Activation of an Industrial Catalyst for Propylene Polymerization and Development of a Novel Method for the Controllable Formation of Ziegler-Natta Catalyst Supports

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Die Dissertation wurde am 22.01.2010 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 08.04.2010 angenommen.
This thesis was produced at the Institut für Anorganische Chemie II, Universität Ulm (02/2005–01/2007) and WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München (02/2007–01/2009), under the supervision of Prof. Dr. Dr. h.c. Bernhard Rieger.

It is a pleasure to thank the many people who made this thesis possible.

I would like to express my sincere gratitude to my supervisor, Prof. Dr. Dr. h.c. Bernhard Rieger. With his enthusiasm, his inspiration and his great efforts to explain things clearly and simply, he helped to make this thesis fun for me. Throughout my thesis period, he provided encouragement, sound advice, good teaching and lots of good ideas.

I would like to thank all my colleagues in Ulm and Munich. Most notably I would like to thank Dr. Carsten Troll for his patient help with all the machinery, Dr. Sergei Vagin for his help with all sorts of analytics, Dr. Florian Mögele for being a great lab mate and Felix Schulz for the great discussions and NMR measurements. And to all the “Makros”: It was great to spend my time with you all and I wish you success in all of your endeavours.

Special thanks go to Dr. Liyi Chen: Your help, advice and our discussions were invaluable. Thank you!

I would also like to thank my parents for their support and help during the course of this thesis: Thank you!

Last but not least, I would like to thank my wife, Katrin, for her help, patience, endurance and love: I would have been lost without you!
Abstract

The aim of this work was twofold: First, the activity of a pre-commercial industrial Ziegler-Natta catalyst was to be enhanced (“activated”) and second, a novel method for the controllable formation of Ziegler-Natta catalyst supports was to be developed.

Activation of an Industrial Catalyst for Propylene Polymerization

Two granular and three spherical pre-commercial industrial Ziegler-Natta catalysts from an industry partner were tested for their performance in slurry polymerizations of propylene. All catalysts had very good activities. The catalyst with the best activity (S3) was chosen to be activated with four different hydrocarbon solvents (n-hexane, n-heptane, toluene and ethylbenzene) and mixtures of toluene with titanium tetrachloride. S3 was heated in the various solvents and solvent mixtures at different temperatures and for different amounts of time. The activation procedure had a negative effect on the activity. The mildest activation condition (30 min in toluene at 95°C) removed 9.5% of the titanium from the catalyst, resulting in a 4.1% drop of activity. The harshest condition (90 min in toluene at 111°C in a Soxhlet apparatus) removed 50% of the titanium from the catalyst and resulted in a drop of activity by 71.7%. The removal of titanium species led to a decrease of the polydispersity index of the subsequently synthesized polypropylene samples from 3.6 down to 2.8.

Over the course of the polymerization experiments, a more suitable setup for dosing the catalyst into the pressurized reactor, the solid burette, was developed, drastically reducing the variation of results between equal experiments. Compared to the traditional syringe method, the relative standard deviation of the activity of two equal experiments could be reduced from 15.56% to 0.41%.

A video microscopy analysis of S3 was conducted to observe the polymerization in situ. An indirect activation with the co-catalyst, aiming at a simplified experiment preparation, was implemented. Although polymer growth was observable, the indirect activation proved to be unsuitable.

Development of a Novel Method for the Controllable Formation of Ziegler-Natta Catalyst Supports

Inspired by a process, known as polymer induced liquid precursor (PILP), a novel method for the controllable formation of spherical Ziegler-Natta catalyst supports
via composites of liquid inorganics and polymers (CLIP) was developed. Common support synthesis procedures only control the morphology deliberately on a macroscopic scale. The yielded spherical particles are composed of a single bulky phase, with a low degree of morphological control on the microscopic scale. Using the CLIP method, small primary submoieties are controllably assembled to a final support particle, enabling morphological control on both the microscopic and macroscopic scale.

Magnesium chloride, the support material, was melted in the presence of ethanol, a common process to lower its melting point from 713 °C to well under 100 °C, depending on the amount of ethanol used. 1-Decanol was added, forming a non-stoichiometric network with the MgCl₂-ethanol adducts. The 1-decanol served as an internal surfactant, forming the primary submoieties. PEG-200 was added, binding separate adducts together, like a cement. At 130 °C and under vigorous agitation, the CLIP phase formed. The droplets were then quickly solidified in n-pentane at ca. −45 °C, yielding a perfectly spherical support precursor with a particle diameter of \( x_{a,\text{max}} = 58 \mu m \). Different short-chain alcohols (methanol, ethanol, 1-propanol), long chain alcohols (1-octanol, 1-decanol), different binders (PEG-200, PEG-400, PPG-425, PDMS, PolyTHF-250), different reaction temperatures and different reactant ratios were tested for their performance to yield spherical support precursors. A precursor, synthesized with the optimal combination of the reactants (ethanol, 1-decanol, PEG-200), was dealcoholated to obtain the final support material. Several thermal and chemical procedures were tested to remove the alcohol from the support precursor, of which the treatment with tetrachlorosilane proved to be the most suitable. Two catalysts were synthesized from the dealcoholated support precursor, one catalyst was made directly from the precursor. The catalyst synthesis comprised a treatment with TiCl₄ and DIBP (internal donor). The catalysts had very low polymerization activities. Remarkably, the highest activity \((0.07 \text{ kg}_\text{polymer} \text{g}^{-1}_\text{catalyst} \text{ h}^{-1})\) was obtained with the support which had not been dealcoholated prior to the catalyst synthesis. Polypropylene, generated from said catalyst, had a very low PDI (2.9) and good stereoregularity (96.3 % \textit{mmm}m-pentads).
Zusammenfassung

Mit dieser Arbeit wurden zwei Ziele verfolgt: Zum einen sollte die Aktivität eines sich im Entwicklungsstadium befindlichen industriellen Ziegler-Natta Katalysators erhöht werden (»Aktivierung«). Zum anderen sollte eine neuartige Methode entwickelt werden, um Ziegler-Natta Katalysatorträger mit einem hohen Maß an Morphologiekontrolle zu synthetisieren.

Aktivierung eines Industriellen Katalysators für die Propylenpolymerisation

Zwei granulare und drei sphärische sich im Entwicklungsstadium befindliche Ziegler-Natta Katalysatoren eines Industriepartners, wurden auf ihre Leistungsfähigkeit bei Slurrypolymerisationen getestet. Alle Katalysatoren wiesen sehr gute Aktivitätswerte auf. Der Katalysator mit der höchsten Aktivität (S3) wurde ausgewählt, um ihn mit vier verschiedenen kohlenwasserstoffhaltigen Lösungsmitteln (n-Hexan, n-Heptan, Toluol und Ethylbenzol) und Mischungen von Toluol mit Titan(tetrachlorid zu aktivieren. S3 wurde in den verschiedenen Lösungsmitteln und Lösungsmittelgemischen bei unterschiedlichen Temperaturen und für unterschiedlich lange Zeiten erhitzt. Die Aktivierung hatte einen negativen Einfluss auf die Aktivität. Unter den mildesten Bedingungen (30 min in Toluol bei 95 °C) wurde 9,5 % des Titans vom Katalysator entfernt, was zu einer Verringerung der Aktivität um 4,1 % führte. Unter den drastischsten Bedingungen (90 min in Toluol bei 111 °C in einer Soxhletapparatur) wurde 50 % des Titans entfernt, worauf die Aktivität um 71,7 % sank. Die partielle Entfernung der Titanspezies führte außerdem zu einer Verringerung des Polydispersitätsindex der nachfolgend hergestellten Polypropylenproben von 3,6 auf 2,8.

Während der Durchführung der Polymerisationsexperimente wurde eine geeignete Methode entwickelt, den Katalysator in den unter Druck stehenden Reaktor zu dosieren, wodurch die Abweichung zwischen zwei identischen Experimenten drastisch reduziert werden konnte. Mithilfe der Feststoffbürette konnte im Vergleich zur traditionellen Spritzenmethode die relative Standardabweichung von zwei identischen Experimenten von 15,56 % auf 0,41 % gesenkt werden.

Eine Videomikroskopieanalyse wurde durchgeführt, um die Polymerisation von S3 in situ zu beobachten. Eine indirekte Methode der Aktivierung mit dem Co-
Katalysator wurde implementiert, um die Durchführung des Experiments zu vereinfachen. Obgleich ein Polymerwachstum zu beobachten war, zeigte sich, dass die indirekte Aktivierung nicht für eine optimale Durchführung geeignet war.

**Entwicklung einer Neuartigen Methode für die Kontrollierte Synthese von Ziegler-Natta Katalysatorträgern**

Inspiriert durch den PILP-Prozess (polymer induced liquid precursor) wurde eine neuartige Methode für die kontrollierte Synthese sphärischer Ziegler-Natta Katalysatorträger durch Komposite flüssiger Anorganika und Polymere (composites of liquid inorganics and polymers, CLIP) entwickelt. Übliche Trägersynthesen haben nur auf makroskopischer Ebene einen Einfluss auf die Morphologie. Auf diese Weise synthetisierte sphärische Partikel bestehen aus einer einzig Bulkphase mit geringer Morphologiekontrolle im mikroskopischen Maßstab. Mit der CLIP-Methode werden kleine primäre Subeinheiten kontrolliert zu einem fertigen Trägerpartikel zusammengesetzt, wodurch sowohl im mikroskopischen als auch im makroskopischen Maßstab eine Morphologiekontrolle ermöglicht wird.

Das Trägermaterial Magnesiumchlorid wurde in Gegenwart von Ethanol geschmolzen – eine übliche Methode, um den Schmelzpunkt von 713 °C bis weit unter 100 °C (je nach Menge an Ethanol) zu bringen. Nach der Zugabe von 1-Decanol bildete sich ein nichtstöchiometrisches Netzwerk mit den MgCl$_2$-Ethanol Addukten. 1-Decanol fungierte dabei als internes Tensid bei der Bildung der primären Subeinheiten. Weiter wurde PEG-200 hinzugegeben, wodurch die verschiedenen Addukte zusammengefügt wurden. Bei 130 °C und unter starkem Rühren bildete sich dann die CLIP-Phase. Die Tröpfchen wurden daraufhin zügig in n-Pentan bei ca. −45 °C eingebracht, wodurch sich eine perfekt sphärische Trägervorstufe mit einem Partikeldurchmesser von $x_{a,\text{max}} = 58 \mu\text{m}$ bildete. Verschiedene kurzketttige Alkohole (Methanol, Ethanol, 1-Propanol), langketttige Alkohole (1-Octanol, 1-Decanol), verschiedene Bindesubstanzen (PEG-200, PEG-400, PPG-425, PDMS, PolyTHF-250), unterschiedliche Reaktionstemperaturen und unterschiedliche Reaktandenverhältnisse wurden auf ihre Fähigkeit hin untersucht, sphärische Trägervorstufen zu bilden. Eine Vorstufe, synthetisiert mit der optimalen Kombination von Reaktanden (Ethanol, 1-Decanol, PEG-200), wurde entalkoholisiert, um fertiges Trägermaterial zu erzeugen. Unterschiedliche thermische und chemische Methoden wurden untersucht, um die Alkohole von der Vorstufe zu entfernen. Es stellte sich heraus, dass eine Behandlung
mit Tetrachlorsilan die hierfür geeignete Methode war. Zwei Katalysatoren wurden mit der entalkoholisierten Vorstufe, einer mit der reinen Vorstufe synthetisiert. In der Katalysatorsynthese wurden die Partikel mit TiCl$_4$ und DIBP (interner Donor) behandelt. Die Katalysatoren zeigten eine sehr geringe Polymerisationsaktivität. Erstaunlicherweise war der Katalysator am aktivsten ($0,07 \text{kg}\text{Polymer} \text{g}^{-1}\text{Katalysator h}^{-1}$), der aus der nicht entalkoholisierten Vorstufe synthetisiert wurde. Das mit diesem Katalysator erzeugte Polypropylen hatte einen sehr niedrigen PDI (2,9) und eine gute Stereoregularität (96,3\% mmmm-Pentaden).
Für Katrin
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Nomenclature

\( a \) Activity
\( A \) Area
BSE Back-scattered electron
CED Circle-equivalent diameter
CLIP Composites of liquid inorganics and polymers
CPM Charge percolation mechanism
CSM Core-shell model
DBP Diisobutyl phthalate
DIPS Diisopropylidimethoxy silane
DMSO Dimethyl sulfoxide
EB Ethylbenzoate
ED External donor
EDX Energy-dispersive X-ray spectroscopy
FT-IR Fourier transform infrared spectroscopy
GPC Gel permeation chromatography
HT-GPC High-temperature gel permeation chromatography
ICI Imperial Chemical Industries
ID Internal donor
LM Light microscopy
\( M_n \) Number average molecular mass
\( M_w \) Weight average molecular mass
MGM Multi grain model
MMD Molecular mass distribution
MPI Max-Planck-Institute
NMR Nuclear magnetic resonance
PDI Polydispersity index
PDMS Poly(dimethyl siloxane)
PE Polyethylene
PEG Poly(ethylene glycol)
PFM Polymer flow model
PILP Polymer induced liquid precursor
POC \( o \)-Phthaloyl chloride
<table>
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<tr>
<th>Acronym</th>
<th>Definition</th>
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<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPG</td>
<td>Poly(propylene glycol)</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>R &amp; D</td>
<td>Research and Development</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>$S_{\text{mmmm}}$</td>
<td>Area of the $\text{mmmm}$-pentad methyl peak in $^{13}\text{C}$-NMR spectroscopy.</td>
</tr>
<tr>
<td>$S_{\text{total methyl}}$</td>
<td>Area of all methyl peaks in $^{13}\text{C}$-NMR spectroscopy.</td>
</tr>
<tr>
<td>SB</td>
<td>Solid burette</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SEV</td>
<td>Sphere-equivalent volume</td>
</tr>
<tr>
<td>TCB</td>
<td>1,2,4-Trichlorobenzene</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylaluminum</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>VM</td>
<td>Video microscope</td>
</tr>
<tr>
<td>$x_{50}$</td>
<td>Median value of particle size distribution</td>
</tr>
<tr>
<td>$x_{\text{a,max}}$</td>
<td>Mode value of particle size distribution</td>
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<tr>
<td>ZN</td>
<td>Ziegler-Natta</td>
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*Note:*
SI units, common non-SI units, elemental symbols and chemical formulae are not itemized.
Publication included in this thesis

Chapter 1

Introduction

«Fatto il polipropilene» (“made the polypropylene”)\(^1\) — a small note in Giulio Natta’s lab book marked the beginning of a success story. Polypropylene is at present the second most produced polymer worldwide (45.1 Mt, 2007\(^2\)), with only the varieties of polyethylene having a larger market share (71.0 Mt, 2007\(^3\)). Natta’s discovery of stereospecific polymerization of \(\alpha\)-olefins\(^4-10\) is closely related to the breakthrough works of Karl Ziegler on organometallic mixed catalysts for the polymerization of olefins, the “Mülheim mixed catalysts” for which Natta later coined the term “Ziegler catalysts”.\(^11\) It was on October 26, 1953, when one of Ziegler’s diploma students, Heinz Breil, produced polyethylene at so far unprecedented mild conditions (approx. 100 °C and 100 bar) using zirconium acetylacetonate, leading to the publication of Ziegler’s famous patent in 1953.\(^12\) So far, (low density) polyethylene was only accessible via technically demanding routes, such as free radical polymerization in the ICI process with pressures up to 3000 bar.\(^13\) Ziegler’s initial experiments were quickly extended and it was soon thereafter when it was discovered, that another late transition metal component – titanium tetrachloride – in combination with triethylaluminum is even more active in the polymerization of ethylene than zirconium, yielding high-molecular-weight polyethylene.\(^14\) The catalyst system was soon optimized to work at normal pressure,\(^15\) which was emphasized by choosing a modified food-preserving jar as a polymerization reactor (a photograph of this reactor can be found in Mülhaupt’s review article from 2003\(^16\)). Besides the scientific relevance, Ziegler’s findings had a great impact on the economic situation of the Max-Planck-Institut (MPI) für Kohlenforschung, whose director he was from 1949 until 1969. Among the first licensees was Montecatini in Italy, a company closely affiliated to
Giulio Natta. As part of an earlier license agreement between Montecatini and the MPI in Mülheim – covering new organoaluminum reactions – Natta had been able to place research assistants in Ziegler’s laboratory. Natta had closely been following Ziegler’s work, especially after he had attended his lecture at the Annual Meeting of the Gesellschaft Deutscher Chemiker 1952 in Frankfurt. Due to the license agreement between the Mülheim institute and Montecatini, Natta had access to extensive information on Ziegler’s research and on March 11, 1954, Natta was able to polymerize propylene using Ziegler’s catalyst system. The heptane-insoluble fraction of the yielded substance had a melting point above 160 °C. Natta, being an expert in X-ray spectroscopy, identified this reaction product as highly crystalline isotactic polypropylene and the other fractions as crystalline syndiotactic polypropylene and amorphous atactic polypropylene. The greek names of the stereoregular polymers were devised by Natta’s wife, Rosita, well versed in classical languages. Actually, Natta’s first publication on these findings, in the Journal of the American Chemical Society, submitted on December 10, 1954, was initially rejected because Natta didn’t disclose detailed information on the catalyst, because of his ties to Montecatini. His close relations to Montecatini were also the reason, why Natta did not tell Ziegler about his findings while visiting Mülheim until after the first publication, which was resented by Ziegler after all the help he had given him. The first patent on the synthesis of polypropylene with Ziegler catalysts was filed by Ziegler in August 1954 who had also been investigating the polymerization of propylene early on. The industrial production of high-density polyethylene (Hostalen) started 1955 at Farbwerke Hoechst in Frankfurt. The production of isotactic polypropylene (Moplen) started 1957 at Montecatini’s plant in Ferrara, Italy. Ziegler and Natta were awarded the Nobel Prize in Chemistry 1963 “for their discoveries in the field of the chemistry and technology of high polymers”. Arne Fredga, who introduced the laureates during the ceremony, said about Natta: “Nature synthesizes many stereoregular polymers, for example, cellulose and rubber. This ability has so far been thought to be a monopoly of Nature operating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly.”
(a) Outside of the Max-Planck-Institut für Kohlenforschung in Mülheim/Ruhr.

