but is soft, has a low glass transition temperature, and has poor adhesion to metal and silicon oxides\(^5\). The organic polymers described in the following sections are examples of materials being currently used, evaluated or having properties that may make them suitable for process integration.
1.3.1 Polyimides

Polyimides constitute an important class of materials because of their many desirable characteristics: excellent mechanical properties, low dielectric constant (i.e. low relative permittivity), high breakdown voltage, low dielectric losses over a wide range of frequency, good planarization, relatively good albeit multi-step processability, high wear resistance, good radiation resistance, inertness to solvents, good adhesion properties, high thermal stability, low thermal expansion, good hydrolytic stability, high glass transition temperatures and long-term stability.\textsuperscript{54,55}

![Figure 1.8: Chemical structure of a common polyimide.](image)

Because of these traits, polyimides have found applications in a host of technologies as inter-metal dielectric, high-temperature adhesive, photoresist, nonlinear optical materials and membranes. The applications of polyimides range from aerospace and microelectronics to optoelectronics and composites. However, polyimides are lacking in several key performance properties. The dielectric constants are higher than desired and generally fall between 3.0 and 3.5; fluorinated polyimides have lower dielectric constants $\varepsilon_r = 2.5\text{-}3.3$. The moisture uptake is as high as 2.0 % and, due to the related significant increase in $\varepsilon_r$, can be detrimental to the functionality of a device. The processing of polyimides themselves is usually prevented by their limited solubility and high glass transition temperatures. Therefore, polyamic acid, a precursor of polyimide, has to be spin-coated and subsequently the respective polyimide is only obtained after a thermal conversion step. The fabrication of polyimides typically requires the use of an adhesion promoter resulting in additional processing steps. The latter unfavorable aspects of polyimides cause high processing costs for these materials. Another major disadvantage of polyimides is the usually rather high degree of dielectric anisotropy.\textsuperscript{53}
1.3.2 Hydrophobic Polymers

1.3.2.1 Cyclobutane Derivatives

Benzocyclobutane (BCB) undergoes a ring-opening reaction upon heating, resulting in a diene that can react with a carbon-carbon double bond, yielding a cyclohexane ring fused to a benzene moiety. By choosing an appropriate benzocyclobutane derivative, such as divinylsiloxanebenzocyclobutane (DVS-BCB) or a perfluorocyclobutane derivative with pendant perfluorovinyl ether groups, a crosslinked polymeric film is obtained upon heating these monomers. The crosslinked DVS-BCB film has a dielectric constant of 2.7 (perfluorocyclobutane derivative: 2.24) and generally is isotropic. While polyimides can have a thermal-stability advantage over these materials, DVS-BCB and perfluorocyclobutane derivatives have much less moisture absorption, and feature impressive, isotropic εr-values.

![Scheme 1.1: General reaction scheme for the BCB cycloaddition reaction (a) and chemical structure of an appropriate DVS-BCB monomer (b), which can be used for the formation of crosslinked, polymeric films.](image)

1.3.2.2 Polynorbornenes

Polynorbornenes, already introduced in Section 1.2.4, have dielectric constants from 2.4 to 2.6, depending on the attached side-chain substituents. Properties that make polynorbornene polymers particularly attractive as insulating interlayer are this rather low dielectric constant, good adhesion to metals and substrates without the use of adhesion promoters, good mechanical properties, low moisture uptake, and a high Tg. They can easily be processed by spin-coating.
1.3.2.3 Parylene® Derivatives

Parylene® or poly(p-xylylene) derivatives (Section 1.2.5 and Section 3) are commonly synthesized by means of chemical vapor deposition polymerization. There are several advantages to vapor-deposited polymers: The vapor deposition process is a solvent-free process and, thus, attractive from environmental considerations. The process can provide an extremely uniform coating over a very large area. Many vapor-deposited polymers possess superior gap-filling capability. The dielectric constant of poly(p-xylylene) was determined to be 2.45.56 However, there still are some shortcomings in vapor deposition of polymeric thin films. For example, the manufacturing equipment is not well-developed. Another difficulty is the lack of availability of suitable source materials.

1.3.2.4 Plasma Enhanced Chemical Vapor Deposition Films

If organic compounds, e.g. C_{3}F_{6}/H_{2} or C_{n}F_{2n+2}/H_{2} mixtures, in the gaseous state, are treated with electric glow-discharges (plasma), free radicals and ions are formed which can deposit on surfaces that are brought into the plasma region, and thin, fully coherent, crosslinked, polymeric films are formed.57,58 The low-pressure plasma technique is the basis for a large variety of surface modification techniques; it is able to produce void-free, well adherent thin films with thicknesses between 100 and 10,000 Å. One of the major advantages of glow-discharge produced thin films is the possibility of continuously varying the chemical composition of treated surfaces and their physical and chemical properties over a very broad range. Properties, which can be tuned, include wettability, adhesion, refractive index, hardness, barrier characteristics, chemical inertness and biocompatibility. A peculiarity that makes plasma-enhanced chemical vapor deposition especially attractive is the feasibility of scaling up reactors to production needs and to obtain fast and homogeneous processes.59

1.4 Conclusions

The above-enumerated collection of hydrocarbon polymers has clearly illustrated that there is in fact a substantial number of hydrophobic polymers which cover an extremely broad range of materials properties and applications. However, focusing on simple, well-defined, readily crystallizing, high-melting polymers, which can be used as
processable engineering plastics, for protective coatings, low-ε, and high-strength fiber applications it is obvious that a wide gap exists between the low-melting, highly processable polyethylene and the almost intractable poly(p-xylylene) (PPX; Figure 1.6 and Figure 1.9: y=2). Considering the chemical structures and properties of polyethylene and poly(p-xylylene), it seems to be apparent that polymers with chemical structures in between these two cornerstones with y>2 may exhibit very attractive and useful materials properties (Figure 1.9).

![Figure 1.9: Forgotten class of hydrocarbon polymers (with y>2) between poly(p-xylylene) (y=2) and polyethylene (y=∞).](image)

Rather surprisingly, the series of polymers, depicted in Figure 1.9 with y>2, has been little explored. An overview of the "prior art" of related polymers is given in Chapters 4 and 6. The reason for this situation might be the lack of an adequate synthetic route to produce these materials and the possible necessity to develop a new synthetic path for each representative of this series. Hence, in view of the significant potential and the structural simplicity of this family of hydrocarbon polymers, we set out to develop new synthetic routes for this group of polymers and to investigate their structure-property relationships.

### 1.5 References


34) Ticona *Thermoplastisches Olefin-Polymer amorpher Struktur TOPAS (COC)*; Ticona GmbH: Frankfurt am Main, 1997.


Chapter 2
Scope and Objectives

Driven by the goal to produce crystalline polymeric materials which combine the outstanding processability of polyethylene and at least some of the unique materials properties of poly(p-xylylene) (PPX) (Figure 2.1: y=2), the objective of this thesis is to further explore the family of poly(p-phenylene alkylene)s (Figure 2.1: y>2), here referred to as alkarotic polymers, since they exclusively consist of alkane and aromatic moieties.

![Chemical structure of poly(p-phenylene alkylene)s](image)

Figure 2.1: Chemical structure of poly(p-phenylene alkylene)s ("Alkarotic Polymers").

The approach employed is based on the notion that adjusting the number of methylene units in the backbone allows to control the flexibility of the polymer chain and, therewith, the melting temperature and processability; a concept that has been successfully applied in the design of both novel hydrocarbon polymers\(^1\)\(^-\)\(^6\) and polyamides.\(^7\)\(^-\)\(^9\) Based on the above, the primary goal of the present thesis is to investigate whether alkarotic polymers according to Figure 2.1 exist that meet the requirements for a potential new engineering plastic and that are able to close the property gap between polyethylene and poly(p-xylylene).

In Chapter 3, a literature overview is given of synthetic methods which are used for the production of hydrocarbon polymers, mostly originating from the field of conjugated polymers. Their suitability for the preparation of the present target polymers is discussed.

Apart from the investigation of a variety of synthetic routes to poly(p-phenylene alkylene)s and the production and characterization of the respective materials (Chapters 4, 6 and 7), a novel approach has been developed to gain insight and understanding of the melting behavior of certain series of polymers with homologous repeat units (Chapter 5). This semi-empirical method enabled estimation of the melting
temperatures of unknown polymers within a particular series. Finally, conclusions of the present work and an outlook and suggestions for future work are summarized in Chapter 8.

References
Chapter 3
Potential Synthetic Approaches to Poly(p-phenylene alkylene)s

Summary
A literature overview of potential synthetic routes to the present target polymers is given. Among the myriad of carbon-carbon bond-forming reactions organic chemists have developed in the past century, few selected examples are discussed for their suitability to the synthesis of the present poly(p-phenylene alkylene)s. Among them, the Heck reaction, the Suzuki cross-coupling and acyclic diene metathesis polymerization, which seemed to be the most viable and encouraging tools for the production of the target polymers of this thesis.

3.1 Introduction
Polyolefins or vinylic polymers represent the by far largest volume of plastics with an entire carbon atom backbone in daily life and technology (Scheme 3.1). Vinylic polymers can be synthesized by various routes, including ionic polymerization,1,2 free radical initiation,1,3 or heterogeneous Ziegler-Natta catalyzed polymerization;4,5 more recently vinylic polymerization was conducted using metallocene-based catalyst systems.5-7

\[
R \xrightarrow{\text{vinylic polymerization}} R_n
\]

Scheme 3.1: General reaction scheme for the synthesis of polyolefins.6

Unfortunately, the present poly(p-phenylene alkylene)s, can hardly be synthesized by vinylic polymerization because the incorporation with this method of an aromatic

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6 The correct stoichiometry of a polymerization would, of course, be: \( nA \rightarrow [A]_n \). For the sake of clarity, the \( n \) on the side of the monomers is omitted in all the polymerization schemes within this thesis.
moiety into the polymer backbone appears unlikely, if not impossible. Established routes for the synthesis of polymers, which are able to overcome this fundamental problem are rare, and only very few can be used for the production of commercial polymers. Certainly, there are many procedures known in organic chemistry to form carbon-carbon bonds, but very few actually satisfy the demands of technological polymer synthesis. A critical requirement is the realization of high yields under mild reaction conditions. The simple equation of Carothers which relates the number-average degree of polymerization $\bar{X}_n$ (produced by step polymerization) to the turnover $p$ (Equation 3.1), reflects the need to attain a very high conversion of reaction in order to produce polymers of the high molecular weight.

$$\bar{X}_n = \frac{1}{1-p}$$

*Equation 3.1: Dependence of the degree of polymerization on the conversion of the polymerization.*

Normally, degrees of polymerization $\bar{X}_n$ of the order of a few hundred and higher are required in order to produce materials that exhibit useful mechanical properties, hence demanding values of $p \geq 0.99$. Moreover, many reactions in organic synthesis are restricted to specific solvents, which very often happen to be a non-solvent for the desired polymer. A further desire, and likely difficulty is the development of direct methods that yield the envisioned alkarotic polymers, i.e. in one step without further modifications. In the following, an overview is given of direct and indirect, synthetic pathways that might be candidates for the synthesis of the target polymers.

Most of the routes are transition-metal catalyzed cross-coupling reactions, such as the Heck reaction, Suzuki, and Kumada-cross-coupling and the Pd-catalyzed cross-coupling of organotin reagents with organic electrophiles according to Stille. Further, perhaps unusual candidates for the polymer synthesis might be reductive dehalogenation, Wurtz coupling, Wittig reaction, Friedel-Crafts alkylation, polycondensation of $p$-arylene-dialkyltetrahydrothiophenium salts, electrolysis, ring-opening polymerization via a $\pi$-allyl complex, and the McMurry reaction. Ring-opening metathesis polymerization (ROMP) and acyclic diene...
metathesis (ADMET)\textsuperscript{33} polymerization are methods that have already found successful applications in the commercial manufacture of other plastics and they seem to be novel, very promising approaches towards the desired polymers. Another potential process, of course, is the polymerization of derivatives of the extremely reactive p-xylylene, the so-called Gorham route.\textsuperscript{34} Remarkably, with the exception of metathesis polymerization and the vapor-coating process of poly(p-xylylene), hardly any of these synthetic approaches are being used in industry for the large scale production of polymers.

3.2 Polymers Produced from p-Xylylene Derivatives

3.2.1 General

Poly(p-xylylene) (PPX) has already been discussed in Sections 1.2.5 and 1.3.2.3. Considering the unique chemistry for the production of PPX, the idea appears tempting to adapt its chemistry to the synthesis of poly(p-phenylene alkylene)s. The monomer of which PPX and its derivatives (depicted in Scheme 3.2) are made of is p-xylylene (PX). p-Xylylene or 1,4-quinodimethane (Scheme 3.3) is an extremely reactive, intermediate species.

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{scheme3_2.png}
\caption{Poly(p-xylylene) PPX derivatives.}
\end{scheme}

The monomeric p-xylylene is diamagnetic in its ground state, i.e., all electron spins are paired.\textsuperscript{35} An electronically excited state of p-xylene, which is substantially more energetic than the ground state (\(\Delta E = 50 \text{ kJmol}^{-1}\)), is the biradical (triplet) form (Scheme 3.3). Many authors ascribe the reactivity of p-xylylene to this “biradical nature”, because it behaves chemically as if it was a biradical, owing to its centers of high electron availability at the two terminal methylene groups although it cannot constitute any appreciable amount of the biradical species at the equilibrium, even at pyrolysis temperatures (600 °C).\textsuperscript{35} Therefore, p-xylylene is more likely a conjugated tetraolefin with a quinonoide structure, whose particular arrangement gives it extreme reactivity at its end carbons.\textsuperscript{35}
Scheme 3.3: Ground state (left) and excited state (right) of p-xylylene.

p-Xylylene and PPX were for the first time synthesized in 1904 by Thiele and Balhorn. Although the synthesis of quinonoid hydrocarbons was investigated, Thiele et al. did not realize that they in fact had succeeded in the synthesis of the latter. The polymers that can be generated from 1,4-quinodimethane derivatives range from the classic, rather intractable poly(p-xylylene) PPX (Parylene-N®, R₁ to R₈ = H), halogen-(Parylene-C®, R₅ = Cl and Parylene-D®, R₂ = R₈ = Cl), nitro-, SO₂H-, methyl- and dimethyl-, phenyl- or phenethyl-substituted PPX, to polymonochloro-p-xylylene (R₁ = Cl), polytrichloro-p-xylylene (R₁ = R₂ = R₃ = Cl), polytetrachloro-p-xylylene, polymethyl-p-xylylene, polyphenyl-p-xylylene, polytetrafluoro-p-xylylene (Parylene-F®), to derivatives in which the phenylene ring is replaced by naphthalene, pyrazine, lutidine, quinoline, thienylene or furylene moieties. In addition, Errede reported the polymerization of spiro-di-o-xylylene to high molecular weight poly(o-xylylene). Even poly(p-phenylene vinylene)s PPVs can be obtained by chemical vapor deposition of a correspondent 1,4-quinodimethane derivative and subsequent thermal conversion. For the synthesis of p-xylylene and subsequent polymerization two principally different ways exist, the procedure in the gaseous phase (the so-called “dry” route) and the method in solution (the so-called “wet” route).

3.2.2 Generation of p-Xylylene in the Gas Phase

The generation of gaseous p-xylylene PX under reduced pressure and at elevated temperatures can be accomplished by means of several approaches, such as the direct pyrolysis of p-xylene at 950 °C, the thermal cleavage of its dimer, a [2.2]paracyclophane, the thermal conversion of a monomeric α-halogeno-1,4-
xylene\textsuperscript{41} or diesters of $\alpha,\alpha'$-dihydroxy-1,4-xylene\textsuperscript{50,51} at 600-900 °C and under reduced pressure (Scheme 3.4).

Scheme 3.4: Generation of gaseous $p$-xylylene (PX) under reduced pressure.

As discussed in the previous Section, $p$-xylylene is a very reactive compound and it is only stable as a gas at low pressure. Upon condensation, e.g. upon contact with a cold surface, it spontaneously polymerizes to yield a uniform coating of a high molecular weight poly($p$-xylylene). The special features of the so-called "vapor deposition" process of $p$-xylylene imply certain practical disadvantages, namely the related application restriction of PPX to thin films and the limitation of size of the substrates resulting from the dimensions of the vapor-deposition chamber.

3.2.3 Generation of $p$-Xylylene in Solution

The formation of $p$-xylylene by the "wet route" can be accomplished by the procedure of Gilch and Wheelwright.\textsuperscript{40,52} Here, $p$-xylylene is generated by means of base-induced dehydrohalogenation of $\alpha$-chloro-1,4-xylene (Scheme 3.5). Unlike in the case of vapor deposition polymerization, here $p$-xylylene reacts directly in solution, forming PPX that precipitates from the reaction mixture when approaching a critical (i.e. solubility limiting) molecular weight. The resulting white, solid powder is poorly soluble and virtually intractable. A further method, which pertains to the so-called wet chemistry, is the preparation of PPX-derivatives by the Wurtz reaction.\textsuperscript{22} For reviews covering
almost all aspects of the synthesis of p-xylylene and the corresponding poly(p-xylylene)s we refer to the works of Iwatsuki and Greiner.\textsuperscript{53-55}

\[ \text{Scheme 3.5: Synthesis of PPX by “wet” chemistry.}^{40,52} \]

Another possibility to produce a p-xylylene derivative in solution is the sulfonium salt approach. Early attempts by Kanbe and Okawara to synthesize a saturated \( \alpha \)-substituted poly(p-xylylidene) by the polymerization of p-xylylene-bis(dimethylsulfonium tetrafluoroborate) resulted in the formation of an insoluble oligomeric PPV.\textsuperscript{56} Similar investigations by Wessling and Zimmermann involving the polymerization of several bis-sulfonium salts yielded high molecular weight, water-soluble polyelectrolytes, which generated PPV after treatment with base or exposure to elevated temperatures (Scheme 3.6).\textsuperscript{27-29} The complete mechanism for this polymerization is still unresolved. However, the reaction scheme proposed by Wessling\textsuperscript{57} involving ylid formation and elimination to form either a diradical or a p-xylylene intermediate, which polymerizes to yield polyelectrolyte A, is widely accepted.

\[ \text{Scheme 3.6: PPV synthesized by the sulfonium salt precursor route.}^{27-29} \]
In the past decades, this procedure has evolved to one of the most popular and frequently used method to produce PPV and derivatives.\textsuperscript{58-63} It has been long recognized that unsubstituted conjugated polymers tend to be infusible and insoluble. Hence, the method is of utmost attractiveness due to the generation of a processable polyelectrolytic precursor polymer, which allows the preparation of films and fibers. Subsequent thermal treatment leads to the elimination of the thioalkyl hydrochloride salt yielding the final polymer.

### 3.2.4 Applicability to Poly(p-phenylene alkylene)s

Even though there are many ways to prepare quinonoide hydrocarbons and a variety of chemically very different polymers exist that are synthesized from the latter,\textsuperscript{64} the macromolecules that are formed from quinonoide hydrocarbons almost exclusively comprise in their repeat unit two carbon atoms between the aromatic moieties. One exception can be found in the work of Sonoda et al. who attempted to apply this approach to conjugated polymers with more than two carbon atoms between the aromatic moieties (Scheme 3.7).\textsuperscript{65}

\begin{equation}
\text{Scheme 3.7: Sulfonium salt approach to produce alkarotic polymers with more than two carbon atoms between the aromatic moieties.}^{65}
\end{equation}

The pyrolysis of the MeOH-soluble precursor polymer shown in Scheme 3.7 resulted, however, only in carbonyl-containing compounds, rather than the desired conjugated polymers. Nevertheless, this method may be promising regarding the adaption to poly(p-phenylene alkylene)s. Considering the polymerization mechanism\textsuperscript{66,67} of the 1,4-quinodimethanes, it is, however, rather difficult to apply this method to longer aliphatic segments between the aromatic units. The reason for that might be the exceptional, chemical nature of carbon atoms at the benzylic position, that are able to delocalize a radical or a charge into the aromatic ring. An attempt to produce a
precursor for poly(p-phenylene butylene) (PPPB) employing a quinoidal hydrocarbon with more than two carbon atoms between the aromatic moiety is described in Section 6.2.4.

Although there are only very few successful experiments reported in the literature, and only random copolymers can initially be expected, another interesting approach towards the desired alkarotic polymers might be the copolymerization of $p$-xylylene with olefins, such as ethylene, styrene, methyl methacrylate.

### 3.3 The Heck Reaction

#### 3.3.1 General

The Heck reaction probably is one of the most exploited monomer and polymer forming transition metal catalyzed carbon-carbon coupling reaction. With the Heck reaction, organic halides and vinylic compounds are, Pd-catalyzed and under the elimination of HX ($X = \text{Cl, Br, I}$), coupled to generate a carbon-carbon bond. Conceivable syntheses of precursors of poly($p$-phenylene alkylene)s by means of the Heck reaction are depicted in Scheme 3.8. The respective poly($p$-phenylene alkylene)s may be obtained by subsequent hydrogenation of the respective precursors.

**Scheme 3.8: Conceivable synthesis of alkarotic polymers by the Heck reaction.**
3.3.2 The Heck Reaction in Polymer Synthesis

Greiner and Heitz employed this useful organic chemistry tool to the synthesis of monomers and polymers, such as poly(p-phenylene vinylene) (PPV) (Scheme 3.9), derivatives of PPV and other poly(arene vinylene)s from dibromoarenes and ethylene.\textsuperscript{72-75}

\[
\begin{align*}
\text{Br} & + \text{H}_2\text{C}=\text{CH}_2 \xrightarrow{\text{Pd(OAc)}_2, \text{base}} \text{HBr} \\
\text{Br} & \quad \text{Pd(OAc)}_2 \\
\text{H}_2\text{C}=\text{CH}_2 & \quad \text{base}
\end{align*}
\]

\textit{Scheme 3.9: Preparation of PPV by the Heck reaction.}\textsuperscript{72-75}

Apart from the synthesis of novel polymers, model reactions of bromobenzene and ethylene to trans-stilbene were investigated in order to analyze the presence of structural defects of the polymer caused by side-reactions and to optimize the synthesis of polymers.\textsuperscript{76} Among other minor by-products, the mainly formed side-product was found to be 1,1-diphenylethylene (5-10\%) which stems from a $\beta$-addition of the intermediately formed palladium(aryl)complex to the olefin.\textsuperscript{76} The quantity of these defects is dependent on the nature of the halogenated arenes used. Low catalyst concentrations and low reaction temperatures can minimize defects. Bao et al. employed the Heck Reaction for the production of PPVs as well, but in contrast to Greiner et al. divinylbenzene was used as the olefin source (Scheme 3.10).\textsuperscript{77}

\[
\begin{align*}
\text{OAlkyl} & + \text{AlkylO} \xrightarrow{\text{Pd(OAc)}_2, \text{base}} \text{AlkylO} \\
\text{OAlkyl} & \quad \text{base} \quad \text{base-HI} \\
\text{AlkylO} & \quad \text{AlkylO}
\end{align*}
\]

\textit{Scheme 3.10: Preparation of PPV by the Heck reaction according to Bao et al.}\textsuperscript{77}

The production of soluble and fusible PPVs with number-average molecular weights ($M_n$) in the range of 8,000-22,000 by the Heck reaction was found to be faster than that
by Stille reaction. Several other groups used the Heck reaction for the synthesis of novel polymers, such as polycinnamamides of rather high molecular weights ($M_n = 93,000$),\textsuperscript{78} cinnamoyl skeleton polyesters,\textsuperscript{79} or main-chain type liquid crystalline polymers with distyrylbenzene mesogenic groups (Scheme 3.11).\textsuperscript{80}

\begin{align*}
\text{Scheme 3.11: Polymers produced by the Heck reaction.}^{78,80}
\end{align*}

The Pd-catalyzed coupling reaction of aryl dibromides or -iodides with acetylenes is also a widely used and versatile method for the synthesis of conjugated poly(arylene ethynylene)s. In general, dihalogenated aryl or heteroaryl compounds can react with terminal diethynyl compounds and form polymers according to Scheme 3.12.\textsuperscript{81}

\begin{align*}
\text{Scheme 3.12: General reaction scheme of the Heck coupling of aryl halogenides with aryl acetylenes.}
\end{align*}

The usage and mechanism of the Pd-catalyzed coupling reaction of aryl halogenides with aryl acetylenes have been independently studied by three different research groups.\textsuperscript{82-84} The yields of these reactions are, in general, very good, e.g. as high as
It is, thus, not surprising that this fact stimulated significant activities in the field of semi-conducting (or conjugated) polymers; most prominently, poly(p-phenylene ethynylene)s PPEs are routinely synthesized with this procedure which led to PPEs with number average degrees of polymerization of up to 125. In addition to the preparation of PPEs, this method was also used for the synthesis of main-chain liquid-crystalline polymers based on a tolan mesogen (Scheme 3.13). However, it is known that in the presence of oxygen and copper salts, terminal acetylenes are able to react with themselves (homo-coupling according to Glaser) leading to defects in the overall polymer structure.

![Scheme 3.13: Synthesis of a hydrocarbon main-chain LC polymer by the Heck reaction.](image)

3.3.3 **Applicability to Poly(p-phenylene alkylene)s**

As outlined above, the classical Heck arylation of terminal olefins has successfully been used for the development of a variety of polymers. Significant drawbacks, however, remain in view of the synthesis of the present target polymers. Considering the reaction mechanism proposed by Heck et al., three constitutional possibilities exist for the addition of the terminal olefin to the palladium(aryl)complex and, subsequently for the addition of the olefin to the aryl halide, which leads, of course, to defects in the structure of the polymer. The number of such defect sites created in the synthesis of PPV by the Heck reaction is usually rather low, due to the comparably high regioselectivity of the monomers employed. However, in the case of poly(p-phenylene alkylene) synthesis the selectivities and reactivities of useful monomer systems differ drastically. The ratio at which the three constitutional isomers are formed under
standard reaction conditions was exemplarily studied for the reactions of bromobenzene or iodobenzene with 1-hexene, which represent ideal model reactions for the synthesis of poly(p-phenylene alkylene)s by this method (Scheme 3.14). This reaction indeed results in a mixture of at least three isomeric products; the typical structures and ratios of which are given in Scheme 3.14.

\[
\text{Scheme 3.14: Model Heck reaction for the coupling of an aliphatic terminal olefin with bromo- or iodobenzene.}
\]

Thus, the poor regioselectivity and the inferior yield of the actually desired product prevent the synthesis of well-defined alkarotics by this route. Electron-withdrawing substituents at or near the double bond would favor terminal substitution and increase the reactivity. Hence, activation of the terminal olefin would be necessary, which increases the reactivity and enables a selective attack of the terminal carbon atom (Suzuki cross-coupling, Section 3.4).

The problem with respect to regioselectivity is not existent in the case of the Pd-catalyzed coupling reaction of aryl halides with terminal alkyl acetylenes; however, the issue of the limited reactivity possibly remains. While a number of such couplings have been described for low-molecular weight compounds, to the best of our knowledge, all polymerizations described in the literature utilize aryl acetylenes for the cross-coupling, which might exhibit a better reactivity than alkyl acetylenes. However, the model reaction of 1-pentyne with iodobenzene that has been described in the literature revealed a yield of 97% and the absence of any by-products (Scheme 3.15). Due to these very promising results, it was elected to investigate and explore this approach in the
context of this work. Scheme 3.16 shows the envisioned synthesis of alkarotic polymers by the Heck reaction of diynes with diiodobenzene, followed by the catalytic reduction of the resulting precursor polymers.

\[
\text{Scheme 3.15: Model Heck reaction for the coupling of a terminal alkyl acetylene with iodobenzene.}^{83,97}
\]

\[
\text{Scheme 3.16: Envisioned synthesis of poly(p-phenylene alkylene)s by means of the Heck reaction.}
\]

### 3.4 Suzuki Cross-Coupling

#### 3.4.1 General

The Suzuki cross-coupling was developed in the late 1970s and 1980s, when several research groups became interested in the development of novel carbon-carbon bond formation reactions based on Pd-catalyzed mechanisms. With the Suzuki reaction, alkenylboranes, alkylboranes, aryl boronic acids or esters are coupled with aryl halides in the presence of palladium or thallium salts and a base, yielding products in excellent stereoselectivities and high turnovers (up to 100 %).\textsuperscript{11,98-103} A conceivable synthesis of poly(p-phenylene alkylene)s by means of the Suzuki cross-coupling reaction is depicted in Scheme 3.17. A bifunctional $B$-alkyl-9-borabicyclo[3.3.1]nonane ($B$-alkyl-9-BBN) is reacted with diiodobenzene in the presence of a palladium salt and a base.
3.4.2 The Suzuki Cross-Coupling in Polymer Synthesis

Despite the mild reaction conditions and the excellent yields of this reaction of up to 99%, the attention of polymer chemists to the Suzuki cross-coupling has been limited, at least when compared to the Heck reaction. The most prominent application of the Suzuki cross-coupling reaction is the synthesis of poly(p-phenylene)s; arylboronic acids or esters were successfully coupled with aryl halides by several groups for the preparation of soluble poly(p-phenylene)s of high molecular weights.\textsuperscript{104-106} Most interestingly, Percée et al. actually employed the coupling of alkylboranes with arylhalogenides according to Scheme 3.17 for the production of poly(p-phenylene octylene). However, apart from a $^1$H NMR spectrum, the authors did not disclose any other physical properties of the materials prepared.\textsuperscript{107,108}

3.4.3 Applicability to Poly(p-phenylene alkylene)s

As discussed in Section 3.3, the classical Heck cross-coupling of organometallic reagents, e.g. phenylpalladium acetate, with olefinic compounds such as propylene, 1-hexene, allyl alcohol, and allyl acetate is severely limited due to the formation of appreciable amounts of internal substitution.\textsuperscript{9} Those difficulties and the lack of reactivity of terminal aliphatic olefins, such as 1-hexene, are readily overcome with the preliminary hydroboration of the olefin with a suitable borane. Those considerations and the prior work of Percée et al.\textsuperscript{107,108} make the Suzuki cross-coupling a promising method for the synthesis of poly(p-phenylene alkylene)s. A minor drawback might be the use of a borane intermediate which may be difficult to isolate and purify, and therefore has to be formed \textit{in situ} directly before the polymerization. This could result in stoichiometric problems if two monomers of the AA- and BB-type are employed, and, of course, requires a 100 % efficiency of the activation step. Nevertheless, the Suzuki
cross-coupling will explicitly investigated in the course of this work (Chapters 4 and 6).

### 3.5 Nickel-Catalyzed Cross-Coupling

#### 3.5.1 General

It has been known for fifty years that catalytic amounts of transition metal salts induce the coupling reaction of Grignard reagents with organic halides. In 1972, two groups independently reported that certain nickel-phosphine complexes efficiently catalyze the selective cross-coupling of Grignard reagents with aryl and alkenyl halides (Scheme 3.18).12-14

\[
R - \text{MgX} + R' - X' \xrightarrow{[\text{NiL}_2\text{Cl}_2]} R - R' + \text{MgXX'}
\]

*Scheme 3.18: Ni-catalyzed cross-coupling of Grignard reagents with organic halides according to Kumada*.

#### 3.5.2 Nickel-Catalyzed Cross-Coupling in Polymer Synthesis

The applicability of nickel-catalyzed cross-coupling reactions in polymer chemistry has been demonstrated in a number of publications. Ueda et al. synthesized aromatic poly(ether ketone)s (Scheme 3.19, a)).109 Kantor et al. used the Kumada-coupling for the preparation of main-chain liquid crystalline polymers based on a biphenyl moiety (Scheme 3.19, b)).110,111 Perée et al. described aryl sulfonates undergoing Ni(0)-catalyzed homocoupling for the manufacture of novel functional poly(p-phenylene)s (Scheme 3.19, c)).112 However, the molecular weights obtained were rather low (2,000-7,000), which is at least in part explained by the early precipitation of the growing polymers from the polymerization solvent.110-112
Scheme 3.19: Polymers produced by different Ni-catalyzed cross-coupling reactions.109-112

3.5.3 Applicability to Poly(p-phenylene alkylene)s

The model reaction that reflects the catalytic activity of NiL2Cl2 systems for the cross-coupling of n-butyl-MgBr with phenyl chloride is extremely promising, since the best catalyst systems afford conversions and yields up to 100%.12 It is, thus, surprising that up to now, to the best of our knowledge, the Kumada coupling has not been used for the synthesis of polymers by forming the carbon-carbon bond between an aromatic sp2- and an aliphatic sp3-carbon atom. It should be noted, however, that a rather severe disadvantage of the Nickel-catalyzed cross-coupling reactions is the restricted number of solvents that can be used. It is well known that the preliminary species (e.g. Grignard reagents) can only be synthesized in solvents such as diethyl ether or THF, which are not necessarily good solvents for poly(p-phenylene alkylene)s. In addition, the reactive Grignard intermediate cannot be isolated and purified, but has to be formed in situ directly before the polymerization. In analogy to the Suzuki coupling (Section 3.4.3),
this situation could result in stoichiometric problems leading to polymers with limited molecular weight. Thus, for these reasons, we elected to not utilize nickel-catalyzed cross-couplings for the polymerization step within the scope of this thesis.

### 3.6 Stille Cross-Coupling

#### 3.6.1 General

Palladium complexes can also catalyze the coupling of tetraorganotin compounds with a variety of organic electrophiles, thus providing yet another method for generating a carbon-carbon bond. Various functional groups are tolerated by this versatile reaction and generally high yields of the cross-coupled products are obtained. In this reaction, essentially only one of the alkyl or aryl groups bound to tin enters into the coupling reaction (Scheme 3.20).

$$ R-X + R'Sn(R'')_3 \rightarrow [PdLn] \rightarrow R-R' + XSn(R'')_3 $$

*Scheme 3.20: General scheme of the Stille cross-coupling reaction.*

Fortunately, different groups are transferred rather selectively from tin, the simple alkyl group having the slowest transfer rate. Thus, an asymmetrical organotin reagent containing three simple, linear alkyl groups (such as methyl or butyl) is chosen; the fourth group, which is elected to undergo transfer, is usually an alkynyl, alkenyl, aryl, benzyl, or an allyl group.

#### 3.6.2 The Stille Cross-Coupling in Polymer Synthesis

Bochmann et al. were the first to apply these tin reagents to the synthesis of polymers. They reported the synthesis of a range of aromatic polymers by this route (Scheme 3.21, a). Unfortunately, none of their polymeric products showed any appreciable solubility in organic solvents and therefore the molecular weights remained modest. Deeter et al. succeeded in the preparation of high molecular weight ($M_n$ up to 52,000) aromatic polyketones employing the Stille reaction (Scheme 3.21, b). The Stille cross-coupling was used for the preparation of PPPs as well; however, the number-
average molecular weights of the substituted poly(p-phenylene)s obtained by Qian et al. were only in the range 2,000 to 3,800 (Scheme 3.21, c)).

\[
a) \text{Bu}_3\text{Sn}--\text{Ar}--\text{SnBu}_3 + \text{Br}--\text{Ar}''--\text{Br} \xrightarrow{[\text{Pd}]} \left[\text{Ar}--\text{Ar}'\right]_n + 2 \text{R}_3\text{SnX}
\]

![Chemical structures](image)

**Scheme 3.21: Polymers synthesized by Stille cross-coupling reactions.**

**3.6.3 Applicability to Poly(p-phenylene alkylene)s**

Only few precursors of alkarotic polymers prepared through the Stille cross-coupling have been described in the literature. The average molecular weights of the polymers obtained with the reaction conditions depicted in Scheme 3.22 are 8,000 for polymer D and 7,500 for polymer E.
The above described results of Wright et al. clearly demonstrate that it is in principal possible to apply the Stille cross-coupling to synthesize polymers forming \( \text{sp}^2-\text{sp}^2 \) or \( \text{sp}^3-\text{sp}^2 \)-carbon-carbon bonds.\(^{115,116}\) However, the few results available and the modest molecular weights obtained in the latter work did not cause us to consider this method as a viable alternative.

### 3.7 The McMurry Reaction

#### 3.7.1 General

The McMurry reaction is a titanium-induced reductive coupling of two carbonyl compounds that was invented\(^{32}\) and developed\(^{117}\) in the seventies. The reducing agent is a low-valent titanium species, which can be prepared \textit{in situ} by treatment of TiCl\(_3\) or TiCl\(_4\) with metals (e.g., zinc) or LiAlH\(_4\). It is well established that the McMurry reaction proceeds in two steps. First, the carbonyl groups are reduced to 1,2-pinacolates that are converted into alkenes. Due to incomplete reduction, 1,2-diols and epoxides are in a second step common by-products of the McMurry reaction.\(^{118}\) A conceivable synthesis of poly(p-phenylene alkylene)s by means of the McMurry reaction is depicted in Scheme 3.23.
3.7.2 The McMurry Reaction in Polymer Synthesis

Many publications discuss the coupling of monofunctional keto- or aldehyde-groups, but only in a few cases the McMurry reaction was used to prepare homopolymers from bifunctional compounds. For example, Iwatsuki et al. applied this method for the synthesis of a soluble poly(thienylene vinylene) derivative with a rather high number average molecular weight of 35,000 (Scheme 3.24).