(b) Karl Ziegler’s 1963 Nobel Prize medal and diploma, on display at the MPI in Mülheim.

Figure 1.1: Max-Planck-Institut für Kohlenforschung in Mülheim/Ruhr.
In 1967, Montedison (a joint venture of Montecatini and Edison) decided to license a polyethylene process from Philips Petroleum – a short-sighted decision, probably promoted by the Edison people who had no polymer background and little interest in research. The Philips and competitor processes applied so called first generation Ziegler-Natta catalysts, basically aluminum-reduced TiCl$_3$. However, the activity and stereoregularity (for the polymerization of propylene) was poor, necessitating post processing steps, such as deashing and extraction. Licensing a polymerization process was much to the dismay of the R & D director Crespi, for it was his company being closely involved in the discovery of crystalline polypropylene before. Crespi – who had been one of the researchers, placed by Natta in Ziegler’s group in Mülheim – wanted Montedison to take the scientific lead again and persuaded the top management that the scientists at Ferrara were given the go-ahead to develop an own PE process within one year, outperforming the process from Philips. On their search for a novel catalyst system, the scientists found that MgCl$_2$ – which was known to be a suitable support for TiCl$_4$ leads to much higher activities, if it was transformed into its active form by ball milling beforehand. Within the year given, the Ferrara laboratory was able to develop a heterogeneous catalyst, highly active for the polymerization of α-olefins, such as ethylene, bypassing the patents from Philips and Solvay, another competitor for polymerization processes. In defiance of decision-makers with a lack of visions, the persistence of individuals, the hard work and the passion of a group of chemists to be the leaders in their field, paved the way to the development of MgCl$_2$-based Ziegler-Natta catalysts, widely adopted up until the present day.
Chapter 2

Background

2.1 Ziegler-Natta Catalysts

Since 1953 and 1954, the years Ziegler and Natta conducted their breakthrough polymerization experiments, the Ziegler-Natta (ZN) catalysts have steadily been developed further by a multitude of scientists around the globe. Even though homogeneous single-site catalyst systems, such as metallocenes\textsuperscript{28–32} and late-transition metal complexes,\textsuperscript{33,34} principally offer a number of advantages over conventional ZN systems through ligand design, the advanced heterogeneous “Mülheim mixed catalysts” still produce the largest share of the global polyolefin market. This is due to such catalyst systems meeting certain objectives, such as very high mileage, stereoregularity (for propylene and other \(\alpha\)-olefins), control of polymer properties (mainly molecular mass and molecular mass distribution) and morphology control over both the catalyst and polymer particles. These abilities were adapted by the catalyst system through a series of scientific achievements, namely the discovery of the active form of magnesium chloride, the stereoregulating effect of electron donors and the exploitation of the catalyst-polymer replication phenomenon. Today, modern MgCl\(_2\)-based Ziegler-Natta catalyst systems evolved to the sixth (often referred to as “next”) generation. The generation describes the donor system used (see Chapter 2.1.2), which is one of the key starting points for future developments and improvements. Modern MgCl\(_2\)-based systems (fourth generation and higher) offer productivities well over 100 kg\(_{\text{pol}}\) kg\(_{\text{cat}}^{-1}\), extremely high isotacticities (\(m_{m_{m_{m_{m}}}} = 99\%\)) and molecular mass distributions in the range of 4.5 until 15 in bulk phase polymerizations.\textsuperscript{35}
As outlined in the following sections, extensive research is still conducted by many research groups throughout the world, over half a century after the groundbreaking discoveries of Ziegler and Natta in late transition metal catalyzed polymerizations and the stereoselective polymerization of α-olefins.

2.1.1 Mechanism

Insertion Mechanism

The most widely approved – yet not conclusively confirmed – mechanism for polymerizations by Ziegler-Natta catalysts is the insertion mechanism. It is believed that the polymer chain propagates by insertion of monomer molecules between the metal and the polymer chain. The most important mechanisms proposing insertion are the Cossee-Arlman monometallic mechanism\textsuperscript{36–38} and the bimetallic mechanism proposed by Sinn et al.\textsuperscript{39} and Natta.\textsuperscript{40} Sinn et al. and Natta proposed, that an interaction in complexes of both titanium and aluminum leads to the monomer insertion. According to the widely accepted mechanism of Cossee and Arlman (Figure 2.1), an octahedrally coordinated ion of a transition metal, carrying one alkyl group and having a vacant position, is the active center of a Ziegler-Natta catalyst. The alkyl group is introduced through alkylation with aluminum alkyls (formation of a Ti–C bond). The polymerization occurs in two steps: coordination of the olefin at the vacant coordination position, with the formation of a four-center activated complex, followed by cis opening of the double bond and insertion of the olefin into the Ti–C bond. The chain grows in length after each monomer insertion. Cossee also describes the back skip, an isomerization of the active center. After each monomer insertion there is an interchange of the positions of the vacancy and the growing chain.

In order for the catalyst to yield isotactic, syndiotactic or atactic polymers of α-olefins (Figure 2.2), it has to select the correct enantioface (\textit{re} or \textit{si}) of the monomer for insertion. There are two possible sources of enantioface selectivity: the chirality of the active center or the growing chain itself. In the case of polypropylene made from TiCl\textsubscript{4}-MgCl\textsubscript{2} systems, the enantioface selectivity is under control of the active center (enantiomorphic site control). If a monomer is erroneously inserted with the wrong enantioface, the selectivity of the active center is not altered, thus only single stereo errors are produced.
Figure 2.1: Cossee and Arlman’s mechanism of the Ziegler-Natta polymerization of propylene.

Figure 2.2: Isotactic, syndiotactic and atactic polypropylene.
Charge Percolation Mechanism

Recently, the charge percolation mechanism (CPM) has been proposed by Stoiljković et al.\textsuperscript{41–43} According to this proposition, the titanium species and the monomer are the reactants of the polymerization and the support is the catalyst. Stoiljković et al. elaborate that the late transition metal on the support exists in different oxidation states (e.g. +2, +3 and +4 for Ti) after the activation with alkyl aluminum compounds (see Chapter 2.1.3) and that they can be easily transformed from one oxidation state to another. In contrast to the insertion mechanism, the CPM acts on the assumption, that the monomer is adsorbed on the entire support surface, not only at the active center during insertion. The “total adsorption” has been hinted at quite early,\textsuperscript{44} yet it had been mostly abandoned due to the widespread adoption of the insertion mechanism. According to the CPM, the monomer aides the immobilized metal centers to equilibrate their varying oxidation states. A chain of adsorbed monomer molecules connects two immobilized metal ions (oxidation states +2 and +4) by overlapping π-bonds, with the terminal molecules being inserted into the metal vacancies (see Figure 2.3).

![Figure 2.3: Schematics of the monomer coordination in the Charge Percolation Mechanism.](image)

This leads to an excited stage of the monomer bridge, as the π-electrons are drawn towards the metal with the higher oxidation state (electron acceptor). Subsequently, a proton is attracted by the partial negative charge of the terminal monomer, leaving an electron pair on the alkyl group. The resulting positive charge on the other
end of the monomer cluster repels a proton, which is moved to the metal center with the lower oxidation state. The now exposed electron pair leads to the simultaneous polymerization of the bridge monomers, whereas the electron pair on the alkyl group moves to the empty orbital of the metal with the higher oxidation state (agostic interaction\textsuperscript{45}). During the equilibration of the oxidation states of the metal ions, the entire monomer bridged is polymerized at once. Both the metal centers and the monomer bridge are chemically altered during the polymerization. The former are deactivated and the latter are polymerized, hence they are defined as reactants. The support allows both the oxido-reduction of the metals and the polymerization of the monomer at the same location, in the same process. The support is not chemically changed by immobilizing the metal and by adsorption of the monomer. Therefore it is the catalyst for the polymerization. Stoišjković et al. report of a high compatibility of the CPM with empirical experience and experimental results achieved since the discovery of ZN polymerization. Quite descriptive is a finding of Xu and Cheng: In the case of styrene polymerization using four different titanocene/methylaluminoxane systems, they were able to show that the polymer yield correlates with increasing Ti\textsuperscript{3+} and decreasing Ti\textsuperscript{2+} and Ti\textsuperscript{4+} concentrations.\textsuperscript{46}

**Chain Termination**

The termination of the growing chain is mostly caused by chain transfer reactions, including transfer to monomer, to metal alkyls and to the transfer agent, and also caused by thermal cleavage of the active center involving \(\beta\)-hydrogen elimination. In many cases, a transfer agent, such as H\textsubscript{2}, is deliberately introduced into the polymerization system for control of the molecular weight of the product.

### 2.1.2 Magnesium Chloride as a Support Material

The discovery of MgCl\textsubscript{2} being a suitable support for TiCl\textsubscript{4} by Shell in 1962\textsuperscript{25} was of rather serendipitous nature, yet it was soon thereafter scientifically justified. The ionic radii of Mg\textsuperscript{2+} and Ti\textsuperscript{4+} are very similar (Pauling ionic radius: Mg\textsuperscript{2+} = 0.65 Å and Ti\textsuperscript{4+} = 0.68 Å). Furthermore, both Mg\textsuperscript{2+} and Ti\textsuperscript{3+} ions coordinate octahedrally and have comparable metal-chlorine bond lengths (Mg−Cl = 2.57 Å and Ti−Cl = 2.51 Å\textsuperscript{47}), thus enabling the epitactic adsorption of TiCl\textsubscript{4} on the MgCl\textsubscript{2} surface. The crystalline structure of MgCl\textsubscript{2} (\(\alpha\) and \(\beta\) forms) is not active towards coordination.
The platlet-like morphology of MgCl\textsubscript{2} crystals exposes the coordinatively saturated basal (001) planes, where a magnesium atom is coordinated by six chlorine atoms and hence has no free coordination site.\textsuperscript{48}

MgCl\textsubscript{2} can be activated to develop crystallites with coordination sites for other molecules by transformation into the δ form. The activation can be achieved by mechanical and chemical procedures. In the former case the activation is attained by milling MgCl\textsubscript{2} for several days.\textsuperscript{49,50} For the chemical activation there exists a multitude of possibilities. Predominant are the reaction of metallic magnesium with suitable alkyl chlorides\textsuperscript{51} and the treatment of MgCl\textsubscript{2} with Lewis bases.\textsuperscript{52,53} Active MgCl\textsubscript{2} can also be gained through recrystallization via precipitation of MgCl\textsubscript{2}-solutions with SiCl\textsubscript{4}.\textsuperscript{54} A very effective method, applying the approach with Lewis bases, is the formation of MgCl\textsubscript{2}-ethanol adducts.\textsuperscript{55,56} The ethanol considerably lowers the melting point of the MgCl\textsubscript{2} (713 °C) and allows – usually with the aid of a suitable surfactant\textsuperscript{57} – the formation of spherical catalyst supports.\textsuperscript{58}

Activating MgCl\textsubscript{2} will result in crystallites made up from lateral cut surfaces corresponding to the (110) and (100) planes with four-coordinated (with two chlorine vacancies) and five-coordinated (with one chlorine vacancy) magnesium atoms.\textsuperscript{59} In case of ball milling, the (110) surface is generated more rapidly than (100).\textsuperscript{60}

During catalyst synthesis, monomeric TiCl\textsubscript{4} molecules and TiCl\textsubscript{3} fragments preferentially complex along the (110) lateral cuts of activated MgCl\textsubscript{2} rather than on the (100) cuts, whereas dimeric Ti\textsubscript{2}Cl\textsubscript{8} favorably complexes along the (100) lateral cuts.\textsuperscript{61,62} Busico et al. proposed that the dimeric species were highly isospecific and the monomeric species were aspecific.\textsuperscript{63} This proposition was recently backed by the “island-model”, stating that Ti species close to each other (as if they were on an island in a sea of MgCl\textsubscript{2}) are isospecific and monomeric species are aspecific.\textsuperscript{64,65} Furthermore, Correa et al. state that active centers on the (110) face are atactic unless flanked by two donors (110)-bridge coordinated (i.e., the two oxygen atoms of a donor molecule coordinate to different Mg atoms).\textsuperscript{66} FT-IR and Raman spectroscopic studies by Brambilla et al. show that the complexes can be separated by their stability: Monomeric titanium species in a tetrahedral coordination on (110) and dimeric species in an octahedral coordination on (100) are unstable. Only monomeric titanium species in an octahedral coordination on (110) are stable. Washing with n-hexane removes such unstable complexes as well as excess (physisorbed) TiCl\textsubscript{4}.\textsuperscript{60,67}
Corradini et al. and Busico et al. proposed a three-sites model in terms of equilibrium interconversion between three kinds of stereospecific active sites namely highly isospecific, poorly isospecific and syndiospecific sites to explain the stereoblock characteristics of PP synthesized by MgCl$_2$ supported ZN catalysts. Based on this model, Liu et al. proposed a plausible mechanism of the formation and transformation of stereospecific active sites. They reported, that the highest isospecificity of active sites is derived from the introduction of bulky alkyl groups into the ligand positions during pretreatment with the Al-alkyl co-catalyst.

The surface environment of Ziegler-Natta catalysts is highly complex. The multiplicity of different active species involved and the complexity of the MgCl$_2$ surface structures impeded a full understanding of the mechanisms involved until the present day. After a re-evaluation of the crystal structure of MgCl$_2$ supports, Busico et al. concluded that the surface with five-coordinate Mg cations should be indexed as (1 0 4) rather than (1 0 0) and that this is the dominant lateral termination in activated MgCl$_2$. Four-coordinate Mg cations on (1 1 0) edges and other Mg sites of higher unsaturation make up only a small fraction (ca. 10–20 %) of activated Mg.