3.7.3 Applicability to Poly(p-phenylene alkylene)s

Although the McMurry reaction has been very successfully applied in polymer synthesis, an obstacle to the synthesis of poly(p-phenylene alkylene)s might – again – be the limitation to specific solvents needed. Due to its specific role in the reductive reaction mechanism, THF is typically employed. However, THF or other ethers are not expected to be the solvents of choice for the envisioned hydrocarbon polymers. Another drawback is the necessity of a polymer-analogous step to produce alkarotic polymers, namely the hydrogenation of the double bond of the precursor polymer. For all these reasons the McMurry reaction was not employed in this thesis.
3.8 The Wittig Reaction

3.8.1 General

The Wittig reaction is a very common and frequently used reaction in organic chemistry. Typically, an alkyl- or aryl-phosphonium ylid reacts with an aldehyde or a ketone to an alkene.\textsuperscript{122,123} A conceivable synthesis of poly(p-phenylene alkylene)s by means of the Wittig reaction is depicted in Scheme 3.25.

![Scheme 3.25: Possible synthesis of alkarotic polymers by the McMurry reaction.](image)

3.8.2 The Wittig Reaction in Polymer Synthesis

Campbell et al. were the first to apply the Wittig reaction to polymer synthesis.\textsuperscript{25} Unsubstituted (and therefore intractable) PPV was synthesized from \textit{p}-xylylene-bis(triphenylphosphonium chloride) and terephthalaldehyde (Scheme 3.26, a)). This procedure was used by Kang et al. in the preparation of a confined-conjugated trimethylsilyl-substituted PPV derivative (Scheme 3.26, b)).\textsuperscript{63}
Interestingly, the Wittig reaction can also be used for the synthesis of conjugated\(^{26}\) (Scheme 3.27, a)) or confined-conjugated\(^{24}\) (Scheme 3.27, b)) polymers where the number of methylene- and/or methylidene units between the phenylene moieties is more than two. One of these latter polymers is depicted in Scheme 3.27, b); it is obvious that this polymer could be prepared as a precursor for the preparation of alkarotic polymers. After hydrogenation of the olefinic bonds between the two aromates the respective poly(\(p\)-phenylene alkylene) would be obtained.
3.8.3 Applicability to Poly(p-phenylene alkylene)s

Although the Wittig reaction is supposed to be able to generate structures with long alkyl segments between aromatic moieties, it is questionable whether significantly higher molecular weights than $\overline{M}_n = 2.100^{63}$ or $\overline{M}_n = 3.900^{26}$ can be obtained with this method. Hence, we did not employ the Wittig reaction for the synthesis of the target polymers.
3.9 Ring-Opening Metathesis Chemistry

3.9.1 General

Metathesis chemistry, now more than thirty years old, pertains to a unique reaction of olefins that can be used to synthesize both small molecules and a broad spectrum of polymers. When cyclic olefins are employed, cleavage of the ring leads to the formation of a difunctional moiety, which effectively forms the building block for a polymer chain (Scheme 3.28).

\[ 
\text{Scheme 3.28: Ring-opening metathesis polymerization (ROMP)}
\]

Conceivable cyclic monomers that may be used for the production of poly(p-phenylene alkylene)s with ring-opening metathesis polymerization (ROMP) are depicted in Scheme 3.29.

\[ 
\text{Scheme 3.29: Proposed synthetic pathway for the synthesis of poly(p-phenylene alkylene) by ROMP.}
\]

3.9.2 Ring-opening Metathesis Polymerization

Ring-opening metathesis polymerization was for the first time used by Anderson and Merckling at DuPont de Nemours and Co. for the polymerization of norbornene with titanium-based catalysts, as early as 1954. However, the decisive contributions stem
from three laboratories which recognized and carefully investigated the general concept of metathesis, namely the group of Robert L. Banks at Phillips Petroleum, Giulio Natta's team in Milano and Nissil Calderon and coworkers at Goodyear and Co. In 1954, Natta et al. reported the ring-opening of cyclobutene with a TiCl₄/Al(C₂H₅)₃ system¹²⁶-¹²⁸ and cyclopentene with Mo- or W-systems¹²⁹ yielding high molecular weight 1,4-polybutadienes or polypentenamers. In addition, cyclohexene, cycloheptene, cyclooctene, and cyclododecene in the presence of the same catalyst systems were polymerized as well.¹³⁰ Calderon and coworkers investigated the polymerization of cyclic olefins more thoroughly, and, indeed, accomplished homogeneous disproportionation for the first time and named the ring-opening polymerization of cycloolefins as a special case of olefin metathesis.¹³¹ They disproved the earlier assumption of the Truett- and Natta-groups that the ring-opening site was the bond adjacent to the double bond, i.e. α-scission, and correctly proposed the ring-opening to take place at the double bond itself.¹³² Those early developments unleashed an enormous research effort around the world in the development of new catalysts¹³³-¹³⁸ and in the application of metathesis to the synthesis of both polymeric materials¹³⁹ and low molecular weight compounds.¹⁴⁰ The development of highly active, well-defined Lewis-acid-free catalysts by the groups of Schrock and Grubbs in the mid-eighties has triggered a renaissance in metathesis chemistry. The synthesis of alkylidene complexes of molybdenum¹⁴¹,¹⁴² tungsten,¹⁴³ ruthenium¹⁴⁴ and others¹⁴⁵,¹⁴⁶ has caused a revitalization of the design of polymeric materials based on living ring-opening metathesis polymerizations.¹⁴⁷-¹⁵² Cyclic olefins differ in one major respect from their acyclic counterparts in that the reaction is usually (but not necessarily) accompanied by the release of ring strain. Thus, an additional driving force exists which results in shifting the reaction equilibrium in favor of the polymer. However, ring strain is not a prerequisite, since entropy alone can drive the polymerization of strain-free monomers to high polymers if the ring size is sufficiently large.

Considering the amount of patents and applications of olefin metathesis in industry (more than 1,100), it is obvious that this is a very versatile and powerful synthetic tool of polymer- and petrochemistry.¹²⁴
3.9.3 Applicability to Poly(p-phenylene alkylene)s

The persuasive enumerations given above suggest that ROMP is a prime candidate for the synthesis of high molecular weight poly(p-phenylene alkylene)s. The structure of the cyclic monomers (Scheme 3.29) reveals the one serious disadvantage of ROMP, namely the difficult accessibility of the respective ROMP monomers. Despite the favorable features of ROMP, the number of monomers that can be used for this polymerization technique is limited or their synthesis is rather sophisticated such as in the case of [4.4]paracyclophane derivatives.153-157 Nevertheless, once the respective monomers are synthesized, ROMP might be a potent candidate for the formation of poly(p-phenylene alkylene)s.

3.10 Acyclic Diene Metathesis (ADMET) Polymerization

3.10.1 General

Although the suggestion of polycondensation metathesis chemistry was not new,134 the first relevant efforts to employ olefin metathesis in a step propagation, condensation-type polymerization were made in the group of Ken Wagener.158 For acyclic diene metathesis (ADMET) polymerization (Scheme 3.30) a variety of acyclic dienes are suitable monomers in a polymerization that is driven by the removal of a small molecule, in most cases ethylene. Thus, it became possible to significantly broaden the scope of metathesis polymerization, which had been restricted to cyclic olefins (Section 3.9.3). A synthetic route for poly(p-phenylene alkylene)s is suggested in Scheme 3.31. Of course, a polymer-analogous step is required, namely the reduction of the double bond formed by the ADMET polymerization step.

\[
\text{Scheme 3.30: Acyclic diene metathesis (ADMET) polymerization.}
\]
Scheme 3.31: Proposed synthetic pathway for the synthesis of poly(p-phenylene alkylene)s by ADMET polymerization.

3.10.2 Literature Overview

The initial limitations of ADMET that were mainly related to the vinyl addition chemistry in the original tungsten hexachloride-ethyl aluminum dichloride catalyst system\textsuperscript{158} has been eliminated by choosing a Lewis-acid-free metathesis catalyst system\textsuperscript{159} With the latter, perfectly linear 1,4-polybutadiene\textsuperscript{160} polymers\textsuperscript{161-163} and copolymers\textsuperscript{164,165} of 1,5-hexadiene and 1,9-decadiene with number-average molecular weights, $M_a$, up to 57,000\textsuperscript{161} were synthesized. In addition to the relatively high molecular weights and the readily available monomers, ADMET polymerization proved to be a viable synthetic route to polymers possessing various functionalities such as ethers,\textsuperscript{166} thioethers,\textsuperscript{167} silanes,\textsuperscript{168} siloxanes,\textsuperscript{169} esters,\textsuperscript{170} ketones,\textsuperscript{171} carbonates,\textsuperscript{172} amines,\textsuperscript{173} boronates,\textsuperscript{174} stannanes,\textsuperscript{175} and alcohols.\textsuperscript{176}

3.10.3 Applicability to Poly(p-phenylene alkylene)s

According to the discussion in the previous section, ADMET polymerization was deemed to be a very attractive option for the synthesis of the present target polymers. Compared to the monomers required for ROMP, the synthesis of the appropriate acyclic dienes needed for ADMET seems to be significantly easier, which is a relevant advantage of ADMET. A fundamental drawback of ADMET might be the fact that ADMET is a step-propagation, condensation-type polymerization. It is well known that the molecular weights of such polymerizations are, in principle, lower than those obtained from polyadditions or living polymerizations. Also the required polymer analogous step is a minor disadvantage of this methodology.

3.11 Conclusions

In the previous Sections 3.2-3.10, different possible synthetic approaches for the synthesis of poly(p-phenylene alkylene)s have been discussed. As described in Section
3.1, the requirements for a chemical reaction to be suitable for the synthesis of high polymers are multifold. Hence, methods such as Friedel Crafts alkylation, Wurtz coupling or others have not even been discussed in this Chapter, since they are not a priori expected to be suitable for the synthesis of polymers. As is evident from the arguments in the respective Sections, the suitability of the different synthetic routes differ significantly. Whereas the polymerization of $p$-xyylene derivatives (Section 3.2) initially is not expected to be suitable for the synthesis of poly($p$-phenylene alkylene)s due to mechanistic aspects, the probability to obtain high-molecular weight polymers by applying the Kumada-(Section 3.5), Stille-(Section 3.6) or Wittig-type (Section 3.8) reactions may be small because of preparative reasons. However, the Heck reaction (Section 3.3), the Suzuki cross-coupling (Section 3.4) and metathesis polymerization (Sections 3.9 and 3.10) seem to be viable and promising tools for the production of the target polymers, and will be experimentally explored in the next Chapters of this thesis.

3.12 References

4) Ziegler, K. Kunststoffe 1955, 45, 506.
36) Thiele, J.; Balhorn, H. Ber. 1904, 37, 1463.
Chapter 4

Synthesis and Properties of Poly(p-phenylene octylene)

Summary

Suzuki cross-coupling and acyclic diene metathesis (ADMET) polymerization followed by catalytic reduction of the resulting, unsaturated prepolymer were successfully used as synthetic routes to a class of processable, hydrophobic, crystalline polymers, which contain only aromatic and aliphatic hydrocarbon units in their backbone. Poly(p-phenylene octylene) (PPPO) was prepared with weight-average molecular weights in the range of 13,000-25,000. Besides Suzuki-cross coupling and ADMET polymerization, the Heck reaction was employed to explore its suitability to synthesize this class of polymers. Poly(p-phenylene octylene) was found to be highly soluble in common solvents and to have an unexpectedly low melting temperature of around 90 °C, which enabled melt-processing into fibers and films without decomposition. Wide-angle X-ray diffraction and annealing experiments on PPPO revealed two different crystal modifications. The polymer, as precipitated from the reaction mixture, predominantly forms the kinetically preferred Modification α; while the annealing of pristine PPPO almost exclusively leads to the thermodynamically more stable Modification β.

4.1 Introduction

To our knowledge, the only studies on poly(p-phenylene alkylene)s that have been described in the literature were conducted by Cramer and Percec on poly(p-phenylene octylene) (PPPO),1,2 and Brown and Farthing.3 While Cramer et al. discussed the synthesis of poly(p-phenylene octylene) (PPPO) – unfortunately without disclosing any physical characteristics – Brown and Farthing described an attempt to produce poly(p-phenylene butylene) (PPPB) by the Wurtz-condensation of 1,4-bis-(2-chloroethyl)-benzene. The experiments of Brown and Farthing resulted in a material which was reported to be amorphous but – rather inconsistently – to have a melting temperature between 395-415 °C; thus, in a temperature regime in which thermoplastic processing is still stifled by thermal decomposition. Guided by the results of Brown and Farthing,3 we elected to synthesize PPPO as the first representative of the present target polymers. In this chapter, the evaluation of different synthetic approaches for the production of poly(p-phenylene octylene) (PPPO) is given special emphasis.
4.2 Results and Discussion

4.2.1 Polymer Synthesis via Heck-Arylation of Terminal Acetylenes

Compared to the arylation of double bonds, the problem of poor regioselectivity is excluded in the case of the Heck-arylation of terminal acetylenes (Chapter 3). The Pd-catalyzed coupling of diiodobenzene with 1,7-octadiyne or 1,9-decadiyne employing Pd-complexes, CuI, diisopropylamine in toluene, in fact, led to the expected unsaturated precursors P1 or P2, respectively (Scheme 4.1).

\[
\text{Pd} / \text{CuI} \quad \text{diisopropylamine}
\]

\[
\begin{align*}
\text{Pd(II)} / \text{Cu} & \quad \text{diisopropylamine} \\
\text{P1} & \quad \text{n} \\
\text{P2} & \quad \text{n}
\end{align*}
\]

Scheme 4.1: Synthesis of alkarotic polymers by the Heck reaction.

In a set of experiments, the influence of the nature of Pd catalyst employed, different monomer ratios, and the use of endcappers were investigated. In addition, in one experiment an even more extended flexible moiety, 1,9-decadiyne, was employed. In the initial experiments regarding the synthesis of P1, exactly equimolecular amounts of the two monomers were employed, in order to prepare high-molecular weight polymers. The polymers obtained with this method were found to be only partially soluble, and the molecular weights of the soluble fraction were limited to degrees of polymerization of 12. In addition, it was found that the two different Pd-catalysts employed, Pd(PPh₃)₄ and PdCl₃(PPh₃)₂, did not lead to significantly different results (Experimental Section 4.4.5: P1.1, P1.2). Since it is known that, in the presence of oxygen and copper salts, terminal acetylenes are able to react among themselves (homo-coupling according to Glaser) we elected to employ an excess of the diyne monomer in order to compensate for the “loss” of this monomer. In fact, these experiments resulted in polymers, the degrees of polymerization of which were significantly higher (Experimental Section 4.4.5: P1.3, P1.4). In a further experiment it could be shown that the degree of polymerization could
be controlled by the use of a monofunctional endcapper, e.g. iodobenzene (Experimental Section 4.4.5: P1.4).

A problem that could not be fully elucidated was the occasionally occurring limited solubility of the materials obtained, which might have several causes. One explanation could be the significant overall rigidity of the polymer backbone, which (in view of the lack of specific interactions with the solvent) gives rise to an inherent low solubility. Another important aspect is the tendency of double or triple bonds adjacent to an aromatic ring to crosslink, potentially even already during the condensation step. This assumption is supported by DSC measurements which clearly exhibit an irreversible exothermic transition, starting at around 120 °C (Figure 4.1), which can be assigned to the crosslinking of the benzylic acetylenes. Apparently, the cross-linking step can occur either during polymerization or, later on, if the respective materials are excessively heated, leading, of course, to hardly, if at all soluble materials.

![Figure 4.1: Differential scanning calorimetry of precursor polymer P1 prepared by the Heck reaction.](image)

In order to obtain the desired alkarotic polymer, the triple bond of the produced Heck precursor polymer had to be saturated. To evaluate the best hydrogenation conditions, initial experiments were based on oligomeric P1 in order to avoid solubility problems. Soluble oligomers of polymer P1, P1.1 and P1.5 with a degree of polymerization of 6 and 8, respectively, were attempted to hydrogenate using different catalytic reduction
methods. However, attempts to fully hydrogenate the precipitated precursors P1 using Pd on activated charcoal Pd(C), PtO₂, Raney-Nickel, or Pd(OAc)₂ with hydrogen pressures between 1 and 50 bar, failed (Experimental Section 4.4.5.3). In the same way, the reduction of the triple bonds of precipitated P1 by employing p-toluenesulfohydrazide and tri-n-propylamine was not successful. Nevertheless, precursor polymer P1 could be successfully hydrogenated by directly treating the polymerization mixture with p-toluenesulfohydrazide and tripropylamine (Experimental Section 4.4.5.4). The ¹H NMR spectrum of the resulting black residue confirmed clearly the formation of PPPO. Unfortunately, attempts to purify the black, sticky residue by reprecipitation failed.

The hydrogenation of the model compound phenylacetylene to ethylbenzene employing Pd(C)/H₂ (5 bar) at room temperature proceeded without problems (Experimental Section 4.4.5.5), which clearly indicated that the reason for the insufficient hydrogenation of P1 under those conditions was not determined by the limited reactivity of the reactants.

In a supplementary experiment, 1,9-decadiyne was employed instead of 1,7-octadiyne as the acetylenic monomer (Scheme 4.1). In analogy to the polymerization of 1,7-octadiyne with diiodobenzene, the polymer obtained was found to be highly insoluble in toluene, chloroform, and xylene. However, the ¹H NMR spectrum of a small fraction that proved to be soluble in hot chloroform clearly proved the postulated structure as depicted in Scheme 4.1 (Experimental Section 4.4.5). The limited solubility, also with a representative with a more extended methylene segment, could be an indication for the cross-linking aspect as discussed above.

In this Chapter it has been shown that with the Heck coupling of aliphatic diacetylenes and diiodobenzene well-defined, alkarotic precursors with a reasonable molecular weight can be produced. In one case, we succeeded in reducing the triple bonds resulting in a first PPPO sample.

Thus, although the Heck-arylation of terminal acetylenes in principle seems to be a viable way to produce precursors of poly(p-phenylene alkylene)s, substantial disadvantages, such as the poor solubility of e.g. polymers P1 and P2, together with their inherent chemical reactivity towards crosslinking, prevented further efforts in this direction.
4.2.2 Polymer Synthesis via Suzuki Cross-Coupling

As discussed in Chapter 3, the difficulties related to internal substitution and the limited reactivity of terminal aliphatic olefins are readily overcome with the preliminary hydroboration of the olefin with a suitable borane. In fact, PPPO was successfully prepared by the Suzuki cross-coupling of hydroborated 1,7-octadiene (1) and diiodobenzene (Method A) as suggested by Cramer et al. (Scheme 4.2).

![Scheme 4.2: Monomer synthesis and Suzuki cross-coupling polymerization.](image)

The reaction conditions of Cramer et al. were modified and different experimental parameters were varied in order to possibly optimize the polymerization procedure. The reported reaction conditions for the coupling of dibromo- or diiodobenzene with dihydroborated octadiene were based on PdCl₂(dppf) (3 mol%) as catalyst and dichlorobenzene as the solvent; the reaction temperature was between 50 and 60 °C, aqueous NaOH or KOH were employed as the base forming a two-phase system with the apolar solvent, and, thus, a phase transfer catalyst (PTC), such as tetrabutylammonium hydrogensulfate or crown ethers had to be used. The conditions
of Cramer et al. were reproduced in entries PPPO.1 and PPPO.2 (Table 4.1), resulting in polymers with number-average molecular weights of up to 2,800. Unfortunately, it was not possible to compare these values to the ones in the original paper since the authors did not disclose any physical data of their polymers. Although PdCl$_2$(dppf), C1, is mostly used in Suzuki cross-couplings, Pd(PPh$_3$)$_4$ is, according to Suzuki et al.,$^{13}$ equally suitable for this coupling reaction. However, the molecular weights of polymers obtained in experiments with Pd(PPh$_3$)$_4$, employing an aqueous base (10 M KOH), were not as high as the ones obtained with the Cramer conditions (Entries PPPO.3 and PPPO.4 in Table 4.1). Amazingly, the experiment conducted without PTC (Entry PPPO.4 in Table 4.1) did result in a higher molecular weight than the one with PTC (Entry PPPO.3). Therefore, it was decided to employ an alkoxy base, in order to avoid a phase separation and, particularly, to avoid water in the polymerization system, because water is a non-solvent for the target polymers. In the following experiments, in which NaOEt or NaOMe were employed as the base, no significant improvement of the molecular weights could be achieved compared to the Cramer conditions (Entries PPPO.5 to PPPO.6 in Table 4.1). Also, removal of THF after the hydroboration and carrying out the reaction in pure xylene at elevated temperatures did not lead to higher molecular weights (Entry PPPO.7 in Table 4.1). A slight improvement was observed when a solvent mixture of THF and toluene was used, and THF was distilled off during the first three hours of the polymerization (Entry PPPO.8 in Table 4.1). In another experiment (Entry PPPO.9 in Table 4.1), we attempted to evaluate the minimum temperature at which the polymerization set in. At a temperature of 60 °C the polymerization usually started in less than an hour, as indicated by a significant clouding of the reaction mixture, probably due to the formation of borane salts. When the polymerization was started at RT, no reaction could be detected after two hours. Even after 18 h at RT, no polymer could be precipitated if a small sample of the mixture was given into MeOH. When conducting the reaction at 50 °C, after two hours a slight, but continuously increasing clouding indicated the start and the progress of the reaction. Thus, it was concluded that a temperature of around 50 °C is needed for the induction of the Suzuki cross-coupling.

In the course of this work it was established that a possibility to significantly increase the molecular weight of poly(p-phenylene octylene) prepared with the Suzuki cross-coupling was the use of the asymmetrical monomer 2 (Method B: Scheme 4.2). In this
context, the asymmetrical monomer 8-(4'-bromophenyl)-1-octene (2) was employed for Suzuki cross-coupling reactions (Entries PPPO.10 and PPPO.11 in Table 4.1) under otherwise similar conditions. The use of this asymmetrical monomer represents an improvement of the original route, because limitations with respect to equimolarity of the originally two monomers are eliminated, and the number of condensation steps required to obtain a certain molecular weight is reduced by 50%. In fact, the molecular weights obtained with this route were approximately twice as high compared to the ones obtained with two symmetrical monomers under similar reaction conditions. All relevant reaction parameters for the Suzuki polycondensations are summarized in Table 4.1 and for further details see the Experimental Section.
<table>
<thead>
<tr>
<th>Entry</th>
<th>method</th>
<th>catalyst</th>
<th>base</th>
<th>solvent</th>
<th>THF/Polym. solvent</th>
<th>Temp./°C</th>
<th>reaction time, h</th>
<th>mp, °C</th>
<th>$\bar{M}_n$ b)</th>
<th>9-BBN g)</th>
<th>yield, %</th>
<th>Specials</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPO.1</td>
<td>A</td>
<td>PdCl$_2$(dppf)</td>
<td>KOH</td>
<td>toluene</td>
<td>0.80</td>
<td>60</td>
<td>18</td>
<td>96</td>
<td>1,500</td>
<td>1</td>
<td>71</td>
<td>PTC</td>
</tr>
<tr>
<td>PPPO.2</td>
<td>A</td>
<td>PdCl$_2$(dppf)</td>
<td>KOH</td>
<td>m-DCB</td>
<td>0.76</td>
<td>60</td>
<td>3.25</td>
<td>97</td>
<td>2,800</td>
<td>1</td>
<td>72</td>
<td>PTC</td>
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<tr>
<td>PPPO.3</td>
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<td>Pd(PPh$_3$)$_2$</td>
<td>KOH</td>
<td>toluene</td>
<td>0.73</td>
<td>60</td>
<td>15</td>
<td>97</td>
<td>380</td>
<td>1</td>
<td>86</td>
<td>PTC</td>
</tr>
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<td>Pd(PPh$_3$)$_2$</td>
<td>KOH</td>
<td>toluene</td>
<td>0.73</td>
<td>60</td>
<td>16</td>
<td>91</td>
<td>1,300</td>
<td>1</td>
<td>94</td>
<td>without PTC</td>
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<tr>
<td>PPPO.5</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOEt</td>
<td>toluene</td>
<td>0.80</td>
<td>60</td>
<td>15</td>
<td>69</td>
<td>560</td>
<td>1</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>PPPO.6</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.79</td>
<td>60</td>
<td>96</td>
<td>93</td>
<td>1,880</td>
<td>1.1</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>PPPO.7</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>xylene</td>
<td>0</td>
<td>120</td>
<td>17.5</td>
<td>75</td>
<td>1,500</td>
<td>1.1</td>
<td>33</td>
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<td>PPPO.8</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>xylene</td>
<td>0.03–1.0</td>
<td>100–110</td>
<td>18</td>
<td>90</td>
<td>1,880</td>
<td>1.1</td>
<td>56</td>
<td>THF removed</td>
</tr>
<tr>
<td>PPPO.9</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.99</td>
<td>RT–50</td>
<td>48</td>
<td>73</td>
<td>1,300</td>
<td>1.1</td>
<td>23</td>
<td>temp. exp.</td>
</tr>
<tr>
<td>PPPO.10</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.54</td>
<td>60</td>
<td>14</td>
<td>50</td>
<td>560</td>
<td>1</td>
<td>51</td>
<td></td>
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<td>PPPO.11</td>
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<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.71</td>
<td>60</td>
<td>15</td>
<td>84</td>
<td>1,100</td>
<td>1</td>
<td>73</td>
<td></td>
</tr>
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<td>PPPO.12</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.81</td>
<td>60</td>
<td>18</td>
<td>85</td>
<td>1,100</td>
<td>1</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>PPPO.13</td>
<td>A</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.78</td>
<td>60</td>
<td>18</td>
<td>91</td>
<td>1,500</td>
<td>1.1</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>PPPO.14</td>
<td>B</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.4</td>
<td>60</td>
<td>24</td>
<td>93</td>
<td>3,200</td>
<td>1.1</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>PPPO.15</td>
<td>B</td>
<td>Pd(PPh$_3$)$_2$</td>
<td>NaOME</td>
<td>toluene</td>
<td>0.38</td>
<td>60</td>
<td>24</td>
<td>94</td>
<td>3,400</td>
<td>1.1</td>
<td>69</td>
<td></td>
</tr>
</tbody>
</table>

*a* A: polymerization of 1 and diiodobenzene; B: polymerization of hydroborated 2 (cf. Scheme 4.2 and Experimental Section). b determined by $^1$H NMR endgroup analysis. c $M_w$ (GPC-visco) = 2,000; $M_w$ / $M_n$ = 1.89. d $M_s$ (VPO) = 4,500; $M_w$ (GPC-visco) = 9,300; $M_w$ / $M_n$ = 4.14. e $M_v$ (GPC-visco) = 3,500; $M_w$ / $M_s$ = 2.30. f aqueous solution (10 M). g ratio 9-BBN/olefinic group.

Table 4.1: Suzuki polymerization: Methods and results.
All PPPO samples prepared by Suzuki cross-coupling were satisfactorily characterized by NMR spectroscopy, DSC and – in selected cases – TGA and elemental analysis. Elemental analysis show a slight but systematic offset from the calculated values, in well agreement with the presence of a significant amount of end groups. All PPPO samples prepared with the Suzuki polymerization could be fully and easily dissolved in solvents such as toluene, xylene, benzene, dichloromethane, CHCl₃ or THF under ambient conditions and, thus, exhibited the attempted ease of solubility. Molecular weight data were obtained using ¹H NMR-endgroup analysis for oligomers and gel permeation chromatography (GPC) for polymers. All molecular weight data of oligomers and polymers produced by Suzuki cross-coupling are given together with the reaction conditions in Table 4.1. The maximum number-average molecular weights of PPPOs prepared by Suzuki cross-coupling were around 3,500. The use of the asymmetric monomer 2, as suggested in this work, was found to lead to a significantly improved molecular weight when compared to the route used by Cramer et al.¹⁻² The investigation and the discussion of the morphology and thermal properties of PPPO will follow in Chapter 4.2.4.

Hence, it is concluded that the direct Suzuki cross-coupling is sufficient for a first estimation of the thermal properties of a new alkarotic polymer. However, since it is not expected that the molecular weights can be significantly improved with this approach it is necessary to focus on other synthetic procedures.

### 4.2.3 Polymer Synthesis via ADMET Polymerization

As discussed in Chapter 3, acyclic diene metathesis polymerization has been recently established as a suitable synthetic route to high-molecular-weight, unsaturated polymers, that are perfectly linear and free from branching and other defects.¹⁴⁻¹⁸ ADMET polymerization is here for the first time used for the synthesis of a class of hydrophobic and (potentially) high-melting polymers containing only aromatic and aliphatic hydrocarbon units in their backbone.

#### 4.2.3.1 Monomer Synthesis

The ADMET polymerizations were based on the monomer 1,4-bis(pent-4-ene)benzene (3), having two terminal olefinic functions. 3 was prepared in a one-step method, using
the nickel-complex catalyzed cross-coupling of 1-pentenylmagnesium bromide with \( p \)-dibromobenzene or \( p \)-dichlorobenzene as shown in Scheme 4.3, according to a general reaction scheme introduced elsewhere.\(^{19-21}\)

![Scheme 4.3: Monomer synthesis catalyzed by different Ni-complexes.](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Halide</th>
<th>Yield of 3</th>
<th>Yield of by-product(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiCl}_2(\text{dppp}) ) C2</td>
<td>( p )-dichlorobenzene</td>
<td>18 %</td>
<td>15 %</td>
</tr>
<tr>
<td>( \text{NiCl}_2(\text{dmpe}) ) C3</td>
<td>( p )-dibromobenzene</td>
<td>52 %</td>
<td>20 %</td>
</tr>
</tbody>
</table>

\(^a\)By-product: 4-chloro-1-(pent-4-ene)-benzene.

Table 4.2: Dependence of the yield of 3 on the Nickel-complex and on the aromatic halide employed.

The yield of this reaction was found to strongly depend on the type of nickel-catalyst and/or aromatic halide used. With the commercially available dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II), \( \text{NiCl}_2(\text{dppp}) \), (C2) only modest yields and significant amounts of the monoalkylated by-product, 4-chloro-1-(pent-4-ene)-benzene, could be achieved. Higher yields of up to 52 % were obtained when employing dichloro-[1,2-bis(dimethylphosphino)ethane]nickel(II), \( \text{NiCl}_2(\text{dmpe}) \), (C3), which has successfully been used in the past for the preparation of compounds containing olefinic groups.\(^{20}\) The preparation of this catalyst followed the methods given before.\(^{22,23}\)
4.2.3.2 Synthesis of the ADMET Precursor Polymer

As will be evident from the below description, ADMET polymerization of diene 3 indeed led to the PPPO-precursor polymer P3 (Scheme 4.4). 2,6-Diisopropylphenylimidophenylenediamine(molybdenumbis(hexafluoro-α-butoxide) (C4), also known as “Schrock’s Mo-catalyst”, was employed as the polymerization catalyst. The choice of this particular catalyst was triggered by its successful use in polymerizations of rather similar monomers (Chapter 3) and by its commercial availability. The typical reaction times were in the range of 48 h, the evolution of ethylene and the increasing viscosity of the reaction mixtures were taken as an indication for the progress of the polymerization. The removal of ethylene from the catalytic equilibrium system under a static vacuum was earlier found to be an effective driving force for the polymerization and, thus, was also applied here.

Scheme 4.4: Acyclic diene metathesis (ADMET) polymerization of diene 3.

Three different sets of reaction conditions were investigated. In a first method, the polymerization was carried out in bulk (P3.1; Method C), i.e. the catalyst was added to the liquid monomer, and, when the solidification set in, the reaction mixture was heated, in order to continue the reaction in the melt. In the second method, the polymerization was also started in bulk, but when the reaction mixture started to solidify, it was redissolved by adding toluene (P3.2; Method D). In a third method, the monomer was
dissolved in toluene before the catalyst was added, and the entire polymerization was carried out in solution (P3.3, P3.4; Method E). While no significant difference between the two latter methods was observed, and polymers with comparable molecular weight and molecular weight distribution were obtained, the polymerization in bulk (method A) led to a significantly broader polydispersity ($\overline{M}_w / \overline{M}_n \approx 8$) and a low melting point of the resulting PPPO.

By means of a post-condensation (P3.5; Method F), attempts were made to further improve the molecular weight of the precursor polymer. An ADMET polymer was redissolved in the polymerization solvent and, again, treated with catalyst C4. The pressure and the temperature were kept at the same values as in the previous polymerizations. However, the degree of polymerization could only be slightly improved by this procedure; the molecular weights of the two polymers (as determined by GPC), starting material P3.4 and post-condensation product P3.5, were within the margins of error of the measurement (Table 4.3). The reaction parameters for all ADMET polymerizations are compiled in Table 4.3.
### Table 4.3: ADMET polymer precursors P3: Methods and results.

<table>
<thead>
<tr>
<th>Polymer precursor</th>
<th>Method</th>
<th>Reaction temperature, °C</th>
<th>Toluene, % w/w</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;, °C</th>
<th>( \overline{M}_{w} ) b)</th>
<th>( \overline{M}<em>{w} / \overline{M}</em>{n} ) b)</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPO.16</td>
<td>P3.1</td>
<td>C</td>
<td>72</td>
<td>98</td>
<td>46-77</td>
<td>25,700</td>
<td>7.9</td>
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<tr>
<td>PPPO.17</td>
<td>P3.2</td>
<td>D</td>
<td>24</td>
<td>99</td>
<td>95</td>
<td>1,300</td>
<td>1.4</td>
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<tr>
<td>PPPO.18</td>
<td>P3.3</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>82</td>
<td>14,800</td>
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<td>PPPO.19</td>
<td>P3.3</td>
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<tr>
<td>PPPO.20</td>
<td>P3.3</td>
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<td>24</td>
<td>98</td>
<td>79</td>
<td>18,000</td>
<td>3.3</td>
</tr>
<tr>
<td>PPPO.21</td>
<td>P3.4</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>98</td>
<td>6,600</td>
<td>2.5</td>
</tr>
<tr>
<td>PPPO.22</td>
<td>P3.4</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>99</td>
<td>7,500</td>
<td>2.2</td>
</tr>
<tr>
<td>PPPO.23</td>
<td>P3.5</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>90</td>
<td>13,900</td>
<td>3</td>
</tr>
</tbody>
</table>

a) C: bulk; D: bulk/solution; E: solution; F: post-condensation (for details cf. Experimental Section).

b) Material fully amorphous.

c) Determined by GPC-visco.

### Table 4.4: PPPO polymers prepared by reduction of the ADMET-precursor polymers P3.

<table>
<thead>
<tr>
<th>Polymer precursor</th>
<th>Method</th>
<th>Reaction time, h</th>
<th>Toluene, % w/w</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;, °C</th>
<th>( \overline{M}_{w} ) b)</th>
<th>( \overline{M}<em>{w} / \overline{M}</em>{n} ) b)</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPO.16</td>
<td>P3.1</td>
<td>C</td>
<td>72</td>
<td>98</td>
<td>46-77</td>
<td>25,700</td>
<td>7.9</td>
</tr>
<tr>
<td>PPPO.17</td>
<td>P3.2</td>
<td>D</td>
<td>24</td>
<td>99</td>
<td>95</td>
<td>1,300</td>
<td>1.4</td>
</tr>
<tr>
<td>PPPO.18</td>
<td>P3.3</td>
<td>E</td>
<td>24</td>
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<td>82</td>
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<tr>
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<td>P3.3</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>78</td>
<td>15,500</td>
<td>3.0</td>
</tr>
<tr>
<td>PPPO.20</td>
<td>P3.3</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>79</td>
<td>18,000</td>
<td>3.3</td>
</tr>
<tr>
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<td>P3.4</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>98</td>
<td>6,600</td>
<td>2.5</td>
</tr>
<tr>
<td>PPPO.22</td>
<td>P3.4</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>99</td>
<td>7,500</td>
<td>2.2</td>
</tr>
<tr>
<td>PPPO.23</td>
<td>P3.5</td>
<td>E</td>
<td>24</td>
<td>98</td>
<td>90</td>
<td>13,900</td>
<td>3</td>
</tr>
</tbody>
</table>

a) Refers to the method used for the preparation of the unsaturated prepolymer P3 (cf. Table 4.3).

b) Determined by GPC-visco.
4.2.3.3 Catalytic Reduction of the Precursor Polymer

The PPPO-precursor polymers P3 were reduced to yield the fully reduced PPPO, employing the catalytic hydrogenation with palladium on activated charcoal as the reduction method (Scheme 4.5). In contrast to the precursor polymers obtained by the Heck reaction, the reduction of the ADMET precursors proceeded smoothly and essentially completely.