Internal donors (ID) – Lewis bases of vital importance for polymerization because of their stereoregulating effect (see below) – have the ability to steer the formation of a particular MgCl$_2$ crystallite face during catalyst preparation. For example, using a monoester such as ethyl benzoate (EB) or a diester such as diisobutyl phthalate (DIBP) as an internal donor leads to the formation of both the (1 1 0) and (1 0 4) crystallite faces of MgCl$_2$, yet in the presence of a 1,3-diether, the (1 1 0) plane is preferentially generated.

It is well known, that internal (or external) donors, added to MgCl$_2$-supported Ziegler-Natta catalysts, stereoregulate the active centers, thus improving the isotacticity of polypropylene. In the absence of such donors, only 40–50 % of the polymer is isotactic. The donor systems used have evolved over time, which is also reflected in the catalyst “generation”: The first family of internal/external donors consisted of ethylbenzoate (ID) and aromatic esters such as methyl p-toluate (ED). They were replaced with the couple diisobutyl phthalate (ID)/alkylalkoxysilane (ED) and, more recently, with diethers, such as 2,2-disubstituted-1,3-dimethoxypropane. The above electron donors/donor couples define, respectively, the third, fourth, and fifth generation of Ziegler-Natta catalyst systems. Quite recently, a “next” generation of MgCl$_2$-TiCl$_4$ systems was developed, which is based
on succinates as internal donors. It is able to provide both controlled polymer stereoregularity (either very high or low) and broad MMD. Like phthalate donors they are quite flexible in their coordination behavior because of their four-atom spacer between coordinating oxygen atoms. This results in a broader variety of active sites and leads to larger PDI values of the produced polymer. In diethers and alkoxysilanes the short spacer imposes (1 1 0)-chelate coordination, resulting in a larger homogeneity of active sites. Chadwick et al. presented a correlation between the PDI and the diisobutyl phthalate and diether donor system: The active species in the diether donor system are quite uniform, significant 2,1-insertion takes place at both highly isospecific and weakly isospecific active species. The active species in phthalate systems undergo less 2,1-insertion and are therefore less responsive to chain transfer with hydrogen. This will therefore lead to the formation of a high molecular weight fraction, broadening the molecular mass distribution (MMD). Ribour et al. report, that a decreasing titanium and active site content of the catalyst leads to a narrowing of the MMD. Terano et al. furthermore report, that a lowering of the titanium concentration in catalyst systems with an ID, increases the stereoregularity.

An anecdote, underlining that pure luck sometimes leads to great findings, is the discovery of alkylalkoxysilanes as ED. An alkoxysilane/TEA mixture, resulting in poor polymerization performance, was left on the shelf for several weeks and was then tried again. It had reacted to the alkyl-species and had a very positive effect on the stereoregularity of the polymerization.

According to the proposed mechanism for the stereoregulation of IDs, they create the bulkiness for the monomer to be oriented at the active center in a certain way. Isolated Ti sites may be aspecific or have low isospecificity because steric hindrance around them may be insufficient. Accordingly, Wada et al. suggest that the donors work best on such aspecific isolated monomeric Ti species. The donors can coordinate around the titanium sites and make them highly stereospecific.

The co-adsorption of the ID and TiCl₄ is non competitive because the TiCl₄ complexes are much weaker than those of the ID on the surface. The ID covering is a matrix for TiCl₄. After the ID has occupied all the accessible Mg cations, the TiCl₄ occupies the rest ID-free adsorption sites. Recently, Lee et al. reported a different mechanism for the 1,3-diether: Such an ID doesn’t transform aspecific sites on the (1 1 0) face to isospecific sites. It rather prevents – by selective adsorption
on (110) – the formation of aspecific active sites which elevates the concentration of isospecific sites on the (100) planes, thus resulting in a higher isotacticity and productivity.\textsuperscript{91}

The ID, coordinated to MgCl\textsubscript{2}, must not be displaced to ensure high stereospecificity. Yet, up until 80\% of IDs like ethyl benzoate and diisobutyl phthalate is removed from the support by alkylation and complexation reactions with the aluminum-alkyl co-catalyst\textsuperscript{24} (see Chapter 2.1.3), necessitating the use of an external donor in the polymerization to prevent this.\textsuperscript{53} As outlined above, external donors are aromatic esters and diesters in third and fourth generation ZN catalysts, respectively. In contrast, diethers such as 2,2-disubstituted-1,3-dimethoxypropanes remain strongly coordinated to the support when the catalyst is brought into contact with the co-catalyst, so that high stereospecificity can be attained even in the absence of an external donor.\textsuperscript{77}

### 2.1.3 Activation with Aluminum Alkyls

For an olefin insertion into a catalytic site, the site must first be activated by a co-catalyst, leading to the formation of a Ti-alkyl bond by replacement of one chlorine atom coordinated to the titanium with an alkyl chain. The co-catalyst, AlEt\textsubscript{3}, is combined – if necessary (see above) – with the external donor. The fourth generation catalysts portrayed in this work, contain an internal donor compound as component of the solid catalysts and an external donor compound as component of the co-catalyst mixture. On the surface, complexes of the DIBP with MgCl\textsubscript{2} and TiCl\textsubscript{4} are formed, as well as complexes of MgCl\textsubscript{2} and o-phthaloyl chloride (POC),\textsuperscript{92} which is formed in a reaction between DIBP and TiCl\textsubscript{4}. Approximately 80\% of the adsorbed carbonyl species react with AlEt\textsubscript{3} during contact with the co-catalyst mixture, leading to the formation of various dialkylaluminum alkoxides and a complete removal of the POC from the surface.\textsuperscript{24,93,94} The complexes of the silane with AlEt\textsubscript{3} are strongly adsorbed on the surface of the solid catalyst and on the surface of the products of its reactions with excess AlEt\textsubscript{3}.\textsuperscript{94}

The addition of AlEt\textsubscript{3} ultimately leads to Ti–C bond and vacant orbital formation on the titanium, which is reduced from Ti\textsuperscript{+4} to Ti\textsuperscript{+3}.\textsuperscript{95} This activation process is a prerequisite for either monomer insertion or terminal monomer coordination, depending on the applied mechanism.
2.1.4 Replication and Fragmentation

A prominent detail of supported ZN catalysts is their ability to replicate their shape during polymerization.\textsuperscript{96,97} For example, a spherical catalyst particle will yield a spherical polymer particle after fragmentation and polymerization. Such behavior is exhibited for example by catalyst N26 (Figure 2.5a) and the corresponding polymer N29 (Figure 2.5b). The synthesis of N26 will be explained in Chapter 5. Three models, explaining the replication phenomenon of MgCl\textsubscript{2}-based ZN catalysts, are most often used.

Core-Shell Model

According to the core-shell model (CSM), the catalyst particle does not break up during polymerization. A growing shell of polymer is formed on the outer surface of the catalyst (the core).\textsuperscript{98–102} The monomer has to diffuse through the polymer shell to gain access to the active sites. Obviously, the final polymer particle will have the same shape as the catalyst. According to some, catalysts with low porosity exhibit this growth model during slurry polymerizations.\textsuperscript{103,104}
(a) SEM image of a spherical catalyst (N26).

(b) SEM image of a polymer (N29), made with spherical catalyst N26.

Figure 2.5: Exemplification of the replication phenomenon.

Figure 2.6: Polymer growth according to the core-shell model.
Multigrain Model

Very often applied, the multi grain model (MGM) explains the polymerization especially in porous supports. According to the MGM, the monomer quickly reaches a large number of active sites on the surface and inside the catalyst, resulting in a simultaneous polymerization throughout the entire catalyst. This leads to an immediate fragmentation of the catalyst particle. The polymerization on the microparticles follows the core-shell model leading to a macroparticle replicating the shape of the catalyst.

![Figure 2.7: Polymer growth according to the multigrain model.](image)

Polymer Flow Model

In the polymer flow model (PFM), the catalyst fragments at the beginning of the polymerization. The catalyst and the polymer build one phase and the polymerization occurs at embedded active sites, moving radially outwards with the forming polymer.

The MGM and the PFM are the most widely adapted models explaining the replication phenomenon.
Figure 2.8: Polymer growth according to the polymer flow model.
Chapter 3

Motivation

Activation of an Industrial Catalyst for Propylene Polymerization

The first aim of this work was the screening of highly active industrial catalysts for propylene polymerization. Afterwards a method of activating one of said catalysts (i.e., enhancing the activity) was to be applied and the resulting activated catalyst samples were to be tested for polymerization performance.

Pre-commercial fourth generation Ziegler-Natta catalysts were supplied by an industry partner. The screening was to be carried out by means of slurry polymerizations in laboratory autoclave systems. A video microscope autoclave was also to be used for polymerizations to gain visual insight into the growth of the polymer on the support.

The activation was supposed to be an additional step after the actual catalyst synthesis. Instead of enhancing the synthesis of the support and the impregnation with catalytically active species, a simple washing step was to be introduced to the supplied ready-to-use catalysts. They were to be treated (“activated”) with different hydrocarbon solvents and mixtures thereof with titanium tetrachloride at elevated temperatures and later tested in slurry polymerizations.

Development of a Novel Method for the Controllable Formation of Ziegler-Natta Catalyst Supports

The second aim of this work was the development of a novel method for the controllable formation of spherical Ziegler-Natta catalyst supports. As opposed to well-
known synthesis procedures, I wanted to synthesize spherical particles by a con-
trolled stepwise assembly of microscaled submoieties, thus yielding a substance with
high porosity and large surface area able to act as a good support for Ziegler-Natta
catalysts.
Chapter 4

Activation of an Industrial Catalyst

4.1 Overview

A series of pre-commercial industrial fourth generation Ziegler-Natta catalysts were tested for their propylene polymerization performance prior to the intended catalyst activation project. It helped developing an own standard procedure for polymerization experiments with heterogeneous catalysts. Based on a statistical analysis of these preliminary results, an improved method for catalyst injection was developed.

Spherical catalyst S3 was chosen for the subsequent activation experiments. It was tested if the catalyst activity could be increased by a treatment with different hydrocarbon solvents or mixtures of toluene with TiCl₄. The modification of the catalyst could not be directly observed, because of the very low concentration of active sites on the support. The modification is indirectly evidenced by the polymerization performance of the catalysts and by the analysis of polymer properties. The methods applied had a negative effect on the catalyst activity. However, the activation project delivered supplemental insight into the phenomena accompanying polymerizations with industrial heterogeneous Ziegler-Natta catalysts. Accompanying the decrease of titanium concentration due to the applied procedure, was a narrowing of the molecular mass distribution at constant levels of high stereoregularity. Furthermore, the development of the improved catalyst injection method proved to be a vital element for better polymerization control in future experiments.
4.2 Catalysts

4.2.1 Pre-Commercial Catalysts

The industry partner supplied a selection of pre-commercial fourth generation Ziegler-Natta catalysts (G1, G2 and S1, S2, S3), optimized for the polymerization of propylene.

Granular Catalysts

G1 and G2 are granular type catalysts, optimized for gas-phase polymerizations. Figure 4.1a and Figure 4.1b show light microscopy (LM) and scanning electron microscopy (SEM) images of G1. As opposed to spherical catalysts, they exhibit a characteristic irregular shape. A particle size distribution (PSD) analysis of G1 is shown in Figure 4.3a. It reveals a bimodal distribution with mode values $x_{a,max1} = 4 \mu m$ and $x_{a,max2} = 20 \mu m$ and a median $x_{50} = 14 \mu m$. The mode $x_{a,max}$ represents the most populated class in a histogram. Multimodal distributions have several mode values. The median $x_{50}$ separates the higher half of a population from the lower half.

![LM image of G1.](image1)

![SEM image of G1.](image2)

Figure 4.1: Granular catalyst G1.

As can be recognized from the LM and SEM images (Figure 4.2a and 4.2b) the shape of G2 is very similar to that of G1. Its particle size, shown in Figure 4.3b, is also bimodally distributed ($x_{a,max1} = 8 \mu m$, $x_{a,max2} = 16 \mu m$ and $x_{50} = 17 \mu m$) but the different classes are more evenly populated.
Figure 4.2: Granular catalyst G2.

Figure 4.3: PSDs of G1 and G2.
Spherical Catalysts

S1, S2 and S3 are spherical type catalysts. S1 is an early development. Figure 4.4a shows acceptable spherically shaped particles with a minor amount of small fragments. However, energy dispersive X-ray spectroscopy (EDX) analysis and PSD reveal problematic issues. Figure 4.4b shows an SEM-EDX mapping image. The SEM image captured by the back-scattered electron (BSE) detector is located in the upper right-hand corner (grey). The EDX data for three different elements of choice (red: titanium; green: nickel; blue: magnesium) was added to the SEM image. Stronger colors imply a higher density of the respective element on the surface. The signals of magnesium and titanium are the strongest because the catalyst consists mainly of magnesium chloride (support) and titanium chloride (active species). The few nickel signals can be attributed to background noise. For a detailed introduction to the design and synthesis of Ziegler-Natta catalysts, please refer to Chapter 2.1. On closer inspection, the titanium signals are unevenly distributed on the surface. Such hotspots are undesirable. The intricate catalytic system is inhibited by an excess amount of titanium chloride on the surface. As explained in Chapter 2.1.1, effective Ziegler-Natta catalysis only takes place if the proper amount of active species is attached to the proper lattice of the MgCl₂ surface.

![Image of S1](image1.jpg)

(a) LM image of S1.

![Image of SEM-EDX mapping of S1](image2.jpg)

(b) SEM-EDX mapping image of S1.

Figure 4.4: Spherical catalyst S1.

A closer look at the catalyst by SEM reveals more details. Large cracks on the catalyst surface can be seen on Figure 4.5a and 4.5b. During polymerizations, the catalyst is supposed to break up deliberately. The fragmentation during the so
A porous support structure is necessary for monomer mobility but large cracks as observed in S1 will lead to catalyst damage during polymerization and eventually to the formation of undesired polymer fines.

A PSD is shown in Figure 4.6. It is monomodal ($x_{a,\text{max}} = 8 \, \mu m$ and $x_{50} = 13 \, \mu m$) but not narrow. There is a long tail with well populated classes larger than $x_{a,\text{max}}$.

S2 exhibits properties similar to S1. A large amount of particles are spherical but the catalyst’s surface is permeated by large cracks (Figure 4.7a and 4.7b).
The PSD of $S_2$ (Figure 4.8a) has improved compared to $S_1$ ($x_{a,max} = 4 \, \mu m$ and $x_{50} = 4 \, \mu m$). It can be considered fairly narrow. There is no considerable large tail of highly populated classes above the mode value. The mode of $S_2$ is smaller than the mode of $S_1$. An EDX analysis of $S_2$ is presented in Figure 4.8b. Again, titanium (green) is unevenly distributed on the support and hotspots are visible.

$S_3$ is more advanced than both $S_1$ and $S_2$. As the LM image (Figure 4.9a) indicates, the particles are mostly spheres, yet there are still small fragments visible. The surface structure of the catalyst has greatly improved. There are no large
cracks visible. The distribution of active species on the surface has improved as well (Figure 4.10b). Titanium (green) is now evenly distributed over the surface with no hotspots visible. The PSD of S3 is shown in Figure 4.10a. The particles have a slightly larger size than S1 and S2 ($x_{a,\text{max}} = 12\,\mu m$ and $x_{50} = 13\,\mu m$).

![LM image of S3.](image1)

![SEM closeup of S3.](image2)

(a) LM image of S3.  
(b) SEM closeup of S3.

Figure 4.9: Spherical catalyst S3.

![PSD of S3.](image3)

![SEM-EDX mapping of S3.](image4)

(a) PSD of S3.  
(b) SEM-EDX mapping of S3.

Figure 4.10: Spherical catalyst S3.

All catalysts had decent activities in slurry polymerizations. A summary, including a statistical inspection, of the catalysts’ activities in polymerization experiments can be found in Table 4.5 (Page 36). S3, being the most advanced of the supplied spherical catalysts at that time, was chosen for the subsequent activation study. No
granular catalysts were selected for activation. The main focus of the activation project and the development of a novel method for the controllable formation of catalyst supports (see Chapter 5) was on spherical particles.