![Scheme 4.5: Catalytic hydrogenation of the precursor polymer P3.](image)

The polymers obtained were characterized to satisfaction by $^1$H and $^{13}$C NMR spectroscopy and elemental analysis. The $^1$H NMR spectra of polymers P3 and PPPO are shown in Figure 4.2. The spectra are consistent with the postulated chemical structure, and it is evident that the olefinic signals (5.49-5.36 ppm) have fully disappeared after reduction. The reaction parameters for the reductions are compiled in Table 4.4.

All PPPO samples prepared by means of ADMET polymerization could be fully and easily dissolved in solvents such as toluene, xylene, benzene, dichloromethane, CHCl₃, or THF under ambient conditions and, thus, exhibited the desired improved solubility. Molecular-weight data were obtained using $^1$H NMR-endgroup analysis for oligomers and gel permeation chromatography (GPC) for polymers. All molecular-weight data for polymers prepared by ADMET polymerization are given in Table 4.3 and Table 4.4 together with the reaction conditions. The weight-average molecular weights ($M_w$) obtained with ADMET were in the range of 13,000-25,000, with polydispersities of typically between 2 and 3, and, thus, in the typical molecular weight regime available with ADMET reactions.¹⁴⁻¹⁸
4.2.4 Thermal Properties and Morphology

The thermal properties of PPPO, prepared by all methods, have been investigated using wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at heating rates of 10 °C/min. TGA experiments
reveal that **PPPO** is stable under dynamic heating up to around 350 °C under nitrogen atmosphere, as well as in air (Figure 4.3). The DSC traces (Figure 4.4) for the **PPPOs** show well-defined melting points between 55 and 100 °C, indicative for a significant crystallinity of these polymers. The graphic representation of the influence of the degree of polymerization (DP) on the melting temperature of the **PPPOs** reveals an interesting behavior (Figure 4.5). As can be expected, the melting temperature initially increases with increasing DP before levelling off at a temperature of about 100 °C at a number-average molecular weight ($\bar{M}_n$) of about 2,000 (DP = 10). However, at a $\bar{M}_n$ of about 5,000 (DP = 25), a significant drop of the melting temperature to a new plateau of about 80 °C can be observed. In addition, as can be seen from Figure 4.4, the shape of the endothermic melt transition changes from a fairly narrow, well-resolved peak to a significantly broader signal. This behavior can be related to different causes. The observed effect is consistent with a possible change from extended chain to folded chain crystals, as it is well known for e.g. polyethylene in a comparable molecular-weight regime.\(^{26}\) The observed behavior is also in well agreement with the existence of different crystal structures; in fact, polymorphism is also well known to play an important role in the case of PPX.\(^{27-29}\)

![Graph showing thermogravimetric analysis of PPPO.16 under nitrogen and air.](image-url)
Figure 4.4: Differential scanning calorimetry of low-molecular weight (PPPO.17, $\bar{M}_w = 1,300$) and high-molecular weight (PPPO.19, $\bar{M}_w = 15,500$) PPPO.

Figure 4.5: Melting temperatures of PPPO for different degrees of polymerization.
To investigate the thermal behavior of PPPO in more detail, thermal annealing experiments, combined with wide-angle X-ray diffraction experiments, were carried out. WAXD patterns of all pristine PPPO samples (independent on the molecular weight and the method of preparation) are identical and show a significant crystallinity (Figure 4.6). A (weak) reflection corresponding to the largest spacing is found at 11.9 Å. This value represents the distance between the repeat units and is in well agreement with the one calculated from standard bond lengths and angles (12.5 Å). In addition, the diffractograms of pristine PPPO show prominent reflections at 5.2 and 3.7 Å, which were found to be characteristic for a crystal structure that was designated as modification α. When the same polymers were molten under inert atmosphere for 60 minutes and subsequently annealed for 48 h at 75 °C, the WAXD-patterns (also shown in Figure 5), show the most prominent reflection at 4.5 Å, which were found characteristic for a crystal structure that was designated as modification β. While the reflection corresponding to the largest spacing at 11.9 Å remained unchanged in the latter, the reflections at 5.2 and 3.7 Å disappeared almost completely. These observations suggest that virgin PPPO, as precipitated from the reaction mixture, apparently predominantly forms a crystal structure of the α-form, while the annealing of pristine PPPO almost exclusively leads to the β-modification. It was, therefore, concluded that modification α is kinetically preferred, while modification β is of higher thermodynamic stability. Independent of the molecular weight, it is therefore possible to selectively generate PPPO of the desired crystal modification. Samples of the different crystal modifications did not display significantly different thermal behavior. Hence, the above referred melting temperature/chain length development was attributed to the standard transition of melting of extended chain crystals to that of folded chain crystals.
Finally, it is noteworthy that PPPO-samples of a $\bar{M}_w$ higher than about 14,000 have fiber-forming properties. PPPO monofilaments could easily be drawn from their melts (Figure 4.7).

Figure 4.6: Wide-angle X-ray diffraction patterns of PPPO of modification $\alpha$ (left) and modification $\beta$ (right).

Figure 4.7: Optical micrograph of a melt-drawn PPPO fiber.
4.3 Conclusions

It was demonstrated that the Suzuki cross-coupling and acyclic diene metathesis (ADMET) polymerization can be used as synthetic routes to poly(p-phenylene octylene) (PPPO). The highest molecular weight was obtained when PPPO was prepared by the ADMET polymerization of 1,4-bis(pent-4-ene)benzene, followed by the catalytic reduction of the resulting unsaturated polymer. The weight-average molecular weight of the polymers obtained with this method were in the range of 13,000-25,000, significantly higher than PPPO which, for the purpose of comparison, was prepared by the Suzuki cross-coupling of hydroborated olefins and aryl halogenides.

Wide-angle X-ray diffraction and annealing experiments on PPPO revealed two different crystal modifications. The polymer, as precipitated from the reaction mixture, predominantly forms the kinetically preferred modification α, while the annealing of pristine PPPO almost exclusively leads to the thermodynamically more stable modification β.

All PPPO-samples prepared in this work are highly soluble in common solvents; the low melting temperature enabled melt-processing into homogeneous fibers and films, hence, demonstrating a first proof of principle for the concept to design melt-processable PPX-analogs. Analyses of the crystallization kinetics and the evaluation of the equilibrium melting temperature of PPPO are given in the Appendix.

4.4 Experimental Section

4.4.1 General

All reagents and solvents were purchased from FLUKA, Aldrich Chemical Co. and Merck. Catalyst C4 was purchased from Strem Chemicals, Inc. All experiments were carried out under a nitrogen or argon atmosphere by applying standard Schlenk, vacuum-line or glove-box techniques. All ADMET polymerizations were carried out in a glove-box, under a N₂-atmosphere with water and oxygen concentrations of lower than 1 ppm. A stationary vacuum was used for the polymerizations. DSC and TGA measurements were performed on Netzsch CC 200 and Netzsch TG 209 instruments. ¹H NMR and ¹³C NMR spectral data are expressed in ppm relative to internal TMS and were obtained on various Bruker NMR spectrometers. GPC measurements were
performed on a Knauer GPC (detectors: differential refractometer Knauer, Viscotek H502 differential-viscosimeter, conditions: flow 1.1 mL/min, solvent tetrahydrofuran, 45 °C). Elemental analyses and mass spectra were carried out by the Microanalysis and Mass Spectra Laboratories of the Department of Chemistry of ETH Zürich. Wide-angle X-ray diffraction experiments were performed with a Seifert ISO-Debeyflex 2002, using Ni-filtered CuKα-radiation as the ray source (conditions: 12 h, 30 mA, 35 kV).

4.4.2 Purification of Monomers, Reagents, and Solvents

Due to the very high sensitivity of the ADMET catalyst, all chemicals used in conjunction with this catalyst were of outmost purity. Monomer 3 was purified by column chromatography, dried over calcium hydride for 24 h, distilled onto molecular sieve (4 Å), and subsequently deoxygenated by sparging with Ar for at least 2 h prior to use. ¹H NMR and elemental analysis was used to verify the purity of the monomer. The absence of water was confirmed by the observation of a persistent purple color, after a sodium/benzophenone indicator solution was added to the monomer.

4.4.3 Catalyst Synthesis

Dichloro-{l,1'-bis(diphenylphosphino)ferrocene}palladium(II) (C1) PdCl₂(dppf).³¹

A solution of 1,1'-bis(diphenylphosphino)ferrocene (dppf) (391.3 mg, 0.7058 mmol) in benzene (8 mL) was added to a stirred suspension of dichloro-bis(acetonitrile)palladium(II) (183.1 mg, 0.7058 mmol) in benzene (7 mL). After the reaction mixture was stirred at room temperature for 15 h, the reddish brown precipitate formed was collected by filtration, washed with benzene, and dried in vacuo to give 510 mg (99 %) of an orange solid. DSC: Tm and dec 270 °C (Lit.³¹ 265 °C). ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.93-7.86 (m, 8H), 7.51-7.46 (m, 4H), 7.41-7.38 (m, 8H), 4.40-4.39 (m, 4H), 4.20-4.19 (m, 4H). ³¹P NMR (122 MHz, CDCl₃) δ 34.37.

Dichloro-{l,2-bis(dimethylphosphino)ethane}nickel(II) (C3) NiCl₂(dmpe).²²-²³

A solution of NiCl₂(H₂O)₆ (661 mg, 2.78 mmol) in ethanol (5 mL) was added to a stirred solution of 1,2-bis(dimethylphosphino)ethane (850 mg, 5.66 mmol) in ethanol (14 mL). After concentration of the resulting mixture to low volume and the addition of a mixture of acetone/toluene (14 mL/28 mL), orange crystals precipitated which were filtered off,
dried and redissolved in ethanol (14 mL). A second portion of NiCl₂(H₂O)₆ (1.074g, 4.521 mmol) in ethanol (18 mL) was added to this latter solution and the reaction mixture was stirred for 90 min at 85 °C. The resulting precipitate was collected and recrystallized from ethanol to yield gold-red C3 (810 mg, 2.90 mmol, 51 %). ¹H NMR (300 MHz, CDCl₃, 298 K) δ 1.75 - 1.73 (m, 4H, CH₂), 1.70 - 1.54 (m, 12H, CH₃); ³¹P NMR (120 MHz, CDCl₃, 298 K) δ 50.86 (s, 2P). Anal. Calcd for NiC₆H₁₆P₂Cl₂: C, 25.76; H, 5.76; P, 22.15; Cl, 25.35. Found: C, 25.95; H, 5.51; P, 22.37; Cl, 25.50.

4.4.4 Monomer Synthesis

8-(4'-Bromophenyl)-1-octene (2).³² A solution of 1,4-bis(bromomagnesio)butane in diethyl ether (40 mL), which was prepared from 1,4-dibromobutane (16.343 g, 75.693 mmol) and magnesium turnings (18.397 g, 0.757 mol), was added to a solution of 4-bromobenzyl bromide (9.459 g, 37.85 mmol) in diethyl ether (20 mL) at 0 °C. After stirring for 4.5 h at 0 °C, the reaction mixture was cooled to -40 °C and a solution of allyl bromide (12.8 mL, 0.151 mol) in diethyl ether (20 mL) was slowly added such that the temperature of the reaction mixture was kept between -45 to -60 °C. After the addition was complete, the mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched with water, the mixture was extracted with diethyl ether. The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuo. Column chromatography (silicagel 60, n-hexane) of the resulting yellow oil yielded a 10/14-mixture (5.0 g) of 4-(4'-bromophenyl)-1-butene and 2. Pure 2 (1.8 g, 18%) was obtained by vacuum distillation, bp 80-85 °C (4.0 x 10⁻² mbar). ¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.38 (d, J = 8.34, 2H), 7.03 (d, J = 8.20, 2H), 5.86-5.73 (m, 1 H), 5.02-4.90 (m, 2H), 2.55 (t, J = 7.47, 2H), 2.06-2.00 (m, 2 H), 1.63-1.53 (m, 2 H), 1.41-1.26 (m, 6 H). ¹³C NMR (75 MHz, CDCl₃, 298 K) δ 141.74 (Ar), 139.04 (-HC=CH₂), 131.25 (Ar), 130.15 (Ar), 119.27 (Ar), 114.24 (-CH=CH₂), 35.31, 33.74, 31.24, 29.00, 28.91, 28.81 (all CH₂). Anal. calcd for C₁₄H₁₀Br: C, 62.93; H, 7.17. Found: C, 62.83; H, 7.39.

Synthesis of 1,4-Bis(pent-4-ene)benzene (3) Employing NiCl₂(dpdp) C2. 1-Pentenyl-magnesium bromide was prepared by reacting 5-bromopent-1-ene (25.69 g, 172.4 mmol) and magnesium turnings (5.24 g, 216 mmol) in absolute diethyl ether (160 mL)
for 2 h at 0 °C. The mixture was added dropwise to a stirred mixture of p-
dichlorobenzene (10.20 g, 69.37 mmol), NiCl₂(dppp) (482 mg, 0.89 mmol) and diethyl ether (65 mL) at RT and the resulting mixture was refluxed for 69 h at 35 °C. Finally, the reaction was quenched with aqueous HCl (2 N, 125 mL), the organic phase was separated off and washed with water (3 x 50 mL), and the aqueous layer was extracted with diethyl ether (3 x 80 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuo. After distillation of the resulting oil, two compounds were obtained: 1,4-Bis(pent-4-ene)benzene (3) (2.65 g, 18 %; bp 75 °C, 4.3 x 10⁻² mbar) and 4-chloro-1-(pent-4-ene)-benzene (1.90 g, 15 %; bp 47 °C, 9.0 x 10⁻² mbar). The desired diene (3): ¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.09 (s, 4H, Ar), 5.90-5.76 (m, 2H, C=CH), 5.06-4.94 (m, 4H, C=CH₂), 2.59 (t, J(₁H) = 7.74 Hz, 4H, Ar-CH₂), 2.13-2.05 (m, 4H, CH₂-CH=CH₂), 1.76-1.65 (m, 4H, C-CH₂-C).

Synthesis of 1,4-Bis(pent-4-ene)benzene (3) employing NiCl₂(dmpe) C3. 1-Pentenyl-magnesium bromide was prepared by reacting 5-bromopent-1-ene (9.58 g, 64.3 mmol) and magnesium turnings (1.73 g, 71.0 mmol) in absolute diethyl ether (60 mL) for 150 min at RT. The remaining solids were filtered off, the solution was added dropwise to a stirred mixture of p-dibromobenzene (6.07 g, 25.7 mmol), NiCl₂(dmpe) (90.3 mg, 0.32 mmol) and diethyl ether (20 mL) at RT and the resulting mixture was refluxed for 24 h at 35 °C. Another portion of NiCl₂(dmpe) (30.9 mg, 0.11 mmol) was added to the reaction mixture, which was then allowed to reflux for another 6 h. Finally, the reaction was quenched with aqueous HCl (2 N, 125 mL), the organic phase was separated off and washed with water (3 x 50 mL), and the aqueous layer was extracted with diethyl ether (3 x 80 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuo. Column chromatography (silicagel 60, n-hexane) of the resulting oil yielded 3 (2.87 g, 52 %) as a colorless oil; bp 58 °C (7.5 x 10⁻² mbar). ¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.08 (s, 4H, Ar), 5.90-5.77 (m, 2H, C=CH), 5.06-4.94 (m, 4H, C=CH₂), 2.59 (t, J(₁H) = 7.75 Hz, 4H, Ar-CH₂), 2.13-2.05 (m, 4H, CH₂-CH=CH₂), 1.75-1.65 (m, 4H, C-CH₂-C); ¹³C NMR (75 MHz, CDCl₃, 298 K) δ 139.96 (s, 2C, Ar-C), 138.70 (s, 2C, C=CH₂), 128.36 (d, 4C, Ar), 114.64 (t, 2C, H₂C=C), 34.93 (t, 2C, C-C=), 33.35 (t, 2C, C-Ar), 30.70 (t, 2C, C(CH₂)₂); mass spectrum m/e 214 (M⁺ parent). Anal. Calcd for C₁₆H₂₂: C, 89.66; H, 10.34. Found: C, 89.58; H, 10.17.
4.4.5  Polymer Synthesis by the Heck Reaction

4.4.5.1  Synthesis of Poly(p-phenylene oct-1,7-diynylene) (P1)

(P1.1). A solution of 1,7-octadiyne (0.983 g, 9.25 mmol), 1,4-diiodobenzene (3.053 g, 9.254 mmol), Pd(PPh₃)₄ (149 mg, 0.129 mmol) and CuI (24.6 mg, 0.129 mmol) in toluene (150 mL) and diisopropylamine (88 mL) was heated to 70 °C. After stirring at 70 °C for 19 h, the orange suspension was cooled to ambient temperature, filtered, and 50 % (120 mL) of the total volume of the filtrate were poured into MeOH (900 mL). The precipitate was collected and washed with hot EtOH, acetonitrile and acetone. After drying in vacuo, 820 mg (49 % of the total yield) of poly(p-phenylene oct-1,7-diynylene) was obtained as a cream-colored solid that was soluble at room temperature in toluene, CH₂Cl₂ and THF. DSC: No Tₘ detectable, degradation (probably crosslinking) starts at 120 °C. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.60 (d, J = 8.32, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.32, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H). DPₙₑorrh: 8.

(P1.2). A solution of 1,7-octadiyne (0.1592 g, 1.499 mmol), 1,4-diiodobenzene (0.4946 g, 1.499 mmol), PdCl₂(PPh₃)₂ (31.3 mg, 0.045 mmol), CuI (8.4 mg, 0.044 mmol) and diisopropylamine (15 mL) in toluene (35 mL) was heated to 70 °C. After 43 h, the suspension was cooled to ambient temperature and added to rapidly stirred acetone (400 mL). The precipitate was collected and washed with hot EtOH and acetonitrile. After drying in vacuo, 120 mg (44 %) of a cream-colored solid was obtained. This material was only partially soluble in xylene, toluene, and chloroform. DSC: No Tₘ detectable, degradation (probably crosslinking) starts at around 130 °C. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.60 (d, J = 8.32, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.32, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H). DPₙₑorrh (of soluble fraction): 8.

(P1.3). A solution of 1,7-octadiyne (0.1604 g, 15.11 mmol), 1,4-diiodobenzene (4.0676 g, 12.330 mmol), PdCl₂(PPh₃)₂ (221.1 mg, 0.315 mmol), CuI (89.8 mg, 0.472 mmol) and diisopropylamine (28 mL) in toluene (140 mL) was heated to 70 °C. After 15 h, the

* the remaining 50 % v/v were employed in Section 4.4.5.4.
suspension was cooled to ambient temperature and added to rapidly stirred acetone (600 mL). The precipitate was collected and washed with hot EtOH and acetonitrile. After drying in vacuo, 1.99 g (90 %) of a cream-colored solid was obtained that was fully soluble in toluene and chloroform. DSC: No T_m detectable, degradation (probably crosslinking) starts at around 120 °C. ^1H NMR (300 MHz, CDCl_3, 297 K) δ 7.29 (s, phenylene, 4H), 2.47 (m, 4H), 1.77 (m, 4H). DP_NMR: Not measurable, due to the lack of endgroups.

(P1.4). A solution of 1,7-octadiyne (1.6124 g, 15.19 mmol), 1,4-diiodobenzene (4.0475 g, 12.27 mmol), iodobenzene (561 mg, 2.74 mmol), PdCl_2(PPh_3)_2 (310.6 mg, 0.4425 mmol), CuI (89.3 mg, 0.469 mmol) and diisopropylamine (60 mL) in toluene (140 mL) was heated to 70 °C. After 19 h the suspension was cooled to ambient temperature and added to rapidly stirred acetone. The precipitate was collected and washed with hot EtOH and acetonitrile. After drying in vacuo 2.11 g (78 %) of a cream-colored solid was obtained that was fully soluble in chloroform. DSC: No T_m detectable, degradation (probably crosslinking) starts at around 115 °C. ^1H NMR (300 MHz, CDCl_3, 297 K) δ 7.42-7.38 (m, phenyl-endgroups, traces), 7.30 (s, phenylene, 4H), 2.47 (m, 4H), 1.78-1.77 (m, 4H). DP_NMR: 25.

(P1.5). A solution of 1,7-octadiyne (0.5115 g, 4.818 mmol), 1,4-diiodobenzene (1.900 g, 8.759 mmol), Pd(PPh_3)_4 (107 mg, 0.092 mmol) and CuI (32 mg, 0.17 mmol) in toluene (53 mL) and diisopropylamine (23 mL) was heated to 70 °C. After 19 h, the orange suspension was cooled to ambient temperature, filtered, and poured into EtOH (250 mL). The precipitate was collected and washed with EtOH and acetone. After drying in vacuo, 658 mg (56 %) of a cream-colored solid that was soluble at room temperature in toluene, CH_2Cl_2 and THF. DSC: No T_m detectable, degradation (probably crosslinking) starts at 120 °C. ^1H NMR (300 MHz, CDCl_3, 300 K) δ 7.60 (d, J = 8.32, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.32, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H). DP_NMR: 6.

(P1.6). A solution of 1,7-octadiyne (0.1601 g, 1.508 mmol), 1,4-diiodobenzene (0.4976 g, 1.508 mmol), Pd(PPh_3)_4 (52.3 mg, 0.045 mmol), CuI (7.7 mg, 0.040 mmol) and
diisopropylamine (15 mL) in toluene (35 mL) was heated to 70 °C. After 43 h, the suspension was cooled to ambient temperature and added to rapidly stirred acetone (400 mL). The precipitate was collected and washed with hot EtOH and acetonitrile. After drying in vacuo, 121 mg (45 %) of a cream-colored solid was obtained. This material was only partially soluble in xylene, toluene, and chloroform. DSC: No $T_m$ detectable, degradation (probably crosslinking) starts at around 115 °C. $^1$H NMR (300 MHz, CDCl$_3$, 297 K) δ 7.60 (d, $J = 8.37$, phenyl iodide-endgroups, traces), 7.29 (s, phenylene, 4H), 7.11 (d, $J = 8.37$, phenyl iodide-endgroups, traces), 2.47-2.45 (m, 4H), 1.77 (m, 4H). DP$_{NMR}$ (of soluble fraction): 12.

4.4.5.2 Synthesis of Poly($p$-phenylene deca-1,9-diynylene) (P2)

(P2.1). A solution of 1,9-decadiyne (2.0825 g, 15.52 mmol), 1,4-diiodobenzene (4.9493 g, 15.00 mmol), PdCl$_2$(PPh$_3$)$_2$ (317 mg, 0.452 mmol) and CuI (86.5 mg, 0.454 mmol) in toluene (140 mL) and diisopropylamine (60 mL) was heated to 70 °C. After 15 h, the yellow suspension was cooled to ambient temperature and poured into acetone (600 mL). The yellow precipitate was collected and washed with hot EtOH, acetonitrile and acetone. After drying in vacuo, 3.19 g (167 %) of a yellow powder was obtained that was almost fully insoluble in toluene, CHCl$_3$ and xylene. DSC: No $T_m$ detectable, degradation (probably crosslinking) starts at 100 °C. $^1$H NMR (300 MHz, CDCl$_3$, 297 K) of the chloroform soluble fraction δ 7.28 (s, phenylene, 4H), 2.41 (t, $J = 6.9$, 4H), 1.62-1.43 (m, 8H).

4.4.5.3 Attempts to Hydrogenate Poly($p$-phenylene oct-1,7-diynylene) (P1)

With Pd(C). (R1). Palladium on charcoal (10.2 mg, 10 % Pd) was added to a mixture of P1.5 (102 mg, 0.565 mmol) in toluene (10 mL) and the reaction mixture was stirred at RT under a hydrogen pressure of 5 bar. After 2 h, EtOH (0.5 mL) was added. After a total reaction time of 72 h, the catalyst was removed by filtration through a silica gel. After concentration of the reaction mixture in vacuo, 66 mg (62 %) of an orange solid were obtained. DSC: No $T_m$ detectable, degradation (probably crosslinking) starts at 100 °C. $^1$H NMR (300 MHz, CDCl$_3$, 300 K) δ 7.61 (d, $J = 8.35$, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, $J = 8.35$, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.5.
(R2). Palladium on charcoal (9.6 mg, 10 % Pd) was added to a mixture of P1.5 (86.9 mg, 0.482 mmol) in toluene (8 mL) and the reaction mixture was stirred at RT under a hydrogen pressure of 8 bar. After 48 h, the hydrogen pressure was raised to 44 bar. After a total reaction time of 52 h, the mixture was concentrated in vacuo and directly dissolved in CDCl₃. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.60 (d, J = 8.34, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.34, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.5.

(R3). Palladium on charcoal (133 mg, 10 % Pd) was added to a mixture of P1.1 (284 mg, 1.58 mmol) in toluene (70 mL, absolute) and the reaction mixture was stirred at 30 °C under a hydrogen pressure of 5 bar. After 24 h, the hydrogen pressure was raised to 50 bar. After a total reaction time of 48 h, the mixture was filtered through Celite, the resulting solution was concentrated in vacuo and directly dissolved in CDCl₃. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.60 (d, J = 8.15, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.21, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.1.

(R4). Palladium on charcoal (30 mg, 10 % Pd) was added to a mixture of P1.1 (71 mg, 0.39 mmol) in toluene (20 mL, absolute) and hexane (4 mL) and the reaction mixture was stirred at RT under a hydrogen pressure of 39 bar. After 24 h the mixture was filtered, the resulting solution was concentrated in vacuo and directly dissolved in CDCl₃. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.60 (d, J = 8.41, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.41, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.1.

With Pd(OAc)₂ (R5). Pd(OAc)₂ (1.5 mg, 6.7 μmol) and P1.5 (59.3 mg, 0.329 mmol) in benzene (5 mL) was stirred at RT and under a hydrogen pressure of ca. 1.5 bar. After a total reaction time of 18 h, the mixture was added to MeOH (20 mL). The resulting dispersion was concentrated in vacuo, redissolved in toluene (5 mL) and, again, dropwise added to MeOH (20 mL). The resulting solution was filtered through silica gel. After concentration of the resulting solution in vacuo, 13 mg (22 %) of an orange solid were obtained. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.61 (d, J = 8.51, phenyl
iodide-endgroups of P1.5, traces), 7.30 (s, phenylene of P1.5, traces), 7.11 (d, J = 8.50, phenyl iodide-endgroups of P1.5, traces), 7.07 (s, phenylene of PPPO, 4H), 2.55 (t, J = 7.54, Ar-CH2- of PPPO, 4H), 2.49-2.45 (m, -CH2- of P1.5, traces), 1.77 (m, -CH2- of P1.5, traces), 1.579 (m, -CH2- of PPPO, 4H), 1.305-1.258 (m, -CH2- of PPPO, 8H): Ratio P1.5/PPPO = 1:5.

With PtO2 hydrate (R6). A suspension of PtO2 hydrate (2.6 mg) and P1.5 (48 mg, 0.27 mmol) in toluene (5 mL) were stirred at RT under a hydrogen pressure of 1.5 bar. After a total reaction time of 24 h, the mixture was concentrated in vacuo and directly dissolved in CDCl3. 1H NMR (300 MHz, CDCl3, 300 K) δ 7.60 (d, J = 8.40, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.40, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.5.

With Raney-Nickel (R7). Raney-Nickel (2 mL, 50 % slurry in water) was added to a solution of P1.1 (71 mg, 0.394 mmol) in toluene (10 mL) and the reaction mixture was stirred at RT under a hydrogen pressure of 1.5 bar. An additional amount of toluene (5 mL) was added. After a total reaction time of 17 h, the catalyst was removed by filtration. After concentration of the mixture in vacuo 71 mg (96 %) of a partially insoluble, orange solid were obtained. 1H NMR (300 MHz, CDCl3, 300 K) δ 7.60 (d, J = 8.30, phenyl iodide-endgroups, traces), 7.30 (s, phenylene, 4H), 7.11 (d, J = 8.32, phenyl iodide-endgroups, traces), 2.47 (m, 4H), 1.77 (m, 4H): Only starting material P1.1.

4.4.5.4 Preparation of PPPO by Reduction of P1 (R8). To the other 120 mL (50 % v/v) of the reddish filtrate of P1.1 were added p-toluenesulfonylhydrazide (4.31 g, 23.1 mmol) and tripropylamine (3.31 g, 23.1 mmol) at room temperature. The resulting solution was heated to reflux (110 °C). After 2 h, the color of the reaction mixture had become black. After 3.5 h, additional portions of p-toluenesulfonylhydrazide (2.07 g, 11.12 mmol) and NPr3 (3.31 g, 23.14 mmol) were added. After a total time of 4.5 h, the reaction mixture was concentrated and poured into MeOH (300 mL). The oily, black residue was washed with EtOH, acetone and acetonitrile. After drying in vacuo, 646 mg (74 %) of a black solid were obtained. DSC: No clear Tm
detectable. $^1$H NMR (300 MHz, CDCl$_3$, 300 K) $\delta$ 7.07 (s, Ar, 4H), 2.55 (t, $J = 7.6$, Ar-CH$_2$, 4H), 1.57-1.55 (m, Ar-C-CH$_2$, 4H), 1.30 (s, -CH$_2$-, 8H).

4.4.5.5 Reduction of Phenylacetylene with Pd(C)

(R9). Palladium on charcoal (17.7 mg, 10 % Pd) was added to a solution of phenylacetylene (300 mg, 2.94 mmol) in hexane (2 mL) and the reaction mixture was stirred at RT under a hydrogen pressure of 5 bar. After a total reaction time of 22 h, the catalyst was removed by filtration. After concentration of the solution in vacuo, 150 mg (48 %) of ethylbenzene were obtained as colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$, 300 K) $\delta$ 7.30-7.13 (m, 5 H, Ar), 2.64 (q, $J = 7.6$, 2H), 1.24 (t, $J = 7.5$, 3H).

4.4.6 Polymer Synthesis by Suzuki Cross-Coupling Polymerization

4.4.6.1 Two Symmetrical Monomers

**PPPO.1.** After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 12.7 mL, 6.37 mmol) to 1,7-octadiene (0.3511 g, 3.186 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless, clear solution was added to a suspension of diiodobenzene (1.0511 g, 3.186 mmol), PdCl$_2$(dpdf) (69.94 mg, 95.58 μmol) and tetrabutylammonium hydrogensulfate (TBAH) (108.18 mg, 0.3186 mmol) in toluene (16 mL). Finally, aqueous 10 M KOH (1.91 mL, 19.1 mmol) was added to the orange suspension. The mixture was heated to 60 °C and stirred under reflux for 18 h. After cooling to RT, the reaction mixture was added dropwise into rapidly stirred methanol (220 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, hot ethanol and acetonitrile. Drying at room temperature in vacuo overnight yielded PPPO.1 as an off-white powder (425 mg, 71 %). DSC: $T_m$ 96 °C. $^1$H NMR (300 MHz, CDCl$_3$, 297 K) $\delta$ 7.48 (d, $J = 7.9$, phenyl iodide-endgroups, traces), 7.07 (s, 4H), 5.87-5.73 (m, olefins, traces), 5.01-4.91 (m, olefins, traces), 2.55 (t, $J = 7.4$, 4H), 1.58 (m, 4H), 1.30 (br s, 8 H). $\text{DP}_{\text{NMR}}$: 8.

**PPPO.2.** After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 15.2 mL, 7.59 mmol) to 1,7-octadiene (0.4184 g, 3.797 mmol) at 0 °C, the reaction mixture was
allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. Subsequently, the 9-BBN solution was degassed with argon. The colorless clear solution was added to a suspension of diiodobenzene (1.2526 g, 3.7968 mmol), PdCl2(dpff) (41.673 mg, 56.95 μmol) and TBAH (128.9 mg, 0.3797 mmol) in 1,3-dichlorobenzene (degassed) (20 mL). Finally, aqueous 10 M KOH (1.139 mL, 11.39 mmol) was added to the orange-red suspension. The two-phase system was heated to 60 °C and stirred under reflux for 3.25 h. After cooling to RT, the reaction mixture was added dropwise into rapidly stirred methanol (200 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPO.2 as an off-white powder (540 mg, 72 %). DSC: Tm 97 °C. 1H NMR (500 MHz, CDCl3, 300 K) δ 7.09 (s, 4H), 2.57 (t, 7 = 7.62, 4H), 1.59-1.58 (m, 4H), 1.32 (br s, 8 H). DPNMR: 15.

PPPO.3. After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 11.7 mL, 5.83 mmol) to 1,7-octadiene (0.3211 g, 2.914 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless clear solution was added to a suspension of diiodobenzene (0.96128 g, 2.9138 mmol), Pd(PPh3)4 (101 mg, 87.4 μmol) and TBAH (98.94 mg, 0.2914 mmol) in toluene (16 mL). Finally, aqueous 10 M KOH (0.874 mL, 8.741 mmol) was added to the yellow suspension. The mixture was heated to 60 °C and stirred under reflux for 16 h. After cooling to RT, the reaction mixture was carefully treated with 5 mL of an oxidation solution (50 % v/v 3 M NaOH and 50 % v/v H2O2, 35 %) and added dropwise into rapidly stirred methanol (200 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol and water. Drying at room temperature in vacuo overnight yielded PPPO.3 as an off-white powder (472 mg, 86 %). DSC: Tm 43 °C. 1H NMR (500 MHz, CDCl3, 300 K) δ 7.58 (d../ = 8.18, phenyl iodide-endgroups, traces), 7.07 (s, 4 H), 6.92 (d, J = 8.24, phenyl iodide-endgroups, traces), 2.57-2.51 (m, 4H), 1.57-1.56 (m, 4H), 1.30-1.28 (br s, 8 H). DP NMR: 2.

PPPO.4. After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 11.7 mL, 5.85 mmol) to 1,7-octadiene (0.3222 g, 2.9238 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for
another 5 h. The colorless, clear solution was added to a suspension of diiodobenzene (0.9646 g, 2.924 mmol) and Pd(PPh₃)$_4$ (101.36 mg, 87.71 µmol) in toluene (16 mL). Finally, aqueous 10 M KOH (0.877 mL, 8.77 mmol) was added to the yellow suspension. The mixture was heated to 60 °C and stirred under reflux for 16 h. After cooling to RT, the reaction mixture was carefully treated with 4 mL of an oxidation solution (50 % v/v 3 M NaOH and 50 % v/v H₂O₂, 35 %) and added dropwise into rapidly stirred methanol (200 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol and water. Drying at room temperature in vacuo overnight yielded PPPO.4 as a gray powder (514 mg, 94 %). DSC: Tm 91 °C. $^1$H NMR (500 MHz, CDCl₃, 300 K) δ 7.57 (d, J = 8.20, phenyl iodide-endgroups, traces), 7.07 (s, 4 H), 6.92 (d, J = 8.14, phenyl iodide-endgroups, traces), 5.83-5.76 (m, olefins, traces), 5.41-5.40 (m, olefins, traces), 5.00-4.92 (m, olefins, traces), 2.55 (t, J = 7.60, 4H), 1.59-1.56 (m, 4H), 1.30 (br s, 8 H). DP$_{NMR}$: 7.

PPPO.5. After adding 9-BBN (0.5 M in THF, 14.95 mL, 7.47 mmol) to 1,7-octadiene (0.4118 g, 3.736 mmol) in dry THF (1.7 mL) at 0 °C, the reaction mixture was allowed to warm to RT and subsequently stirred at this temperature for another 5 h. The mixture was slowly heated to RT and stirred for 3 h at this temperature. An equivalent of hydroborated octadiene of the colorless solution (4.387 mL, 0.9529 mmol) was given to a suspension of diiodobenzene (0.3144 g, 0.9529 mmol), NaOEt (154.45 mg, 2.859 mmol) and Pd(PPh₃)$_4$ (33.038 mg, 28.59 µmol) in toluene (5.5 mL). The mixture was heated to 80 °C and stirred under reflux for 15 h. After cooling to RT, the reaction mixture was carefully treated with 1 mL of an oxidation solution (50 % v/v 3 M NaOH and 50 % v/v H₂O₂, 35 %) and added dropwise into rapidly stirred methanol (100 mL), and after stirring for 1 h, the precipitated polymer was collected, dried at room temperature in vacuo overnight yielded PPPO as a brown powder (155 mg, 86 %). DSC: Tm 69 °C. $^1$H NMR (300 MHz, CDCl₃, 297 K) δ 7.59-7.53 (m, phenyl iodide-endgroups, traces), 7.07 (s, 4 H), 6.92 (d, J = 7.00, phenyl iodide-endgroups, traces), 2.55 (t, J = 7.53, 4H), 1.58-1.53 (m, 4H), 1.31 (br s, 8 H). DP$_{NMR}$: 3.