Particle Size Distributions

Table 4.1 presents an overview of the PSD data of the supplied catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>distribution</th>
<th>mode $x_{a,\text{max}} \ [\mu m]$</th>
<th>median $x_{50} \ [\mu m]$</th>
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</thead>
<tbody>
<tr>
<td>G1</td>
<td>bimodal</td>
<td>4; 20</td>
<td>14</td>
</tr>
<tr>
<td>G2</td>
<td>bimodal</td>
<td>8; 16</td>
<td>17</td>
</tr>
<tr>
<td>S1</td>
<td>monomodal</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>S2</td>
<td>monomodal</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>S3</td>
<td>monomodal</td>
<td>12</td>
<td>13</td>
</tr>
</tbody>
</table>

4.2.2 Commercial Catalysts

At a later stage, the industry partner was able to provide me with two commercial catalysts (G3, S4). However, since the activation project had advanced far already with S3, they have not been considered for any activation experiments. SEM images of G3 and S4 are presented only for reference in Figure 4.11 and 4.12.

4.3 Polymerizations Before Activation

All catalysts were tested for their propylene polymerization performance prior to the projected activation. Standard polymerization conditions were implemented in close contact with the industry partner. The execution of numerous polymerizations under standard conditions prior to the activation experiments ensured a high degree of steady and uniform results. These preliminary experiments also led to the development of an enhanced method of catalyst dosing (see Chapter 4.3.4).
Screening polymerizations were all carried out in a 1 L double-mantle stirred steel autoclave. The polymerization conditions were aimed to be kept constant, as outlined in Table 4.2. The detailed procedure of the polymerization experiments is outlined in Chapter 6.1.4

Table 4.2: Standard Slurry Polymerization Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
</tr>
<tr>
<td>Reactor volume</td>
<td>$V_{\text{reactor}}$</td>
</tr>
<tr>
<td>Propylene pressure</td>
<td>$p_{\text{propylene}}$</td>
</tr>
<tr>
<td>Hydrogen partial pressure</td>
<td>$p'_{\text{H}_2}$</td>
</tr>
<tr>
<td>Solvent volume</td>
<td>$V_{\text{solvent}}$</td>
</tr>
<tr>
<td>Catalyst amount</td>
<td>$m_{\text{catalyst}}$</td>
</tr>
<tr>
<td>Polymerization duration</td>
<td>$\Delta t_{\text{polymerization}}$</td>
</tr>
<tr>
<td>Al:Si:Ti ratio</td>
<td></td>
</tr>
</tbody>
</table>

Note: Applying the ideal gas law, a molar ratio of 6.8% hydrogen in the reactor can be calculated.

To ensure significant data for the catalyst activity, it is important to comply with the polymerization time that has been agreed upon. The activity is an average value, calculated from the polymer mass after the polymerization time. At the beginning of a polymerization, a large quantity of propylene is consumed. The catalyst frag-
ments due to the growing polymer chains and fresh active sites become accessible (see Chapter 2.1.4 for a detailed explanation of the fragmentation and replication phenomena). Over the course of the polymerization the propylene consumption decreases. This is attributed to the fact that a growing layer of polymer is limiting access to the active centers of the catalyst. It takes an increasingly longer time for the monomer to diffuse through the catalyst and this layer. As a result less polymer is generated and the activity decreases. Thus, shorter polymerization times of the same catalyst would lead to higher values for the activity.

The polymerization is an isothermal reaction in a semibatch reactor. In order to examine the hydrogen response, preliminary experiments were also carried out in the absence of hydrogen. It was expected that the hydrogen acts as a chain length limiting agent, thus lowering the molecular weight and broadening the MMD of the polymer. Moreover, it was expected that the addition of hydrogen improves the activity of the catalyst. The dosing procedure for the hydrogen is explained in Chapter 6.1.4.

### 4.3.1 Polymerization Preparation

The catalyst has to be activated, prior to the polymerization. As outlined in Chapter 2.1.3, the sample is contacted with a mixture of TEA (co-catalyst) and DIPS (ED) and then brought into the reactor, which has already been pressurized with propylene. A detailed, step-by-step, illustration is given in Chapter 6.1.4.
4.3.2 Catalyst Activity

All catalysts exhibited activities in a mutual range, yet differences between each were significant. The chosen polymerization conditions met the requirements of the catalysts. It was unproblematic to remove the heat of the exothermic polymerization from the system with a cryostat. The amount of polymer produced in each experiment was low enough not to cause heat transfer problems due to overfilling of the reactor space. A summary of the preliminary polymerizations prior to the activation project is found in Table 4.3.

Table 4.3: Summary of the Catalyst Activities Before Activation

<table>
<thead>
<tr>
<th>catalyst</th>
<th>hydrogen</th>
<th>activity $a$ $\left[ \frac{kg\text{polymer}}{g\text{catalyst} \cdot h} \right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>yes</td>
<td>1.15</td>
</tr>
<tr>
<td>G2</td>
<td>yes</td>
<td>1.40</td>
</tr>
<tr>
<td>S1</td>
<td>yes</td>
<td>2.08</td>
</tr>
<tr>
<td>S2</td>
<td>yes</td>
<td>1.05</td>
</tr>
<tr>
<td>S3</td>
<td>yes</td>
<td>1.80</td>
</tr>
<tr>
<td>G1</td>
<td>no</td>
<td>1.09</td>
</tr>
<tr>
<td>G2</td>
<td>no</td>
<td>1.60</td>
</tr>
<tr>
<td>S1</td>
<td>no</td>
<td>1.56</td>
</tr>
<tr>
<td>S2</td>
<td>no</td>
<td>0.99</td>
</tr>
<tr>
<td>S3</td>
<td>no</td>
<td>1.92</td>
</tr>
</tbody>
</table>

G2 is more active than G1. S1 seems to be the spherical catalyst with the highest activity. An investigation of the catalyst dosing technique, which is discussed in Chapter 4.3.4, revealed that S3 has a higher activity than S1.

A comparison of the activities with and without hydrogen is shown in Figure 4.13. It can be seen that hydrogen has no definite effect on the catalysts’ activities. Hydrogen has a positive effect on the activity of G1 (5.5 % higher), S1 (33.3 % higher) and S2 (6.1 % higher). The activity is lowered in the presence of hydrogen for G2 (12.5 % less) and S3 (6.3 % less). This is consistent with the findings of Kouzai et al. who report that hydrogen has no effect on the activity of isospecific and aspecific
active sites.\textsuperscript{90}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.13.jpg}
\caption{Comparison of activities with and without the presence of hydrogen.}
\end{figure}

A comparison of the SEM-EDX mapping images of titanium (Figures 4.4b, 4.8b and 4.10b) and the activities (incl. statistical considerations, Table 4.5 in Chapter 4.3.4) of $S_1$, $S_2$ and $S_3$ (please take the solid burette experiments into account) suggests, that titanium hotspots impair the activity. Catalysts with titanium hotspots ($S_1$ and $S_2$) have a lower activity than catalysts without ($S_3$).

4.3.3 Molecular Mass

A determination of the chain length distribution is an important aspect of polymer characterization. Polypropylene is a linear homopolymer, thus the molecular mass $M_i$ of each polymer chain is a measure for its length. The molecular masses of the polymers were determined with high-temperature gel permeation chromatography (HT-GPC).\textsuperscript{111} In a statistical analysis of the HT-GPC data, the number average molecular mass $M_n$ and weight average molecular mass $M_w$ can be calculated. $M_n$ represents an arithmetic mean of the molecular masses of all polymer chains. With $N_i$ being the number of chains with the molecular mass $M_i$, the number average molar mass is

$$M_n = \frac{\sum_{i=1}^{k} N_i \cdot M_i}{\sum_{i=1}^{k} N_i} \quad (4.1)$$

The weight average molecular mass $M_w$ takes the weight fraction $w_i$ of polymers with the molecular mass $M_i$ into account. The weight of each fraction $i$ is calculated with
weight = \( N_i \cdot M_i \)  \( (4.2) \)

Thus the weight fraction is

\[ w_i = \frac{N_i \cdot M_i}{\sum_{i=1}^{k} N_i \cdot M_i} \]  \( (4.3) \)

The weight average molecular mass \( M_w \) is then calculated with

\[ M_w = \sum_{i=1}^{k} w_i \cdot M_i \]  \( (4.4) \)

The ratio between the weight average molecular mass and the number average molecular mass is called polydispersity index PDI and is a measure of the distribution of molecular mass in a sample:

\[ \text{PDI} = \frac{M_w}{M_n} \]  \( (4.5) \)

A hypothetical polymer consisting only of chains with the same length has a polydispersity index of \( M_w/M_n = 1 \). Homogeneous single-site catalysts have a PDI \( \approx 2 \).\(^{112}\) Similar values can be achieved with novel, silica-supported Ni(II) catalysts.\(^{113}\) Ziegler-Natta catalysts typically have a molecular mass distribution from 5 to 15.\(^{114}\)

A summary of \( M_n \), \( M_w \) and PDI of the examined catalysts is displayed in Table 4.4.

The hydrogen response is visible for both granular and spherical catalysts. Polymerizations in the absence of hydrogen generate polymers with weight average molecular masses between 600 000 g mol\(^{-1}\) and 800 000 g mol\(^{-1}\). The introduction of hydrogen to the reactor (6.8 %, see Table 4.2) lowers the molecular masses considerably to values in the range of 250 000 g mol\(^{-1}\). This is also visualized in Figure 4.14a. The polydispersity index is not consistently influenced by the introduction of hydrogen. As visible in Figure 4.14b, hydrogen lowers the PDI of \( \text{G2, S1 and S2} \), but elevates the value for \( \text{G1} \).

A comparison of the SEM-EDX mapping images of titanium (Figures 4.4b, 4.8b and 4.10b) reveals, that \( \text{S1 and S2} \) exhibit a higher Ti concentration on the surface than \( \text{S3} \). The PDI of the generated polymers (see Table 4.4) decreases with less titanium on the surface. \( \text{S1 and S2} \) have a PDI of 4.4 and 5.0, respectively. \( \text{S3} \) has a PDI of 3.6. As has been pointed out in Chapter 2.1.2, the PDI correlates with the degree of heterogeneity of active sites on the surface. A lower amount of titanium yields catalysts with a higher homogeneity of active sites, thus producing polymers with lower PDIs.
Table 4.4: Summary of the Molecular Mass Averages and PDIs before Activation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Hydrogen</th>
<th>$M_n$ [g/mol]</th>
<th>$M_w$ [g/mol]</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>yes</td>
<td>50 000</td>
<td>250 000</td>
<td>5.0</td>
</tr>
<tr>
<td>G2</td>
<td>yes</td>
<td>70 000</td>
<td>230 000</td>
<td>3.3</td>
</tr>
<tr>
<td>S1</td>
<td>yes</td>
<td>50 000</td>
<td>220 000</td>
<td>4.4</td>
</tr>
<tr>
<td>S2</td>
<td>yes</td>
<td>50 000</td>
<td>250 000</td>
<td>5.0</td>
</tr>
<tr>
<td>S3</td>
<td>yes</td>
<td>70 000</td>
<td>250 000</td>
<td>3.6</td>
</tr>
<tr>
<td>G1</td>
<td>no</td>
<td>140 000</td>
<td>600 000</td>
<td>4.3</td>
</tr>
<tr>
<td>G2</td>
<td>no</td>
<td>150 000</td>
<td>700 000</td>
<td>4.7</td>
</tr>
<tr>
<td>S1</td>
<td>no</td>
<td>120 000</td>
<td>650 000</td>
<td>5.4</td>
</tr>
<tr>
<td>S2</td>
<td>no</td>
<td>150 000</td>
<td>800 000</td>
<td>5.3</td>
</tr>
</tbody>
</table>

(a) Side-by-side comparison of the weight-average molecular mass after polymerization with and without hydrogen.

(b) Side-by-side comparison of the polydispersity indices after polymerization with and without hydrogen.

Figure 4.14: Weight average molecular mass and polydispersity index against hydrogen presence.
4.3.4 Statistical Considerations

An ongoing fluctuation of catalyst activity in identical experiments could not be explained at first. It was revealed that the then applied syringe-dosing technique was the cause of this.

Dosing exactly 15 mg of catalyst into the pressurized reactor under inert conditions was challenging if not impossible applying the traditional syringe-method. For this method, a portion of the catalyst – larger than needed for a single experiment – was suspended in a hydrocarbon solvent (e.g., n-heptane) and stored in a Schlenk tube. Prior to injecting the catalyst during a polymerization experiment, the slurry was agitated and an appropriate amount was extracted with a syringe. The portion was then transferred into a small pressure cylinder and injected into the reactor. Two problems arise using this method:

1. The catalyst concentration of the sample inside the syringe can differ from the overall slurry concentration because the solid settles inside the Schlenk tube. It is uncertain whether the sampled volume contains the desired amount of catalyst. Using a liquid with a higher viscosity (e.g., paraffin) is of no avail. It becomes difficult to suspend and properly distribute the catalyst in such media. Gas bubbles form often during agitation and stay in the slurry. The true amount of catalyst in a sample taken with a syringe from a slurry cannot be determined with a high degree of certainty.

2. During each instance of catalyst sampling, a significant amount of catalyst adheres to the outer wall of the syringe’s cannula. There is more catalyst taken out of the Schlenk tube than intended. As a consequence the next experiment will be conducted with an underdose of catalyst, since the operator anticipates a slurry with a higher catalyst concentration.

For the reasons outlined above, the results of the polymerization experiments fluctuated, visible in a large standard deviation of the activity. Fluctuations of activity in allegedly equal experiments were unacceptable. As a consequence, the solid burette, a more suitable setup for dosing sensitive solid catalysts, was developed and deployed. Its development and advantages over the traditional method are explained in detail in Chapter 6.2.6. The results of the screening of all unmodified catalysts supplied are summarized in Table 4.5. The standard deviation of the activity $a$ is
indicated. Additionally, the relative standard deviation is presented for clarification as it visualizes the fluctuation of the results. It is calculated as follows:

$$\text{relative standard deviation} = \frac{\text{standard deviation} \cdot 100}{\text{arithmetic mean}}$$ (4.6)

Table 4.5: Comparison of Dosing Techniques on the Basis of Activity Before Activation

<table>
<thead>
<tr>
<th>catalyst</th>
<th>dosing method</th>
<th>activity $a$</th>
<th>standard deviation</th>
<th>relative standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>syringe</td>
<td>1.15</td>
<td>0.50</td>
<td>43.48%</td>
</tr>
<tr>
<td>G2</td>
<td>syringe</td>
<td>1.40</td>
<td>0.28</td>
<td>20.00%</td>
</tr>
<tr>
<td>S1</td>
<td>syringe</td>
<td>2.08</td>
<td>0.34</td>
<td>16.35%</td>
</tr>
<tr>
<td>S2</td>
<td>syringe</td>
<td>1.05</td>
<td>0.21</td>
<td>20.00%</td>
</tr>
<tr>
<td>S3</td>
<td>syringe</td>
<td>1.80</td>
<td>0.28</td>
<td>15.56%</td>
</tr>
<tr>
<td>S1</td>
<td>solid burette</td>
<td>1.83</td>
<td>0.06</td>
<td>3.28%</td>
</tr>
<tr>
<td>S3</td>
<td>solid burette</td>
<td>2.44</td>
<td>0.01</td>
<td>0.41%</td>
</tr>
</tbody>
</table>

The fluctuation of the results was dramatically decreased when the catalysts were injected into the reactor with the solid burette. The relative standard deviation of the single experiments could be lowered considerably, giving the values for the activity significantly more credibility. The solid burette was later used for all polymerizations with all catalysts. A comparison between S1 and S3 – the former contestants for highest activity – revealed that in fact S3 has the highest activity.

### 4.4 Activation

During catalyst synthesis, stable and unstable titanium complexes form on the surface. There might even be excess titanium – still physisorbed – present (visible as Ti-hotspots on SEM-EDX mapping images at sufficient concentrations). A slight detitanation (e.g., washing with $n$-hexane) is a suitable method to remove the species that are not tightly attached to the surface and to lower the overall titanium concentration. A strong detitanation, as applied by Ribour et al. with vacuum and
elevated temperatures (up to 140°C) will remove large amounts of the titanium on the catalyst, leading to a drastic drop of activity by 80% up to 100%. Moderately lowering the relative amount of titanium on the surface could enhance the stereospecificity or the PDI; the relative concentration of the ID is enlarged (it coordinates stronger than the Ti species to MgCl₂) and the distribution of active sites will be more homogeneous. Depending on the amount (and type) of Ti species removed, there might be a lower activity but an improved, more narrow, PDI.