PPPO.6. After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 14.9 mL, 7.46 mmol) to 1,7-octadiene (0.3739 g, 3.3929 mmol) at 0 °C, the reaction mixture was
allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 16 h. The colorless, clear solution was then added to a suspension of diiodobenzene (1.1193 g, 3.3929 mmol), Pd(PPh₃)₄ (39.21 mg, 33.93 μmol) and sodium methylate (0.550 g, 10.18 mmol) in toluene (19 mL), the mixture was heated to 60 °C and stirred under reflux for 96 h. After cooling, the reaction mixture was added dropwise into rapidly stirred methanol (250 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, H₂O, hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPO.6 as an off-white powder (424 mg, 66 %). DSC: T_m 93 °C. ¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.07 (s, 4H), 2.55 (t, J = 7.45, 4H), 1.65-1.54 (m, 4H), 1.40-1.20 (br s, 8 H). ¹³C NMR (75 MHz, CDCl₃, 298 K) δ 140.02 (Ar), 128.20 (Ar), 35.55, 31.56, 29.44, 29.36 (all CH₂). DP_NMR: 10. Anal. Calcd for C₁₄H₁₈: C, 89.30; H, 10.70. Found: C, 85.80; H, 10.60.

PPPO.7. After adding 9-BBN (0.5 M in THF, 17.2 mL, 8.59 mmol) to 1,7-octadiene (0.4305 g, 3.907 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 22 h. The THF was distilled off at 68-72 °C and subsequently, at 40 °C, a vacuum of 3 mbar was applied to remove the last traces of THF. The resulting colorless oil, dissolved in xylene (20 mL), was added to a suspension of diiodobenzene (1.2888 g, 3.9066 mmol), Pd(PPh₃)₄ (45.14 mg, 39.07 μmol) and sodium methylate (0.6332 g, 11.72 mmol) in xylene (15 mL). The mixture was slowly heated to 120 °C and stirred under reflux for 17.5 h. After cooling, the reaction mixture was filtered and added dropwise into rapidly stirred methanol (250 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with hot EtOH, acetonitrile and acetone. Drying in vacuo overnight yielded PPPO.7 as a white powder (244 mg, 33 %). DSC: T_m 75 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.07 (s, 4H), 5.81-5.76 (m, olefins, traces), 5.01-4.91 (m, olefins, traces), 2.55 (t, J = 7.43, 4H), 1.58 (m, 4H), 1.30 (br s, 8 H). DP_NMR: 8.

PPPO.8. After adding 9-BBN (0.5 M in THF, 20.6 mL, 10.3 mmol) to 1,7-octadiene (0.5155 g, 4.678 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 22 h. Approximately 60 %
v/v of the colorless solution was given to a refluxing suspension of diiodobenzene (1.5433 g, 4.6779 mmol), Pd(PPh₃)₄ (54.06 mg, 46.78 μmol) and sodium methylate (0.7581 g, 14.03 mmol) in toluene (20 mL) at 110 °C. The THF was slowly allowed to distill off the reaction mixture. In two steps, the remaining 9-BBN solution was added to the flask. After 3 additional hours the distillation apparatus was changed to a reflux condenser. The mixture was stirred under reflux for 18 h. After cooling, the reaction mixture was filtered and added dropwise into rapidly stirred methanol (250 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with hot EtOH, acetonitrile and acetone. Drying in vacuo overnight yielded PPPO as an off-white powder (492 mg, 56%). DSC: Tm 90 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.07 (s, 4H), 5.87-5.74 (m, olefins, traces), 5.01-4.91 (m, olefins, traces), 2.55 (t, J = 7.98, 4H), 1.58 (m, 4H), 1.30 (br s, 8 H). DPNMR: 10.

PPPO.9. After adding 9-BBN (0.5 M in THF, 18.8 mL, 9.39 mmol) to 1,7-octadiene (0.4703 g, 4.268 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 22 h. The resulting colorless solution was added to a suspension of diiodobenzene (1.4079 g, 4.2677 mmol), Pd(PPh₃)₄ (49.32 mg, 42.68 μmol) and sodium methylate (0.6917 g, 12.80 mmol) in toluene (19 mL). The resulting mixture was stirred at RT. After 18 h a sample was taken from the yellow solution and added to MeOH. Since no precipitation was observed, the reaction mixture was slowly heated to 40 °C. After 4 h, the temperature was raised to 50 °C. After two more hours a slight clouding indicated the starting of the polymerization. After a total reaction time of 48 h the polymerization mixture was cooled to RT and added dropwise into rapidly stirred methanol (250 mL). The precipitated polymer was collected and washed with hot EtOH, acetonitrile and acetone. Drying in vacuo overnight yielded PPPO.9 as an off-white powder (184 mg, 23%). DSC: Tm 73 °C. ¹H NMR (500 MHz, CDCl₃, 300 K) δ 7.59 (d, J = 8.0, phenyl iodide-endgroups, traces), 7.07 (s, 4 H), 6.93 (d, J = 8.0, phenyl iodide-endgroups, traces), 7.07 (s, 4H), 2.51-2.50 (m, 4H), 1.61-1.54 (m, 4H), 1.35-1.32 (br s, 8 H). DPNMR: 7.

PPPO.12. After adding 9-BBN (0.5 M in THF, 4.88 mL, 2.44 mmol) to 1,7-octadiene (0.1343 g, 1.219 mmol) at 0 °C, the reaction mixture was allowed to warm to RT and
subsequently stirred at this temperature for another 5 h. To the colorless, clear solution was added a yellow suspension of diiodobenzene (0.4021 g, 1.2187 mmol), Pd(PPh₃)₄ (42.25 mg, 36.561 μmol) and NaOMe (0.1975 g, 3.656 mmol) in toluene (9 mL). The mixture was heated to 60 °C and stirred under reflux for 14 h. After cooling to 0 °C, the reaction mixture was carefully treated with 1 mL of an oxidation solution (50 % v/v 3 M NaOH and 50 % v/v H₂O₂, 35 %) and added dropwise into rapidly stirred methanol (70 mL). The precipitated polymer was collected, dried in vacuo overnight to yield PPPO.12 as an off-white powder (117 mg, 51 %). DSC: T_m 50 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.57 (d, J = 8.24, phenyl iodide-endgroups, traces), 7.07 (s, 4 H), 6.91 (d, J = 8.21, phenyl iodide-endgroups, traces), 2.55 (t, J = 7.47, 4H), 1.58-1.55 (m, 4H), 1.31 (br s, 8 H). DPNMR: 3.

PPPO13. After adding 9-borabicyclo[3.3.1]nonane (9-BBN) (0.5 M in THF, 11.4 mL, 5.69 mmol) to 1,7-octadiene (0.3137 g, 2.8467 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless, clear solution was added to a suspension of diiodobenzene (0.9391 g, 2.8467 mmol), NaOMe (461 mg, 8.54 mmol) and Pd(PPh₃)₄ (98.6 mg, 85.4 μmol) in toluene (16 mL). The mixture was heated to 60 °C and stirred under reflux for 15 h. After cooling of the pink suspension to RT, the reaction mixture was carefully treated with 4 mL of an oxidation solution (50 % v/v 3 M NaOH and 50 % v/v H₂O₂, 35 %) and added dropwise into rapidly stirred methanol (200 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol and water. Drying at room temperature in vacuo overnight yielded PPPO.13 as a black solid (392 mg, 73 %). DSC: T_m 84 °C. ¹H NMR (500 MHz, CDCl₃, 300 K) δ 7.28-7.26 (m, phenyl-endgroups, traces), 7.07 (s, 4 H), 5.83-5.76 (m, olefins, traces), 5.41-5.40 (m, olefins, traces), 5.00-4.91 (m, olefins, traces), 2.55 (t, J = 7.60, 4H), 1.59-1.56 (m, 4H), 1.30 (br s, 8 H). DP_NMR: 6.

PPPO.14. After adding 9-BBN (0.5 M in THF, 13.0 mL, 6.52 mmol) to 1,7-octadiene (0.3593 g, 3.261 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless, clear solution was added to a suspension of diiodobenzene (1.0757 g, 3.2605 mmol), NaOMe
(528.5 mg, 9.782 mmol) and Pd(PPh₃)₄ (113.0 mg, 97.8 µmol) in toluene (16 mL). The yellow mixture was heated to 60 °C and stirred under reflux for 18 h. After cooling of the orange suspension to RT it was added dropwise into rapidly stirred methanol (220 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, water, hot EtOH, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPO as a white solid (375 mg, 61%). DSC: Tm 85 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.07 (s, 4 H), 5.85-5.73 (m, olefins, traces), 5.01-4.91 (m, olefins, traces), 2.55 (t, J = 7.46, 4H), 1.58-1.55 (m, 4H), 1.31 (br s, 8 H). DPNMR: 6.

PPPO.15. After adding 9-BBN (0.5 M in THF, 14.9 mL, 7.47 mmol) to 1,7-octadiene (0.3741 g, 3.3948 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5.5 h. The colorless, clear solution was added to a suspension of diiodobenzene (1.1200 g, 3.3948 mmol), NaOMe (550.2 mg, 10.184 mmol) and Pd(PPh₃)₄ (40 mg, 35 µmol) in toluene (19 mL). The mixture was heated to 60 °C and stirred under reflux for 18 h. After cooling of the olive-green suspension to RT, the reaction mixture was added dropwise into rapidly stirred methanol (220 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, water, hot EtOH, acetonitrile and acetone. Drying in vacuo overnight yielded PPPO.15 as an off-white solid (342 mg, 54%). DSC: Tm 91 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.07 (s, 4 H), 2.55 (t, J = 7.52, 4H), 1.60-1.54 (m, 4H), 1.31 (br s, 8 H). DPNMR: 8. GPC-visco: $M_w = 2,000$; $M_w / M_n = 1.89$.

4.4.6.2 One Asymmetrical Monomer

PPPO.10. After adding 9-BBN (0.5 M in THF, 6.5 mL, 3.2 mmol) to 8-(4'-bromophenyl)-1-octene (0.7837 g, 2.9329 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 7 h. The colorless, clear solution was then added to a suspension of Pd(PPh₃)₄ (33.89 mg, 29.33 µmol) and sodium methylate (0.2377 g, 4.399 mmol) in toluene (16 mL), the mixture was heated to 60 °C and stirred under reflux. After 17 h, another portion of Pd(PPh₃)₄ (36.5 mg, 31.6 µmol) was added. After a total reaction time of 24
h, the reaction mixture was cooled and added dropwise into rapidly stirred methanol (175 mL). After stirring for 1 h, the precipitated polymer was collected, washed with methanol, hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPO.10 as an off-white powder (260 mg, 47%). DSC: T_m 93 °C. \(^\text{1}^\text{H} \text{NMR} (300 \text{ MHz}, \text{CDCl}_3, 298 \text{ K}) \delta 7.07 (s, 4H), 2.55 (t, J = 7.51, 4H), 1.60-1.50 (m, 4H), 1.31 (br, 8 H). \(^{13}\text{C} \text{NMR} (75 \text{ MHz}, \text{CDCl}_3, 298 \text{ K}) \delta 140.12 \text{ (Ar), 128.29 \text{ (Ar), 35.63, 31.64, 29.53, 29.45 (all CH}_2) \text{. GPC-visco}: \overline{M}_w = 9,600; \overline{M}_w/\overline{M}_n = 4.14. \text{DP}\_\text{NMR}: 17. \text{Anal. Calcd for C}_{14}\text{H}_{18}: \text{C, 89.30; H, 10.70. Found: C, 86.18; H, 11.01.}

PPPO.11. After adding 9-BBN (0.5 M in THF, 4.58 mL, 2.29 mmol) to 8-(4'-bromophenyl)-1-octene (0.5565 g, 2.083 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless solution was then added to a suspension of Pd(PPh\(_3\))\(_4\) (24.07 mg, 20.83 \text{ mmol}) and sodium methylate (0.1688 g, 3.124 mmol) in toluene (12 mL). The resulting, almost clear, yellow solution was heated to 60 °C and stirred under reflux. After a total reaction time of 24 h, the reaction mixture was cooled to RT and added dropwise into rapidly stirred methanol (150 mL). After stirring for 1 h, the precipitated polymer was collected, washed with ethanol and acetone. Drying in vacuo overnight yielded PPPO.11 as an off-white powder (270 mg, 69 %). DSC: T_m 94 °C. \(^\text{1}^\text{H} \text{NMR} (300 \text{ MHz}, \text{CDCl}_3, 300 \text{ K}) \delta 7.07 (s, 4H), 2.55 (t, J = 7.56, 4H), 1.58-1.55 (m, 4H), 1.30 (br, 8 H). \text{GPC-visco}: \overline{M}_w = 3,500; \overline{M}_w/\overline{M}_n = 2.30. \text{DP}_{\text{NMR}}: 18.

4.4.7 PPPO Synthesis by ADMET Polymerization

4.4.7.1 Preparation of the Precursor Polymer P3

Bulk Polymerization of Diene 3 (Method C). Poly(p-phenylene oct-4-enylene) (P3.1). C4 (10.0 mg, 0.013 mmol) was added to rapidly stirred 1,4-bis-(pent-4-ene)benzene (3) (472.0 mg, 2.20 mmol) at 50 °C. The resulting yellow mixture started to vigorously evolve gas (ethylene). After about 5 minutes, the evolution of gas decreased, a dynamic vacuum of about 200 mbar was established, and the reddish reaction mixture became highly viscous. After 60 min, the temperature was increased to 75 °C and a second portion of catalyst C4 (4 mg, 5 \text{ mmol}) was added, enhancing the
evolution of gas, now under a further reduced pressure (0.04 mbar). After 7 h, toluene (0.93 g) and C4 (7 mg, 9 µmol) were added to the highly viscous reaction mixture and the reaction was continued for another 45 h. After a total reaction time of 52 h the dark viscous solution was diluted with another portion of toluene (2 mL) and precipitated into methanol (50 mL). Polymer P3.1 (310 mg, 76 %) was obtained as a dark, waxy material. $^1$H NMR (300 MHz, CDCl₃, 298 K) δ 7.07 (s, 4H, Ar), 5.44-5.37 (m, 2H, -CH=CH-), 2.65-2.51 (m, 4H, Ar-CH₂), 2.02-2.01 (m, 4H, -CH₂-CH=CH-), 1.68-1.63 (m, 4H, CH₂). $^{13}$C NMR (75 MHz, CDCl₃, 298 K) δ 139.80 (Ar), 130.37 (HC=CH), 128.30 (Ar), 34.94, 32.18, 31.37 (all CH₂). Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.20; H, 9.81. GPC: $\bar{M}_w = 15,000; \bar{M}_w / \bar{M}_n = 4.27$.

**Bulk/Solution Polymerization of Diene 3 (Method D). Poly(p-phenylene oct-4-ylene) (P3.2).** C4 (10.0 mg, 0.013 mmol) was added to rapidly stirred 1,4-bis-(pent-4-ene)benzene (3) (480.0 mg, 2.52 mmol) at room temperature. The resulting yellow solution started to vigorously evolve gas (ethylene). After about 5 minutes, the reaction mixture solidified and was redissolved in toluene (350 mg) and heated to 50 °C. A second portion of catalyst C4 (6 mg, 0.008 mmol) was added, enhancing the evolution of gas, now under a reduced pressure (600 mbar). After 15 min, the solution turned red and the evolution of gas stopped slowly. A third portion of catalyst C4 (7.5 mg, 0.010 mmol) was added, and the vacuum was adjusted to 350 mbar. After a total reaction time of 42 h, the highly viscous reaction mixture was precipitated into methanol. Polymer P3.2 (374.0 mg, 78 %) was obtained as an olive-green, waxy material. DSC: $T_m$ 43 °C. $^1$H NMR (300 MHz, CDCl₃, 298 K) δ 7.07 (s, 4H, Ar), 5.49-5.38 (m, 2H, -CH=CH-), 2.63-2.50 (m, 4H, Ar-CH₂), 2.03-2.01 (m, 4H, -CH₂-CH=CH-), 1.70-1.57 (m, 4H, CH₂). $^{13}$C NMR (75 MHz, CDCl₃, 298 K) δ 139.82 (Ar), 130.37 (HC=CH), 128.31 (Ar), 34.94, 32.19, 31.37 (all CH₂). Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.24; H, 9.67. GPC: $\bar{M}_w = 14,600; \bar{M}_w / \bar{M}_n = 3.60$.

**Solution Polymerization of Diene 3 (Method E). Poly(p-phenylene oct-4-ylene) (P3.3).** In analogy to P3.4, polymer P3.3 (365 mg, 81 %) was obtained as an olive-green, waxy material. DSC: $T_m$ 40.5 °C. $^1$H NMR (300 MHz, CDCl₃, 298 K) δ 7.07 (s,
4H, Ar), 5.49-5.38 (m, 2H, -CH=CH-), 2.65-2.50 (m, 4H, Ar-CH₂), 2.03-2.01 (m, 4H, -CH₂-CH=CH-), 1.70-1.57 (m, 4H, CH₂). GPC-visco: \( \bar{M}_w = 20,000; \bar{M}_w / \bar{M}_n = 5.60. \)

(P3.4). 1,4-Bis(pent-4-ene)benzene (3) (571 mg, 2.66 mmol) was dissolved in toluene (446 mg). C4 (9 mg, 0.012 mmol) was added to the rapidly stirred solution at room temperature. The resulting yellow solution started to vigorously evolved gas (ethylene). After about 5 minutes, an additional portion of C4 (8 mg, 0.011 mmol) was added, the reaction temperature was increased to 50 °C, and the pressure was reduced (350 mbar). The solution became dark-red and further evolved ethylene. After 2 h, a third portion of catalyst C4 (9 mg, 0.012 mmol) was added to the slightly viscous solution. After a total reaction time of 42 h, the reaction mixture was precipitated into methanol (20 mL). Polymer P3.4 (422.0 mg, 85%) was obtained as an olive-green, waxy material. DSC: \( T_m = 51 \) °C. \(^1\)H NMR (300 MHz, CDCl₃, 298 K) \( \delta 7.07 \) (s, 4H, Ar), 5.49-5.36 (m, 2H, -CH=CH-), 2.65-2.53 (m, 4H, Ar-CH₂), 2.05-2.01 (m, 4H, -CH₂-CH=CH-), 1.71-1.60 (m, 4H, CH₂). \(^1^3\)C NMR (75 MHz, CDCl₃, 298 K) \( \delta 139.81 \) (s, 2C, Ar-C), 130.38 (d, 2C, HC=CH), 128.31 (d, 4C, Ar), 34.95 (t, 2C, C-C=C), 32.19 (t, 2C, C-Ar), 31.38 (t, 2C, C(CH₂)₂). Anal. Calcd for C₁₄H₁₄: C, 90.26; H, 9.74. Found: C, 90.20; H, 10.15. GPC: \( \bar{M}_w = 13,500; \bar{M}_w / \bar{M}_n = 4.0. \)

Attempt of an “ADMET Post-Condensation” (Method F). Solution Polymerization of P3.4. Poly(p-phenylene oct-4-enylene) (P3.5). Poly(p-phenylene oct-4-enylene) (P3.4) (210 mg, 1.13 mmol) was dissolved in toluene (550 mg). C4 (10 mg, 0.013 mmol) was added to the rapidly stirred solution at room temperature. Under reduced pressure (275 mbar, dynamic) the solution was stirred at 50 °C. After 25 minutes, an additional portion of C4 (10 mg, 0.013 mmol) was added. After 2 h, the reaction mixture was precipitated into methanol. The polymer was collected and dried in vacuo. Polymer P3.5 (164.5 mg, 78%) was obtained as an olive-green, waxy material. DSC: \( T_m = 44 \) °C. \(^1\)H NMR (300 MHz, CDCl₃, 300 K) \( \delta 7.07 \) (s, 4H, Ar), 5.44-5.39 (m, 2H, -CH=CH-), 2.65-2.51 (m, 4H, Ar-CH₂), 2.03-2.01 (m, 4H, -CH₂-CH=CH-), 1.71-1.61 (m, 4H, CH₂). GPC-visco: \( \bar{M}_w = 16,200; \bar{M}_w / \bar{M}_n = 4.29. \)
4.4.7.2 Catalytic Hydrogenation of the Precursor Polymer P3

(PPPO.16). Palladium on charcoal (80 mg, 10% Pd) was added to a solution of P3.1 (240 mg, 1.28 mmol) in toluene (10 mL) and the reaction mixture was stirred for 72 h under a hydrogen pressure of 5 bar. The catalyst was removed by centrifugation and filtration through a PTFE-filter (pore size = 1 μm). Precipitation of the resulting solution into methanol yielded the white polymer PPPO.16 (235 mg, 97%). DSC: T_m 46-77 °C. 1H NMR (300 MHz, CDCl3, 298 K) δ 7.06 (s, 4H, Ar), 2.55 (t, J(HH) = 7.7 Hz, 4H, Ar-CH2), 1.60-1.55 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). 13C NMR (75 MHz, CDCl3, 298 K) δ 140.01 (Ar), 128.19 (Ar), 35.54, 31.56, 29.44, 29.37 (all CH2). Anal. Calcd for C14H18: C, 89.30; H, 10.70. Found: C, 89.30; H, 10.83. GPC: M_w = 25,700; M_w/M_n = 7.96.

(PPPO.17). In analogy to PPPO.19, PPPO.17 was obtained from P3.2 as a white powder (81.4 mg, 56%). DSC: T_m 95 °C. 1H NMR (200 MHz, CDCl3, 300 K) δ 7.07 (s, 4H, Ar), 2.55 (t, J(HH) = 7.32 Hz, 4H, Ar-CH2), 1.58-1.52 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). Anal. Calcd for C14H18: C, 89.30; H, 10.70. Found: C, 89.30; H, 10.77. GPC: M_w = 1,300; M_w/M_n = 1.43.

(PPPO.19). Palladium on charcoal (84 mg, 10% Pd) was added to a solution of P3.3 (166.0 mg, 0.891 mmol) in toluene (5 mL) and the reaction mixture was stirred for 24 h under a hydrogen pressure of 5 bar. The catalyst was removed by filtration through a paper filter. Precipitation of the resulting solution into methanol yielded PPPO.19 as a white powder (114.5 mg, 69%). DSC: T_m 78 °C. 1H NMR (300 MHz, CDCl3, 298 K) δ 7.07 (s, 4H, Ar), 2.55 (t, J(HH) = 7.71 Hz, 4H, Ar-CH2), 1.58-1.55 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). Anal. Calcd for C14H18: C, 89.30; H, 10.70. Found: C, 89.53; H, 10.81. GPC: M_w = 15,500; M_w/M_n = 2.95.

(PPPO.20). In analogy to PPPO.19, PPPO.20 was obtained from P3.3 as a white powder (100.2 mg, 97%). DSC: T_m 82 °C. 1H NMR (300 MHz, CDCl3, 300 K) δ 7.07 (s, 4H, Ar), 2.55 (t, J(HH) = 7.53 Hz, 4H, Ar-CH2), 1.60-1.51 (m, 4H, CH2-C-Ar), 1.32-
1.30 (s, 8H, CH2). $^{13}$C NMR (75 MHz, CDCl3, 300 K) $\delta$ 140.06 (Ar), 128.22 (Ar), 35.56, 31.57, 29.46, 29.39 (all CH2). Anal. Calcd for C14H18: C, 89.30; H, 10.70. Found: C, 89.53; H, 10.81. GPC: $\overline{M}_n = 18,000$; $\overline{M}_w/\overline{M}_n = 3.28$.

(PPPO.21). In analogy to PPPO.19, PPPO.21 was obtained from P3.4 as a white powder. DSC: $T_m$ 98 °C. $^1$H NMR (300 MHz, CDCl3, 300 K) $\delta$ 7.07 (s, 4H, Ar), 2.55 (t, $J_{HH} = 7.48$ Hz, 4H, Ar-CH2), 1.60-1.52 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). $^{13}$C NMR (75 MHz, CDCl3, 300 K) $\delta$ 140.04 (Ar), 128.21 (Ar), 35.56, 31.57, 29.45, 29.38 (all CH2). Anal. Calcd for C14H18: C, 89.30; H, 10.70. Found: C, 89.09; H, 10.79. GPC: $\overline{M}_n = 6,600$; $\overline{M}_w/\overline{M}_n = 2.49$.

(PPPO.22). In analogy to PPPO.19, PPPO.22 was obtained from P3.4 as a white powder (51.0 mg, 50 %). DSC: $T_m$ 99.1 °C. $^1$H NMR (300 MHz, CDCl3, 298 K) $\delta$ 7.07 (s, 4H, Ar), 2.55 (t, $J_{HH} = 7.73$ Hz, 4H, Ar-CH2), 1.60-1.52 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). GPC: $\overline{M}_n = 7,500$; $\overline{M}_w/\overline{M}_n = 2.19$.

(PPPO.23). In analogy to PPPO.19, PPPO.23 was obtained from P3.5 as a white powder (68.4 mg, 73 %). DSC: $T_m$ 90.3 °C. $^1$H NMR (300 MHz, CDCl3, 298 K) $\delta$ 7.07 (s, 4H, Ar), 2.54 (t, $J_{HH} = 7.72$ Hz, 4H, Ar-CH2), 1.60-1.52 (m, 4H, CH2-C-Ar), 1.30 (s, 8H, CH2). GPC: $\overline{M}_n = 13,900$; $\overline{M}_w/\overline{M}_n = 3.00$.

4.5 References

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Chapter 5

Semi-Empirical Approach for the Estimation of Melting Temperatures of Polymers

Summary

In this Chapter, a semi-empirical method is described that allows to predict the melting temperature of different members of a particular series of copolymers if certain experimental data are available. The key feature of this approach is the linear connection of the ratio $n_r/n_f$ (the number of rigid segments $n_r$ divided by the respective number of flexible segments $n_f$ in the copolymer repeat unit, herein termed RRF) and the melting temperatures of a particular copolymer series. This semi-empirical method is not only valid for the hydrophobic polymers under investigation but seems to be rather universal and can also be applied to hydrophilic polymers such as polyamides, as was demonstrated on different polymer series for which the predicted and the experimental melting temperatures were in well agreement. Importantly, by means of this approach, it was possible to predict the melting temperatures of other representatives of the poly(p-phenylene alkylene) family, i.e. poly(p-phenylene hexylene) ($T_m = 127 ^\circ C$) and poly(p-phenylene butylene) ($T_m = 202 ^\circ C$). The predicted values were of assistance for the selection of an adequate alkarotic target polymer.

5.1 Introduction

Surprised by the unexpectedly low melting temperature, $T_m$, of PPPO, we have studied methods which allow to predict the melting temperature of polymers and could help to choose an appropriate alkarotic target polymer. It is remarkable that practically no $T_m$-structure relationships have been proposed in the literature, although the crystalline melting temperature is very important for the processing behavior and properties of semicrystalline polymers.\(^1\) Unlike the glass transition temperature, melting is a first-order thermodynamic phase transition where the first derivatives of the free energy change discontinuously.\(^2\) In addition, melting is free of the kinetic effects which occur around the glass transition, and $T_m$ is a property of a well-ordered crystalline material while $T_g$ is a characteristic of an amorphous material, and therefore, it may be imagined that the prediction of $T_m$ should be easier than the prediction of $T_g$. In fact, just the opposite is true.\(^3\) The reason for this may be the fact that in addition to the two key
features determining $T_m$ and $T_g$ (being chain stiffness and interchain cohesive forces), the interchain packing, which is not relevant for the calculation of $T_g$, is of major importance for the determination of the melting temperature. Furthermore, $T_m$ very often depends on the morphology of the crystalline phase, such as whether the crystalline domains consist of folded or extended chain crystallites and on the crystalline unit cell scale. The equilibrium melting temperature $T_{m}^{e}$ of a polymer does not depend on morphological factors, since it is defined as the (hypothetical) temperature at which an infinitely large polymer crystal would be in equilibrium with its melt (see also the Appendix of this thesis). Nevertheless, the methods reported in the literature (see below) exclusively use the experimentally determined melting temperature $T_m$ of semi-crystalline polymer samples, which is, therefore, also adopted in the present Chapter.

Considering all these factors that influence the melting temperature of polymers it is not surprising that there is, to the best of our knowledge, no way to predict $T_m$ from ab initio calculations.

5.2 Results and Discussion

5.2.1 General

"Science consists of data (experimental facts), correlations (rules, laws), and theories (concepts, models, hypotheses). Basic science is the search for insight and understanding; it tries to develop theories which merge data and correlations into a consistent whole in order to understand the properties of matter on the basis of a structural image ... It is useful as far as it enables us to estimate or predict the required numerical values of properties and correlations which are not yet measured or discovered ... In the field of polymers the semi-empirical approach is mostly necessary and sometimes the only possible way. What is needed in practice is a formulation, which is designed to deal directly with the phenomena and make use of the language of observation. This approach is pragmatic and designed specifically for use; it is a completely nonspeculative procedure. The value of estimation and prediction techniques largely depends on their simplicity. Complicated methods have to be rejected."

These statements, made by Dirk Van Krevelen, are the guiding principles in this chapter. Van Krevelen was the first to systematically develop and use semi-empirical
methods that allow to predict polymer properties through “extrapolation” processes. Bicerano\textsuperscript{3} and Askadskii\textsuperscript{5} followed this conceptual approach and developed these theories further.

5.2.2 Van Krevelen’s Group Contribution Techniques

A powerful tool in the semi-empirical approach to the study of physicochemical properties in general, and of polymer properties in particular, is the use of the additivity principle. This principle means that many properties, or combinations of properties, may be calculated by summation of either atomic, group, or bond contributions. The \textit{additive molar melt transition contribution function}, \( Y_m \), according to Van Krevelen (Equation 5.1)\textsuperscript{1,3} is one of the very few empirically developed methods to estimate the melting temperature from the chemical structure. The function \( Y_m \) has the dimension [K·kg/mol], and the group increments for this function were derived from the available literature data on crystalline melting points of polymers.\textsuperscript{1}

We have undertaken to verify the validity of \( T_m \) calculated by the additive, molar melt transition function \( Y_m \) according to Van Krevelen (Equation 5.1) for different polymers:\textsuperscript{1}

\[
Y_m = \sum_i Y_{mi} = T_m \cdot M \rightarrow T_m = \frac{Y_m}{M}
\]

\textit{Equation 5.1: Additive molar melt transition function }\( Y_m \).

The \( Y_{mi} \)-values are calculated from additive increments for a respective functional group in the polymer backbone, which can be arbitrarily combined according to the desired repeat unit.\textsuperscript{1} The term \( M \) corresponds to the molecular weight of the respective moiety. For example, the \( Y_{mi} \)-value of a \(-\text{CH}_2\)- group is reported to be 5.7 K·kg·mol\textsuperscript{-1} with a molar mass \( M \) of 14 g·mol\textsuperscript{-1}.\textsuperscript{1} Employing Equation 5.1, the melting temperature of PE is calculated to be 134 °C. With the respective \( Y_{mi} \)-values of a \(-\text{CH(CH}_3)\)- (13 K·kg·mol\textsuperscript{-1}), a phenylene- (38 K·kg·mol\textsuperscript{-1}) and an amide-functionality (45 K·kg·mol\textsuperscript{-1}) the melting temperatures of the polymers in Table 5.1 were determined.\textsuperscript{1}
As is evident from Table 5.1, a reasonable agreement between the estimated and experimental $T_m$ could be obtained in the case of PE and PP, but the relation failed to adequately describe the melting behavior of many other polymers, such as PPX, PPPO, and n-Nylons (Table 5.1). Due to these unsatisfactory results, we have focused on an alternative approach that is based on the connection of the melting temperature with the enthalpy and entropy of fusion, which relies on the fact that at the melting temperature, $T_m$, the following relation is valid:\[2\]

\[ T_m = \frac{\Delta H_m}{\Delta S_m} \]

*Equation 5.2: Relation between the enthalpy ($\Delta H_m$) and entropy ($\Delta S_m$) of fusion and the melting temperature at $T_m$.\]

Equation 5.2 suggests that a method for predicting $T_m$ could be based on calculation of both $\Delta H_m$ and $\Delta S_m$ by Van Krevelen’s group contribution methods, employing the additivity principle, i.e.:

\[ \Delta H_m = \sum_i \Delta H_{mi} \]

\[ \Delta S_m = \sum_i \Delta S_{mi} \]
Indeed, somewhat better results for the estimation of $T_m$ were obtained (compared to the above described approach) when expressing $T_m$ by Equation 5.2, and estimation of $\Delta H_{mi}$ and $\Delta S_{mi}$ by group contribution calculations (Table 5.2)\(^1\) using Equation 5.3:

$$T_m = \frac{\sum_{i} \Delta H_{mi}}{\sum_{i} \Delta S_{mi}}$$

*Equation 5.3: Application of the additivity principle for the calculation of $T_m$ with the enthalpy and the entropy of fusion.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Delta H_m$ (VK)/kJmol(^{-1})</th>
<th>$\Delta S_m$ (VK)/Jmol(^{-1})K(^{-1})</th>
<th>$T_m$(VK)/°C</th>
<th>$T_m$(exp)/°C</th>
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</thead>
<tbody>
<tr>
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<td>135</td>
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<tr>
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<td>170</td>
</tr>
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</tr>
</tbody>
</table>

*Table 5.2: Melting temperature, calculated from values for $\Delta H_m$ and $\Delta S_m$ determined from additive group contributions according to Van Krevelen, $T_m$(VK), and comparison with the experimental data, $T_m$(exp).*

However, also this modified group contribution approach clearly has its limits and a variety of polymers has been identified for which the predictions did not fit the experimental melting temperature, e.g. polyoxymethylene POM, various n-Nylons, PPX, and PPPO (Table 5.2). The mismatch between the experimental and calculated values of $T_m$ compiled in Table 5.1 and Table 5.2 seems to suggest that the values for
the different increments are not universal. Therefore, it is compelling to calibrate the respective increments for a certain series of polymers.

5.2.3 Estimating Properties Using the Bicerano Method

The work of Bicerano is a further methodology to describe quantitative structure-property relationships of polymers. With the Bicerano method the formalism of connectivity indices\textsuperscript{6,7} was used as the starting point.\textsuperscript{3} Connectivity indices were utilized as the principal descriptors of the topology of the repeat unit of a polymer. Properties are then correlated using these connectivity indices. In addition, simple additivity corrections for special groups and structures are incorporated in the correlation equations to improve accuracy of prediction. Copolymer properties using the Bicerano method are calculated using weighted averages for all extensive properties and appropriate relationships for intensive properties in terms of the extensive properties.\textsuperscript{3} With the Bicerano methodology, a wealth of properties is supposed to be predictable, such as Van der Waals volume, density, thermal expansion coefficients, glass transition temperature, solubility parameters etc. However, among all these polymer properties the melting temperature is, unfortunately, missing, at least within the scope of this thesis, a serious lack of this approach.

5.2.4 Estimating Properties Using the Askadskii Method

The approach developed by Andrey A. Askadskii,\textsuperscript{5} is also based on the principle of additivity but in this case each equation for properties calculation is based on physical models. This method represents the polymer repeat unit as a set of inharmonic oscillators, which describe the thermal motion of atoms in the field of intra- and intermolecular forces, including weak dispersion forces, dipole-dipole interactions, hydrogen and valence bonds. The critical temperature of such a set of inharmonic oscillators is associated either with the glass transition temperature or with the temperature of the onset of intense thermal degradation. The incorporation of a few simplifying assumptions in the theory results in an additive calculation technique, which utilizes a set of atomic increments and a small number of empirical parameters independent of the chemical structure of the polymer. Strictly speaking, this method cannot be referred to as an additive method because the properties estimated are not
assumed to be additive with respect to the constituent atoms, groups, or bonds. The
additive principle, however, is applied to properties that are truly additive, such as molar
volume, molecular weight, and various energies. However, even though many physical
properties of polymers, such as the polymer density, thermal coefficient of volumetric
expansion, the glass transition temperature, the temperature of onset of intense thermal
degradation, optical and optico-mechanical properties, equilibrium rubbery modulus for
polymer networks, solubility and miscibility of polymers, and even effects of branching
and end groups on the physical properties of polymers can be predicted with the
Askadskii method, it should be noted that the approach to estimate the melting
temperature is of limited applicability.5

The latter is mainly related to the fact that the approach of Askadskii is based on the
assumption that for many polymers the ratio $\gamma = T_g/T_m$ is constant and which adopts a
value of between 0.25-0.97. The calculations carried out by Askadskii show that the
value for $\gamma$ depends on the ratio $k_a/k_{cr}$, where $k_a$ is the coefficient of molecular packing
for the amorphous polymer and $k_{cr}$ is the coefficient of molecular packing for the ideal
crystal. It was shown that the $\gamma$ value increases linear proportional to the $k_a/k_{cr}$ ratio.
Consequently, the ratio of glass transition temperature to melting temperature, $\gamma$,
depends on the difference between the intensity of packing of the macromolecules in
amorphous and crystalline states. However, the inadequacies in the method of Askadskii
in the estimation of the melting temperature of polymers seem to be founded in the
various values that have to be determined in advance, such as the ratio $k_a/k_{cr}$ and $T_g$. The
determination of these values already contains a certain error, which is even augmented
with the calculation of $T_m$.