Applying an additional washing step with different solvents on S3 (the most active spherical catalyst of the series) to reduce the amount of titanium was deemed suitable to enhance the performance, most notably the interaction of activity and PDI. Such an activation procedure would be able to wash away residue of physisorbed TiCl₄, coordinated unstable and even stable titanium species still left from previous washing steps applied during the catalyst synthesis. If successful, this cost-effective approach could be easily implemented in the catalyst production.

4.4.1 Activation Procedure

As outlined above, a moderate activation procedure was chosen to remove excess titanium while inhibiting extreme detitanation. The experiments were conducted in glass flasks in an inert argon atmosphere using standard Schlenk technique. The catalyst was suspended in the solvent and activated according to the parameters found in Table 4.6. Instead of agitation with a magnetic stir bar the flask was gently shaken to assure mechanical integrity of the catalyst particles. Alternatively, a Soxhlet extractor was tested for the activation procedure. After the activation, the solvent was removed and the activated sample was washed three times with n-heptane at RT. The samples were dried overnight under vacuum (≈ 1·10⁻² mbar) at RT.

Two linear (n-hexane and n-heptane) and two aromatic hydrocarbon solvents (toluene and ethylbenzene) were chosen as activation reagents. TiCl₄ exhibits excellent solubility in these solvents and they are well available in industry. Two mixtures of toluene with TiCl₄ (volume ratios 1:1 and 10:1) were also chosen as activation reagents to investigate if this would lead to a higher homogeneity of active sites and lower PDIs.
Table 4.6: Activation Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T_{\text{activation}}$</td>
<td>95°C</td>
</tr>
<tr>
<td>Solvent volume</td>
<td>$V_{\text{solvent}}$</td>
<td>250 mL</td>
</tr>
<tr>
<td>Catalyst sample weight</td>
<td>$m_{\text{catalyst}}$</td>
<td>2.5 g</td>
</tr>
<tr>
<td>Duration</td>
<td>$\Delta t_{\text{activation}}$</td>
<td>90 min</td>
</tr>
</tbody>
</table>

*Note: Temperature was 65 °C for $n$-hexane.*

4.5 Polymerizations After Activation

The polymerizations were conducted applying the same set of parameters (see Table 4.2 in Chapter 4.3) as during the initial testing of the pure catalysts. The preparation of the catalyst, its reaction with the external donor and the activation with the co-catalyst is identical to the procedure outlined in Chapter 4.3.1. The solid burette was used for the injection of the catalyst.

4.5.1 Catalyst Activity

The catalyst activity was affected by the activation procedure; it always dropped below the value of the unactivated catalyst. A summary of the activities and the titanium concentrations of all activated samples is listed in Table 4.7. $n$-Hexane, $n$-heptane and toluene have a relatively low effect on the activity; the values remain within 10% deviation of the unactivated catalyst. The effect of ethylbenzene on the activity was surprisingly strong; an activity loss of more than 35% was determined. The activity losses correlate with the Ti concentration (see below, Figure 4.15).

Effect of Activation Duration

The duration of the activation influences the degree of activity loss, as can be seen in a comparison of S3A5 (toluene, $\Delta t_{\text{activation}} = 30$ min) and S3A3 (toluene, $\Delta t_{\text{activation}} = 90$ min). The activity drops 4.1% and 8.2%, respectively. Judging from the Ti concentrations of S3A5 and S3A3 (3.8% and 3.4%), the detitanation is a function of contact time.
Table 4.7: Summary of Catalyst Activities After Activation

<table>
<thead>
<tr>
<th>catalyst</th>
<th>activation reagent</th>
<th>activity $a \left[ \frac{\text{kg polymer}}{\text{g catalyst} \cdot \text{h}} \right]$</th>
<th>relative deviation of activity</th>
<th>Ti conc. [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>—</td>
<td>2.44</td>
<td>—</td>
<td>4.2</td>
</tr>
<tr>
<td>S3A5</td>
<td>toluene (30 min)</td>
<td>2.34</td>
<td>−4.1%</td>
<td>3.8</td>
</tr>
<tr>
<td>S3A2</td>
<td>$n$-heptane</td>
<td>2.28</td>
<td>−6.6%</td>
<td>3.5</td>
</tr>
<tr>
<td>S3A3</td>
<td>toluene</td>
<td>2.24</td>
<td>−8.2%</td>
<td>3.4</td>
</tr>
<tr>
<td>S3A1</td>
<td>$n$-hexane</td>
<td>2.22</td>
<td>−9.0%</td>
<td>3.6</td>
</tr>
<tr>
<td>S3A8</td>
<td>toluene/TiCl$_4$ (10:1)</td>
<td>1.84</td>
<td>−24.6%</td>
<td>2.6</td>
</tr>
<tr>
<td>S3A7</td>
<td>toluene/TiCl$_4$ (1:1)</td>
<td>1.72</td>
<td>−29.5%</td>
<td>2.9</td>
</tr>
<tr>
<td>S3A6</td>
<td>ethylbenzene</td>
<td>1.57</td>
<td>−35.7%</td>
<td>2.8</td>
</tr>
<tr>
<td>S3A4</td>
<td>toluene (Soxhlet)</td>
<td>0.69</td>
<td>−71.7%</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*Note:* Data sorted by relative deviation of activity.

**Effect of Activation Temperature**

The activation temperature has a drastic effect on the activity, as it is revealed by a comparison of S3A3 (toluene, $\Delta t_{\text{activation}} = 90$ min, $T = 95$ °C) and S3A4 (toluene, Soxhlet extraction, $\Delta t_{\text{activation}} = 90$ min, $T = 111$ °C/b.p. of toluene). The activity decreases by 8.2% and 71.7%, respectively. The Soxhlet extraction removed 50.0% of the titanium present in S3. It is to be assumed, that the detitaniaion accelerates considerably at elevated temperatures.

**Effect of additional TiCl$_4$ in the Activation Reagent**

The addition of extra-TiCl$_4$ leads as well to a decrease in the titanium concentration of S3A7 and S3A8, accompanied by a decrease of activity. Compared to S3A3 (toluene), the loss of activity of S3A8 (toluene/TiCl$_4$, 1:1) and S3A7 (toluene/TiCl$_4$, 10:1) was remarkable. However, an analysis of the effect of the activation on the PDI revealed a positive effect of the additional TiCl$_4$ (see below, Chapter 4.5.2).
Correlation with Titanium Concentration

Figure 4.15 shows a diagram of the activity against the titanium concentration. A decrease of titanium – as observed during all activation experiments – leads to a decrease of activity. The fitting function is non-linear. Each activation reagent (see Table 4.7) has a characteristic effect on the titanium concentration and thus the activity of S3.

The activation experiments revealed, that S3 was already optimized regarding the presence of excess titanium possibly inhibiting catalytically active sites. Activation – even for a short duration – always led to a decrease of activity. This originates in a removal of active titanium species by the activation reagent. A similar removal had already been described by Brambilla et al., but they only removed weakly coordinated unstable species with n-hexane at RT. Since such a step had already been conducted during the catalyst synthesis of S3, the activation led to a partial removal of stable and active titanium species of S3, down until 2.1 wt%.

4.5.2 Polymer Molecular Masses

A GPC analysis of the synthesized polymers revealed a correlation between the titanium concentration of the catalyst and the polymer properties, most prominent the polydispersity index. Thus, such properties are also dependent on the chosen activation reagent and the activation conditions. Figure 4.16a illustrates this correlation: The PDI values decrease with the titanium concentration. With the exception of one value, a close to linear relationship (see fit line) can be proposed,
considering the large margin of error of GPC measurements (relative standard deviation of 6% to 10% for $M_w$ according to Mori\textsuperscript{115}). The activation procedure will affect those species first, which are most weakly coordinated to the support. As stated by Stukalov et al.,\textsuperscript{72} the ID complexes are much stronger than those of TiCl$_4$. Thus, the activation has a greater effect on the titanium complexes than on the ID, visible in a decrease of the titanium concentration. Considering the increased ID concentration (relative to Ti), it can be assumed that the detitanation also results in a more narrow variety of active sites. This leads to a narrowing of the molecular mass distribution, and smaller values for the PDI.

![Graphs](attachment:graphs.png)

(a) PDI against Titanium Concentration.  
(b) Molecular Mass $M_w$ against Titanium Concentration.

Figure 4.16: Comparison of $M_w$ and PDI against the Titanium Concentration.

Plotting the molecular mass $M_w$ against the titanium concentration (Figure 4.16b) reveals an inconclusive correlation. As in the case of the PDI, a linear fit of the $M_w$ data against the titanium concentration appears to be possible. However, considering the already mentioned large margin of error of GPC measurements, the fluctuation of the values is too large to establish a definite linear fit of all values. There is a tendency for $M_w$ to decrease with the titanium concentrations, a definite correlation can’t be established however. A summary of all values is found in Table 4.8.

### 4.5.3 Stereoregularity Determination by NMR Spectroscopy

It has been pointed out in Chapter 2.1.2, that the removal of titanium species from the support surface results in an increased homogeneity of the active sites, visible
Table 4.8: Summary of the Molecular Mass Averages and PDIs After Activation

<table>
<thead>
<tr>
<th>catalyst</th>
<th>activation reagent</th>
<th>$M_n$ [g mol$^{-1}$]</th>
<th>$M_w$ [g mol$^{-1}$]</th>
<th>PDI</th>
<th>Ti concentration [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>—</td>
<td>70 000</td>
<td>250 000</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>S3A6</td>
<td>ethylbenzene</td>
<td>50 000</td>
<td>190 000</td>
<td>3.8</td>
<td>2.8</td>
</tr>
<tr>
<td>S3A1</td>
<td>n-hexane</td>
<td>70 000</td>
<td>240 000</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>S3A3</td>
<td>toluene</td>
<td>70 000</td>
<td>220 000</td>
<td>3.1</td>
<td>3.4</td>
</tr>
<tr>
<td>S3A2</td>
<td>$n$-heptane</td>
<td>70 000</td>
<td>222 000</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td>S3A5</td>
<td>toluene (30min)</td>
<td>60 000</td>
<td>200 000</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>S3A7</td>
<td>toluene/TiCl$_4$ (1 : 1)</td>
<td>80 000</td>
<td>240 000</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>S3A8</td>
<td>toluene/TiCl$_4$ (10 : 1)</td>
<td>50 000</td>
<td>140 000</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>S3A4</td>
<td>toluene (soxhlet)</td>
<td>60 000</td>
<td>170 000</td>
<td>2.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Note: Data sorted by PDI (descending).

in lower values for the PDI and improved stereoregularity. The former could be shown above, in Chapter 4.5.2. The effect of the activation on the stereoregularity of the synthesized polymers can be studied by determining the pentad tacticities with $^{13}$C-NMR.$^{30,69,116-119}$ The content of meso pentads ($mmmm\%$) is determined from the methyl carbon resonance data between 19 ppm and 22 ppm:

$$mmmm\% = \left( \frac{S_{mmmm}}{S_{total \: methyl}} \right) \cdot 100$$

$S_{mmmm}$ is the area of the $mmmm$-pentad methyl peak at $\approx 21.8$ ppm and $S_{total \: methyl}$ is the sum of the area of all methyl peaks.

In contrast to the determination of the isotacticity index and the “isotactic” and “atactic” fractions by determining the heptane-insoluble fraction,$^{120}$ a more detailed view can be obtained with $^{13}$C-NMR. This method is more precise, as only 90% of the insoluble (isotactic) fraction is made of $mmmm$ pentads.$^{69}$ Obtaining NMR spectra of the polymers synthesized from pure and activated catalysts ($S3$ and $S3A1-8$, respectively) proved to be challenging due to the low solubility of the polymer in most solvents. A suitable procedure allowing the $^{13}$C-NMR analysis included dissolving the polymer in 1,2,4-trichlorobenzene (TCB) and dimethyl sulfoxide-$d_6$ (5:1 volume ratio) at $T = 410$ K with a polymer concentration of ca. 100 mg mL$^{-1}$. How-
ever, the probe head of the NMR spectrometer used (see Chapter 6.2.4) could not be operated at such a temperature for a sufficiently long time. The data acquisition was limited to 1024 scans to ensure the integrity of the probe head. The accompanied decrease in resolution resulted in spectra in which only strong signals could be detected. The polymers synthesized later in Chapter 5, exhibit several such strong peaks in the methyl region, corresponding to different pentads. However, in the case of all polymers synthesized from $S_3$ and $S_3A1-8$, only the signal corresponding to the $mmm$-pentad could be detected. Figure 4.17 shows the methyl region of the $^{13}$C-NMR spectrum of $S3A4$.

![Figure 4.17: Representative $^{13}$C-NMR spectrum. Displayed is the relevant methyl region (ca. 21.6 ppm–19.7 ppm) of $S3A4$. Only the $mmm$-pentad at $\delta = 21.61$ ppm is visible.](image)

Arithmetically speaking, with $mmmm\% = 100$, the polymers are completely isotactic. However, due to the margin of error, resulting from the low resolution, the polymers should rather be referred to as “highly isotactic”. As a consequence, it is not possible to establish a correlation between the $^{13}$C-NMR data, the titanium
concentration and the polymer properties ($M_w$ and PDI). The literature about similar experiments\textsuperscript{88} suggests, that the isotacticity of the polymer improves when a decrease of the PDI is observed.

4.6 Video Microscopy Polymerization

Polymerizations in a conventional autoclave setup do not offer a direct observation of the evolution of the particle morphology of a single particle. Whereas the catalyst activity can be observed online through the consumption of monomer and displayed in a monomer-flow diagram, the polymer growth on the catalyst particle cannot be observed online in a system closed to an observation from the outside.

This issue was first addressed by Reichert and coworkers in the polymerization of butadiene, by introducing the video microscopy, a method to observe single resting polymerizing particles in a small gas-phase autoclave equipped with a microscope.\textsuperscript{121–125} Weickert et al. and Fink et al. also examined olefin polymerizations with video microscopy.\textsuperscript{126–128} Video microscopy experiments were conducted with S3 to gain insight into the polymerization behavior (especially replication) during polymerization and to test an indirect method of activation with the co-catalyst.

4.6.1 Experimental Preparation and Analysis

A detailed presentation of the video microscopy equipment and the experimental setup is found in Chapter 6.2.2. The reaction conditions were aimed to be similar to the corresponding slurry polymerization:

| Table 4.9: Video Microscopy Polymerization Conditions |
|----------------------------------------------------|---------------------|
| Temperature $T$ | 70°C |
| Propylene pressure $p_{\text{propylene}}$ | 5.00 bar |

To achieve single particle observation, only a few grains of the catalyst were dispersed on top of the sample holder. Due to the high sensitivity towards water and oxygen, the preparation had to take place inside a glove box. A detailed summary of the precautions taken are found in the experimental section (Chapter 6.3.3). As
opposed to Knoke who activated the catalyst in his Ph.D. dissertation directly, it was attempted to activate the catalyst indirectly. A direct contact between the catalyst and the co-catalyst/external donor wets the sample and necessitates an additional drying step prior to polymerization. Therefore, the aluminum alkyl and the silane were brought into the bottom of the autoclave. The activation took place by evaporating co-catalyst/external donor while the reactor was heated to reach polymerization temperature. Initial difficulties arising from the condensation of liquid on the inner side of the window were overcome by heating the window from outside with hot air. During the polymerization, micrographs were taken every 30 seconds, beginning when the reactor reached 70 °C. The reaction was subsequently stopped by depressurizing the reactor and flushing with argon.

Using ImageJ, the micrographs were preprocessed with a thresholding algorithm and the area $A$ of each particle’s projection was measured. The obtained values were then converted to circle-equivalent diameters (CED):

$$\text{CED} = 2 \cdot \sqrt{\frac{A}{\pi}}$$

(4.7)

The CED can be used to further calculate the sphere-equivalent volume (SEV):

$$\text{SEV} = \frac{\pi}{6} \cdot (\text{CED})^3$$

(4.8)

The values were then normalized with the initial CED$_0$ and SEV$_0$, respectively.

### 4.6.2 Video Microscopy Polymerization of S3

Propylene was polymerized for 20 min according to the parameters outlined above. A selection of six micrographs at different points in time is shown in Figure 4.18a – 4.18f.

The polymerization was stopped after 20 min due to increased blurring of the images, prohibiting an exact analysis of the particle properties. The blurring was caused by the propylene and the evaporating co-catalyst/external donor mixture flowing inside the reactor, resulting in changing refraction indices in the line of sight. As can be seen from the selected micrographs, a particle growth was visible. At the same time, it can be seen, that not all particles participated in the polymerization. Thus, the observation was confined to the particles labeled 1 through 5. Figure 4.19 contains two diagrams, showing the course of the normalized CED and SEV values against polymerization time for the selected particles.
(a) $t = 0 \text{ min}$

(b) $t = 4 \text{ min}$

Figure 4.18

(c) $t = 8 \text{ min}$

(d) $t = 12 \text{ min}$

Figure 4.18
Figure 4.18: Catalyst particles, observed at different points of time during polymerization. Five particles have been marked, observed and analyzed for polymer growth.

Figure 4.19: Normalized CED and SEV values, showing the growth of the observed single particles.
The particles did not begin to polymerize at the same time. 1, 2 and 3 began polymerizing from the start (i.e., when the reactor reached 70°C). 1 and 2 polymerized at the same speed (indicated by similar slopes), the growth of 3 was slower. The initial particle growth was quite fast, since initially formed polymer fractionated the catalyst, giving the monomer access to more active sites (please see Chapter 2.1.4 for an introduction to the phenomena of fragmentation and replication). The catalyst surface was then covered by an increasing layer of polymer, inhibiting the diffusion of the monomer to the active sites. The speed of polymerization decreased, made evident in a flattening of the graphs. Ultimately, the polymerization stopped. The dent in the graph of 3 at 12 min was caused by the particle tilting over, presenting a slightly smaller projection area. 4 and 5 began to polymerize after 15 min and 10 min, respectively. The initial speed of growth was similar to 1 and 2.

The replication of the catalyst morphology was not homogeneous, as can be seen in a comparison of 1, 2 and 3 at the beginning and the end of the polymerization (Figures 4.18a and 4.18f, respectively). The polymer grows inhomogeneously, not replicating the initial shape of the catalyst. 4 and 5 on the other hand, replicate the catalyst shape.

The indirect activation of a Ziegler-Natta catalyst like S3 should not be preferred to a direct activation. Even though it eliminates the additional step of contacting the catalyst with the co-catalyst/external donor mixture, followed by drying prior to the polymerization, the experimental results indicate a deficient activation. The catalyst particles do not begin to polymerize at the same time, exhibit a low replication performance and quickly deactivate. The activation is dependent on a sufficient amount of co-catalyst/external donor on the catalyst. As already hinted at by Weickert et al., the aluminum alkyl has a low vapor pressure, thus inhibiting sufficient contact with the catalyst. The experimental data now reveals that the distribution of the co-catalyst/external donor in the proximity of the catalyst is insufficient when activating indirectly, impeding a satisfactory polymerization performance.
Chapter 5

Novel Method for the Synthesis of Catalyst Supports

5.1 Overview

A novel method for the synthesis of a MgCl$_2$-based catalyst support has been developed. Spherical particles were generated by a controlled assembly of microscaled submoieties. The final particles had a narrow particle size distribution and high porosity. Three catalysts were prepared from said particles, with and without an additional donor, having good stereoregularity but low activity in propylene polymerizations.

5.2 Support Precursor Synthesis

5.2.1 Initial Thoughts

Nowadays, synthesis routes for MgCl$_2$-based catalyst support materials aim at the direct formation of final particles.$^{57,58,129-134}$ However, precise morphological control is achieved only on a micrometer scaled level. Properties like surface area and porosity are difficult to fine-tune. Consequentially, developing a method that offered a higher degree of morphological control was an interesting challenge. The idea devised from this incentive comprised the synthesis of nano- or micrometer sized submoieties and their controlled assembly to larger, final support particles. Such an approach would enable morphological control on a smaller scale than currently
feasible.

The development of the novel method for the synthesis of a MgCl$_2$-based catalyst support, presented in this work, was influenced by the so-called PILP process in biomimetic mineralization: In studies by Gower and Tirrell it was shown that low molecular mass polypeptides can alter the crystallizing environment of calcium carbonates in aqueous solutions by inducing a phase-separation of a hydrated calcium carbonate/polypeptide liquid-precursor phase.$^{135}$ Gower and Odom later proposed, that the solution crystallization process is transformed to the polymer-induced liquid-precursor (PILP) process, a solidification process of a liquid-phase mineral precursor, in which it can be deposited on substrates to produce mineral films or spatially limited structures.$^{136}$ The PILP process enables the synthesis of crystalline non-equilibrium morphologies resembling solidified melts or liquid crystals as they form from a fluid-like precursor state and aim at a controlled mineralization with high morphology control and uniform crystallization. As aforementioned, morphology control is a highly sought after feature in the synthesis of Ziegler-Natta catalyst supports, and the performance of the PILP process in this regard is intriguing. However, since MgCl$_2$ is prone to form hydrates, unwanted in Ziegler-Natta catalyst supports, the targeted synthesis procedure was confined to a non-aqueous environment. As a result, the PILP process had to be modified to suit the requirements. It was intended to generate nano- or micrometer scaled submoieties (“microparticles” in Figure 5.1) and assemble them with high morphological control, using binder molecules, yielding “macroparticles” suitable to be used as Ziegler-Natta catalyst supports.

![Figure 5.1: Initial thoughts of a formation of macroscaled particles through a controlled assembly of microscaled submoieties.](image)

The MgCl$_2$-based support material obtained through such a novel synthesis method
had to meet certain requirements, as outlined in Table 5.1

<table>
<thead>
<tr>
<th>Spherical shape</th>
<th>High surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suitable particle size (15 µm ... 80 µm)\textsuperscript{137,138}</td>
<td>MgCl\textsubscript{2} in the active form</td>
</tr>
<tr>
<td>Narrow particle size distribution</td>
<td></td>
</tr>
</tbody>
</table>

**5.2.2 Experimentation Preparation**

Of the multitude of possibilities for the MgCl\textsubscript{2} to be generated in the active form (see Chapter 2.1.2), fast-solidification from MgCl\textsubscript{2}-ethanol adducts was chosen. It was deemed to be the most suitable approach, being superior to an in-situ MgCl\textsubscript{2} formation via the chemical route because the adduct could be prepared in a separate step, preceding the support particle formation. The separation of the adduct synthesis and the actual particle formation simplified control over the entire procedure.

Anhydrous MgCl\textsubscript{2}, its alcohol adducts and especially the final support particles (due to their high surface area) are very sensitive to moisture. In addition, the final Ziegler-Natta catalyst is also very sensitive towards oxygen, because it deactivates the active titanium species.\textsuperscript{139} Therefore, all components of the synthesis and all materials were thoroughly dried prior to use and the experimentation took place in an inert gas (argon) environment. Schlenk technique was applied for the handling of all components and materials – a glovebox was used when necessary.

Experimentation in glass apparatuses proved to be unsuitable: The MgCl\textsubscript{2}-ethanol adducts and later interstage products adhered to the glass because of its OH-functionality, hindering effective mixing and handling (Figure 5.2a). This behavior was countered by a hydrophobization of the glass surface with trimethylchlorosilane (Figure 5.2b), greatly lowering the ability of the reactants to stick to the wall.

However, even more problematic proved to be the effective agitation of the reactants. The only stirring method, that was available for Schlenk vessels was a magnetic stir bar. But the shear energy needed for an effective particle dispersion could not be brought into the system in this way. For these reasons – after a series of experiments in glass apparatuses – all synthesis steps were subsequently carried out
in a steel autoclave. The MgCl₂-ethanol adducts and later interstage products did no longer adhere to the reactor walls. The magnetically coupled blade stirrer of the autoclave proved to be a very effective method for introducing high shear energy without compromising inert gas conditions. Additionally, the autoclave’s double-mantle design in conjunction with an attached cryostat offered excellent temperature control. It also turned out that the release valve at the bottom of the autoclave was very useful for a quick release and subsequent solidification of the reactants.

5.2.3 Novel Synthesis Method

The starting material for all support synthesis experiments was MgCl₂-ethanol adduct. Thus, preceding every subsequent step, anhydrous MgCl₂ was reacted with dry ethanol to yield the adduct MgCl₂(EtOH)₂ (N1).

![Scheme 1](image)

Figure 5.3: Synthesis of the ethanol adduct.
The MgCl$_2$ was brought into the autoclave, to which was charged paraffin. The suspension was stirred at a speed of 400 rpm. Dry ethanol was added to the suspension dropwise at RT. The mixture was stirred at RT for 10 min followed by heating to 70°C for 2 h to form N1 stoichiometrically. Then the mixture was allowed to cool down to RT under mechanical agitation. 1-Decanol was added to the slurry of N1 in paraffin, and the mixture was stirred at 70°C for 1 h, followed by cooling down to RT to give N3.

\[
\text{MgCl}_2(\text{EtOH})_2 + 0.4 \text{C}_{10}\text{H}_{21}\text{OH} \xrightarrow{\Delta} \left[\text{MgCl}_2(\text{EtOH})_2(\text{C}_{10}\text{H}_{21}\text{OH})_{0.4}\right]_x
\]

Figure 5.4: Synthesis of the 1-decanol adduct.

N3 has to be considered a non-stoichiometric network as indicated by the “x” in the formula of Scheme 2. As a simplification, N3 is considered to be a mixture of N1 and N2 as shown in Chart 1 (Figure 5.5). The ability of N2 to act as a surfactant is evident. The long linear carbon chain of the 1-decanol is hydrophobic, whereas the MgCl$_2$-ethanol “head” is more hydrophilic.

As can be seen in verification experiments (see Chapter 5.4.1), N3 will form small micrometer scaled droplets at this stage due to these anchored alcohols.

Poly(ethylene glycol) 200 (PEG-200) was added to N3 at RT, yielding N4, an aggregation of droplets. An again simplified proposal of the possible structure of N4
is given in Scheme 3 (Figure 5.6). The coordination behavior of the PEG-200 cannot be predicted precisely. It can either bind other adducts together (like a cement) or coordinate to only one species.

![Scheme 3](image)

**Scheme 3**

Figure 5.6: Simplified illustration of N4.

N4 in paraffin was stirred at 70°C for 30 min and was finally melted at 130°C under vigorous mechanical agitation (800 rpm). The mechanical stirring dispersed the molten MgCl₂ adducts into droplets. After 30 min, the reactor content was quickly released via the bottom valve of the autoclave and poured into a large amount of pre-cooled (−50°C to −40°C) dry n-pentane in a Schlenk flask. The liquid droplets of MgCl₂ adducts solidified to form spherical particles (N5). As can be seen from SEM images (Figure 5.7), N5 consists of perfectly spherical particles. According to a PSD analysis (Figure 5.7b), the modal value of the diameter is \( x_{a,\text{max}} = 58 \mu m \), the median \( x_{50} = 58 \mu m \).

It can be seen in Figure 5.7d, that N5 is build up from smaller particles. The complex surface structure suggests a high surface area and – after dealcoholation – a high porosity. According to the amount of starting material, a “yield” of 48% can be determined. The weight loss can be attributed to the structural changes of the mixture at elevated temperatures at which ethanol can evaporate. This partial evaporation is accompanied by an increase of the melting point of the adduct mixture, thus leading to a desirable faster solidification.

Measuring the surface area and/or porosity was not possible with the available equipment. Even though utmost care and very fast operation were applied, the samples hydrolized during each analysis, causing highly faulty results. Thus, the porosity and surface area could only be judged qualitatively as being “large”. This assumption is backed to a certain extent by the obtained SEM imagery.
Figure 5.7: Spherical catalyst support precursor N5.
5.3 Dealcoholation

Judging from the visual impression, N5 is a suitable support material for Ziegler-Natta catalysts. However, it is still a precursor. The alcohols have to be removed prior to catalyst synthesis, otherwise the TiCl$_4$ would form catalytically inactive alkoxides with the alcohols.$^{54}$ Several methods for the dealcoholation of such support precursors are known. They can be categorized in thermal$^{140}$ and chemical treatments.$^{54}$ Whereas the former is targeted to a removal by evaporation of the alcohols, the latter chemically modifies the alcohols to be later removed or to be inactivated towards TiCl$_4$. Variants of both methods have been applied and – where necessary – adapted for the specific needs of the precursor.

5.3.1 Thermal Dealcoholation

Thermal Dealcoholation under Vacuum

A sample of N5 was suspended in n-decane and heated up to 50°C under vacuum (approx. 8·10$^{-3}$ mbar) for 2 h. The yielded product (N6) was filtered off, washed with n-pentane and dried under vacuum ($\approx$ 1·10$^{-2}$ mbar). A weight loss of 13.8% was determined. As can be seen in Figure 5.8a, N6 lost its macroscaled spherical morphology. Figure 5.8b shows a macroparticle which was still spherical in shape. It can be seen that it is made from smaller particles.

Figure 5.8: Support N6 (precursor N5, thermally dealcoholated under vacuum).
Thermal Dealcoholation in an Argon Stream

A sample of N5 was brought into a Schlenk frit. A stream of argon was heated up to 70°C by letting it flow through copper tubing, submerged in an appropriately heated oil bath. The argon was attached to the Schlenk frit and the sample was dried for 2 h, yielding N7. A weight loss of 9.5 % was determined. It can be seen in Figure 5.9 that the macroscaled morphology is mostly preserved. However, a closer inspection revealed a strong smoothing of the surface, attributed to a degradation of the nanoscaled morphology.

Figure 5.9: Support N7 (precursor N5, thermally dealcoholated in an inert gas stream).

5.3.2 Chemical Dealcoholation

Chemical Dealcoholation with Tetrachlorosilane

A sample of N5 was suspended in n-heptane and cooled down in an ice bath. Tetrachlorosilane (SiCl4) was added, generating HCl. The suspension was gently shaken until the reaction was over. The liquid was siphoned off and washed with n-pentane. The product was then dried under vacuum (≈ 1·10⁻² mbar), yielding N8. A weight loss of 15.0 % was determined. Applying SiCl4 to remove the alcohol has a favorable side effect. As shown in Scheme 4 (Figure 5.10), it reacts with the alcohols, forming alkoxysilanes, which can act as a stereoregulating donor (see Chapter 2.1.2). The alkoxysilanes remain on the support until further treatment with TiCl4.
Scheme 4

\[
\text{MgCl}_2(\text{ROH})_n + \text{SiCl}_4 \xrightarrow{-\text{HCl}} \text{MgCl}_2\text{(OR)}_n\text{Cl}_{4-n}
\]

Figure 5.10: Reaction of \textbf{N5} with \textbf{SiCl}_4.

The macroscaled morphology was partially lost, as apparent from Figure 5.11. Many particles broke in half, they seemed to have become very brittle. The particles show a higher porosity while retaining nanoscaled integrity, suggesting a successful dealcoholation. An observation of both Figure 5.11a and 5.11b supports the assertion that \textbf{N5} really is assembled from small particles. \textbf{N8} was chosen for a subsequent catalyst preparation (see Chapter 5.6), because it largely kept its macro- and nanoscaled morphology.

Figure 5.11: Support \textbf{N8} (precursor \textbf{N5}, chemically dealcoholated with \textbf{SiCl}_4).