The Askadskii method is still under development in order to extend the list of properties
that can be estimated. The number of characteristics that can be estimated at present
using the Askadskii method is less than those for the Bicerano or the Van Krevelen
methods.5
5.2.5 Development of the RRF Approach

Since neither the Bicerano nor the Askadskii method adequately allow to estimate melting temperatures, the Van Krevelen approach seems to be the only methodology that enables the prediction of this quantity, with a, however, sometimes severely limited accuracy. We therefore used the Van Krevelen approach as a starting point to develop a methodology to describe the melting temperatures of "AB-copolymers" consisting of "rigid" (A) and "flexible" (B) moieties in the repeat unit (see Figure 5.1).

![Diagram of a copolymer repeat unit divided into rigid and flexible moieties.]

*Figure 5.1: Division of the "copolymer" repeat unit into a rigid and a flexible component.*

The lengths of the rigid and flexible moieties are expressed by the number of rigid and flexible segments $n_r$ and $n_f$, respectively (Figure 5.2). It is obvious that the quotient $n_r/n_f$ (Ratio of Rigid and Flexible segments, RRF-value) is an indication for the stiffness of the copolymer chain; the flexible homopolymer will have an RRF-value of zero, whereas the rigid homopolymer exhibits an RRF-value that tends towards infinity.

---

*In the following Sections, the term "copolymer" is not used in the classical sense as a polymer synthesized from two or more monomers, but the expression "copolymer" is strictly related to the nature of the repeat unit.*
It is well known that the flexibility of a macromolecule chain is related to the melting temperature of the corresponding polymeric material. Hence, the question arose whether this dependence directly could result in a simple relation between the RRF-value and the melting temperature $T_m$ of a specific series of copolymers.

The following graphs (Figure 5.3-5.5) clearly show a linear relation between the RRF-value and the melting or isotropization temperature of a particular series of copolymers. This linear behavior is valid for many different copolymers, such as hydrophobic hydrocarbon copolymers, and aromatic and/or aliphatic polyamides, and many others.

In the case of the copolymers described in Figure 5.3, the rigid moiety was defined to be the biphenyl unit (a: with phenyl rings as the rigid segments) and the tolan unit (b: with two phenyl rings and an acetylene unit as the rigid segments), respectively.
**Figure 5.3**: Experimentally determined isotropization temperatures of liquid-crystalline hydrocarbon copolymers vs. the RRF-value (lines represent least square fit).

In the case of the polyamides illustrated in the following two figures, the rigid moiety was defined to be the terephthalamide (Figure 5.4) and the amide functionality unit (Figure 5.5), respectively.
Figure 5.4: Experimentally determined melting temperatures of semi-aromatic polyamides (a: \(x\) is even; b: \(x\) is odd) vs. RRF according to Equation 5.5 (lines represent least square fit).
Figure 5.5: Experimentally determined melting temperatures of n-Nylons (a: x is even; b: x is odd) vs. RRF (lines represent least square fit).

In analogy, a linear relation between the RRF-value and $T_m$ could also be confirmed for other copolymer series, such as oligo(alkynes) with chemical structures as depicted in Figure 5.6.

Figure 5.6: Chemical structure of a series of oligo(alkyne)s.
Thus, a linear relation between $T_m$ and the RRF-value was empirically demonstrated for a number of different copolymer systems. Although only comparably few systems were considered (due to the limited availability of $T_m$ data for homologous copolymer series), no system was found, for which this relation did not hold. This initially surprising finding can be rationalized by thermodynamic considerations. Again, it is assumed that the melting temperature, $T_m$, can be expressed by the ratio of the enthalpy and entropy of fusion, $\Delta H_m$ and $\Delta S_m$ (Equation 5.2). Conceptually following the group contribution approach of Van Krevelen, $\Delta H_m$ and $\Delta S_m$ of a copolymer are expressed by additively composing the respective increments of the rigid and the flexible segments of the copolymer repeat unit:

$$T_m = \frac{\Delta H_m}{\Delta S_m} = \frac{n_r(\Delta H^r_m) + n_f(\Delta H^f_m)}{n_r(\Delta S^r_m) + n_f(\Delta S^f_m)} = \frac{n_r(\Delta H^r_m)}{n_f(\Delta S^r_m)} + \frac{n_f(\Delta H^f_m)}{n_f(\Delta S^f_m)}$$

$\Delta H^r_m$ : Melting enthalpy of the rigid segment
$\Delta H^f_m$ : Melting enthalpy of the flexible segment
$\Delta S^r_m$ : Melting entropy of the rigid segment
$\Delta S^f_m$ : Melting entropy of the flexible segment
$n_r$ : Number of rigid segments per repeat unit
$n_f$ : Number of flexible segments per repeat unit

Equation 5.4: $T_m$ as a function of the ratio $n_r/n_f$.

For limiting situations, Equation 5.4 can be simplified significantly. For example, under the often very reasonable assumption that the melting entropy contribution of the rigid segment can be neglected, the following equation is obtained (Equation 5.5):
Equation 5.5: Transformation of Equation 5.4 under the assumption that $\Delta S_m^t$ is small, so that \( \frac{n_r}{n_f} \Delta S_m^c \ll \Delta S_m^t \).

It is evident that the above equation adequately describes the previously observed linear relation between the RRF-value \( (n_f/n_f) \) and \( T_m \), since the values for $\Delta H_m$ and $\Delta S_m$ for the respective rigid and flexible segments are constant within a given series of polymeric homologues.

We have also plotted the melting temperatures calculated for a number of copolymer series by Van Krevelen’s original group contribution approach (according to Equation 5.1 and following the procedures given in Section 5.2.2) vs. the RRF-value \( (n_f/n_f) \), also resulting in a linear relationship, as can be seen exemplarily for \( n \)-Nylons in Figure 5.7. However, the function thus determined significantly differs from the experimental values, clearly indicating that the values of $\frac{\Delta H_m^r}{\Delta S_m^r}$ and $\frac{\Delta H_m^f}{\Delta S_m^f}$ in Equation 5.5 should be regarded as fitting parameters for a specific copolymer series, and cannot be calculated from group contributions. Thus, we think that an initial calibration of a specific copolymer series with two experimentally determined melting temperatures is necessary. Ideally, the two calibration copolymers should have significantly different RRF-values. Equation 5.5, subsequently becomes a reliable tool to predict the melting temperature of all other copolymers of the particular series under consideration. As can be seen from, e.g., Figure 5.7, the respective odd and even members from a particular copolymer series have to be considered separately. It is well known that within a homologue series of copolymers the representatives with an odd number of certain repeating elements in the backbone behave remarkably different than their respective even brothers. Usually, the odd members exhibit lower melting temperatures (cf. Chapter 7).
Figure 5.7: Experimentally determined melting temperatures of $n$-Nyons ($a$: $x$ is even; $b$: $x$ is odd) compared to $T_m$ estimated by Van Krevelen's group contribution approach (Equation 5.1).

Substituting the melting temperature of the flexible homopolymer $T_m^f$ in Equation 5.5 (Equation 5.6) shows that, in principle, for a given series of copolymers, the melting temperature of the calculated copolymer cannot fall below the melting temperature of the flexible homopolymer. Indeed, for most of the copolymer series described before (Figure 5.3 and Figure 5.5), the extrapolated lines tend, with a decreasing RRF-value, towards the melting temperature of the flexible homopolymer (in these cases polyethylene).
Equation 5.6: Reformulation of Equation 5.5.

\[ T_m = \frac{n_r}{n_f} \left( \frac{\Delta H^f_m}{\Delta H^f} \right) T^f + T^f = RRF \left( \frac{\Delta H^f_m}{\Delta H^f} \right) T^f + T^f \]

5.2.6 Application to Poly(p-phenylene alkylene)s

If the RRF-approach is applied to the present target poly(p-phenylene alkylene)s, the significantly different experimental melting temperatures of PPX \((T_m = 425 \, ^\circ\text{C}; \ RRF = 0.5)\) and PPPO \((T_m = 90 \, ^\circ\text{C}; \ RRF = 0.125)\) can be used to “calibrate” Equation 5.5 resulting in:

\[ T_m / K = 893 \cdot RRF + 251 \]

Equation 5.7: Melting temperature of poly(p-phenylene alkylene)s.

Figure 5.8: Graphical evaluation of the desired target polymer (● used for “calibration”; ♦ predicted).

Thus, from Equation 5.7 it is possible to calculate the melting temperatures of poly(p-phenylene hexylene) \((T_m = 127 \, ^\circ\text{C}; \ RRF = 0.167)\) and poly(p-phenylene butylene) \((T_m = 202 \, ^\circ\text{C}; \ RRF = 0.25)\) (Figure 5.8). Considering the requirements for a new thermoplastically processable engineering polymer as discussed in Chapter 2, it seems obvious that poly(p-phenylene butylene) is the most promising polymer from the series of alkarotic polymers, having a predicted melting temperature of 202 °C.
5.3 Conclusions

With the above developed semi-empirical methodology for which we have coined the term “RRF-approach”, the melting temperatures of poly(\(p\)-phenylene butylene) and poly(\(p\)-phenylene hexylene) could be calculated. Based on these results, the following work focused on the preparation of poly(\(p\)-phenylene butylene) (PPPB). In the following Chapter, it will be shown that the experimentally determined melting temperature of PPPB in fact perfectly matches the predicted value. Additional support for this approach could be gained with the experimental determination of the melting temperature of poly(\(p\)-phenylene hexylene) (PPPH). Detailed studies focused on this polymer are discussed in Chapter 7.

The separation of the polymer repeat unit into rigid and flexible parts is, in principle, quite semantic. It is our current understanding that the described methodology can also be applied for copolymer series (and also for low-molecular weight compounds), in which the ratio of two (or more) in any kind different moieties (e.g. a hydrophobic and a hydrophilic moiety) are varied in a regular manner.

5.4 References


Chapter 6

Synthesis and Properties of Poly(p-phenylene butylene)

Summary

With the objective to produce a processable, high-melting, hydrophobic, and crystalline polymer, and with the results of the two previous chapters in mind, we embarked on the synthesis of poly(p-phenylene butylene) (PPPB) as a new representative of the class of polymers which contain only aromatic and aliphatic hydrocarbon units in their backbone. While also employing Suzuki cross-coupling condensation, the Heck reaction, and dehydrohalogenation, acyclic diene metathesis (ADMET) polymerization of p-diallylbenzene followed by catalytic reduction of the resulting unsaturated polymer was used as the primary synthetic route to PPPB. For the ADMET polymerizations, Schrock’s alkylidene molybdenum complex, Grubbs’ benzylidene ruthenium catalyst, and two classical systems (WOCl₂(OAr)₂/Bu₄Sn and WCl₆/Bu₄Sn) were employed, and different reaction conditions were compared. WOCU₂(OAr)₂/Bu₄Sn in refluxing toluene proved to be the most appropriate catalyst system to produce the crystalline and high-melting poly(p-phenylene but-2-ylene) precursor polymer in high molecular weight and chemically pure form. Catalytic hydrogenation of the latter led to poh(p-phenylene butylene) with number-average molecular weights of up to 14,000. The latter polymer was found to have a melting temperature of between 200 and 215 °C and to be highly crystalline and melt-processible. Thus, PPPB indeed represents a high-melting, hydrophobic polymer, which permits conventional processing technologies as opposed to its “homologue” poly(p-xylylene) (PPX). The melting temperature of PPPB that has been predicted by the RRF-approach, discussed in Chapter 5, could be confirmed.

6.1 Introduction

Erroneously guided by results of Brown and Farthing,¹ PPPO was previously synthesized in an attempt to produce a melt-processible poly(p-phenylene alkylene) (Chapter 4). However, to our surprise, this highly-crystalline polymer was found to have a melting temperature as low as 90 °C (Chapter 4). Employing the semi-empirical method described in Chapter 5 that allows to extrapolate the melting temperature of different representatives of homologous classes of polymers, and using the melting temperatures of PPX and PPPO as calibration temperatures, the melting temperatures of poly(p-phenylene hexylene) (PPPH) and poly(p-phenylene butylene (PPPB) were
interpolated to be 127 and 202 °C, respectively. Based on these estimations, and with the above discussed technological potential of a high-melting, melt-processable hydrophobic polymer in mind, the synthesis of PPPB was revisited. In this Chapter, various routes for the synthesis of PPPB including the Suzuki polymerization, the Heck reaction, acyclic diene metathesis (ADMET) polymerization and dehydrohalogenation (Gilch route) were investigated. The produced materials were characterized and their physical and chemical properties were investigated.

6.2 Results and Discussion

6.2.1 Polymer Synthesis via Suzuki Cross-Coupling

In analogy to the synthesis of PPPO described in Chapter 4, PPPB was prepared by Suzuki cross-coupling polycondensation. The utilization of two symmetrical monomers, i.e. hydroborated 1,3-butadiene and diiodobenzene (Scheme 6.1), was found to be experimentally difficult, since 1,3-butadiene has a boiling point of -4.5 °C.2 The condensation and subsequent hydroboration of 1,3-butadiene3 had to be performed at -50 °C or below, in order to avoid the evaporation of the highly volatile starting compound. Nevertheless, the polycondensation of hydroborated 1,3-butadiene and diiodobenzene to PPPB was, in principle, successful and could be proved by 1H NMR spectroscopy, however, in a yield of only 2 % (Experimental Section 6.4.4).

Thus, although the synthesis of PPPB via the Suzuki coupling of 1,3-butadiene with diiodobenzene was demonstrated to be possible, the use of less volatile monomers seemed to be more appropriate. Consequently, the asymmetrical monomer 4-(4’-bromophenyl)-1-butene (4), which could readily be hydroborated with 9-BBN, was synthesized according to a procedure of Quelet et al.4 The polymerization of the activated olefin was carried out in a toluene/THF mixture (2.4/1.0 v/v) using Pd(PPh₃)₄ as catalyst and NaOMe as the base (Scheme 6.1), yielding PPPB.2. All PPPB samples prepared by the Suzuki cross-coupling reaction were satisfactorily characterized by elemental analysis and NMR spectroscopy. Elemental analysis shows a slight, but systematic offset from the calculated values, in agreement with the presence of a significant amount of end groups.
Scheme 6.1: Monomer synthesis and Suzuki cross-coupling polymerizations.

PPPB prepared by the Suzuki polycondensation could be dissolved in solvents such as toluene, o-xylene, decalin, chloroform, and THF at elevated temperatures (> 60 °C) and, thus, exhibited the desired improved solubility compared to poly(p-xylylene), PPX. The melting temperatures of the materials were at around 160 °C, which represented a significant increase compared to PPPO. The maximum number-average molecular weights obtained (determined by endgroup analysis in the $^1$H NMR spectrum) were below 2,100, which corresponds to a degree of polymerization of only 16. The low molecular weights of the materials obtained by the Suzuki cross-coupling are attributed to the use of the solvent mixture required by the Pd-catalyst; the latter is rather unfavorable for the present polymer because it prevents the conduction of the polymerization at temperatures above 100 °C, and, thus leads to early precipitation of the polymer.

From these experimental findings we conclude that the PPPBs synthesized by the Suzuki cross-coupling indeed exhibited a promising melting behavior but were characterized by a rather limited molecular weight. Hence, a better synthetic procedure had to be found in order to improve the degree of polymerization.
6.2.2 Heck Polymerization of Side-Chain Derivatized Monomers

From the experiments carried out in the connection with the synthesis of PPPO (Chapter 4), it was learned that polymers having a 1,4-bis(ethynyl)phenylene moiety tend to be rather insoluble and intractable even if these moieties are interrupted by four flexible methylene groups. Hence, it seemed to be unreasonable to adapt an analogous strategy for the synthesis of a precursor of PPPB. An increase of the solubility of the precursor polymer appeared to be inevitable in order to enable the polymerization under mild conditions.

A well-known concept to increase the solubility of rigid-rod polymers is the introduction of flexible, linear or sterically hindered side chains. This strategy was for example successfully employed in the synthesis of a variety of processable polyesters, polyamides, and a variety of conjugated polymers. In contrast to the above concepts that rely on the derivatization of phenylene moieties, we here envisioned to introduce solubilizing alkoxy groups at the benzylic positions of the polymer repeat unit.

Scheme 6.2: Synthesis of the branched monomers used for Heck polymerization.
The fundamental idea of solubilizing side chains at the benzylic position is based on the assumption that they can be cleaved after polymerization under the same conditions as the reduction of a non-aromatic carbon-carbon double or triple bond. In synthetic organic chemistry, the benzyl group is a well-known protection group for amines and alcohols, which can be removed e.g. by hydrogenolysis.\(^{11}\) For this purpose, the monomers depicted in Scheme 6.2 were synthesized.

1-(4-Bromophenyl)-3-butyn-1-ol (5) was synthesized in 78 % yield from 4-bromobenzaldehyde according to a procedure of Nakagawa et al.\(^ {12}\) The resulting alcohol offers the opportunity of an alkylation with an appropriate side chain. In order to have an optimally soluble precursor polymer the branch has to fulfil some requirements. Usually the introduction of long aliphatic side-chains increases the dissolution entropy contribution, whereas the substitution of the polymer backbone with sterically hindered, bulky side-chains enhances the disorder in the overall structure and, therefore, prevents crystallization of the macromolecule. As an alternative to apolar side chains, which enhance the solubility essentially because of entropic contributions, pendant polar groups also lead to an increase of the solution enthalpy, and, thus, could further enhance the solubility of the precursor polymer.

Etherification of the propargyl alcohol 5 with various electrophiles was found to be difficult, since many standard procedures could not be adapted to alcohol 5 (Scheme 6.3, Table 6.1). For example, alcohol 5 could not be alkylated with 2-ethylhexyl bromide neither employing KOH/DMSO\(^ {9,13}\) nor in a refluxing NaOMe/MeOH mixture,\(^ 8\) nor with NaH/THF at 45 °C.\(^ {14}\) The presence of hexamethylphosphoramide (HMPA) did not result in any alkylation of 5 neither with 2-ethylhexyl bromide nor with octyl bromide as the primary alkylating agent.\(^ {15}\) The use of 2-methoxy-ethoxymethyl chloride (MEM chloride) as the electrophile was slightly more successful. Whereas the use of a weak base (NEt\(_3\)) did not lead to any reaction in the presence of MEM chloride, the utilization of a stronger base (NaH) resulted in a turnover of 80 to 100 %.\(^ {16}\) However, the purification of the MEM-protected alcohol unfortunately turned out to be difficult. The application of an aliphatic halide without β-hydrogen atoms, such as neopentyl iodide, allowed to increase the alkylation temperature because an elimination of the respective hydroiodic acid was excluded. But neither the KOH/DMSO\(^ {9,13}\) nor the NaH/THF conditions\(^ {14}\) led to the desired neopentyl ether (Scheme 6.3). Thus, the
above experiments seem to suggest that the respective alcoholate 5 – somewhat surprisingly – is not nucleophilic enough to be alkylated by the latter electrophiles. Besides MEM chloride, the only reagent that was able to smoothly alkylate alcohol 5 to the corresponding ether was methyl iodide, though, only if the reaction temperature was raised to 45 °C (Table 6.1). Of course, considering the above discussed requirements for a suitable side chain, a methoxy branch is not expected to contribute significantly to the solubility of the polymer and, hence, is not the side chain of choice.

Scheme 6.3: Attempts to alkylate alcohol 5.

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\(^{a}\) Ethylhexyl bromide, KOH, DMSO, RT. \(^{b}\) Ethylhexyl bromide, NaOMe, MeOH, 65 °C. \(^{c}\) Ethylhexyl bromide, NaH, THF, 45 °C. \(^{d}\) Neopentyl iodide, KOH, DMSO, 60 °C. \(^{e}\) Neopentyl iodide, NaH, THF, 45 °C. \(^{f}\) MEM chloride, NEt\(_3\), RT. \(^{g}\) MEM chloride, NaH, THF. \(^{h}\) Mel, NaH, THF, 0 °C to RT. \(^{i}\) Mel, NaH, THF, 0 °C to 45 °C.
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<th>Electrophile</th>
<th>Turnover&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>0 °C – 45 °C</td>
<td>methyl iodide</td>
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<sup>a</sup> Determined by <sup>1</sup>H NMR and/or thin layer chromatography TLC (Legend: "-" = no turnover; "+" = partial turnover; "++" = full turnover, no starting material left), for details see Experimental Section 6.4.3.

Table 6.1: Attempts to alkylate alcohol 5.

The reductive cleavage of an alkoxy group in the benzylic position is not necessarily restricted to ethers but fundamentally also should work e.g. with esters. Thus, since the etherification was found to be difficult, alcohol 5 was derivatized into an ester employing 2-ethylhexanoyl chloride. The esterification was found to occur readily (Scheme 6.2), and the attached side-chain favorably combines both entropy contribution (through its long chain) as well as prevention of crystallinity (through its stereoirregularity)<sup>9,10</sup>. Subsequently, the produced, branched monomers were polymerized in Heck type reactions, employing the same conditions as in Chapter 4 for the production of a PPPO-precursor (Scheme 6.4).
Scheme 6.4: Polymerization of monomers 5, 6 and 7 employing the Heck reaction.

As usually with Heck reactions, after about 10 min the formation of a cloudy precipitate (diisopropylamine hydroiodide salts) in the reaction mixture indicated the start and the smooth proceeding of the Heck polycondensation. After characterization of the respective materials by means of NMR spectroscopy, DSC, GPC and elemental analysis, it was concluded that the Heck reaction performed well with all three monomers and the expected polymers were obtained in a reasonable molecular weight. The synthesized side-chain derivatized polymers were found to be amorphous and, with the exception of P4 which was exclusively soluble in DMSO, readily soluble in a variety of common solvents at ambient temperature (Table 6.2). However, polymers P5 of a degree of polymerization exceeding a value of around 15, were found to be of limited solubility. The number-average molecular weights of the 2-ethylhexanoate substituted polymers P6, determined by GPC, were in the range of 3,900-4,400 and exhibited polydispersities between 1.4 and 2.2 (Experimental Section 6.4.5). The change of the catalyst from Pd(PPh3)4 to PdCl2(PPh3)2 did not lead to significantly higher molecular weights.
Table 6.2: Solubility of the side-chain derivatized PPPB-precursors (++ = well soluble; - = insoluble).

Together with the experiments in Chapter 4 (Pd-catalyzed coupling of 1,7-octadiyne with diiodobenzene), the polymerization of the branched monomers described above is, to the best of our knowledge, the first time that the Heck reaction is used for the polymerization of an aliphatic acetylene with an aromatic halide and, thus, is a further demonstration for the versatility of this unique synthetic tool.

However, attempts to cleave the side-chains in a polymer-analogous step somewhat unexpectedly failed. When a solution of the respective polymers was treated with palladium on activated charcoal and hydrogen (5-8 bars) the triple bond could partially be reduced, at least in the case of polymer P5. But the side-chains, and in case of polymer P6 also the acetylenic function, persisted (Scheme 6.5) in the backbone. Having not investigated this problem in detail and with only limited experimental information at hand, it is difficult to say why these reductions did not proceed as expected. Of course, polymer-analogous steps very often cause problems, probably due to the limited mobility of the chains in solution. In the case of polymer P6, the sterical

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<td>-</td>
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<tr>
<td>1,4-Dioxan</td>
<td>-</td>
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<td>3 M NaOH</td>
<td>-</td>
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<tr>
<td>DMSO</td>
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\# Polymers P5 of a dp higher than around 15 proved to be insoluble (Experimental Section).
hindrance of the bulky side-chains may have prevented the binding of the polymer to
the heterogeneous catalyst surface.

\[ \text{Scheme 6.5: Catalytic hydrogenation of the soluble, side-chain substituted polymers.} \]

Thus, by means of the Heck-polymerization of side-chain derivatized monomers the
molecular weights of the respective polymers could slightly be improved compared to
the Suzuki cross-coupling condensation (Chapter 6.2.1) and also when compared to the
non-sidechain derivatized Heck polymers of Chapter 4.2.1. However, since the cleavage
of the alkoxy side-chains proved to be somewhat difficult, a better synthetic procedure
had to be found to produce PPPB and to further improve the degree of polymerization.

6.2.3 Polymer Synthesis via ADMET Polymerization

6.2.3.1 Monomer Synthesis

As in the case of PPPO (Chapter 4), ADMET was also used for the synthesis of PPPB.
All ADMET polymerizations were based on \( p \)-diallylbenzene (8), which was prepared
in a two-step, one-pot procedure shown in Scheme 6.6, adapting a general method
described elsewhere.\(^{17}\)
Scheme 6.6: Monomer Synthesis.

6.2.3.2 Synthesis of the ADMET Precursor Polymer

ADMET polymerization of 8 yielded the unsaturated PPPB-precursor polymer P7 (Scheme 6.7). Four ADMET catalyst systems in various solvents, utilized at different temperatures were investigated in this work (Table 6.3 and Experimental Section): Schrock’s 2,6-diisopropylphenylimido neophyldenemolybdenum (VI) bis(hexafluoro-t-butoxide) (C4), Grubbs’ bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (C5) and the classical tungsten systems trans-dichlorobis(2,6-dibromophenoxy)oxotungsten (VI)/Bu₄Sn (C6) and tungsten (VI) chloride/Bu₄Sn (C7) shown in Scheme 6.8.

Scheme 6.7: Acyclic diene metathesis (ADMET) polymerization and catalytic reduction of the unsaturated precursor polymer P7.
Scheme 6.8: ADMET catalyst systems employed in this work; 2,6-diisopropylphenylimido neophyldenemolybdenum (VI) bis(hexafluoro-t-butoxide) (C4) ("Schrock's Mo-catalyst"), bis(tricyclohexyl-phosphine)benzylidene ruthenium (IV) dichloride (C5) ("Grubbs' Ru-catalyst"), trans-dichlorobis(2,6-dibromophenoxoy)oxotungsten (VI)/Bu4Sn (C6) and tungsten (VI) chloride/Bu4Sn (C7).

In a first series of ADMET polymerizations of 8, Schrock's alkylidene molybdenum complex C4 was used, which has been successfully applied in the earlier synthesis of PPPO (Chapter 4). Bulk polymerization of 8 was hampered by the relatively high crystalline melting temperature (Figure 6.4) of the precursor polymer P7 (Table 6.3, Exp. P7.A1 and P7.C1) resulting in premature precipitation of P7, which occurred typically within several minutes after the polymerization was initiated. Consequently, only low-molecular weight materials were obtained under these conditions. Therefore, all subsequent polymerizations were conducted in solution and at elevated temperatures (Table 6.3). However, also when conducting the polymerization with C4 at temperatures of 55 °C and changing the solvent to 1,2,4-trichlorobenzene (TCB) (which appeared to be a slightly better solvent for P7 than toluene), early precipitation of P7 was observed, leading to polymers of relatively low molecular weights (Table 6.3, Exp. P7.A4). Further increase of the reaction temperature to 60 or 75 °C resulted in a color...
change of the reaction mixture from red to dark brown and a reduction in molecular weight of the products, indicating the decomposition of catalyst C4 (Table 6.3, Exp. P7.A3 and P7.A5). In addition to the rapidly decreasing activity of C4 under those conditions, signals related to a significant fraction of arylvinylic protons were observed in the $^1$H NMR spectra of the respective polymers P7.A3 and P7.A5, indicating the emergence of unwanted side reactions. Thus, the thermal stability of the Schrock-Mo catalyst C4, under the employed conditions, appeared to be limited to temperatures below about 60-70 °C, which is in excellent agreement with results of Wagener et al.,$^{18}$ who reported decomposition of C4 to occur in the temperature range of 65-75 °C.

Hence, in view of the inherent, limited solubility of P7 at low temperatures – which arises from the rigidity of its backbone and the lack of favorable enthalpic interactions with solvents – and in order to avoid early precipitation of the polymer P7 during polymerization, the use of a catalyst that is stable at significantly higher temperatures appeared to be a prerequisite. In experiments with Grubbs' ruthenium catalyst C5 at 110 °C (Table 6.3, Exp. P7.B1 and Experimental Section) the initially lively evolution of ethylene gas diminished within few minutes and was accompanied with a color change of the reaction mixture from violet to dark. In addition, a dark solid residue that was formed, possibly originating from the decomposed catalyst, clearly demonstrated that 110 °C is beyond the thermal stability of this catalyst. No improvements with respect to the molecular weight of P7 resulted from employing C5.

Wagener and co-workers recently described ADMET polymerizations using different classical tungsten systems that are activated and used at higher temperatures (65-120 °C).$^{19,20}$ Indeed, the experiments indicated that use of trans-dichlorobis(2,6-dibromo phenoxo)oxotungsten(VI)/Bu4Sn (C6) allowed increase of the polycondensation temperature up to 120 °C without significant decay of the catalyst during the course of the reaction. Thus, various polymerization conditions were investigated for the WOCl2(OAr)2/Bu4Sn-system C6. At solvent concentrations below 60 % w/w (all solvent concentrations in this work are given as a percentage of the total weight of the reaction mixture), precipitation of the prepolymer P7 occurred in less than 15 minutes (Table 6.3, Exp. P7.C1, P7.C2, P7.C3), which produced materials of only slightly improved $M_n$ of around 6,000 (Table 6.3, Exp. P7.C2). At a toluene concentration of around 90 % w/w, systematic increase of the polymerization temperature from 97 °C to reflux resulted in delay of the precipitation of P7 from 1 to 5
h (Table 6.3, Exp. P7.C4, P7.C5, P7.C6) yielding polymers with a concomitantly increased molecular weight. In the case of P7.C6, endgroup analysis with \(^1\text{H} \text{NMR}\) in fact was no longer possible due to high molecular weight of the polymer. A change of the solvent from toluene to 1,2,4-trichlorobenzene at comparable reaction conditions did not lead to further increased polymer molecular weights. To the contrary, a significantly lower degree of polymerization was achieved, indicating that TCB might be a less suitable solvent for the present ADMET reaction (Table 6.3, Exp. P7.C7). Similar results were obtained with \(\alpha\)-xylene at 105 °C (Table 6.3, Exp. P7.C8), but when elevating the reaction temperature up to 125 °C number-average molecular weights of up to 7,800 were achieved. Unfortunately, analogously to the experiments with C4 and C5, significant fractions of arylvinylic protons were detected in \(^1\text{H} \text{NMR}\) analysis of P7.C9 and P7.C10; which again resulted from the side reactions that took place under reaction conditions close to the thermal limit of the catalyst system C6. Further evidence for the thermal application limit of C6 was obtained with an attempted post-condensation of a polymer P7 with C6 at 130 °C. The material obtained under these conditions (Table 6.3, Exp. P7.C11) was found to be insoluble and not meltable, indicative of crosslinking.

Summarizing the results presented above, it is concluded that the optimum reaction conditions investigated here are use of catalyst C6 in refluxing toluene; and at rather dilute concentrations (Table 6.3, Exp. P7.C6) in which polymer P7 could be kept in solution for approximately 5 h. After the catalytic reduction of P7.C6 the respective poly(\(p\)-phenylene butylene) PPPB.4 had a polydispersity of 3.0 and a HT-GPC- \(M_n\) of 26,000 (Table 6.4), which due to the overestimation of the \(M_n\) by GPC (below) translates into a more realistic value of \(M_n\) of the order of 14,000. These observations seem to suggest that the nature of the solvent, if at all, has only a minor effect on the nature of the polymer produced, while the reaction temperature was found to be the dominating factor. A significant increase in molecular weight was observed when increasing the latter from 100 °C (P7.C4) to 125 °C (P7.C6 and P7.C9). A further increase to 125 °C or 130 °C seemed to exceed the thermal stability limit of C6 (P7.C10 and P7.C11). Also WCl\(_6\)/Bu\(_4\)Sn (C7)\(^{21}\) another classical tungsten system, used at this temperature was unsuccessful, as the resulting polymer (P7.D1) was not meltable and insoluble in boiling \(\alpha\)-xylene.
The above mentioned occasional production of insoluble materials (P7.C11, P7.D1) can be explained in view of the emergence of arylvinyllic protons (6.15-6.40 ppm) in the $^1$H NMR spectra of the polymers P7, when the respective decomposition temperatures of the catalysts or catalyst systems were approached. At elevated temperatures these arylvinyllic functions, caused by undesired side reactions, can readily trigger vinylic polymerization and, hence, yield crosslinked materials.

It is well known that the olefinic groups of polymers formed by ADMET can be present in either trans (E) or cis (Z) form. The ratio Z/E of the repeat units in P7 was determined from $^1$H NMR spectra (Figure 6.1), in which the chemical shift of benzylic protons of a cis repeat unit (3.43 ppm) differs significantly from the one of the trans conformation (3.29 ppm). The assignment of these NMR signals was established by $^1$H-$^1$H and $^1$H-$^1$C correlation spectroscopy (COSY) experiments. The Z/E ratio of the repeat units in P7 was found to be independent of the catalyst system and typically around 0.20 (except in materials obtained under conditions that involved a significant amount of side-reactions), which is comparable to results obtained by other authors. All relevant reaction parameters for the ADMET polymerizations are compiled in Table 6.3.
<table>
<thead>
<tr>
<th>polymer</th>
<th>catalyst</th>
<th>polymerization temperature, °C</th>
<th>solvent, % w/w</th>
<th>equivalents catalyst</th>
<th>precipitation of P7 after time, h</th>
<th>reaction yield, %</th>
<th>$T_m$, °C</th>
<th>$d_P$ b)</th>
<th>$\overline{M}_n$ b)</th>
<th>side reactions c)</th>
<th>% cis°</th>
</tr>
</thead>
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<tr>
<td>P7.A1</td>
<td>C4</td>
<td>RT-50 toluene, 0/84 e)</td>
<td>0.0025</td>
<td>30 min</td>
<td>24</td>
<td>42</td>
<td>147</td>
<td>14±1.6</td>
<td>1,800</td>
<td>0.05</td>
<td>20</td>
</tr>
<tr>
<td>P7.A2</td>
<td>C4</td>
<td>RT-50 toluene, 96</td>
<td>0.0025</td>
<td>60 min</td>
<td>24</td>
<td>53</td>
<td>150</td>
<td>14±1.4</td>
<td>1,800</td>
<td>0.06</td>
<td>17</td>
</tr>
<tr>
<td>P7.A3</td>
<td>C4</td>
<td>75 toluene, 89</td>
<td>0.0023</td>
<td>3 h</td>
<td>52</td>
<td>53</td>
<td>162</td>
<td>9.5±1</td>
<td>1,200</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>P7.A4</td>
<td>C4</td>
<td>55 TCB, 69</td>
<td>0.0026</td>
<td>9 h</td>
<td>23</td>
<td>58</td>
<td>130</td>
<td>20±2.4</td>
<td>2,600</td>
<td>0.08</td>
<td>24</td>
</tr>
<tr>
<td>P7.A5</td>
<td>C4</td>
<td>60 TCB, 95</td>
<td>0.0046</td>
<td>CRT f)</td>
<td>94</td>
<td>78</td>
<td>157</td>
<td>14±3</td>
<td>1,800</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>P7.B1</td>
<td>C5</td>
<td>110 toluene, 51</td>
<td>0.0023</td>
<td>CRT f)</td>
<td>6</td>
<td>75</td>
<td>105-136</td>
<td>38±31</td>
<td>4,900</td>
<td>0.15</td>
<td>30</td>
</tr>
<tr>
<td>P7.C1</td>
<td>C6</td>
<td>100 toluene, 0/86 e)</td>
<td>0.002</td>
<td>10 min</td>
<td>18</td>
<td>73</td>
<td>178</td>
<td>20±1.6</td>
<td>2,600</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>P7.C2</td>
<td>C6</td>
<td>105 toluene, 28</td>
<td>0.0032</td>
<td>5 min</td>
<td>7</td>
<td>98</td>
<td>184</td>
<td>47±6</td>
<td>6,100</td>
<td>0</td>
<td>19</td>
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<tr>
<td>P7.C3</td>
<td>C6</td>
<td>107 toluene, 58</td>
<td>0.0072</td>
<td>12 min</td>
<td>4</td>
<td>98</td>
<td>182</td>
<td>30±2.2</td>
<td>3,900</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>P7.C4</td>
<td>C6</td>
<td>97 toluene, 93</td>
<td>0.0024</td>
<td>1 h</td>
<td>6</td>
<td>88</td>
<td>191</td>
<td>40±0.5</td>
<td>5,200</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>P7.C5</td>
<td>C6</td>
<td>110 toluene, 91</td>
<td>0.0032</td>
<td>3 h</td>
<td>20</td>
<td>90</td>
<td>193</td>
<td>42±6</td>
<td>5,500</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>P7.C6</td>
<td>C6</td>
<td>reflux toluene, 89</td>
<td>0.0035</td>
<td>5 h</td>
<td>15</td>
<td>93</td>
<td>186</td>
<td>n.a. k)</td>
<td>n.a. k)</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>P7.C7</td>
<td>C6</td>
<td>100 TCB, 92</td>
<td>0.002</td>
<td>CRT f)</td>
<td>31</td>
<td>93</td>
<td>180</td>
<td>12.4±1.0</td>
<td>1,600</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>P7.C8</td>
<td>C6</td>
<td>105 o-xylene, 93</td>
<td>0.0044</td>
<td>10 h</td>
<td>31</td>
<td>85</td>
<td>181</td>
<td>17±1.5</td>
<td>2,200</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>P7.C9</td>
<td>C6</td>
<td>125 o-xylene, 94</td>
<td>0.0024</td>
<td>CRT f)</td>
<td>30</td>
<td>84</td>
<td>177</td>
<td>56±16</td>
<td>7,300</td>
<td>0.02</td>
<td>21</td>
</tr>
<tr>
<td>P7.C10</td>
<td>C6</td>
<td>125 o-xylene, 66</td>
<td>0.0022</td>
<td>4 h</td>
<td>22</td>
<td>94</td>
<td>178</td>
<td>62±12</td>
<td>8,000</td>
<td>0.06</td>
<td>22</td>
</tr>
<tr>
<td>P7.C11</td>
<td>C6</td>
<td>130 o-xylene, 93</td>
<td>0.0084</td>
<td>n.a. b)</td>
<td>48</td>
<td>54</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P7.D1</td>
<td>C7</td>
<td>130 o-xylene, 66</td>
<td>0.028</td>
<td>n.a. b)</td>
<td>52</td>
<td>92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a referring to the amount of monomer, b degree of polymerization (dp) or number-average molecular weight, respectively, determined by $^1$H NMR end-group analysis. c arbitrarily evaluated by the ratio of arylvinylic protons per internal olefinic protons in the $^1$H NMR spectrum. d fraction of cis-configuration of the olefinic groups as determined by $^1$H NMR measurements. e start of the polymerization in the bulk, addition of solvent after 1 h (P7.A1) and after 10 min (P7.C1), respectively. f CRT: cooling reaction mixture to room temperature. g postcondensation of P7.C5. h not available. i material insoluble and not meltable. j no endgroups detectable in $^1$H NMR spectrum due to high degree of polymerization.