Chemical Dealcoholation with Trimethylchlorosilane

Trimethylchlorosilane was chosen as a variant in comparison to tetrachlorosilane. In contrast to \textbf{SiCl}_4, the reaction had to be heated instead of cooled for the reaction to take place at a decent speed. A sample of \textbf{N5} was suspended in \textit{n}-heptane. After the addition of trimethylchlorosilane the solution was heated to 70°C for 4.5 h and
gently shaken. The mixture was washed at 70°C with \(n\)-heptane. The product was then dried under vacuum (\(\approx 1\cdot10^{-2}\) mbar), yielding \(\text{N9}\). A weight loss of 21.3% was determined. As can be seen in Figure 5.12a, \(\text{N9}\) largely lost its macroscaled spherical morphology. Figure 5.12b shows a macroparticle which was still spherical in shape. Similar to Figure 5.11b, it can be seen that the support is made from smaller particles and has a porous structure.

Figure 5.12: Support \(\text{N9}\) (precursor \(\text{N5}\), chemically dealcoholated with ClSi(Me)\(_3\)).

5.4 Verification Experiments

In order to investigate the different functions of 1-decanol and PEG-200, and to show the dependency on each other, a series of verification experiments were conducted. In the course of experimentation it became evident that the presented synthesis procedure is very sensitive to the amount of the reactants used and to the parameters chosen. Subsequently, a series of experiments is presented, in which different alcohols and/or polymer binders were used.

5.4.1 1-Decanol

The particles in Figure 5.14a and 5.14b were produced by reacting \(\text{N1}\) with 1 equivalent of 1-decanol in paraffin (see Scheme 5 in Figure 5.13). The mixture was stirred at 130°C under vigorous mechanical agitation and was then quickly poured into a large amount of pre-cooled dry \(n\)-pentane at ca. \(-45^\circ\)C, yielding \(\text{N10}\). A “yield”
of 79% was determined. The figure clearly shows that lots of chunks, having an irregular shape, were formed and that the precursor has no spherical macroscaled morphology. However, a close look suggests that these chunks are composed of small sub-particles in a size of only several micrometers (Figure 5.14b). These small particles aggregate without control and are sensitive to moisture in the air. A mixture of N1 and 1-decanol alone will not generate spherical support precursor particles. However, the findings indicate the formation of sub-particles, which can be assembled to form macroscaled spherical particles.

Scheme 5

\[
\text{MgCl}_2(\text{EtOH})_2 + \text{C}_{10}\text{H}_{21}\text{OH} \xrightarrow{\Delta} \left[ \text{MgCl}_2(\text{EtOH})_2(\text{C}_{10}\text{H}_{21}\text{OH}) \right]_x
\]

Figure 5.13: Synthesis of N10.
5.4.2 PEG-200

Adduct N1 was reacted with 0.34 equivalents of PEG-200 in paraffin (see Scheme 6 in Figure 5.15), yielding N11. A “yield” of 83% was determined. Irregular chunks were produced almost exclusively (Figure 5.16a and 5.16b). Unlike N10, these chunks show a smooth surface structure and seem not to consist of small sub-particles. This is consistent with the stronger coordinating ability of PEG-200 to MgCl₂ as opposed to that of 1-decanol due to the existence of multi electron donors in the backbone of PEG-200. A mixture of N1 and PEG-200 alone yields smooth particles of highly irregular shape and size. The smooth surface, attributed to the strong coordination behavior of the PEG-200, indicates the ability of PEG-200 to bind N1 strongly together. It is thus considered a cement for N1.

Scheme 6

\[
\text{MgCl}_2(\text{EtOH})_2 + 0.34 \text{ PEG-200} \xrightarrow{\Delta} \left[ \text{MgCl}_2(\text{EtOH})_2(\text{PEG-200})_{0.34} \right]_x \]

Figure 5.15: Synthesis of N11.
5.4.3 Variation of the 1-Decanol/PEG-200 Ratio

The correct molecular ratio of the reactants is – besides the reaction parameters – the key to an efficient synthesis of N5. A slight deviation of the ideal ratio leads to unsatisfactory results. The sensitivity of the method to the reactant ratio is demonstrated in the synthesis of N12-N15. The ratios used are found in Table 5.2. The ideal ratio of N5 is also indicated. SEM images of N12-N15 (Figure 5.17a-5.17d) reveal, that slight deviations of the ideal ratio have a strong effect on the particles and lead to irregular morphologies. The “yields” of N12-N15 were 81%, 76%, 49% and 79%, respectively.

Table 5.2: Variation of Reactant Ratios

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Mg : EtOH : Decanol : PEG-200</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5</td>
<td>1 : 2 : 0.4 : 0.11</td>
</tr>
<tr>
<td>N12</td>
<td>1 : 2 : <strong>0.3</strong> : 0.11</td>
</tr>
<tr>
<td>N13</td>
<td>1 : 2 : <strong>0.5</strong> : 0.11</td>
</tr>
<tr>
<td>N14</td>
<td>1 : 2 : 0.4 : <strong>0.06</strong></td>
</tr>
<tr>
<td>N15</td>
<td>1 : 2 : 0.4 : <strong>0.21</strong></td>
</tr>
</tbody>
</table>
Figure 5.17: Support precursors, made from different reactant ratios.
5.4.4 Variation of the Reaction Temperature

After determining the synthesis method, yielding N5, it became evident that the reaction temperature of the final particle forming step is very important. This can be seen in Figure 5.18. N16 was prepared using exactly the same amounts of reactants and the same set of parameters with the exception of said temperature. For the synthesis of N16, the temperature was lowered from 130°C to 125°C. A “yield” of 54% was determined. Although many spherical particles have already been formed, it can be seen that this final step is still incomplete due to the lower temperature.

![SEM image of N16](image)

Figure 5.18: SEM image of N16.

5.4.5 Variation of the Alcohols and Binder

The ideal system for the novel synthesis method is MgCl₂/ethanol/1-decanol/PEG-200, which has been used for N5. In addition, a variety of different reagents have been tested for the particle synthesis to replace the short chain alcohol, the long chain alcohol and the polymer “binder”. Table 5.3 lists an overview of the experiments with varying reagents. The experiments were conducted using the set of parameters known to yield spherical support precursors (N5).

1-Octanol

The most promising replacement was 1-octanol instead of 1-decanol as the long chain alcohol. However, it was not possible to generate particles using 1-octanol having morphological properties like N5. An SEM image of the best example of a support
Table 5.3: Variation of Reactants

<table>
<thead>
<tr>
<th>Precursor</th>
<th>short alcohol</th>
<th>long alcohol</th>
<th>binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5</td>
<td>ethanol</td>
<td>1-decanol</td>
<td>PEG-200</td>
</tr>
<tr>
<td>N17</td>
<td>ethanol</td>
<td>1-octanol</td>
<td>PEG-200</td>
</tr>
<tr>
<td>N18</td>
<td>methanol</td>
<td>1-decanol</td>
<td>PEG-200</td>
</tr>
<tr>
<td>N19</td>
<td>ethanol</td>
<td>1-decanol</td>
<td>PEG-400</td>
</tr>
<tr>
<td>N20</td>
<td>ethanol</td>
<td>1-decanol</td>
<td>PPG-425</td>
</tr>
<tr>
<td>N21</td>
<td>1-propanol</td>
<td>1-decanol</td>
<td>PEG-200</td>
</tr>
<tr>
<td>N22</td>
<td>1-propanol</td>
<td>1-decanol</td>
<td>PDMS</td>
</tr>
<tr>
<td>N23</td>
<td>1-propanol</td>
<td>1-decanol</td>
<td>PolyTHF-250</td>
</tr>
</tbody>
</table>

precursor synthesized via 1-octanol (N17) is presented in Figure 5.19 (“yield”: 40%). The generated particles are fairly large, with average diameters between 100 µm and 150 µm. It can be seen, that parts of the adduct were unable to attain a spherical macroscaled shape. The surface structure is similar to N5, with substructures visible on the surface.

Figure 5.19: SEM image of N17.
Methanol

Replacing ethanol with methanol to form the primary MgCl$_2$ adduct was unsuccessful. It was not possible to solidify the adduct melt of MgCl$_2$/methanol/PEG-200. Only a waxy substance (N18) was yielded, having no particulate morphology.

Poly(ethylene glycol)-400

Poly(ethylene glycol)-400 (PEG-400) was chosen to investigate the influence of the binder on the formation of the support precursor. PEG-400 is similar to PEG-200, but its average molecular mass is twice as high (400 g mol$^{-1}$, $n = 8$ or 9 in Chart 2b, see below). The SEM images (Figure 5.20a and 5.20b) of a support precursor synthesized with PEG-400 as a binder (N19) show, that the formation of macroscaled particles occurs (“yield”: 51%). However, a large portion of the MgCl$_2$/ethanol/1-decanol adduct was not brought into the desired macroscaled spherical shape.

![SEM image of N19](image)

Figure 5.20: SEM image of N19.

Poly(propylene glycol)-425

Poly(propylene glycol)-425 (PPG-425) was chosen to investigate the influence of the binder on the formation of the support precursor. PPG-425 is a mixture of PPGs with an average molecular mass of 425 g mol$^{-1}$. The predominant species of PPG-425 and PEG-200 are shown in Chart 2 (Figure 5.21). The former has eight oxygen atoms in the backbone, the latter has five. Even though the oxygen atoms in
the backbone of the PPG are slightly sterically hindered due to the methyl groups, compared to PEG, it was expected to have a good coordination ability to the MgCl$_2$ adducts and to be a good binder. The SEM images (Figure 5.22a and 5.22b) of a support precursor synthesized with PPG-425 as a binder (N20) show, that the formation of macroscaled particles occurs (“yield”: 66%). It is even well visible in Figure 5.22b that the large particles are built from an aggregation of smaller sub particles. However, a large portion of the MgCl$_2$ ethanol 1-decanol adduct was not brought into the desired macroscaled spherical shape.

**Chart 2**

\[
\begin{align*}
&\text{a) Predominant Species of PPG-425 (n=7)} & \text{b) Predominant Species of PEG-200 (n=4)} \\
&\text{PEG-400 (n=8/9)}
\end{align*}
\]

Figure 5.21: Predominant species of poly(propylene glycol)-425 and poly(ethylene glycol)-200/400.

![Figure 5.21: Predominant species of poly(propylene glycol)-425 and poly(ethylene glycol)-200/400.](image)

**Figure 5.22: SEM image of N20.**
1-Propanol, Poly(ethylene glycol)-200

It was also investigated to replace ethanol by 1-propanol to form the primary MgCl$_2$ adduct. The results of the support precursor synthesis with 1-propanol/1-decanol/PEG-200 (N21) seemed promising ("yield": 72%). SEM images of N21 are displayed in Figure 5.23a and 5.23b. The closeup image of N21 (Figure 5.23b) reveals single spherical particles which consist of a very homogeneous assembly of smaller subparticles. This is visible on the edges of the cracked open particles. Yet, the majority of the reactants were unable to be assembled to large macroscaled particles.

![SEM image of N21](image)

Figure 5.23: SEM image of N21.

1-Propanol, Poly(dimethyl siloxane)

Hydroxyl terminated Poly(dimethyl siloxane) (PDMS) was used with the MgCl$_2$/1-propanol/1-decanol adduct to investigate its role as a binder. An amount of PDMS was chosen to have approx. the same quantity of oxygen functionalities present. The result of the support precursor synthesis (N22) was similar to the other experiments presented above ("yield": 62%). As can be seen in SEM images (Figure 5.24a and 5.24b), even though some macroscaled particles have formed, most of the reagents are still loosely dispersed as uncontrolled agglomerates. The few single macroscaled particles were built up from smaller subparticles having an oblong, plate-like shape.
1-Propanol, Polytetrahydrofurane-250

Replacing the binder with Polytetrahydrofurane-250 to assemble the adduct MgCl$_2$/1-propanol/1-decanol was unsuccessful. It was not possible to solidify the adduct melt of MgCl$_2$/1-propanol/PolyTHF-250. Only a waxy substance (N23) was yielded, having no particulate morphology.

5.5 Proposed Composite Formation Mechanism

Based on the experiments, a mechanism is proposed for the spherical particle formation, describing the formation of composites of liquid inorganics and polymers (CLIP). As presented above, anhydrous MgCl$_2$ reacted with ethanol and 1-decanol successively in paraffin, yielding N3. N3 is considered a non-stoichiometric network of the adducts MgCl$_2$(EtOH)$_2$ (N1) and MgCl$_2$(EtOH)$_2$(C$_{10}$H$_{21}$OH) (N3), as illustrated in Chart 1 (Figure 5.5 on Page 53). A part of N3 further reacted with PEG-200 giving a mixture, which contains a series of adducts in an equilibrium (N4) because of the complicated coordination behavior of PEG-200. A simplified illustration of this equilibrium is shown in Scheme 3 (Figure 5.6 on Page 54).

During the increase of temperature under vigorous mechanical agitation, the mixture of N3 and N4 (or part of this mixture) was melted and dispersed, which led to the formation of primary spherical composites (Chart 3 in Figure 5.25). Such primary composites were stabilized in the hydrocarbon solvent paraffin by the long
carbon chain anchored on adduct N2. Inside these composites, there were mainly aggregates of the hydrophilic adduct N1 which prefers to stay away from the non-polar solvent paraffin. The chain of PEG-200, having both hydrophilic oxygen atoms and hydrophobic ethylene moieties, can either penetrate through some composites or attach to the surface of these composites and behave as a “tentacle”. Such a “tentacle” has a strong ability to grasp other primary composites like a binder to form the macroscaled final spherical composite as illustrated in Chart 4 (Figure 5.26). Upon rapid heat dissipation, the shape of these final composites was frozen and MgCl2-based spherical catalyst support precursors were generated.

Figure 5.25: Primary spherical composites.

The generation of the composites of liquid inorganics and polymers (CLIP) during the last stage of the synthesis is the specific characteristic of the novel synthesis method. The CLIP method yields spherical support precursor particles, having a narrow particle size distribution and presumably a large surface area and high porosity. The precursors were dealcoholated to be used as catalyst supports. Actual catalyst syntheses and polymerization experiments are presented in the following chapters.
Figure 5.26: Macroscaled final spherical composite.
5.6 Catalyst Synthesis

In order to investigate the performance of the CLIP method to generate materials which can be used as Ziegler-Natta catalyst supports, three catalysts have been synthesized. The approach is similar to that found in a large variety of scientific publications.\textsuperscript{47,141–144} The suitable catalyst supports were impregnated with TiCl\textsubscript{4} at $-20^\circ$C and reacted for 2 h. In the case of N25 and N26, the precursors were suspended in n-heptane prior impregnation with TiCl\textsubscript{4}. The reactants were then heated to room temperature and the liquid was decanted. A mixture of TiCl\textsubscript{4} and n-decane was then added to the catalyst for further reaction. The reactants were then heated to 40°C and diisobutylphthalate (internal donor) was added. After 30 min, the reactants were then heated up to 100°C for 2 h. In the end, the final catalyst was washed with n-pentane and dried. In order not to break up the support particles during the catalyst synthesis by stirring with a magnetic stir bar, the reagents were gently shaken. Table 5.4 lists an overview of the synthesized catalysts. Only N5 was chosen as a support precursor, because it was the best available. It is shown in Chapter 5.7, that Ziegler-Natta catalysts, synthesized from CLIP support precursors, have a low activity in propylene polymerization, but produce polypropylene with good stereoregularity and low PDI.

Table 5.4: Catalysts prepared from CLIP supports

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Precursor</th>
<th>Dealcoholation</th>
<th>Internal Donor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N24</td>
<td>N5</td>
<td>N5</td>
<td>—</td>
<td>DIBP</td>
</tr>
<tr>
<td>N25</td>
<td>N8</td>
<td>N5</td>
<td>SiCl\textsubscript{4}</td>
<td>DIBP</td>
</tr>
<tr>
<td>N26</td>
<td>N8</td>
<td>N5</td>
<td>SiCl\textsubscript{4}</td>
<td>—</td>
</tr>
</tbody>
</table>

Catalyst Synthesis without Dealcoholation

N24 was synthesized from precursor N5 without prior dealcoholation in order to investigate the influence of the alcohols during catalyst synthesis. Figure 5.27a and 5.27b show SEM images of N24. The particles have largely lost the macroscaled morphological properties they exhibited prior to the reaction with TiCl\textsubscript{4}. The reaction of TiCl\textsubscript{4} and the alcohols, yielding various titanium alkoxo species, leads to
a loss of structural integrity. Yet, similar to the dealcoholation with SiCl$_4$, TiCl$_4$ dealcoholates the support precursor by alkoxide formation. The reaction is much stronger however, causing the observed morphological issues.