Table 6.3: ADMET polymerization of p-diallylbenzene: Methods and results.
Table 6.4: Poly(p-phenylene butylene) prepared by reduction of the ADMET-precursor polymers P7.
6.2.3.3 Catalytic Hydrogenation of the Precursor Polymers

A number of precursor polymers P7 could be fully reduced at elevated temperatures (100-150 °C) in solvents such as toluene and o-xylene, to yield PPPB, employing the catalytic hydrogenation with palladium on activated charcoal as the reduction method (Scheme 6.7). The reaction conditions and the relevant properties of these materials are collected in Table 6.4. All polymers were characterized to satisfaction by $^1$H NMR spectroscopy, differential scanning calorimetry, and – in selected cases – elemental analysis. $^1$H NMR spectra of polymers P7 and PPPB, recorded in 1,2-dichlorobenzene at 80 °C, are shown in Figure 6.1. The spectra are consistent with the postulated chemical structure, and it is evident that the olefinic signals (5.64-5.62 ppm) virtually have fully disappeared after reduction. However, a minor amount of olefinic protons (around 1 %) is still visible in the spectrum depicted in Figure 6.1.
In contrast to the reduction of the PPPO-precursor P3, the catalytic hydrogenation of the PPPB-precursor polymer P7 was much more connected with difficulties. It was found to be extremely laborious to obtain a reasonable turnover of the reduction procedure. No matter what conditions were chosen, the last fractions of olefinic protons were extraordinarily persistent and could hardly be reduced. Hence, only very few samples could actually fully be saturated. In addition, it was found that these problems usually increased with increasing molecular weight of the precursor polymers. The main reason for these problems was probably the limited solubility of P7, as already discussed in Chapter 6.2.3.2. Thermal crosslinking processes of the olefinic double bonds, which occur at elevated temperatures, prevent from dissolving the prepolymer at even higher temperatures in solvents like tetralin or 1,2,4-trichlorobenzene. By means of DSC experiments (Figure 6.4) it was found that the thermal stability of P7 is limited to temperatures of 130-140 °C only (for details: 6.2.5). Therefore, the thermal processing
window of the unsaturated precursor P7 is very confined. Unfortunately, the restriction is even more marked with polymers of higher molecular weight.

All polymer samples P7 and PPPB produced thereof could only be dissolved in solvents such as o-xylene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene and tetralin at elevated temperatures (> 80 °C) and, thus, exhibited the desired improved solubility compared to poly(p-xylylene), PPX. Molecular-weight data were estimated using 1H NMR-endgroup analysis and high-temperature gel permeation chromatography (HT-GPC) (Figure 6.2). The molecular-weight values of PPPB obtained by HT-GPC were systematically higher (by a factor of around 1.8) than those of the prepolymer calculated by 1H-NMR endgroup analysis. This behavior is consistent and explained with the fact that a polystyrene (PS) calibration was used for the evaluation of the GPC data, which, due the increased rigidity of the PPPB backbone when compared to PS, leads to a significant overestimation of the molecular weight in HT-GPC. The HT-GPC number-average molecular weights obtained for polymers prepared with ADMET polymerization were in the range of 4,000–26,000 (polydispersities typically of between 1.8 and 3), which translates to realistic values of $\overline{M}_n$ of the order of 2,500–14,000. The synthesis of higher molecular weight PPPB by means of ADMET polymerization, most unfortunately, was prevented due to the limited solubility of P7 and, in particular, the lack of appropriate temperature-resistant ADMET catalysts.
In terms of molecular weight, ADMET polymerization of \( p \)-diallylbenzene has proven to be the by far best synthetic procedure to produce PPPB, compared to the previously described methods. However, there are still problems related to this synthetic route, such as the inherent tendency of precursor polymer \( P7 \) to crosslink at temperatures above around 130-140 °C (Figure 6.4), or the limited solubility of the latter. Hence, the processing of \( P7 \) (i.e. polymerization and catalytic reduction) always has to take place at conditions that are either detrimental to the polymerization catalysts or deleterious to the precursor polymer itself.

The only way to avoid these problems is the use of side-chain derivatized monomers, which should lead to soluble and, therefore, better processable, precursor polymers. However, as described in Chapter 6.2.2 this approach entails other difficulties. The thermal properties of precursor polymer \( P7 \) and PPPB will be discussed in Chapter 6.2.5.
6.2.4 Polymer Synthesis via Dehydrohalogenation (Gilch Route)

Inspired by the unique chemistry of p-xyylene (Chapter 3.2) attempts were made to adapt this mechanism to the production of PPPB or precursors thereof. An essential characteristic of the 1,4-quinodimethane derivatives is the possibility of these reactive species to form either the conjugated tetraolefin with a quinonoide structure or the biradical form (Scheme 6.9 (a)).

\[
\text{PPX} \quad \xrightarrow{\text{highly questionable}} \quad \text{PPPBB} \quad \xrightarrow{?} \quad \text{(c)}
\]

\[\text{Scheme 6.9: Other forms of quinoide hydrocarbons.}\]

In case of p-xyylene, the biradical form can be created because the unpaired electrons at the benzylic positions can be delocalized into the aromatic ring resulting in a stabilization of the overall biradical. For the preparation of a polymer with four carbon atoms between the aromatic moieties one additional methylene group is required (Scheme 6.9 (b)). However, the stabilization of the respective unpaired electrons into the aromatic ring is not existent in this case, and, thus, the required biradical is an...
extremely unfavorable species from a thermodynamic point of view, and therefore hardly accessible. To make use of the particular quinoide feature, an odd number of carbon atoms substituted in para-position of the ring is mandatory, such as in the case of the species depicted in Scheme 6.9 (c), which might enable the synthesis of a precursor of poly(p-phenylene hexylene) (PPPH).

In view of the above, one possible quinoide hydrocarbon to produce a polymer with four carbon atoms separating the aromatic rings from each other seems to be the one depicted in Scheme 6.10. Due to its asymmetric architecture, the formation of head-to-tail and tail-to-tail placements of the repeat unit has to be expected leading to a random distribution of the two possible repeat units. In addition, further problems could arise because the reactive quinoide species, depicted in Scheme 6.10, could form other biradicals, which could also react at the benzyl position, leading to branched, ill-defined polymers.

\[
\begin{align*}
\text{Scheme 6.10: A potential quinoide hydrocarbon to produce an alkarotic polymer.}
\end{align*}
\]

In analogy to the chemistry of the \( p \)-xylylene monomer, the quinoide hydrocarbon described in Scheme 6.10 may be obtained when 4-methylcinnamyl chloride (10) is treated with a strong base. The synthesis of 4-methylcinnamyl chloride (10) could be accomplished by three straightforward synthetic steps, which are summarized in Scheme 6.11. The commercially available 4-methylcinnamic acid was first esterified
with ethanol catalyzed with concentrated sulfuric acid. The resulting ester 11 could be quantitatively reduced to the respective alcohol 12 according to a published procedure. Treatment of 4-methylcinnamyl alcohol (12) with thionyl chloride and pyridine yielded the desired “Gilch” monomer 10.

![Scheme 6.11: Synthesis of 4-methylcinnamyl chloride (10).](image)

When monomer 10 was treated with potassium tert-butoxide under the standard Gilch conditions, only starting material could be isolated, indicating that the basicity of alcoholates might not be sufficient to dehydrohalogenate the chloride 10. When 10 was treated with phenyl lithium, a cloudy mixture was obtained when the reaction mixture was given to MeOH and minor amounts of a polymer-like precipitate could be collected that was characterized by NMR spectroscopy, DSC, GPC and elemental analysis. The off-white solid was found to be soluble in common organic solvents, such as chloroform, THF and toluene. The DSC scans did not reveal any thermal transitions, and by means of GPC only a very low molecular weight was detected ($M_w = 2,700$). The above results and two very broad peaks in the $^1$H NMR spectrum, one in the
aromatic the other in the aliphatic region, indicated that the structure of the solid might be the one postulated in Scheme 6.10. These initial experiments clearly show that this approach may be very promising and exciting. Of course, more experiments are needed to fully elucidate the reaction mechanism and to optimize the reaction parameters.

6.2.5 Thermal Properties and Morphology

The thermal properties of the PPPB prepared by means of Suzuki cross-coupling and ADMET polymerization were investigated using thermogravimetric analysis and differential scanning calorimetry conducted at heating rates of 10 °C/min. TGA experiments revealed that PPPB is remarkably stable under dynamic heating; the new polymer was found to be stable up to around 350 °C under nitrogen atmosphere, as well as in air (Figure 6.3).

![Figure 6.3: Thermogravimetric analysis of PPPB (produced from P7.C8) under nitrogen and air (heating rate 20 °C/min).](image-url)

DSC thermograms of the PPPB-precursor polymer P7 (Figure 6.4) displayed in the first heating scan a broad, exothermic transition with a maximum at around 160 °C. This peak is assigned to the onset of thermal crosslinking of the polymer, clearly evidenced by the fact that unsaturated P7 heated up to 180 °C and kept at this temperature for 10
min is (in contrast to the pristine sample) essentially insoluble in boiling o-xylene. This finding is also consistent with the observation that the sharp melt transition at 193 °C of the first heating scan broadened significantly with a maximum at 179 °C in the second heating scan (Figure 6.4).

DSC scans of PPPB revealed a weak glass transition ($T_g$) at around 55 °C, and a melting range between 180-205 °C (Figure 6.5; a)) and 180-215 °C (Figure 6.5; b)) in the first and second heating scan, respectively. The appearance of two melting peaks very well could be an indication of the presence of two crystal modifications, as is known for PPPO (Chapter 4) and PPX. After recrystallization of virgin (as-polymerized) PPPB at 193 °C, only one pronounced endothermic transition with a maximum at 201 °C was observed (Figure 6.5; c)). Recrystallization at 204 °C of preliminarily molten PPPB failed to yield material with only one pronounced endotherm in subsequent melting experiments (Figure 6.5; d)). Wide-angle X-ray diffraction patterns (Figure 6.6, middle and right) of all these PPPB samples (Figure 6.5; a-d)) were found to exhibit the same d-spacings, which appears to disprove the presumption of the presence of more than one crystal modification. Hence, the observed effects were attributed to phase-segregation into crystal domains of significantly different molecular weights, perhaps combined with the presence or absence of extended chain and folded chain crystals, as is well-documented for, e.g., polyethylene in a comparable molecular-weight regime.

Importantly, the melting temperature of PPPB is in the attractive range that combines temperature stability and thermoplastic processability, and, gratifyingly matches the interpolations with the semi-empirical approach that was developed in Chapter 5. It is noteworthy that the PPPB produced here has a dramatically different melting behavior than the material that was obtained by Brown and Farthing, for which we do not have a plausible explanation; other than that these authors may not have produced PPPB.
Figure 6.4: Differential scanning calorimetry of precursor-polymer P7.C5: a) first heating scan; b) second heating scan.

Figure 6.5: Differential scanning calorimetry (heating scans) of PPPB.9 (produced from P7.C9): a) as-reduced, virgin PPPB.9. b) PPPB.9 crystallized from the melt, cooled down by 10 K/min. c) as-reduced PPPB.9 recrystallized at 193 °C. d) once-molten PPPB.9, recrystallized at 204 °C.
The enthalpy of fusion of PPPB was determined to be about 70 J/g, which is indicative of a significant degree of crystallinity of these polymers. This value is comparable to the heat of fusion of commercially available PPX (80 J/g) and to PPX that was obtained by the so-called Gilch route (60-90 J/g). The high degree of crystallinity of both the precursor polymer P7 and PPPB was also detected in wide-angle X-ray diffraction (WAXD) experiments. The pattern of P7 (Figure 6.6, left) showed a prominent reflection at 4.5 Å and two weaker reflections at d-spacings of 3.68 Å and 5.50 Å. The WAXD patterns of virgin PPPB that was obtained by pouring a hot, concentrated (around 5 % w/w PPPB) PPPB-solution into ethanol displayed ill-resolved reflections resulting from a high degree of disorder (Figure 6.6, middle). On the other hand, the X-ray photograph of a PPPB-sample that was crystallized from the melt exhibited very sharp, well-defined reflections (Figure 6.6, right). The principal spacings of PPPB (Figure 6.6, right) were 5.09 Å and 4.36 Å. The respective d-spacings for the α- (4.0 and 5.2 Å) and β-modification (4.4 Å) of PPX are in a comparable range. Additional weak reflections were observed at 3.47 and 6.58 Å. The (weak) diffraction ring corresponding to the largest value, found at 6.58 Å, likely represents the distance between the polymer repeat units; although the value calculated from standard bond lengths and angles (8.37 Å) is higher, which is indicative of tilting of the polymer chains in the crystal unit cell.

Figure 6.6: Wide-angle X-ray diffraction patterns of precursor polymer P7.C4 (left), virgin PPPB.5 (middle) and PPPB.5 crystallized from the melt (right).
6.3 Conclusions

In Chapter 4, it was demonstrated that acyclic diene metathesis (ADMET) polymerization can be used as an efficient synthetic route to a class of processable, hydrophobic and crystalline polymers, which contain only aromatic and aliphatic hydrocarbon units in their backbone. In the present Chapter, poly(p-phenylene butylene) (PPPB), as a second member of this class of polymers, was synthesized by the use of four different ADMET catalysts and subsequent catalytic reduction. Number-average molecular weights of the polymers obtained exceeded 10,000. WOCl₃(OAr)₂/Bu₄Sn in refluxing toluene proved to be the most appropriate catalyst system to produce the crystalline and high-melting poly(p-phenylene but-2-enylene), the precursor for PPPB, of high-molecular weight. PPPB could also be prepared by the Suzuki cross-coupling of hydroborated olefins. The polymerization of side-chain derivatized monomers was found to be significantly less successful. The entailed polymer-analogous steps, e.g. the reduction of double or triple bonds and the cleavage of side-chains, are usually troublesome and difficult to obtain in decent turnovers.

Wide-angle X-ray diffraction and DSC experiments showed that both the unsaturated precursor-polymer and poly(p-phenylene butylene), displayed a significant degree of crystallinity. In contrast to poly(p-phenylene octylene) (Chapter 4), poly(p-phenylene butylene) PPPB was found to be soluble only at elevated temperatures, and had a high melting temperature in the range from 200 to 215 °C. Thus, PPPB indeed exhibits the thermal properties that close the gap between polyethylene and poly(p-xylylene). The melting temperature for PPPB that has been predicted with the semi-empirical approach, discussed in Chapter 5, could be confirmed. A detailed analysis of the equilibrium melting temperature and crystallization kinetics of PPPB is given in an Appendix of this work.

6.4 Experimental Section

6.4.1 General

A general description concerning the origin of chemicals, purification of monomers, reagents and solvents, common procedures and spectroscopic techniques is given in Chapter 4.5.1. A commercial Parylene N (PPX) film sample (used for the determination of the heat of fusion) was purchased from COMELEC SA, La Chaux-de-Fonds,
Switzerland. HT-GPC measurements carried out at Montell Polyolefins, Ferrara, Italy were performed on a Waters 150C ALC/GPC (detector: refractive index; column type: TSK GMHXL-HT, 13 μm; mobile phase flow rate: 0.5 mL/min; solvent: 1,2,4-trichlorobenzene; column temperature: 135 °C; calibration standards: polystyrene).

6.4.2 Catalyst Synthesis

trans-Dichlorobis(2,6-dibromophenoxy)oxotungsten(VI), WOCl₂(OAr)₂, was synthesized according to a reported procedure.³⁵

6.4.3 Monomer Synthesis

4-(4'-Bromophenyl)-1-butene (4).⁴ A mixture of 4-bromobenzyl bromide (0.246 g, 0.984 mmol) and Mg (0.479 g, 19.9 mmol) in dry diethyl ether (6 mL) was rapidly heated to reflux and the exothermic reaction started instantly. The heating was removed and an additional portion of 4-bromobenzyl bromide (4.675 g, 18.71 mmol) in diethyl ether (14 mL) was slowly added. After the exothermic reaction was finished, the resulting mixture was refluxed for 0.5 h. The greenish solution was allowed to cool to RT and a solution of allyl bromide (2.382 g, 19.69 mmol) in diethyl ether (2.5 mL) was carefully added. After the exothermic reaction had declined, the reaction mixture was refluxed for another 0.5 h. The upper layer of the phase-separated reaction mixture was subsequently quenched with water (50 mL). The aqueous layer was extracted with Et₂O (2 x 50 mL), and the combined organic layers were washed with water (100 mL), dried (MgSO₄) and concentrated in vacuo. The crude product (3.23 g, 78%) was purified by distillation, bp 34 °C (0.2 mbar). ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.38 (d, ³J (H,H) = 8.4 Hz, AA'BB'-system, 2H), 7.04 (d, ³J (H,H) = 8.6 Hz, AA'BB'-system, 2H), 5.88-5.74 (m, 1 H), 5.06-4.94 (m, 2H), 2.68-2.63 (m, 2H), 2.38-2.29 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃, 300 K) δ 140.78 (Ar), 137.60 (-CH=CH₂), 131.36 (Ar), 130.24 (Ar), 119.58 (Ar), 115.32 (-CH=CH₂), 35.29, 34.77 (all CH₂). Anal. calcd for C₁₀H₈Br: C, 56.90; H, 5.25. Found: C, 56.27; H, 5.18.

1-(4-Bromophenyl)but-3-yn-1-ol (5).¹² To a stirred solution of 3-bromo-1-propyne (10.00 g, 0.0841 mol) and Ti(O-i-Pr)₄ (23.91 g, 0.0841 mol) in Et₂O (150 mL) was added i-PrMgBr (127 mL, 1.26 M in Et₂O, 0.160 mol) at -50 °C and the mixture was
stirred for 1 h at −50 °C. Then 4-bromobenzaldehyde (10.879 g, 0.0588 mol) was added at −50 °C and the reaction mixture was warmed to −25 °C over the course of 30 min. Subsequently, the reaction mixture was quenched with aqueous 1 N HCl (100 mL) at this temperature. The resulting mixture was poured into another 200 mL of aqueous 1 N HCl. The aqueous phase was separated and extracted with Et₂O (3 x 200 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The resulting yellow oil was purified by column chromatography on silica gel (eluent: EtOAc/hexane = 1/9 v/v) to yield 9.76 g (74 %) of pure 1-(4-bromophenyl)but-3-yn-1-ol (5). bp 100 °C (0.18 mbar). ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, J (H,H) = 8.5, AA′BB′-system, 2H), 7.27 (d, J (H,H) = 8.3, AA′BB′-system, 2H), 4.84 (dt, J = 6.2, 3.1, 1H), 2.63 (d, J = 2.6, 1H), 2.60 (dd, J = 2.6, 0.9, 1H), 2.41 (d, J = 3.5, 1H), 2.08 (t, J = 2.6, 1H).

1-(4-Bromophenyl)but-3-ynyl Methyl Ether (6). To a solution of alcohol 5 (2.618 g, 0.0116 mol) in THF (20 mL) was added NaH (55-65 % dispersion: 670 mg, 0.0154 mol) at 0 °C and the mixture was stirred for 30 min at this temperature. Then methyl iodide (2.528 g, 0.01781 mol) was added and the reaction mixture was warmed slowly to room temperature. After stirring for further 2.5 h at 45 °C the suspension was poured into H₂O (25 mL). The aqueous phase was separated off and extracted with Et₂O (4 x 50 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The resulting yellow oil was purified by distillation yielding pure 1-(4-bromophenyl)but-3-ynyl methyl ether (6) (2.78g, 98 %) as a colorless oil. bp 60 °C (0.05 mbar). ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, J (H,H) = 8.5, AA′BB′-system, 2H), 7.27 (d, J (H,H) = 8.3, AA′BB′-system, 2H), 4.27 (t, J = 6.5, 1H), 3.26 (s, 3H), 2.74-2.46 (4 x dd, intensity 1:3:3:1, J = 6.4, 2.7, 2H), 1.98 (t, J = 2.7, 1H).

1-(4-Bromophenyl)but-3-ynyl 2-Ethylhexanoate (7). To a solution of alcohol 5 (2.851 g, 12.67 mmol) in pyridine (17 mL) was added 2-ethylhexanoyl chloride (2.33 g, 14.3 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After stirring for another 17 h, the suspension was added to ice water (40 mL). The aqueous phase was separated off and extracted with CHCl₃ (3 x 40 mL). The combined organic layers were dried (CaCl₂) and concentrated in vacuo. The resulting orange, slightly cloudy oil (4.906 g, 110 %) was dissolved in Et₂O (30 mL) and washed with saturated
aqueous NaHCO₃- and NaCl-solution (30 mL each). After drying (MgSO₄) and concentration in vacuo 4.16 g (94 %) of a clear, orange oil was obtained that was further purified by column chromatography on silica gel (eluent: EtOAc/heptane = 1/20 v/v) to yield 3.83 g (86 %) of the colorless ester 7. ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.48 (d, 3J(H,H) = 8.5, AA’BB’-system, 2H), 7.26 (d, 3J(H,H) = 8.4, AA’BB’-system, 2H), 5.85 (t, J = 6.5, 1H), 2.83-2.60 (m, 2H), 2.39-2.25 (m, 1H), 1.96 (t, J = 2.6, 1H), 1.74-1.40 (m, 4H), 1.36-1.07 (m, 4 H), 0.98-0.79 (m, 6H). Anal. calcd for C₁₈H₂₅O₂Br: C, 61.55; H, 6.60. Found: C, 61.48; H, 6.38.

Attempts to Alkylate Alcohol 5 with 2-Ethylhexyl Bromide.⁹ (E1). A suspension of powdered KOH (200 mg, 3.56 mmol) and dry DMSO (24 mL) was stirred and degassed at room temperature for 4 h. Alcohol 5 (175.5 mg, 0.7797 mmol) in DMSO (3 mL) and 2-ethylhexyl bromide (300 mg, 1.55 mmol) were added. The reaction mixture was then stirred for 2.5 h at RT and finally poured into ice water (100 mL). The organic layer was collected and the aqueous layer was extracted with petrol ether (3 x 100 mL). The combined organic layers were dried (MgSO₄), and the solvent was evaporated to give a yellow oil (195 mg). ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, 3J(H,H) = 8.5, AA’BB’-system, 2H), 7.27 (d, 3J(H,H) = 8.4, AA’BB’-system, 2H), 4.95-4.81 (m, 1H), 2.64-2.42 (m, 2H), 2.08 (t, J = 2.6, 1H). This ¹H NMR spectrum is fully consistent with the structure of the starting material 5.

(E2). A suspension of powdered KOH (4 g, 71.29 mmol) and dry DMSO (80 mL) was stirred and degassed at RT for 50 min. Alcohol 5 (3.91 g, 17.4 mmol) in DMSO (10 mL) and 2-ethylhexyl bromide (6.72 mg, 34.8 mmol) were added. The reaction mixture was then stirred for 2.5 h at RT and finally poured into ice water (300 mL). The organic layer was collected and the aqueous layer was extracted with petrol ether (3 x 250 mL). The combined organic layers were dried (MgSO₄), and the solvent was evaporated to yield a yellow oil (4.25 g). ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, 3J(H,H) = 8.50, AA’BB’-system, 2H), 7.27 (d, 3J(H,H) = 8.32, AA’BB’-system, 2H), 4.95-4.80 (m, 1H), 2.64-2.59 (m, 2H), 2.08 (t, J = 2.6, 1H). This ¹H NMR spectrum is fully consistent with the structure of the starting material 5.
(E3). A suspension of powdered KOH (67 mg, 1.194 mmol) and dry DMSO (20 mL) was stirred and degassed at RT for 2.5 h. Alcohol 5 (247 mg, 1.097 mmol) and 2-ethylhexyl bromide (232.5 mg, 1.204 mmol) were added. The reaction mixture was then stirred for 20 h at RT; the temperature was subsequently raised to 80 °C and the reaction was stirred for another 6 h and finally poured into ice water (100 mL). The organic layer was collected and the aqueous layer was extracted with petrol ether (3 x 100 mL). The combined organic layers were dried (MgSO₄), and the solvent was evaporated to give a yellow oil (200 mg). δH NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, δ Jₜ,ₜ = 8.48, AA’BB’-system, 2H), 7.27 (d, δ Jₜ,ₜ = 8.61, AA’BB’-system, 2H), 4.96-4.81 (m, 1H), 2.64-2.59 (m, 2H), 2.08 (t, δ J = 2.6, 1H). The δH NMR spectrum is fully consistent with the structure of the starting material 5.

(E4). To a solution of alcohol 5 (175 mg, 0.777 mmol) in MeOH (10 mL) was added NaOMe (48.5 mg, 0.855 mol) in MeOH (6 mL) and the mixture was refluxed for 20 min at 65 °C. After cooling to RT, 2-ethylhexyl bromide (165 mg, 0.855 mmol) in MeOH (10 mL) was slowly added and the reaction mixture was stirred at 65 °C for 41 h. Finally, the reaction mixture was concentrated in vacuo and the remaining oil was dissolved in Et₂O (30 mL). The organic layer was washed with 2.5 M NaOH (2 x 20 mL) and water (2 x 20 mL), dried (MgSO₄) and concentrated in vacuo to yield a yellow oil (195 mg). δH NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, δ Jₜ,ₜ = 8.52, AA’BB’-system, 2H), 7.27 (d, δ Jₜ,ₜ = 8.38, AA’BB’-system, 2H), 4.84 (t, δ J = 6.29, 1H), 2.63-2.60 (m, 2H), 2.08 (t, δ J = 2.08, 1H). The δH NMR spectrum is fully consistent with the structure of the starting material 5.

(E5). To a suspension of NaH (55-65 %-dispersion: 145 mg, 3.323 mmol) in THF (5 mL) was added 2-ethylhexyl bromide (666 mg, 3.45 mmol) at 45 °C. At this temperature a solution of alcohol 5 (275.5 mg, 1.224 mmol) in THF (20 mL) was added and the mixture was stirred for 4 h at 45 °C. After stirring for another 12 h at RT, the suspension was poured into H₂O (20 mL). The aqueous phase was separated off and extracted with Et₂O (2 x 20 mL). The combined organic layers were washed with brine, dried (MgSO₄) and concentrated in vacuo to yield 865 mg of an orange oil. δH NMR (200 MHz, CDCl₃, 300 K) δ 7.49 (d, δ Jₜ,ₜ = 8.50, AA’BB’-system, 2H), 7.27 (d,
$^3J_{(H,H)} = 8.43$, AA'BB'-system, 2H), 4.89-4.81 (m, 1H), 3.45 (d, $J = 4.57$, ≈ 4H), 2.65-2.59 (m, 2H), 2.37 (d, $J = 3.64$, 1H), 2.08 (t, $J = 2.62$, 1H), 1.70-1.26 (m, ≈ 32H), 0.92-0.85 (m, ≈ 20H). The $^1$H NMR spectrum is fully consistent with a mixture of starting material 5 and 2-ethylhexyl bromide.

(E6). To a suspension of NaH (55-65 %-dispersion previously washed with hexane: 112 mg, 4.67 mmol) in THF (10 mL) was added a solution of alcohol 5 (1.025 g, 4.554 mmol) in THF (6 mL). The resulting mixture was stirred at 66 °C for 2 h. After cooling to RT, HMPA (653 mg, 3.64 mmol) and 2-ethylhexyl bromide (880 mg, 4.58 mmol) were added. Subsequently, the mixture again was stirred at 66 °C. After 20 h, the mixture was cooled to RT and quenched with 10 % HCl solution (26 mL). The aqueous phase was separated off and extracted with hexane (3 x 15 mL). The combined organic layers were washed with saturated aqueous NaHCO$_3$-solution (30 mL), water (30 mL) and saturated aqueous NaCl-solution (30 mL), dried (MgSO$_4$) and concentrated in vacuo to yield 1.351 g of an orange oil. The $^1$H NMR spectrum is fully consistent with a mixture of starting material 5 and 2-ethylhexyl bromide.

Attempt to Alkylate Alcohol 5 with Octyl Bromide (E7). To a suspension of NaH (55-65 %-dispersion previously washed with hexane: 58 mg, 2.4 mmol) in THF (10 mL) was added a solution of alcohol 5 (0.513 g, 2.36 mmol) in THF (4 mL). The resulting mixture was stirred at 66 °C for 2 h. After cooling to RT HMPA (441 mg, 2.46 mmol) and octyl bromide (498.4 mg, 2.581 mmol) were added. Subsequently, the mixture again was stirred at 66 °C. After 18 h, the mixture was cooled to RT and quenched with 10 % HCl solution (5 mL). The aqueous phase was separated off and extracted with hexane (3 x 10 mL). The combined organic layers were washed with saturated aqueous NaHCO$_3$-solution (10 mL), water (10 mL) and saturated aqueous NaCl-solution (10 mL), dried (MgSO$_4$) and concentrated in vacuo to yield 0.877 g of an orange oil. A TLC experiment showed that no turnover had taken place.

Attempts to Alkylate Alcohol 5 with Neopentyl Iodide (E8). Powdered KOH (214 mg, 3.81 mmol) was added to a solution of alcohol 5 (210 mg, 0.933 mmol) in DMSO (5 mL). After 5 min, neopentyl iodide (400.4 mg, 2.022 mmol) was added. The reaction mixture was then stirred for 30 min at RT, and then slowly heated to 60 °C. After 5 h,
the mixture was poured into ice water (100 mL), and hexane (20 mL) was added. Finally, the mixture was extracted with CH₂Cl₂. The combined organic layers were washed with water, dried (MgSO₄), and the solvent was evaporated to give a yellow oil (226 mg). The ¹H NMR spectrum could not confirm the structure of the desired ether.

(E9). To a suspension of NaH (55-65 %-dispersion: 144 mg, 3.30 mmol) in THF (5 mL) was added neopentyl iodide (677 mg, 3.42 mmol) at 45 °C. At this temperature a solution of alcohol 5 (275.5 mg, 1.224 mmol) in THF (5 mL) was added over the course of 25 min and the mixture was stirred for 4 h at 45 °C. After stirring for another 14 h at RT, the suspension was poured into H₂O (20 mL). The aqueous phase was separated off and extracted with Et₂O (2 x 20 mL). The combined organic layers were washed with brine, dried (MgSO₄) and concentrated in vacuo to yield 345 mg of an orange oil. The ¹H NMR spectrum was fully consistent with starting material 5.

Attempts to Alkylate Alcohol 5 with MEM Chloride (E10). To a solution of alcohol 5 (180 mg, 0.800 mmol) in CH₂Cl₂ (5 mL) was added NEt₃ (130 mg, 1.29 mmol) and MEM chloride (160 mg, 1.28 mmol). Subsequently, the mixture was stirred at RT. After 4 h, a TLC experiment clearly indicated only the presence of starting material. The same result was obtained after stirring for another 48 h.

(E11). To a solution of alcohol 5 (159 mg, 0.706 mmol) in THF (5 mL) was added NaH (55-65 %-dispersion: 30.4 mg, 0.696 mmol) at 0 °C. After 5 min at this temperature, MEM chloride (131 mg, 1.05 mmol) was added. After 1.5 h, the mixture was slowly allowed to warm to RT. Subsequently, the mixture was stirred at RT for 4.5 h. After the addition of an additional portion of MEM chloride (150 mg, 1.20 mmol) the mixture was stirred for another 24 h. Finally, the THF was evaporated off, and the resulting oil was redissolved in Et₂O and washed with water. The aqueous phase was extracted with Et₂O. The combined organic layers were dried (MgSO₄) and concentrated in vacuo to yield 237 mg of a yellowish oil. Distillation of the crude product at 0.05 mbar and 100 °C yielded a colorless oil. The ¹H NMR spectrum indicated apart from the desired MEM ether around 25 % starting material. The amount of starting material could be decreased to around 9 % (determined from the ratio of the two respective acetylenic protons in the ¹H NMR spectrum) by means of distillation of
the previously distilled oil suspended with NaH-dispersion at 0.05 mbar and 100 °C. Spectral data of the MEM ether: \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K) \(\delta\) 7.47 (d, \(3\) \(^J\) \(_{\text{H,H}}\) = 8.4, AA'BB'-system, 2H), 7.24 (d, \(3\) \(^J\) \(_{\text{H,H}}\) = 8.4, AA'BB'-system, 2H), 4.83-4.72 (m, 2 H), 4.63-4.57 (m, 1H), 3.90-3.85 (m, 1H), 3.74-3.70 (m, 1H), 3.61-3.47 (m, 2H), 3.39-3.37 (m, 3H), 2.73-2.52 (m, 2H), 1.97 (t, \(J = 2.6\), 1H).

**Attempt to Alkylate Alcohol 5 with Methyl Iodide (E12).**

To a solution of alcohol 5 (3.233 g, 0.01436 mol) in Et\(_2\)O (50 mL) was added NaH (55-65 %-dispersion: 879 mg, 0.0201 mol) at 0 °C and the mixture was stirred for 15 min at this temperature. Then methyl iodide (3.006 g, 0.0212 mol) was added and the reaction mixture was warmed slowly to RT. After stirring for further 1.5 h at RT, the suspension was poured into H\(_2\)O (30 mL). The aqueous phase was separated off and extracted with Et\(_2\)O (3 x 30 mL). The combined organic layers were dried (MgSO\(_4\)) and concentrated in vacuo. The resulting yellow oil was purified by distillation yielding pure 1-(4-bromophenyl)but-3-ynyl methyl ether (5) (3.41g) as an orange oil. The \(^1\)H NMR spectrum is fully consistent with the structure of the starting material 5.

**1,4-Diallylbenzene (8).**

20 mL of a solution of \(p\)-dibromobenzene (28.2341 g, 0.1197 mol) in Et\(_2\)O (85 mL) was added dropwise to a suspension of magnesium turnings (2.9089 g, 0.1197 mol) in Et\(_2\)O (40 mL). After the reaction had started, the remaining aryl bromide solution was carefully added. The resulting mixture was refluxed for 90 min, cooled to RT, and allyl bromide (14.97 g, 0.124 mol) in Et\(_2\)O (30 mL) was slowly added. After refluxing the reaction mixture for 60 min, it was cooled to RT and dropwise added to a suspension of magnesium turnings (2.863 g, 0.1178 mol) in Et\(_2\)O (30 mL). The resulting solution was refluxed for another 60 min. Another portion of allyl bromide (24.175 g, 0.1998 mol) in Et\(_2\)O (50 mL) was added carefully during a period of 30 min. After stirring at reflux for 80 min, the mixture was poured into ice water (300 mL). The aqueous layer was extracted with ether (3 x 200 mL) and the combined organic layers were dried (MgSO\(_4\)) and concentrated in vacuo. Column chromatography (silicagel 60, hexane) and distillation (bp 40 °C at 0.4 mbar) yielded 1 as a colorless oil (6.0 g, 32 %). In addition, a by-product that could be isolated in pure form by column chromatography was 3-(4' -bromophenyl)-1-propene (9).
Data of 8: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta$ 7.12 (s, 4H, Ar), 6.03-5.89 (m, 2H), 5.10-5.02 (m, 4H), 3.36 (d, $J = 6.7$ Hz, 2H). $^{13}$C NMR (50 MHz, CDCl$_3$, 298 K) $\delta$ 137.76 (s, 2C, Ar), 137.59 (d, 2C, CH$_2$-CH=CH$_2$), 128.62 (d, 4C, Ar), 115.62 (t, 2C, CH=CH$_2$), 39.85 (t, 2C, Ar-CH$_2$-CH=CH$_2$). Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 91.16; H, 8.71.

Data of 9: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta$ 7.40 (d, $J_{(HH)} = 8.41$, AA’BB’-system, 2H), 7.06 (d, $J_{(HH)} = 8.54$, AA’BB’-system, 2H), 5.99-5.86 (m, 2H), 5.10-5.03 (m, 1H), 3.33 (d, $J = 6.65$ Hz, 2H).

4-Methylcinnamic Acid Ethyl Ester (11). To a solution of 4-methylcinnamic acid (9.619 g, 59.31 mmol) in EtOH (100 mL) was added concentrated (95-97 %) H$_2$SO$_4$ (1.22 g, 11.9 mmol). The resulting mixture was heated to reflux and stirred for 8 h. After evaporation of approximately 80 % v/v of the solvent, the yellow solution was poured into ice water (100 mL). The organic layer was separated off. The aqueous phase was extracted with Et$_2$O (4 x 75 mL). The combined organic phases were washed with water (100 mL), aqueous NaHCO$_3$ (5 % w/w, 200 mL), water (150 mL), dried (MgSO$_4$) and concentrated in vacuo. The yellow oil (11.05 g, 98 %) was further purified by distillation (bp 78-88 °C at 0.19 mbar) to yield 10.80 g (96 %) of the colorless ester 11. $^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta$ 7.66 (d, $J = 16.0$, 1H), 7.42 (d, $J_{(HH)} = 8.2$, AA’BB’-system, 2H), 7.18 (d, $J_{(HH)} = 8.0$, AA’BB’-system, 2H), 6.39 (d, $J = 16.0$, 1H), 4.26 (q, $J = 7.1$, 2H), 2.37 (s, 3H), 1.33 (t, $J = 7.1$, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K) $\delta$ 167.20 (s, 1C), 144.59 (d, 1C), 140.62 (s, 1C), 131.79 (s, 1C), 129.63 (d, 2C), 128.06 (d, 2C), 117.23 (d, 1C), 60.41 (t, 1C), 21.46 (q, 1C), 14.36 (q, 1C).

4-Methylcinnamyl Alcohol (12).$^{24}$ A solution of 4-methylcinnamic acid ethyl ester (11) (9.74 g, 51.2 mmol) in Et$_2$O (60 mL) was added over a period of about 45 min to a suspension of LiAlH$_4$ (1.596 g, 0.0421 mol) in Et$_2$O (100 mL) at -15 °C. After the addition was completed, the reaction mixture was allowed to warm to RT and stirred over night at this temperature. The mixture was poured into diluted aqueous H$_2$SO$_4$ (~1N, 200 mL). The aqueous phase was separated off and extracted with Et$_2$O (2 x 100 mL). The combined organic layers were washed with water (200 mL) and aqueous Na$_2$CO$_3$ (3 % w/w, 200 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo to yield 7.66 g (101 %) of a colorless oil, which, upon cooling with ice, turned into a white, crystalline
solid. After recrystallization in pentane, a white, crystalline solid was obtained. DSC: $T_m = 50 \, ^\circ C$ (Lit. $24 \, 50 \, ^\circ C$). $^1H$ NMR (300 MHz, CDCl$_3$, 300 K) $\delta$ 7.29-7.25 (m, 2H), 7.13-7.08 (m, 2H), 6.58 (d, $J = 15.9$, 1H), 6.31 (dt, $J = 15.9$, 5.8, 1H), 4.30 (m, 2H), 2.33 (s, 3H). Anal. calcd for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16. Found: C, 78.16; H, 7.90.

**4-Methylcinnamyl Chloride (10).**$^{24, 25}$ A cold (0 °C) solution of pyridine (2.357 g, 29.80 mmol) and SOCl$_2$ (3.35 g, 28.1 mmol) in CHCl$_3$ (3 mL) was added over a period of about 20 min to a solution of 4-methylcinnamyl alcohol (12) (3.344 g, 22.563 mmol) in CHCl$_3$ (5 mL) at 0 °C. After the addition was completed, the resulting suspension was allowed to warm to RT over a period of 2 h. Subsequently, the reaction mixture was refluxed for another 2 h. The orange solution was cooled to RT, washed with water (2 x 30 mL), dried (CaCl$_2$) and concentrated in vacuo to yield 3.39 g of a dark-orange oil. Column chromatography (silica gel 60, eluent: EtOAc/hexane = 1/4 v/v) and recrystallization from pentane yielded 10 as a white, crystalline solid (2.0 g, 53 %). DSC: $T_m = 42 \, ^\circ C$ (Lit. $24 \, 39.5$-40 °C). $^1H$ NMR (300 MHz, CDCl$_3$, 300 K) $\delta$ 7.29 (d, $J = 8.1$, 2H), 7.13 (d, $J = 8.0$, 2H), 6.62 (d, $J = 15.6$, 1H), 6.26 (dt, $J = 15.6$, 7.2, 1H), 4.32 (dd, $J = 7.2$, 1.1, 2H), 2.34 (s, 3H). Anal. calcd for C$_{10}$H$_n$Cl: C, 72.07; H, 6.65. Found: C, 72.00; H, 6.55.

### 6.4.4 Polymer Synthesis by Suzuki Cross-Coupling Polymerization

**Two Symmetrical Monomers.** 9-BBN (0.5 M in THF, 22.2 mL, 11.08 mmol) was added slowly at about -50 °C to liquid 1,3-butadiene (272.5 mg, 5.038 mmol).$^3$ The resulting white suspension was slowly warmed to RT and subsequently stirred at this temperature for 11 h. The resultant colorless solution was then added to a suspension of diiodobenzene (1.662 g, 5.038 mmol), Pd(PPh$_3$)$_4$ (58.2 mg, 50.4 μmol), NaOMe (0.816 g, 15.11 mmol) in toluene (28 mL). The mixture was heated to 60 °C and stirred at this temperature for 22 h. After cooling to RT, the reaction suspension was added dropwise into rapidly stirred methanol (300 mL). The white flakes (PPPBI.1) were collected, washed with ethanol and dried (18 mg, 2 %). $^1H$ NMR (300 MHz, CDCl$_3$, 297 K) $\delta$ 7.06 (s, 4H), 6.05-5.78 (m, traces, -CH$_2$-CH=CH$_2$ endgroups), 5.10-4.93 (m, traces, -CH$_2$-CH=CH$_2$ endgroups), 2.69-2.59 (m, 4H), 1.66-1.64 (m, 4H), 1.26 (m, 8 H, -CH$_2$-probably from 9-BBN).
One Asymmetrical Monomer. 9-BBN (0.5 M in THF, 11.5 mL, 5.73 mmol) was added to 4-(4'-bromophenyl)-1-butene (2) (1.099 g, 5.205 mmol) at 0 °C, and the reaction mixture was allowed to warm to RT within 2 h, and subsequently stirred at this temperature for another 5 h. The colorless, clear solution was then added to a suspension of Pd(PPh₃)₄ (60.15 mg, 52.05 μmol) and sodium methylate (0.422 g, 7.81 mmol) in toluene (28 mL); the mixture was heated to 60 °C, and stirred under reflux. After a total reaction time of 20 h, the reaction mixture was cooled and added dropwise into rapidly stirred methanol (310 mL). After stirring for 1 h, the precipitated polymer was collected, washed with hot ethanol, acetonitrile, and acetone. Drying at room temperature in vacuo overnight yielded PPPB.2 as an off-white powder (365 mg, 53%). DSC: Tm 158 °C. 'H NMR (300 MHz, CDC1₃, 300 K) δ 7.04 (s, 4H), 2.62-2.56 (m, 4H), 1.67-1.62 (m, 4H). ^13C NMR (75 MHz, CDC1₃, 300 K) δ 139.81 (Ar), 128.23 (Ar), 35.36, 31.01 (all CH₂). DPNMR: 14. Anal. Calcd for C₁₄H₁₈: C, 90.85; H, 9.15. Found: C, 88.92; H, 9.86.

6.4.5 Heck Polymerization of Side-Chain Derivatized Monomers

Solution Polymerization of 1-(4-Bromophenyl)but-3-yn-1-ol (5). A solution of alcohol 5 (329 mg, 1.46 mmol), Pd(PPh₃)₄ (62.5 mg, 54.1 μmol), CuI (10.3 mg, 54.1 μmol), toluene (20 mL) and diisopropylamine (8.6 mL) was heated to 65 °C. The initially olive-green solution was stirred at this temperature under reflux for 21 h. The resulting olive-gray suspension was poured into MeOH (200 mL). After filtration and drying in vacuo, 135 mg (64 %) of green-gray polymer P₄ were obtained. DSC: No Tm, degradation starting at 160 °C. 'H NMR (200 MHz, DMSO, 300 K) δ 7.52 (d, 3J (H,H) = 8.4, AA'BB'-system, endgroups, traces), 7.38 (d, 3J (H,H) = 8.3, AA'BB'-system, 2H), 7.27 (d, 3J (H,H) = 8.0, AA'BB'-system, 2H), 6.58-5.61 (m, 1H), 4.77-4.75 (m, 1H), 2.82-2.62 (m, 2H). DPNMR: 3. Anal. Calcd for C₄₀H₃₃O₄Br: C, 73.06; H, 5.06; O, 9.73; Br, 12.15. Found: C, 73.07; H, 5.34.

Solution Polymerization of 1-(4-Bromophenyl)but-3-ynyl Methyl Ether (6). (P₅.1). A solution of methyl ether 6 (1.106 g, 4.625 mmol), Pd(PPh₃)₄ (94 mg, 81 μmol), CuI (15 mg, 79 μmol), toluene (22 mL) and diisopropylamine (10 mL) was heated to 70 °C. The initially yellow solution was stirred at this temperature under reflux for 24 h. The
resulting olive-gray suspension was poured into MeOH (250 mL). After filtration the
grayish residue was dissolved in hot CHCl₃ (20 mL), poured into MeOH (250 mL),
collected, dissolved in hot toluene (20 mL) and filtered through a Celite layer (0.4 cm).
The yellow filtrate solution was then poured into MeOH (250 mL). After filtration and
drying in vacuo the yellow polymer P₅.₁ (232 mg, 32 %) was obtained. DSC: No Tₘ,
degradation starting at 170 °C. ¹H NMR (200 MHz, CDCl₃, 300 K) δ 7.50 (d, 3_J (H,H) =
8.3, AA’BB’-system, endgroups, traces), 7.37-7.26 (m, 4H), 4.35 (t, J = 6.3, 1H), 3.28
(s, 3H), 2.95-2.66 (m, 2H). DP_NMR: 6. Anal. Calcd for C₇₇H₇₁O₇Br: C, 77.83; H, 6.02;
O, 9.42; Br, 6.72. Found: C, 77.79; H, 6.33.

(P₅.₂). A solution of methyl ether 6 (1.007 g, 4.211 mmol), Pd(PPh₃)₄ (175.8 mg, 152
µmol), CuI (30.2 mg, 159 µmol), toluene (10 mL) and diisopropylamine (4.2 mL) was
heated to 70 °C. The initially yellow solution was stirred at this temperature under
reflux for 21 h. The resulting olive-gray suspension was filtered and poured into MeOH
(200 mL). After filtration, the grayish precipitate was dried in vacuo to yield an off-
white solid P₅.₂ (185 mg, 28 %). DSC: No Tₘ, degradation starting at 135 °C. ¹H NMR
(200 MHz, CDCl₃, 300 K) δ 7.50 (d, 3_J (H,H) = 8.4, AA’BB’-system, endgroups, traces),
7.37-7.30 (m, 4H), 4.35 (t, J = 6.4, 1H), 3.28 (s, 3H), 2.95-2.66 (m, 2H). DP_NMR: 8.
The fraction that had precipitated during the polymerization (320 mg, 48 %) and which
was filtered-off during the work-up was tried to dissolve and precipitate. However, this
fraction was not fully soluble in boiling toluene. The soluble part exhibited a very
similar DSC- and ¹H NMR-spectrum as the off-white polymer P₅.₂. DSC: No Tₘ,
degradation starting at around 125 °C. DP_NMR: 13.

Solution Polymerization of 1-(4-Bromophenyl)but-3-ynyl 2-Ethylhexanoate (7)
using Pd(PPh₃)₄. A solution of ester 7 (1.274 g, 3.627 mmol), Pd(PPh₃)₄ (77 mg, 67
µmol), CuI (14.4 mg, 75.6 µmol), toluene (35 mL) and diisopropylamine (15 mL) was
heated to 70 °C. The yellow solution was stirred at this temperature under reflux for 48
h. The resulting yellow suspension was poured into MeOH (200 mL). After filtration
and drying in vacuo, the yellow polymer P₆.₁ (782 mg, 80 %) was obtained. DSC: No
Tₘ, degradation starting at 130 °C. ¹H NMR (300 MHz, CDCl₃, 300 K) δ 7.49 (d, 3_J
(H,H) = 8.2, AA’BB’-system, endgroups, traces), 7.32-7.18 (m, 4H), 5.95 (t, J = 6.4, 1H),
2.99-2.84 (m, 2H), 2.35-2.32 (m, 1H), 1.62-1.46 (m, 4H), 1.30-1.10 (m, 4H), 0.89-0.70
(m, 6H). DP$_{NMR}$: 6. Anal. Calcd for C$_{126}$H$_{155}$O$_4$Br: C, 76.68; H, 7.92; O, 11.35; Br,
4.05. Found: C, 75.98; H, 7.72. GPC (THF): $\bar{M}_w = 8000; \bar{M}_w / \bar{M}_n = 1.80$.

(P6.2). A solution of ester 7 (0.502 g, 1.429 mmol), Pd(PPh$_3$)$_4$ (30 mg, 26 µmol), CuI (5
mg, 26 µmol), toluene (11 mL) and diisopropylamine (5 mL) was heated to 70 °C. The
yellow solution was stirred at this temperature under reflux for 24 h. The resulting
yellow suspension was poured into MeOH (150 mL). After filtration and drying in
vacuo, the yellow polymer P6.2 (205 mg, 53 %) was obtained. DSC: No T$_m$, degradation
starting at around 125 °C. $^1$H NMR (200 MHz, CDC$_3$, 300 K) δ 7.49 (d; $^3J_{(H-H)} = 8.4$, AA'BB'-system, endgroups, traces), 7.32-7.19 (m, 4H), 5.95 (t, $J = 6.0, 1H),
2.99-2.82 (m, 2H), 2.35-2.26 (m, 1H), 1.67-1.43 (m, 4H), 1.20 (m, 4H), 0.89-0.78 (m,
6H). DP$_{NMR}$: 5. GPC (THF): $\bar{M}_w = 5500; \bar{M}_w / \bar{M}_n = 1.43$.

Solution Polymerization of 1-(4-Bromophenyl)but-3-ynyl 2-Ethylhexanoate (7)
using PdCl$_2$(PPh$_3$)$_2$. A solution of ester 7 (0.630 g, 1.79 mmol), PdCl$_2$(PPh$_3$)$_2$ (33 mg,
47 µmol), CuI (9 mg, 47 µmol), toluene (24 mL) and diisopropylamine (10 mL) was
heated to 70 °C. The yellow solution was stirred at this temperature under reflux for 27
h. The resulting yellow suspension was cooled to RT and poured into MeOH (150 mL).
After filtration and drying in vacuo, the gray polymer P6.3 (270 mg, 56 %) was
obtained. $^1$H NMR (300 MHz, CDC$_3$, 300 K) δ 7.49 (d; $^3J_{(H-H)} = 7.8$, AA'BB'-system,
endgroups, traces), 7.31-7.15 (m, 4H), 5.95 (t, $J = 6.3, 1H), 2.99-2.80 (m, 2H), 2.35-
2.33 (m, 1H), 1.61-1.48 (m, 4H), 1.30-1.10 (m, 4H), 0.86-0.79 (m, 6H). DP$_{NMR}$: 5 GPC
(THF): $\bar{M}_w = 8700; \bar{M}_w / \bar{M}_n = 2.23$.

Attempt to Hydrogenate the Methyl Ether Precursor Polymer (P5). Palladium on
charcoal (20 mg, 10 % Pd) was added to a solution of P5.2 (60 mg, 0.38 mmol) in o-
xylene (55 mL) and the reaction mixture was stirred at 100 °C, under a hydrogen
pressure of 5 bar. After a total reaction time of 5 d, the catalyst was removed by
filtration through Celite. After concentration of the filtrate in vacuo to about 2 mL, the
resulting solution was precipitated in MeOH (150 mL). After filtration and drying in
vacuo a gray solid (31 mg) was obtained. DSC: Weak endothermic transition at 126 °C,
degradation starts only at 300 °C. $^1$H NMR (200 MHz, CDCl₃, 300 K) δ 7.46 (d, $^3J_{(H,H)} =$ 8.3, AA’BB’-system, endgroups, traces), 7.37-7.04 (m, 4H), 6.77-6.30 (m, traces), 4.39-4.32 (m, traces), 4.22-4.12 (m, traces), 4.07-4.01 (m, −1H), 3.28-3.16 (m, 3H), 2.88-2.68 (m, traces) 2.95-2.66 (m, 2H), 2.58 (t, $J =$ 7.07, 2H), 2.03-1.26 (m, 4H). From the $^1$H NMR it can be seen that the acetylenic function has almost fully disappeared, while the methoxy group is still present.

**Attempt to Hydrogenate the 2-Ethylhexanoate Precursor Polymer (P6).** Palladium on charcoal (30 mg, 10 % Pd) was added to a solution of P6.2 (120 mg, 0.444 mmol) in o-xylene (50 mL) and the reaction mixture was stirred at 90 °C under a hydrogen pressure of 5 bar. After a total reaction time of 54 h, the catalyst was removed by filtration through Celite. After concentration of the filtrate **in vacuo** to about 2 mL, the resulting solution was precipitated in MeOH (100 mL). After filtration and drying **in vacuo** a gray solid (90 mg) was obtained. DSC and $^1$H NMR are fully consistent with the ester precursor polymer P6.2.

**6.4.6 Polymer Synthesis by ADMET Polymerization**

**Solution Polymerization Employing Schrock-Mo C4. (P7.A1).** To rapidly stirred 1,4-diallylbenzene (8) (0.764 g, 4.83 mmol) was added C4 (10 mg, 13 μmol). The resulting orange solution started to evolve gas (ethylene). After 1 h, toluene (1.4 g) was given to the cloudy mixture. After a total time of 90 min, the temperature was raised to 50 °C. After another 30 min, an additional portion of C4 (8.2 mg, 11 μmol) was added. This procedure was repeated after a total time of 6 h (9 mg C4, 12 μmol) until the evolution of gas ceased. After a total reaction time of 24 h, the pink suspension was precipitated into methanol (50 mL) and stirred for 2 h. After filtration and drying **in vacuo** polymer P7.A1 (267 mg, 42 %) was obtained as a white material. DSC: $T_m$ 147 °C. The $^1$H NMR spectrum was identical to the one of P7.A2. DP$_{NMR}$: 14. Fraction of cis-configuration of the olefinic groups: 20 %.

(P7.A2). 1,4-Diallylbenzene (8) (0.637 g, 4.025 mmol) was dissolved in toluene (6.20 g). C4 (5 mg, 6.5 μmol) was added to the rapidly stirred solution. The resulting orange solution started to evolve gas (ethylene). After 60 min, an additional portion of C4 (4
mg, 5 µmol) was added to the orange, opaque reaction mixture. After a total time of 90 min, the temperature was raised to 50 °C. After another 55 min, an additional portion of C4 (6.5 mg, 8.5 µmol) was added. This procedure was repeated after a total time of 6 h (4.3 mg C4, 5.6 µmol) and after 21 h (4.8 mg C4, 6.3 µmol) until the evolution of gas ceased. After a total reaction time of 24 h, the pink suspension was precipitated into methanol (50 mL). Polymer P7.A2 (279 mg, 53 %) was obtained as a white, slightly waxy material. DSC: Tm 150 °C. "1H NMR (300 MHz, CDCl3, 300 K) δ 7.11 (s, 4H, Ar), 6.40-6.35 (m, traces, arylvinyl), 6.22-6.13 (m, traces, arylvinyl), 6.03-5.89 (m, traces, -CH=CH=CH2 endgroups), 5.70-5.65 (m, 2H, -CH=CH-), 5.10-5.04 (m, traces, -CH2-CH=CH2 endgroups), 3.49-3.47 (m, 0.86H, Ar-CH2-cis), 3.37-3.33 (m, 3.14H, Ar-CH2-trans). 13C NMR (75 MHz, 1,2-dichlorobenzene, 373 K) δ 138.48 (Ar), 130.68 (HC=CH), 128.70 (Ar), 38.75 (CH2). DPN-MR: 14. Fraction of cis-configuration of the olefinic groups: 17 %. Anal. Calcd for C10H10: C, 92.26; H, 7.74. Found: C, 85.77; H, 8.19.

(P7.A3). To rapidly stirred 1,4-diallylbenzene (8) (0.764 g, 4.83 mmol) dissolved in toluene (6.44 g) at 60 °C was added C4 (13 mg, 17 µmol). The resulting orange solution started to evolve gas (ethylene). After 30 min, a dynamic vacuum (around 200 mbar) was established. After 90 min, an additional portion of C4 (5 mg, 7 µmol) was added to the clear solution. This procedure was repeated after a total time of 6 h (7 mg C4, 9 µmol), 9 h (3 mg C4, 4 µmol) and 24 h (3 mg C4, 4 µmol) until the evolution of gas ceased. After a total reaction time of 52.5 h, the brown suspension was precipitated into methanol (180 mL). After filtration and drying in vacuo polymer P7.A3 (810 mg, 53 %) was obtained as a white material. DSC: Tm 162 °C. The "1H NMR spectrum was identical to the one of P7.A2. DP_NMR: 9.5. Fraction of cis-configuration of the olefinic groups: 30 %.

(P7.A4). To rapidly stirred 1,4-diallylbenzene (8) (1.196 g, 7.558 mmol) dissolved in 1,2,4-trichlorobenzene (1.214 g) at 55 °C was added C4 (5 mg, 6.5 µmol). The resulting orange solution started to evolve gas (ethylene). A dynamic vacuum (around 150 mbar) was established immediately. After 330 min, an additional portion of C4 (3 mg, 4 µmol) was added to the reaction mixture. This procedure was repeated after a total time of 9 h
(4 mg C4, 5 μmol) and 22.5 h (3 mg C4, 4 μmol) until the evolution of gas ceased. After a total reaction time of 23 h, the suspension was added to methanol (100 mL). After filtration and drying in vacuo, polymer P7.A4 (545 mg, 58 %) was obtained as a white solid. DSC: Tm 130 °C. The 1H NMR spectrum was identical to the one of P7.A2. DP_NMR: 20. Fraction of cis-configuration of the olefinic groups: 24 %.

(P7.A5). To rapidly stirred 1,4-diallylbenzene (8) (1.14 g, 7.20 mmol) dissolved in 1,2,4-trichlorobenzene (14.7 g) at 60 °C was added C4 (5.8 mg, 7.6 umol). The resulting orange solution started to evolve gas (ethylene). Immediately a dynamic vacuum (around 150 mbar) was established. After 10.5 h, an additional portion of C4 (7 mg, 9 μmol) was added to the reaction mixture. This procedure was repeated after a total time of 31 h (6.5 mg C4, 8.5 μmol), 94 h (4 mg C4, 5 μmol) and 108 h (6.3 mg C4, 8.2 μmol) until the evolution of gas ceased. After a total reaction time of 108 h, the mixture was poured into methanol (250 mL). After filtration and drying in vacuo polymer P7.A5 (730 mg, 78 %) was obtained as a cream-colored solid. DSC: Tm 157 °C. 1H NMR spectrum was identical to the one of P7.A2. DP_NMR: 14. Fraction of cis-configuration of the olefinic groups: 30 %.

Solution Polymerization Employing Grubbs-Ru (C5) (P7.B1). 1,4-Diallylbenzene (8) (1.111 g, 7.021 mmol) was dissolved in toluene (1.15 g) and heated to 111 °C. C5 (13.2 mg, 16.04 umol) was added to the rapidly stirred solution, which immediately vigorously evolved gas (ethylene). After 15 min, the evolution of gas had stopped. An additional portion of C5 (2 mg, 2.4 μmol) was added and, again, initiated the evolution of gas for a short while, indicating the thermal decay of C5 under these conditions. This procedure was repeated several times, until no significant ethylene production could be observed (total amount of C5 added: 26 mg). After a total reaction time of 6 h, the reaction mixture was precipitated into ethanol (150 mL). Polymer P7.B1 (683 mg, 75 %) was obtained as a white material. DSC: Tm 100-145 °C. 1H NMR (200 MHz, 1,2-dichlorobenzene, 353 K) δ 7.12-7.04 (m, 4H, Ar), 6.40-6.33 (m, traces, arylvinyl), 6.26-5.96 (m, traces, arylvinyl and -CH2-CH=CH2 endgroups), 5.65-5.54 (m, 2H, -CH=CH-), 5.13-4.96 (m, traces, -CH2-CH=CH2 endgroups), 3.43-3.41 (m, 1.2H, Ar-CH2-cis), 3.29 (s, 2.8H, Ar-CH2-trans). 13C NMR (75 MHz, 1,2-dichlorobenzene, 373 K) δ 138.49
Solution Polymerization Employing the Classical Tungsten System (C6) (P7.C1). Bu₄Sn (10 mg, 29 µmol) was added to a solution of WOCl₂(OAr)₂ (7.7 mg, 10.0 µmol) in 1,4-diallylbenzene (8) (0.664 g, 4.20 mmol). The resulting red solution was heated to 100 °C. After 10 min, the reaction medium had completely solidified. After the addition of toluene (3 mL) to the reaction mixture, the evolution of gas (ethylene) became visible. The suspension was stirred for 14 h at 100 °C. After a total reaction time of 18 h, the reaction mixture was precipitated into methanol (90 mL). After filtration and drying in vacuo polymer P7.C1 (472 mg, 73 %) was obtained as a white material. DSC: Tₘ 178 °C. The ¹H NMR spectrum was identical to the one of P7.C5. DPNMR: 20. Fraction of cis-configuration of the olefinic groups: 20 %.

(P7.C2). 1,4-Diallylbenzene (8) (0.3196 g, 2.020 mmol) and WOCl₂(OAr)₂ (5 mg, 6.5 µmol) were dissolved in toluene (127 mg) and heated to 100 °C. At a temperature of 105 °C, Bu₄Sn (10 mg, 29 µmol) was added to the red solution. After 6 min, the reaction mixture started vigorously to evolve gas (ethylene). Within 5 min, the polymer started to precipitate and after 15 min the mixture was completely solid. After a total reaction time of 7 h, the reaction mixture was cooled to RT and exposed to air. The slightly gray solid was dissolved in hot o-xylene (2 mL) and precipitated into ethanol (100 mL). After filtration and drying in vacuo polymer P7.C2 (258 mg, 98 %) was obtained as a white material. DSC: Tₘ 184 °C. The ¹H NMR spectrum was identical to the one of P7.C5. DPₙₚₘᵦᵣ: 47. Fraction of cis-configuration of the olefinic groups: 19 %.

(P7.C3). A suspension of WOCl₂(OAr)₂ (26 mg, 34 µmol) and Bu₄Sn (40 mg, 116 µmol) in toluene (300 mg) was added to a solution of 1,4-diallylbenzene (8) (0.993 g, 6.28 mmol) in toluene (1.057 g), kept at 107 °C. After 4 min, the reaction mixture started vigorously to evolve gas (ethylene). Within 10 min, the polymer started to precipitate and after 12 min the mixture was completely solid. The mixture was further stirred at 110 °C. After a total reaction time of 4 h, the reaction mixture was cooled to
RT and exposed to air. The solid was dissolved in hot o-xylene (3 mL) and precipitated into methanol (200 mL). After filtration and drying in vacuo polymer P7.C3 (798 mg, 98 %) was obtained as a white powder. DSC: Tm 182 °C. The $^1$H NMR spectrum was identical to the one of P7.C5. DP$_{NMR}$: 30. Fraction of cis-configuration of the olefinic groups: 14 %.

(P7.C4). 1,4-Diallylbenzene (8) (0.780 g, 4.93 mmol) and WOCl$_2$(OAr)$_2$ (9.1 mg, 12 μmol) were dissolved in toluene (7.9 g) and heated to 90 °C. At a temperature of 100 °C, Bu$_4$Sn (15 mg, 43 μmol) was added to the red solution. After 10 min, the reaction mixture started slowly but increasingly to evolve gas (ethylene). When the evolution of gas had decreased, a slight static vacuum was established, which was renewed from time to time. After approximately 1 h, the polymerization mixture became opaque and after a total reaction time of 2.5 h a dense suspension was obtained. After a total reaction time of 6 h, the reaction mixture was cooled to RT and precipitated into methanol (150 mL). After filtration and drying in vacuo, polymer P7.C4 (564 mg, 88 %) was obtained as a white material. DSC: Tm 191 °C. The $^1$H NMR spectrum was identical to the one of P7.C5. DP$_{NMR}$: 40. Fraction of cis-configuration of the olefinic groups: 15 %.

(P7.C5). 1,4-Diallylbenzene (8) (0.636 g, 4.02 mmol) and WOCl$_2$(OAr)$_2$ (10 mg, 13 μmol) were dissolved in toluene (5.02 g) and heated to 85 °C. After 5 min, Bu$_4$Sn (15 mg, 43 μmol) was added to the red solution. After 18 min, the reaction mixture started slowly but acceleratingly to evolve gas (ethylene). Within 1.5 h, the mixture temperature was raised to 111 °C. After 4.5 h a significant amount of precipitated polymer was observed. After a total reaction time of 21 h, the reaction mixture was precipitated into methanol (200 mL). Polymer P7.C5 (470 mg, 90 %) was obtained as a white material. DSC: Tm 193 °C. $^1$H NMR (300 MHz, 1,2-dichlorobenzene, 353 K) δ 7.09-7.04 (m, 4H, Ar), 5.64-5.62 (m, 2H, -CH=CH-), 3.43-3.41 (m, 0.72H, Ar-CH$_2$-cis), 3.29-3.27 (m, 3.28H, Ar-CH$_2$-trans). $^{13}$C NMR (75 MHz, 1,2-dichlorobenzene, 373 K) δ 138.48 (Ar), 130.68 (HC=CH), 128.70 (Ar), 38.76 (CH$_2$). DP$_{NMR}$: 42. Fraction of cis-configuration of the olefinic groups: 18 %. Anal. Calcd for C$_{10}$H$_{16}$: C, 92.26; H, 7.74. Found: C, 91.08; H, 8.21.
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(P7.C6). 1,4-Diallylbenzene (8) (0.582 g, 3.68 mmol) and WOCl₂(OAr)₂ (10 mg, 13 μmol) were dissolved in toluene (4.84 g) and heated to reflux (111 °C). At the same temperature, Bu₄Sn (22 mg, 63 μmol) was added to the red solution. After 3 min, the reaction mixture started slowly but increasingly to evolve gas (ethylene). After approximately 5 h, the polymerization mixture became slightly opaque and after a total reaction time of 15 h, the reaction mixture was cooled to RT and exposed to air. The resulting suspension was dissolved in hot o-xylene (3 mL) and precipitated into ethanol (150 mL). After filtration and drying in vacuo, polymer P7.C6 (446 mg, 93 %) was obtained as a white material. DSC: Tₘ 186 °C. The ¹H NMR spectrum was identical to the one of P7.C5. DPₙMNR: no endgroups detectable. Fraction of cis-configuration of the olefinic groups: 20 %.

(P7.C7). 1,4-Diallylbenzene (8) (0.975 g, 6.16 mmol) and WOCl₂(OAr)₂ (10 mg, 13 μmol) were dissolved in 1,2,4-trichlorobenzene (8.036 g) and heated to 100 °C. At the same temperature, Bu₄Sn (10 mg, 29 μmol) was added to the red solution. After 5 min, the reaction mixture started vigorously to evolve gas (ethylene). Occasionally, a static vacuum was established. After 24 h an additional portion of WOCl₂(OAr)₂ (10 mg, 13 μmol) and Bu₄Sn (10 mg, 29 μmol) was added and after a total reaction time of 31 h, the reaction mixture was cooled to RT and exposed to air. The resulting suspension was precipitated into methanol (150 mL). After filtration and drying in vacuo, polymer P7.C7 (744 mg, 93 %) was obtained as a white powder. DSC: Tₘ 180 °C. The ¹H NMR spectrum was identical to the one of P7.C5. DPₙMNR: 12. Fraction of cis-configuration of the olefinic groups: 21 %.

(P7.C8). 1,4-Diallylbenzene (8) (0.508 g, 3.21 mmol) and WOCl₂(OAr)₂ (10 mg, 13 μmol) were dissolved in o-xylene (4.93 g) and heated to 105 °C. At the same temperature, Bu₄Sn (15 mg, 43 μmol) was added to the red solution. After 3 min, the reaction mixture started slowly but increasingly to evolve gas (ethylene). Occasionally, a static vacuum was established. After approximately 10 h, the polymerization mixture became slightly opaque and after a total reaction time of 31 h, the reaction mixture was cooled to RT and exposed to air. The resulting suspension was precipitated into methanol (300 mL). After filtration and drying in vacuo, polymer P7.C8 (355 mg, 85
(P7.C9). 1,4-Diallylbenzene (8) (0.871 g, 5.50 mmol) and WOCl$_2$(OAr)$_2$ (10 mg, 13 μmol) were dissolved in o-xylene (9.578 g) and heated to 125 °C. At the same temperature, Bu$_4$Sn (15 mg, 43 μmol) was added to the red solution. After 5 min, the reaction mixture started vigorously to evolve gas (ethylene). After 8.5 h an additional portion of WOCl$_2$(OAr)$_2$ (10 mg, 13 μmol) and Bu$_4$Sn (22 mg, 63 μmol) was added and the solution was continued stirring at 125 °C. After a total reaction time of 30 h, the reaction mixture was cooled to RT and exposed to air. The resulting suspension was precipitated into methanol (200 mL). After filtration and drying in vacuo polymer P7.C9 (602 mg, 84 %) was obtained as an off-white material. DSC: $T_m$ 111 °C. The $^1$H NMR spectrum was identical to the one of P7.C5. DP$_{NMR}$: 56. Fraction of cis-configuration of the olefinic groups: 21 %.

(P7.C10). 1,4-Diallylbenzene (8) (0.562 g, 3.55 mmol) and WOCl$_2$(OAr)$_2$ (6 mg, 8 μmol) were dissolved in o-xylene (1.07 g) and heated to 127 °C. At the same temperature, Bu$_4$Sn (5 mg, 14 μmol) was added to the red solution. After 3 min, the reaction mixture started vigorously to evolve gas (ethylene). After 30 min small amounts of a black precipitate could be observed (possibly degraded catalyst). After a total reaction time of 30 h, the suspension was cooled to RT and precipitated into ethanol (100 mL). After filtration and drying in vacuo polymer P7.C10 (436 mg, 94 %) was obtained as an off-white material. DSC: $T_m$ 178 °C. The $^1$H NMR spectrum was identical to the one of P7.C5. DP$_{NMR}$: 62. Fraction of cis-configuration of the olefinic groups: 22 %.

(P7.C11). Precursor polymer P7.C5 (78 mg, 0.60 mmol) was dissolved at 147 °C in o-xylene (970 mg). The resulting, clear solution was cooled to 130 °C. At this temperature, WOCl$_2$(OAr)$_2$ could not be dissolved in the reaction mixture (probably due to its decomposition). Therefore, a solution of WOCl$_2$(OAr)$_2$ (2 mg, 2.6 μmol) in o-xylene (50 mg) was added to the polymer solution. After a total reaction time of 2 d at
130 °C, the suspension was cooled to RT and precipitated into ethanol (100 mL). After filtration and drying in vacuo, polymer P7.C11 (42 mg, 54 %) was obtained as a yellow material. DSC: no \( T_m \). The material obtained was completely insoluble.

**Solution Polymerization Employing The Classical Tungsten System (C7) (P7.D1).**

To a solution of 1,4-diallylbenzene (1) (0.777 g, 4.91 mmol) in \( \sigma \)-xylene (0.780 g) at 130 °C a solution of WCl\(_6\) (55.3 mg, 0.139 mmol), Bu\(_4\)Sn (89.6 mg, 0.258 mmol) and propyl acetate (48.7 mg, 0.477 mmol) in \( \sigma \)-xylene (0.709 g) were added. After 5 min, the reaction mixture started slowly to evolve gas (ethylene). After 24 h, an additional amount of \( \sigma \)-xylene (0.833 g) was added to the dark reaction mixture, and the temperature was raised to 111 °C. After a total reaction time of 52 h, the dark, highly viscous reaction mixture was cooled to RT and precipitated into ethanol (150 mL). Polymer P7.D1 (591 mg, 92 %) was obtained as an insoluble, brown-gray material. DSC: No \( T_m \). \( T_g \) at 46-52 °C. Anal. Calcd for C\(_{10}\)H\(_{11}\): C, 92.26; H, 7.74. Found: C, 85.65; H, 9.00.

**Preparation of PPPB by Reduction of Poly(p-phenylene but-2-enylene) (P7). (PPPB.3).** Palladium on charcoal (60 mg, 10 % Pd) was added to a solution of P7.A1 (221 mg, 1.70 mmol) in toluene (40 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 100 °C for 24 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (600 mL) yielded the white polymer PPPB.3 (152 mg, 68 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 100 %. DSC: \( T_m \) 129-170 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K) \( \delta \) 7.08-7.06 (br s, 4H, Ar), 2.59-2.52 (m, Ar-CH\(_2\)), 1.64-1.58 (m, 4H, Ar-CH\(_2\)-CH\(_2\)). \( \text{DP}_{\text{NMR}} \): 9.

(PPPB.4). Palladium on charcoal (80 mg, 10 % Pd) was added to a solution of P7.C8 (203 mg, 1.56 mmol) in \( \sigma \)-xylene (75 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 125 °C for 48 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (150 mL) yielded the white polymer PPPB.4 (191 mg, 93 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H
NMR spectrum): 99.2 %. DSC: \( T_m \) 183-195 °C. \(^1\)H NMR (200 MHz, toluene, 353 K) \( \delta \) 6.92 (s, 4H, Ar), 2.44-2.35 (m, Ar-CH\(_2\)), 1.53 (m, 4H, Ar-CH\(_2\)-CH\(_2\)). Anal. Calcd for C\(_{10}\)H\(_{12}\): C, 90.58; H, 9.15. Found: C, 89.62; H, 9.62. HT-GPC: \( M_w = 8,400; \frac{M_w}{M_n} = 2.1. \)

(PPPBP.5). Palladium on charcoal (80 mg, 10 % Pd) was added to a solution of PPPBP.18 (146 mg, 1.12 mmol) in o-xylene (60 mL) and the reaction mixture was stirred at 125 °C for 50 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (120 mL) yielded the white polymer PPPBP.5 (119 mg, 81 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 99.5 %. DSC: \( T_m \) 200-225 °C. \(^1\)H NMR (300 MHz, 1,2-dichlorobenzene, 353 K) \( \delta \) 7.01 (s, 4H, Ar), 2.56-2.53 (m, Ar-CH\(_2\)-), 1.65-1.60 (m, 4H, Ar-CH\(_2\)-CH\(_2\)). \(^1\)C NMR (125 MHz, 1,2-dichlorobenzene, 373 K) \( \delta \) 139.82 (Ar), 128.43 (Ar), 35.61, 31.19 (all CH\(_2\)). Anal. Calcd for C\(_{10}\)H\(_{12}\): C, 90.58; H, 9.15. Found: C, 89.56; H, 10.15. HT-GPC: \( M_w = 20,000; \frac{M_w}{M_n} = 1.8. \)

(PPPBP.6). Palladium on charcoal (22 mg, 10 % Pd) was added to a solution of PPPBP.25 and PPPBP.26 (200 mg, 1.53 mmol) in o-xylene (65 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 125 °C under a hydrogen pressure of 5 bar. After 24 h and 48 h additional portions of catalyst (25 mg each) was added to the autoclave. After a total time of 72 h the catalyst was removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (150 mL) yielded the a gray polymer. Thus, after reprecipitation the polymer was obtained as a white solid PPPBP.6 (100 mg, 50 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 98.6 %. DSC: \( T_m \) 195-210 °C. \(^1\)H NMR (300 MHz, 1,2-dichlorobenzene, 373 K) \( \delta \) 7.01 (s, 4H, Ar), 2.56 (m, Ar-CH\(_2\)-), 1.66-1.61 (m, 4H, Ar-CH\(_2\)-CH\(_2\)). HT-GPC: \( M_w = 78,000; \frac{M_w}{M_n} = 3.0. \)

(PPPBP.7). Palladium on charcoal (60 mg, 10 % Pd) was added to a solution of P7.A4 (482 mg, 3.70 mmol) in toluene (80 mL) and the reaction mixture was stirred in a 250
mL glass-autoclave at 100 °C for 50 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (130 mL) yielded the white polymer PPPB.7 (410 mg, 84 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 100 %. DSC: \(T_m\) 80-170 °C. \(^1\)H NMR (200 MHz, CDCl\(_3\), 300 K) \(\delta\) 7.07-7.06 (br s, 4H, Ar), 2.58-2.50 (m, Ar-CH\(_2\)-), 1.67-1.60 (m, 4H, Ar-CH\(_2\)-CH\(_2\)).

**PPPBB.8**. Palladium on charcoal (90 mg, 10 % Pd) was added to a solution of PPPB.13 (166 mg, 1.28 mmol) in o-xylene (60 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 140 °C for 48 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (200 mL) yielded the white polymer PPPB.8 (410 mg, 84 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 100 %. DSC: \(T_m\) 185-200 °C. \(^1\)H NMR (200 MHz, 1,2-dichlorobenzene, 353 K) \(\delta\) 7.01 (br s, 4H, Ar), 2.59-2.52 (m, Ar-CH\(_2\)-), 1.66-1.59 (m, 4H, Ar-CH\(_2\)-CH\(_2\)).

**PPPBB.9**. Palladium on charcoal (90 mg, 10 % Pd) was added to a solution of PPPB.9 (217 mg, 1.67 mmol) in o-xylene (80 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 125 °C for 48 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (200 mL) yielded the white polymer PPPB.9 (180 mg, 82 %). Turnover (determined by the amount of persistent olefinic protons in the \(^1\)H NMR spectrum): 98.8 %. DSC: \(T_m\) 191-213 °C. \(^1\)H NMR (200 MHz, 1,2-dichlorobenzene, 353 K) \(\delta\) 7.01 (br s, 4H, Ar), 2.56-2.52 (m, Ar-CH\(_2\)-), 1.66-1.63 (m, 4H, Ar-CH\(_2\)-CH\(_2\)).

**PPPBB.10**. Palladium on charcoal (90 mg, 10 % Pd) was added to a solution of PPPB.10 (163 mg, 1.25 mmol) in toluene (65 mL) and the reaction mixture was stirred in a 250 mL glass-autoclave at 110 °C for 48 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite and precipitation of the concentrated solution into methanol (120 mL) yielded the white polymer PPPB.10 (136
mg, 82 %). Turnover (determined by the amount of persistent olefinic protons in the \( ^1H \) NMR spectrum): 98 %. DSC: \( T_m = 189-211 °C \). \( ^1H \) NMR (200 MHz, 1,2-dichlorobenzene, 353 K) \( \delta \) 7.01 (br s, 4H, Ar), 2.55 (m, Ar-CH\(_2\)-), 1.63 (m, 4H, Ar-CH\(_2\)CH\(_2\)).

All other catalytic hydrogenations, depicted in Table 6.4, were carried out in analogy to the procedures described above.

### 6.4.7 Polymer Synthesis via Dehydrohalogenation (Gilch Route)

Phenyllithium (1.8 M in cyclohexane / Et\(_2\)O = 7/3 v/v, 1.4 mL, 2.52 mmol) was added at RT to a solution of chloride 10 (410 mg, 2.46 mmol) in dry o-xylene (4.77 g). The resulting yellow solution was immediately heated to 100 °C accompanied with a change of the color to dark red. After a total time of 24 h the orange suspension was given to rapidly stirred MeOH (75 mL). The resulting cloudy, fine dispersion was allowed to stand for 2 h. After filtration and drying in vacuo 22.2 mg (7 %) of an off-white solid were obtained. DSC: No \( T_m \), no \( T_g \), no degradation detectable. GPC (THF): \( M_w = 2,700; \frac{M_w}{M_n} = 9.4 \). \( ^1H \) NMR (500 MHz, CDCl\(_3\), 300 K) \( \delta \) 7.57-6.20 (m, 4H), 2.67-2.26 (m, 4H).

### 6.5 References

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Chapter 7
Other Poly(p-phenylene alkylene)s

Summary

By means of the Suzuki cross-coupling reaction, two other new representatives of the poly(p-phenylene alkylene) family have been synthesized. Poly(p-phenylene hexylene) exhibited a melting temperature of around 120 °C, and, thus, quite exactly matches the value predicted by the semi-empirical approach as described in Chapter 5. Poly(p-phenylene propylene), as the first member with an odd number of methylene groups in the repeat unit, displayed a melting behavior that strongly contrasts that of the even members, since its melting temperature (110-130 °C) is strikingly lower than that of PPPB. In addition, the solubility of poly(p-phenylene propylene) was found to be comparable to PPPO and PPPH.

7.1 Introduction

In the previous Chapters, we have focused on PPPO and PPPB as the two main representatives of the present series of target polymers. During the course of this thesis, also other members of the poly(p-phenylene alkylene) family have briefly been touched, and will shortly be discussed here. It is the main objective of this Chapter, to describe the synthesis and properties of the latter in the context of the previous discussions.

7.2 Results and Discussion

7.2.1 Poly(p-phenylene hexylene) (PPPH)

In analogy to the experiments described in Chapter 4, poly(p-phenylene hexylene) (PPPH) was prepared by the Pd-catalyzed Suzuki cross-coupling reaction from two symmetrical monomers, diiodobenzene and hydroborated 1,5-hexadiene (Scheme 7.1). PPPH was characterized to satisfaction by means of NMR spectroscopy, DSC as well as elemental analysis and was found to be readily soluble in solvents such as chloroform, toluene and THF. The melting temperature (around 120 °C) of the oligomers produced (DP of 12) was found to be slightly higher than the melting temperature of PPPO.
Scheme 7.1: Preparation of PPPH by means of Suzuki cross-coupling.

Gratifyingly, the experimental $T_m$ of PPPH is in well agreement with the value that has been predicted with the semi-empirical RRF approach (calculated $T_m = 127 \, ^\circ C$) in Chapter 5. In view of the - expected - fact that the $T_m$ of PPPH is not sufficiently higher than the $T_m$ of PPPO, and the (at best) comparable molecular weights of these materials we have omitted any further investigation of PPPH within the scope of this thesis.

7.2.2 Poly(p-phenylene propylene) (PPPPr)

While the odd representatives of the present target polymers, poly(p-phenylene methylene), poly(p-phenylene propylene), poly(p-phenylene pentylene) etc. have deliberately been ignored, the present section attempts to briefly address the latter. It is well known that within a homologue series of polymers the representatives with an odd number of certain repeating elements in the backbone behave remarkably different than their respective even "brothers". Usually, the odd members exhibit lower melting temperatures, different solubility behavior and a sometimes drastically reduced crystallinity. This phenomenon, typically called the "Odd-even Effect", has been observed for example for liquid-crystalline hydrocarbon polymers, poly(3,4-alkoxythiophene)s, and $n$-Nylons. This behavior is usually explained by a less regular structure and a reduced packing capability of the odd representatives compared to their even homologues.

The first "odd" homologue, poly(p-phenylene methylene) or poly(benzyl) (Figure 7.1) consists of one methylene unit between the aromates, leading to an extraordinary stiff backbone. Therefore, the melting temperature of poly(p-phenylene methylene) is very...
high and approximated to be at around 1800 °C, which is, of course, far above the thermal stability of any organic polymer. The estimation has been obtained from the melting temperatures of oligobenzyls extrapolated to infinite molecular weight using the relation of Flory.6

![Figure 7.1: Chemical structure of poly(p-phenylene methylene)](image)

In view of the high melting temperature of poly(p-phenylene methylene), within the scope of this work, the most interesting odd poly(p-phenylene alkylene) was expected to be poly(p-phenylene propylene) PPPPr, also exhibiting a rather rigid backbone, which should actually significantly raise \( T_m \) in comparison to PPPH. However, to which extent the influence of the “Odd-even Effect” would cause a melting point depression, was rather difficult to predict.

Poly(p-phenylene propylene) (PPPPr) was synthesized starting from 3-(4'-bromophenyl)-1-propene (9), which has been obtained as the monoalkylated by-product in the synthesis of \( p \)-diallylbenzene (8) (Chapter 6). By means of hydroboration and subsequent polymerization under standard Suzuki conditions, PPPPr (DP_{NMR}: 20) of typical molecular weight available with Suzuki reactions could be synthesized (Scheme 7.2).

![Scheme 7.2: Synthesis of poly(p-phenylene propylene)](image)

As expected and discussed above, due to the odd number of methylene groups in the repeat unit, PPPPr displayed rather unusual solution and melting properties that contrasted those of the even series of the respective alkarotic polymers. As opposed to
PPPB, PPPPr was found to be readily soluble in chloroform, toluene and o-xylene at ambient temperature. The melting temperature was determined to be between 110 and 130 °C, which is in the same range as with PPPH. According to wide-angle X-ray diffraction experiments, the overall crystallinity of PPPPr was found to be comparable to all other poly(p-phenylene alkylene)s prepared.

7.3 Conclusions

The thermal properties of two further poly(p-phenylene alkylene)s confirm the focus in this work on poly(p-phenylene butylene) (PPPB; $T_m = 200-225$ °C). Whereas the low melting temperatures of PPPH ($T_m = 120$ °C) and PPPO ($T_m = 90$ °C) are probably governed by the flexibility of their backbone, PPPPr ($T_m = 110-130$ °C), although in principle featuring a stiffer backbone than PPPB, is lacking the ability to form an appropriate compact crystal packing. The only polymer in the present series, which apparently perfectly combines all the relevant features that determine the melting temperature of polymers, is PPPB. Hence, PPPB seems to be the only poly(p-phenylene alkylene) that exhibits a melting behavior according to the property matrix established in Chapter 2.

7.4 Experimental Section

7.4.1 General

For a general section concerning the origin of chemicals, purification of monomers, reagents and solvents, common procedures and spectroscopic techniques, see Chapter 4.

7.4.2 Monomer Synthesis

1,5-Hexadiene and diiodobenzene were commercial products. Monomer 9 that was used for the synthesis of PPPPr was obtained as by-product from the synthesis of p-diallylbenzene (8). For the spectral data of 9 see the Experimental Section in Chapter 6.

7.4.3 Polymer Synthesis

Synthesis of PPPH. (PPPH.1). After adding 9-borabicyclo[3.3.1]nonane (9-BBN) (0.5 M in THF, 16.3 mL, 8.14 mmol) to 1,5-hexadiene (0.3345 g, 4.072 mmol) at 0 °C, the
reaction mixture was allowed to warm to RT within 2 h and was subsequently stirred at this temperature for another 4 h. At a temperature of 35 °C and a pressure of 1 mbar, the solvent was distilled off. At the end of the distillation, a vacuum of 0.03 mbar was established to remove the last traces of THF. To the resulting yellow oil, diiodobenzene (1.277 g, 3.873 mmol), Pd(PPh₃)₄ (134 mg, 116 μmol), NaOMe (628 mg, 11.62 mmol) and degassed, absolute toluene (20 mL) were added. The resulting yellow suspension was heated to 60 °C and stirred under reflux for 24 h. After cooling to RT, the reaction mixture was added dropwise into rapidly stirred methanol (220 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, water, hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPH₁ as a slightly gray powder (171 mg, 28 %). DSC: Tₘ = 70-95 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.59-7.30 (m, aromatic endgroups, traces), 7.06 (s, 4H), 2.55 (t, J = 7.43, 4H), 1.59-1.56 (m, 4H), 1.35 (m, 4 H). DPNMR: 4.

(PPPH₂). After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 19.9 mL, 9.93 mmol) to 1,5-hexadiene (0.3707 g, 4.513 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 2-3 h and was subsequently stirred at this temperature for another 13 h. The colorless, clear solution was added to a suspension of diiodobenzene (1.4888 g, 4.5127 mmol), Pd(PPh₃)₄ (52.15 mg, 45.13 μmol) and NaOMe (731 mg, 13.5 mmol) in degassed toluene (25 mL). The mixture was heated to 60 °C and stirred under reflux for 23 h. After cooling to RT, the reaction mixture was added dropwise into rapidly stirred methanol (270 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with methanol, water, hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPH₂ as a white powder (125 mg, 17 %). DSC: Tₘ = 114-119 °C. ¹H NMR (300 MHz, CDCl₃, 297 K) δ 7.63-7.29 (m, aromatic endgroups, traces), 7.06 (s, 4H), 2.55 (t, J = 7.47, 4H), 1.61-1.54 (m, 4H), 1.35 (m, 4 H). DPNMR: 12. Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 85.18; H, 9.50.

Synthesis of PPPPr. After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 27.4 mL, 13.7 mmol) to 3-(4'-bromophenyl)-1-propene (9) (2.4545 g, 12.45 mmol) at 0 °C, the reaction mixture was allowed to warm to RT within 1 h and
subsequently was stirred at this temperature for another 16 h. The colorless, clear solution was added to a suspension of Pd(PPh)_4 (143 mg, 125 μmol) and NaOMe (1.009 g, 18.68 mmol) in degassed toluene (50 mL). The mixture was heated to 70 °C and stirred under reflux for 96 h. After cooling to RT, the reaction mixture was added dropwise into rapidly stirred methanol (750 mL), and after stirring for 1 h, the precipitated polymer was collected and washed with ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded PPPPr as a slightly gray powder (945 mg, 64 %). DSC: \( T_m = 110-130 °C \). \(^1\)H NMR (300 MHz, CDCl₃, 300 K) \( \delta \) 7.70-7.14 (m, aromatic endgroups, traces), 7.08 (s, 4H), 6.04-5.89 (m, olefinic protons, traces), 5.10-5.00 (m, olefinic protons, traces), 2.61 (t, \( J = 7.52 \), 4H), 1.97-1.87 (m, 2H). \( D_P_{NMR} \): 20. Anal. Calcd for C₂H₁₀: C, 91.47; H, 8.53. Found: C, 90.80; H, 8.72.

### 7.5 References


Chapter 8

General Conclusions and Suggestions for Future Work

8.1 Results and Conclusions

The principal objective of this thesis was to explore a forgotten class of hydrocarbon polymers ("alkarotic polymers"). In view of the outstanding materials properties of poly(p-xylylene) and the exceptional processability of polyethylene, we embarked on the search for related polymers of the poly(p-phenylene alkylene) family that favorably combine the attractive features of the above-mentioned cornerstones.

A literature survey and the discussion of various synthetic tools which might be useful for the synthesis of the target polymers clearly demonstrate that the synthesis of these target polymers is, despite their rather simple chemical structure, not a trivial, straightforward task. Among the variety of carbon-carbon-bond forming reactions that are known in organic chemistry, and, more specific, among the synthetic tools experimentally investigated in this thesis, the Suzuki cross-coupling reaction and acyclic diene metathesis polymerization were found to be the most suitable methods for the preparation of "alkarotic polymers". In the course of this work, four new representatives of the poly(p-phenylene alkylene) family, namely poly(p-phenylene octylene) (PPPO), poly(p-phenylene hexylene) (PPPH), poly(p-phenylene butylene) (PPPB) and poly(p-phenylene propylene) (PPPPr) with weight-average molecular weights of up to 25,000 were synthesized. The properties of the latter, in particular the melting temperatures, were found to be governed by the nature of the backbone and strongly depend on the number of methylene groups in the repeat unit. Whereas PPPO (90 °C), PPPH (120 °C) and PPPPr (110-130 °C) have surprisingly low melting temperatures, the highly crystalline PPPB, melting between 200 and 225 °C, somewhat surprisingly is the only polymer of the studied series that exhibits a melting temperature, which is significantly higher than that of polyethylene. The thermal properties of PPPB perfectly fall into the envisioned regime, in which thermoplastic processing without decomposition is possible. Hence, the high-melting PPPB meets many of the requirements that are required for a novel, hydrophobic, processable, engineering polymer. Indeed, PPPB represents a thermoplastic polymer, which might be of interest
as a processable PPX-substitute and that also could be of use in applications typically covered by polymers such as polyethylene, polypropylene or polystyrene.

Within the framework of this thesis, a simple, semi-empirical methodology to estimate melting temperatures of unknown representatives of homologous series of polymers was developed and verified. By means of the so-called RRF-approach (Ratio of Rigid and Flexible segments in the polymer backbone), which is conceptually based on Van Krevelen’s group contribution theory, the melting temperatures of PPPH and PPPB could be predicted with a remarkable accuracy. In addition, it was shown that the application range of the RRF-approach is not restricted to the present alkarotic polymers, but it seems to have a rather broad applicability as evidenced by the successful application to numerous other polymer series, including various liquid crystalline hydrocarbon polymers and different polyamides.

Within the synthetic investigations of the present work, the thermal application window of different ADMET catalysts was explored and the respective limits were evaluated. As a result, the scope of these highly sensitive catalysts was significantly extended to a higher temperature regime, which is of major importance for the synthesis of polymers that are only soluble at elevated temperatures, e.g. for the present high-melting, crystalline PPPB.

In experiments in connection with the Heck reaction, the general viability of the palladium-catalyzed coupling of a terminal, aliphatic acetylene function (i.e. a terminal acetylene that is adjacent to at least one methylene group) to an aromatic halide was investigated. With the synthesis of several corresponding polymers, a, to the best of our knowledge, new synthetic variant of the Heck polymerization has been introduced.

8.2 Suggestions for Future Work

An unsatisfactory aspect of all polymers prepared in the context of this work is their relatively low molecular weight. The maximum weight-average molecular weights obtained in this work were of the order of 25,000. These values are, nota bene, in the typical molecular-weight regime available with transition metal catalyzed cross-coupling reactions or ADMET polymerizations. Many polymers, typically produced
through these methods, belong for example to the family of conjugated polymers. In these cases the length of the conjugated segments in the polymer chains is crucial, the total degree of polymerization is only of secondary importance. Due to strong intermolecular attractive forces, caused by hydrogen bonds, polyamides of a comparable molecular weight exhibit acceptable mechanical properties. However, as opposed to the latter, hydrocarbon polymers, having only relatively weak Van der Waals attractions, require substantially higher molecular weights (at least of the order of 50,000 or more) in order to exhibit adequate mechanical strength. A weight-average molecular weight of 25,000, as was achieved in the case of PPPO, is, without doubt, sufficiently high for the evaluation of properties, such as melting temperature, solubility, morphology (crystallinity) and thermal stability. Even the drawing of short fibers from the melt could be accomplished. However, for the measurement of mechanical properties the physical strength of the produced films and fibers is clearly insufficient.

Thus, if one of the developed polymers, in particular PPPB, should ever gain practical and industrial importance, the molecular weight of the latter has to be significantly improved. In view of the present experiments, the possibility to obtain substantially higher degrees of polymerization by any other metal-catalyzed cross-coupling reaction are regarded as limited, at least, if the polymerizations have to be conducted at temperatures above 100 °C, as it was the case with PPPB.

\[ \text{Scheme 8.1: Possible ring-opening metathesis polymerization for the production of a PPPB-precursor.} \]

Among the latter, as already discussed in Section 3.9.1, ring-opening metathesis polymerization of a [4.4]paracyclophane derivative may be considered to be an encouraging methodology (Scheme 8.1). A particular advantage of this route lies in the fact that it is not a step propagation, polycondensation-type, but a polyaddition-type chemistry. However, as mentioned earlier, one significant drawback of this route is the
troublesome monomer synthesis which prevents a straightforward preparation of the respective monomers.

The attachment of side-chains, which can drastically increase the solubility of the respective precursor polymer, would clearly enable to conduct the polymerization under milder conditions (e.g. lower temperatures). Although the cleavage of side-chains in the benzylic position did not proceed as desired in the experiments discussed in Chapter 6, this approach could very well represent a method of further interest. Certainly, further experiments are needed to optimize the cleavage of the side-groups.

A major challenge for the production of new alkarotic polymers is also the copolymerization of p-xylylene with vinylic monomers, such as styrene, methyl methacrylate, vinyl chloride, etc. Although very few attempts have been made in this direction, as was already discussed in Chapter 3, a small number of monomers were successfully, albeit randomly, incorporated in the PPX backbone, indicating the fundamental viability of this methodology.

\[
\begin{align*}
\text{Scheme 8.2: Suggested copolymerization of p-xylylene and ethylene.}
\end{align*}
\]

An approach, which, due to the most simple and inexpensive monomers, would have a considerable industrial potential, would be the copolymerization of p-xylylene with ethylene (Scheme 8.2). Of course, the crucial issue here would be the regular and alternating incorporation of a p-xylylene and an ethylene moiety in the polymer backbone. This route may be, if at all, possible by means of a sophisticated catalyst system.
Appendix

Crystallization Kinetics

Summary

Using the Hoffman-Weeks method, the equilibrium melting temperatures $T_m^e$ of poly(p-phenylene octylene) (PPPO) and poly(p-phenylene butylene) (PPPB) have been determined to be 99 °C and 241 °C, respectively. The investigations of the crystallization kinetics of the two new alkarotic polymers revealed extraordinarily fast crystal growth rates, which are in the same order of magnitude as the one of polyethylene. Thus, PPPO, and PPPB in particular, are promising candidates for potential new engineering plastics allowing fast processing cycles and have significant advantages compared to other hydrophobic polymers with similar processing and application ranges, such as isotactic and syndiotactic polystyrene.

A.1 Introduction

As discussed in Chapter 1, the crystallization kinetics of polymers are of paramount importance for the practical utilization of these materials. Low crystal growth rates of polymers are not attractive because they prevent fast processing cycles and, hence, raise the production costs of these materials. Slow crystallization is a main drawback of some semi-crystalline polymers such as isotactic polypropylene, where nucleating agents are required in commercial applications, and isotactic as well as syndiotactic polystyrene.

The objective of this Chapter is the qualitative evaluation of the crystallization kinetics of poly(p-phenylene octylene) and poly(p-phenylene butylene), and to estimate their equilibrium melting temperature.

A.2 Results and Discussion

A.2.1 Determination of the Equilibrium Melting Temperature

The equilibrium melting temperature $T_m^e$ is defined as the (hypothetical) temperature at which an infinitely large polymer crystal would be in equilibrium with its melt. At $T_m^e$, the change in free energy for the idealized boundaryless crystal is zero, since melting and crystallization are equally probable. The equilibrium melting temperature $T_m^e$ is
relevant, among other things, in the determination of the supercooling during crystallization; it is conveniently determined by the procedure of Hoffman and Weeks.\textsuperscript{2,3} This method employs the fact that the melting temperature, \( T_m \), of polymers generally significantly (and approximately linearly) depends on the crystallization temperature, \( T_c \). Thus, in a plot of \( T_m \) versus \( T_c \) the point at which the linear extrapolation of the experimental values of \( T_m \) intersect the linear \( T_m = T_c \) yields \( T_m^e \). If, for samples with different thermal history (i.e., cooled from the melt under different conditions), the melting temperatures are plotted versus the peak crystallization temperatures, the respective data reflect a linear relationship and converge toward the single equilibrium melting point \( T_m^e \) of a polymer. In order to evaluate the equilibrium melting temperature \( T_m^e \) of PPPO and PPPB, the dependence of the crystallization temperature \( T_c \) and the melting temperature \( T_m \) of solidified polymer on the cooling rate was studied.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure_a1.png}
\caption{DSC heating scans monitoring the melting (heating rate always 10.0 °C/min) of a PPPO sample (PPPO.23) with different thermal history (crystallized with different cooling rates: a) 0.5, b) 1.0, c) 3.0, d) 5.0, e) 10.0, f) 20.0 °C/min, g) virgin).}
\end{figure}
For this reason, polymer samples were molten and crystallized with different cooling rates ranging from 20 to 0.5 Kmin\(^{-1}\). The corresponding heating scans of the two polymers are depicted in Figure A.1 and Figure A.2. A summary of all peak and onset values for crystallization and melting are compiled in Table A.1. The DSC heating scans of PPPO samples of different thermal history (Figure A.1), exhibit a rather broad melting range with a peak maximum between 85 and 92 °C. The peak melting temperatures, which are attributed to the melting of the folded chain crystals (Chapter 4), were found to be strongly dependent on the cooling rate, as was to be expected. An interesting feature was the fact that, independent of the cooling rate, the (in fact very broad) melting range always ended at around 100 °C. This is consistently explained with the melting of a small fraction of fully extended chain crystals, as was discussed in Chapter 4. Gratifyingly, the determined equilibrium temperature of PPPO (see below) perfectly coincides with this value.

![Figure A.2: DSC heating scans monitoring the melting (heating rate always 10.0 °C/min) of a PPPB sample (PPPBB.9) with different thermal history (crystallized with different cooling rates: a) 0.5, b) 1.0, c) 3.0, d) 5.0, e) 10.0, f) 20.0 °C/min, g) virgin).](image)
The melting behavior of PPPB was found to be more complex and, has already to some extent been discussed in Chapter 6, in which the origin of the two usually occurring endothermic transitions could not be explained with absolute certainty. The fact that the WAXD patterns of all PPPB samples, independently of their thermal history, appear to exhibit the same $d$ spacings initially seemed to disprove the presumption of the presence of more than one crystal modification. The DSC experiments, illustrated in Figure A.2, even raised more questions. The increase of the amount of the lower-melting phase with lower cooling rates, combined with the decrease of the higher-melting fraction, was found to be very unusual for polymers. The relative ratios as determined from their melting enthalpies varied from 3/1 (scan f)) to 11/1 (scan b)). Typically, polymers display the opposite behavior. In all heating scans, a) to f) (Figure A.2), the total heat of fusion of the two melt transitions was found to be constant (between 41 and 51 J/g), independent of the cooling rate.

The speculation that the second endotherm at around 212 to 215 °C could be the transition from a thermotropic liquid crystalline state into the isotropic phase could clearly be refuted. When heating a previously molten and carefully recrystallized PPPB sample under crossed polarizers to 205 °C by means of an optical microscope (Leica DMRX) equipped with a temperature-regulated hot stage (Linkam TMS 92/THMS 600), a first fraction of the crystalline phase was molten. A second part of tiny birefringent crystallites still appeared in the liquid phase of the first fraction. The shape or size of these crystals could not be changed by applying a shear or compression force on the cover glass slide. Finally, when the temperature was raised to approximately 212 °C, the second crystalline fraction melted as well.

However, what can be concluded from the above observations is the following: Apparently two different crystal fractions are present. The data suggest that the maximum growth rate of the higher melting fraction is at a lower temperature than that of the lower-melting fraction. In principle, the two fractions can be of different nature, such as two different modifications, or crystal domains of significantly different molecular weights.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cooling Rate /Kmin⁻¹</th>
<th>T_c (onset)/°C</th>
<th>T_c (peak)/°C</th>
<th>T_m/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPO.23</td>
<td>virgin</td>
<td>-</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>77</td>
<td>72</td>
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<td>1</td>
<td>87</td>
<td>84</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>88</td>
<td>85</td>
<td>92</td>
</tr>
<tr>
<td>PPPB.9</td>
<td>virgin</td>
<td>-</td>
<td>-</td>
<td>188/200</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>189</td>
<td>180</td>
<td>192/212</td>
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<td>1</td>
<td>196</td>
<td>193</td>
<td>195/216</td>
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<tr>
<td></td>
<td>0.5</td>
<td>197</td>
<td>194</td>
<td>195/215</td>
</tr>
</tbody>
</table>

Table A.1: Effect of the cooling rate on the crystallization temperature and on the peak temperatures of melting.

Figure A.3 and A.4 are Hoffman-Weeks graphs in which the peak melting temperatures are plotted versus the peak crystallization temperatures as can be seen for PPPO and PPPB. In the case of PPPB, the second peak endotherm, i.e. the melting of the second crystal fraction, was used as the melting temperature. The intersection of the extrapolated line with $T_m = T_c$ provides a reasonable estimate of the equilibrium melting temperature $T_m^-$. The equilibrium melting temperature of various polymers has been determined by this method, e.g. of polyethylene (145.5 °C), polypropylene (208 °C), isotactic polystyrene (228 °C), syndiotactic polystyrene (285 °C), 288 °C) and poly(dl-propylene oxide) (75 °C). By means of a linear regression of the experimental values, $T_m^-$ was determined to be 99 °C for PPPO and 241 °C for PPPB, respectively.
A.2.2 Evaluation of the Crystal Growth Rate of PPPO and PPPB

Crystal growth of poly(p-phenylene octylene) (PPPO) and poly(p-phenylene butylene) (PPPB) was evaluated in optical microscopy experiments. For this purpose, again, a polarized optical microscope (Leica DMRX) equipped with a temperature-regulated hot stage (Linkam TMS 92/THMS 600) was employed. When the respective poly(p-phenylene alkylene)s were slowly (5 Kmin\(^{-1}\)) cooled from the melt, already abundant

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**Figure A.3:** Evaluation of the equilibrium melting temperature of PPPO.

**Figure A.4:** Evaluation of the equilibrium melting temperature of PPPB.
nucleation occurred. The crystallization behavior of both poly(p-phenylene alkylene)s was, in fact, found to be comparable, in appearance as well as in speed, to the one of polyethylene. The fast nucleation and the rapid formation of numerous small crystals prevented a reasonable estimation of the crystal growth rate.

A.3 Conclusions

Due to their most simple, regular, chemical structure, the present, new representatives of the poly(p-phenylene alkylene) family (PPPO and PPPB), have shown a very favorable crystallization behavior. The determination of the equilibrium melting temperature and the considerations of the crystal growth rate exhibited crystallization features that are most similar to the one of polyethylene. In contrast to many other semi-crystalline polymers, polyethylene and poly(p-phenylene alkylene)s exhibit a very high crystal growth rate, which is of utmost importance for a cost-effective thermoplastic processing. Thus, the presented polymers in this thesis exhibit a very important basic property to make them interesting for potential new engineering plastics candidates.

A.4 References

**Curriculum Vitae**

Birth date: August 12, 1971  
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Education:  
1978 – 1987 Elementary School in Reinach (AG), Switzerland  
1987 – 1991 High School and College at the Alte Kantonsschule (Literargymnasium), Aarau: Awarded Swiss Matura Type B  

Academic training:  
1991 – 1995 Undergraduate student in Chemistry at the Swiss Federal Institute of Technology (ETH) Zürich  
Diploma Thesis: “Synthesis of cellobiose analogous derivatives”  
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1996-1999 Graduate student in Materials Science at ETH Zürich  
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Professional Experience:  
1994 Undergraduate research assistant with Dr. K.-H. Dahmen working on novel organotransition metal clusters as MOCVD-precursors for analytical devices, Department of Chemistry, ETH Zürich.  
1996-1999 Teaching assistant in the courses “Werkstoffpraktikum I” and “Werkstoffpraktikum II”, Department of Materials, ETH Zürich.
Dank

Viele Leute haben auf die eine oder andere Weise dazu beigetragen, dass die Zeit meiner Dissertation an der ETH Zürich ein Lebensabschnitt geworden ist, an den ich mich jederzeit mit Freude zurückerinnern werde.

Mein besonderer Dank gilt Prof. Dr. Paul Smith, dafür dass er mir die Möglichkeit gegeben hat, an diesem faszinierenden Projekt zu arbeiten, für sein Vertrauen und seine Unterstützung, die ich jederzeit gespürt habe.

Prof. Dr. Ulrich W. Suter und PD Dr. Andreas Greiner möchte ich herzlich danken für interessante und anregende Diskussionen und für die spontane Übernahme des Korreferates meiner Doktorarbeit.

Dr. Christoph Weder bin ich zu grossem Dank verpflichtet für seine stete Hilfsbereitschaft in allen Belangen, wo Probleme aufraten. Seine kooperative, offene und motivierende Betreuung habe ich überaus geschätzt. Seine Ideen und Ratschläge haben viel zu dieser Arbeit beigetragen.


Im weiteren danke ich allen Mitgliedern der Polymer Technologie Gruppe, die zum angenehmen Arbeitsklima beigetragen haben und mit denen ich auch ausserhalb der Arbeit eine schöne Zeit erleben durfte.

Ganz zum Schluss möchte ich mich bei meinen Eltern bedanken für die Unterstützung und den Rückhalt, den sie mir in all den Jahren gegeben haben.