Figure 5.27: SEM image of N24.

Catalyst Synthesis after Dealcoholation

N25 and N26 were synthesized from support N8, which is the dealcoholated support precursor N5. DIBP was used as an internal donor for N25, whereas N26 was prepared without a donor. As evident from Figure 5.28 and 5.29, the particle morphology of N25 and N26 was preserved during the catalyst synthesis, because the alcohols reacted with the SiCl$_4$ in the preceding dealcoholation. The assembly of primary particles was preserved as well and agglomerated subparticles are visible, as evident from Figure 5.28b. No smoothing of the surface has occurred. The addition of DIBP during the synthesis did not have an immediate effect on the particle morphology.
Figure 5.28: SEM image of N25.

Figure 5.29: SEM image of N26.
5.7 Polymerizations

The catalysts N24, N25 and N26 were used in propylene polymerizations to investigate their performance. Of great interest were the catalysts' polymerization activities, their fragmentation/replication behavior, their stereoregulating effects and polymer properties such as average molecular mass and PDI. An overview of the polymerization experiments is given in Table 5.5. The polymerization conditions were geared to the established standard conditions as outlined in Chapter 4.3. The Al:Si:Ti ratio was slightly adapted. The polymerization conditions for the catalysts made from CLIP supports are presented in Table 5.6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst</th>
<th>Dealcoholation</th>
<th>Internal Donor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N27</td>
<td>N24</td>
<td>—</td>
<td>DIBP</td>
</tr>
<tr>
<td>N28</td>
<td>N25</td>
<td>SiCl₄</td>
<td>DIBP</td>
</tr>
<tr>
<td>N29</td>
<td>N26</td>
<td>SiCl₄</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 5.5: Polymerizations with CLIP supports

Table 5.6: Slurry Polymerization Conditions for CLIP catalysts

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reactor volume</th>
<th>Propylene pressure</th>
<th>Hydrogen partial pressure</th>
<th>Solvent volume</th>
<th>Catalyst amount</th>
<th>Polymerization duration</th>
<th>Al:Si:Ti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Vₜₐctor</td>
<td>pₚₜropylene</td>
<td>p'ₗ₂</td>
<td>Vₜₗ solvent</td>
<td>mₗ catalyst</td>
<td>Δtₚₜolymerization</td>
<td>800:20:1</td>
</tr>
<tr>
<td>70 °C</td>
<td>1 L</td>
<td>5.00 bar</td>
<td>0.36 bar</td>
<td>350 mL</td>
<td>15 mg</td>
<td>2 h</td>
<td></td>
</tr>
</tbody>
</table>

Note: Applying the ideal gas law, a molar ratio of 6.8% hydrogen in the reactor can be calculated.

The most striking detail of the data is the low activity of all catalyst, as can be seen in Table 5.7. Compared to an industrial spherical catalyst such as S3, which
Table 5.7: Summary of the Polymerization Results with CLIP catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>polymer</th>
<th>activity $\frac{[\text{kg}<em>{\text{polymer}}]}{[\text{g}</em>{\text{catalyst}} \cdot \text{h}]}$</th>
<th>$M_n$ [g mol$^{-1}$]</th>
<th>$M_w$ [g mol$^{-1}$]</th>
<th>PDI</th>
<th>stereoregularity [%$m$m$m$m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N24</td>
<td>N27</td>
<td>0.07</td>
<td>80000</td>
<td>230000</td>
<td>2.9</td>
<td>96.3</td>
</tr>
<tr>
<td>N25</td>
<td>N28</td>
<td>0.004</td>
<td>50000</td>
<td>300000</td>
<td>6.0</td>
<td>91.9</td>
</tr>
<tr>
<td>N26</td>
<td>N29</td>
<td>0.008</td>
<td>90000</td>
<td>400000</td>
<td>4.4</td>
<td>93.8</td>
</tr>
</tbody>
</table>

has an activity of $2.44\frac{\text{kg}_{\text{polymer}}}{\text{g}_{\text{catalyst}} \cdot \text{h}^{-1}}$ in slurry polymerizations, the tested catalysts were close to being considered inactive. Remarkably, although N24 was not dealcoholated, its activity was ten times higher than that of N25 and N26.

Figure 5.30: SEM image of N27.

The most striking detail of the SEM images taken (Figures 5.30–5.32) is the fact, that the catalyst fragmentation was not successful and thus no fresh active sites were accessible for the monomer. It can be seen in Figure 5.31b, that the primary particles began polymerizing. However, due to the low activity of the catalyst, the hydraulic force of the polymer was not strong enough to fragment the catalyst. The catalysts suffered from a lack of access to fresh active sites by fragmentation, and from the low performance of those sites being accessible at the beginning of the polymerization. Although the macroscaled morphology of the catalyst was largely retained, a part of the particles lost structural integrity. This has more likely hap-
pened due to an abrasion from the agitation during the polymerization than due to catalyst fragmentation from growing polymer.

The polymer properties, evaluated by GPC and $^{13}$C-NMR spectroscopy, are also presented in Table 5.7. N27 has a lower molecular mass than both N28 and N29. The PDI of N27 is significantly lower than the values of N28 and N29 and than the values found in literature (see Chapter 2.1). As outlined before (Chapter 2.1.2), a higher homogeneity of active sites on the support leads to lower PDIs and better stereoregularity. N27 also exhibits the highest degree of stereoregularity, indicated by the highest percentage of the $mmmm$-pentads. The results are consistent with the assumption mentioned before, that polymers with low PDI values often exhibit a high degree of stereoregularity. The most favorable set of properties (relatively high activity, good stereoregularity and very low PDI) is exhibited, if the lewis bases (including PEG-200) are not removed by means of dealcoholation.
Figure 5.32: SEM image of N29.
Chapter 6

Experimental Section

6.1 General Remarks

6.1.1 Inert Gas Technique

All material manipulations were conducted using Schlenk technique and glove boxes from mbraun company. Argon 4.8 was used as inert gas of which residual water and impurities were removed in two columns, filled with molecular sieves (4 Å) and Süd-Chemie PolyMax 301, respectively.

6.1.2 Drying

A substance referred to as “dry”, has been dried according to the following procedures: n-Heptane, n-hexane, toluene and ethylbenzene were dried using aluminum oxide (neutral), degassed and stored in the presence of molecular sieves (4 Å). n-Pentane was taken from a solvent purification system (SPS) from mbraun company. Commercial pure ethanol was further dried by refluxing in the presence of magnesium ethoxide$^{145}$ and stored in the presence of molecular sieves. PEG-200, PEG-400, PPG-425, PolyTHF-250, PDMS, DIBP and DIPS were dried with molecular sieves. Propylene was dried and further purified in two columns filled with molecular sieves (4 Å) and BASF BTS catalyst, respectively.
6.1.3 Chemicals

All chemicals were purchased from Merck, Sigma-Aldrich, Fluka, Acros and ABCR. Propylene was obtained from BASF and Linde Gas. Argon was obtained from Linde Gas and Westfalengas.

6.1.4 Polymerization Procedure

The catalyst sample was loaded into the solid burette inside a glove box. Prior to the polymerization, the inside of the autoclave was dried to remove residual water: Under the protection of argon, approx. 300 mL \( n \)-heptane was filled into the autoclave and 6 mL of a 2 M TEA-solution in \( n \)-heptane was added as a water scavenger. The solution was heated for 2 h at 70 °C, vigorously stirred and released afterwards. The actual polymerization was conducted according to the following steps:

1. Fill reactor with 350 mL of dry \( n \)-heptane during a counter current of argon. Close the reactor, release excess pressure and set stirrer to 400 rpm.

2. Introduce propylene, until \( p_{\text{propylene}} = 3 \) bar.

3. Attach solid burette to the reactor, while taking care to properly flush the connections with argon.

4. Add 1) TEA and 2) DIPS to the solid burette under the protection of argon. Wait for 2 min.

5. Pressurize solid burette with \( p_{\text{argon}} = 5 \) bar and introduce the content into the reactor by opening the connection valve.

6. Wash the solid burette with dry \( n \)-pentane three times, each time introducing the content into the reactor by opening the connection valve.

7. Release reactor pressure, until \( p_{\text{propylene}} = 3 \) bar.

8. Introduce hydrogen (see below).

9. Set reactor temperature to \( T = 70 \) °C, set stirrer to 400 rpm.

10. Set \( p_{\text{propylene}} \) to the pressure of the reactor at \( T = 70 \) °C. Depending on the experiment, \( p_{\text{propylene}} \) will be between 5.4 bar and 5.8 bar.
11. Stop the reaction after 2 h.

12. Release the reactor contents through the bottom valve.

13. Wash and dry the yielded polymer.

**Hydrogen Dosing**

50 mL of hydrogen at 5 bar, stored in a small metal cylinder, was dosed into the reactor at room temperature and at $p_{\text{propylene}} = 3$ bar directly after the injection of the catalyst. Applying the ideal gas law, a molar ratio of 6.8% hydrogen in the reactor can be calculated.

**6.1.5 Particle Size Distribution**

According to the procedure described in Chapter 4.6.1, the circle-equivalent diameters (CED) of support/catalyst particles were obtained by analyzing SEM images with ImageJ, using a thresholding algorithm. PSD histograms were prepared after calculating the distribution densities $q_1(x)$ from the CED values.

**6.1.6 Stereoregularity Determination by NMR Spectroscopy**

To gather data about isolated stereo errors, $^{13}\text{C}\{^1\text{H}\}$-NMR spectra of polypropylene samples were obtained. To each NMR tube, approx. 0.5 mL of 1,2,4-trichlorobenzene (TCB), approx. 0.1 mL dimethyl sulfoxide-$d_6$ (DMSO-$d_6$, for field frequency lock and internal standard relative to tetramethylsilane at 0 ppm) and approx. 70 mg of polymer were added. The spectra were recorded at $T = 410$ K, spectrometer frequency $f = 75.47$ Hz, number of scans: 1024. All spectra were calibrated with DMSO-$d_6$, being at 40.76 ppm. If no pentad fraction is specified, only the peak corresponding to $mmm\text{m}$ was visible in the spectrum.

**6.2 Equipment**

**6.2.1 Polymerization Autoclave**

All polymerizations were conducted in a 1 L double-mantle laboratory steel autoclave from büchi glas uster company. The autoclave was equipped with a magnetically
coupled blade stirrer. The fixed top flange featured several openings for manipulations, such as gas charging/venting, addition of reactants, etc. The reactor contents could be released from a bottom valve to keep the inside under inert conditions, thus permitting the conduction of another experiment without a preceding drying step. Alternatively, the autoclave could be opened by removing the lower part from the fixed top flange.

Figure 6.1: 1 L polymerization autoclave. The small gas cylinder for hydrogen dosing can be seen in the top left corner.

The autoclave setup was equipped with a cryostat. PID-temperature control via a thermocouple, located inside the reactor, allowed fast and precise temperature control.

6.2.2 Video Microscopy Setup

The video microscope (VM) is a setup of a window autoclave and a reflected-light microscope (see Figure 6.2a). It allows the direct observation of a chemical reaction (e.g., heterogeneous polymerization) inside the autoclave. A digital camera takes
micrographs at selected time intervals.

(a) VM setup and turbomolecular pump (left).

(b) Closeup of the VM autoclave. The metal cylinder is seen underneath the objective.

Figure 6.2: Video microscopy setup.

A schematic illustration of the VM setup is found in Figure 6.3. The volume of the autoclave (1) was 200 mL. A glass window (2), sustaining pressures and temperatures up until 20 bar and 150°C, respectively, was located between the autoclave body and a threaded lid. The lid and the window was removed to load the catalyst and the co-catalyst/external donor mixture. The catalyst (3) was placed on top of a steel table (4), located closely beneath the window, to reduce the distance of the microscope (5) to the sample in order to obtain focused micrographs (see Figure 6.2b). Since the polished steel table exhibited grooves and scratches at large magnifications, the particles were placed on a microscopy cover slip. The slight elevation of the particles brought the steel surface out of focus and lead to a smooth and homogeneous background. The co-catalyst/external donor mixture was brought to the bottom of the autoclave (6). A digital camera (7), controlled by an
external computer (8), was connected to the microscope. The reactor was equipped with three openings (9), to facilitate gas supply/venting, temperature measurements with a thermocouple and extra manipulations (e.g., dosing of extra reagents; not shown in schematics). The temperature was controlled with a thermocouple, located inside the reactor wall (10). The reactor was electrically heated on a heating plate. A cold light source provided proper illumination (ring light, see Figure 6.2b). The propylene pressure was adapted with a pressure controller. A turbomolecular pump was attached to supply high vacuum (< 1·10⁻⁴ mbar).

Figure 6.3: Schematic illustration of the VM setup.

6.2.3 Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy

SEM-EDX mapping images were taken by the electron microscopy institute at Ulm University. All other SEM images were taken with a Hitachi Tabletop Microscope (TM-1000).
6.2.4 Nuclear Magnetic Resonance Spectrometer

NMR spectra were recorded with a Bruker ARX-300 spectrometer (75.47 MHz).

6.2.5 High Temperature Gel Permeation Chromatograph

HT-GPC measurements were conducted with a Varian PL-GPC 220 integrated GPC system.

6.2.6 Solid Burette

The solid burette (SB) is a device to charge a heterogeneous catalyst into a pressurized autoclave under inert conditions. It was developed to replace the commonly used syringe technique for the reasons outlined in Chapter 4.3.4. The SB is shown in Figure 6.4a.

(a) Solid burette for charging heterogeneous catalysts into a pressurized autoclave under inert conditions.

(b) Three positions of valve 2.

Figure 6.4: Solid burette.
Please note that valve 2 can be set to three different positions (a, b, c, see Figure 6.4b). It is designed to facilitate effective purging with argon and dosing of liquids under inert conditions.

To load a catalyst sample, the SB is opened inside a glove box at fitting 1, making sure valve 5 is closed. After closing fitting 1, valve 2 has to be brought into position a, thus protecting the catalyst from the outside atmosphere. After connecting valve 5 to the autoclave, argon is attached to the SB at 4 ($p_{\text{argon}} > p_{\text{reactor}}$). When opening valve 3, the outer tubing is purged with argon. Afterwards valve 2 is set to position c. The inside of the SB is now accessible, but still protected by argon. As outlined in Chapter 6.1.4, TEA and DIPS can now safely be dosed into the SB. Valve 2 is then set to position b. By opening valve 5, the slurry is injected into the reactor. The procedure has to be repeated for washing with n-pentane.

### 6.3 Activation of Industrial Catalysts

#### 6.3.1 Standard Activation Procedure

125 mL of the selected activation reagent was added to 2.5 g of S3. The slurry was stirred and heated to the desired temperature, whereas the liquid turned yellow. After the chosen reaction time, the slurry was allowed to cool down and settle. The liquid was then siphoned off through a filter and the solid was washed three times with dry n-heptane at RT. The activated catalyst was dried applying Schlenk line vacuum ($\approx 1\cdot10^{-2}$ mbar) overnight.

#### 6.3.2 Syntheses of Activated Catalysts

*Note:* The $^{13}$C-NMR data corresponds to polypropylene, synthesized with the respective catalyst. See Chapter 6.1.4 for a detailed description of the polymerization procedure.

S3A1

S3, activated with n-hexane

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 65^\circ$C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.61 ($mmm\text{m}$), 28.85, 46.43;
S3A2
S3, activated with \textit{n}-heptane

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 95$ °C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.60 ($mmmm$), 28.84, 46.41;

S3A3
S3, activated with toluene

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 95$ °C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.58 ($mmmm$), 28.81, 46.40;

S3A4
S3, activated with toluene in a Soxhlet extractor

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 111$ °C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.59 ($mmmm$), 28.83, 46.41;

S3A5
S3, activated in toluene for 30 min

Duration: $\Delta t_{\text{activation}} = 30$ min. Temperature: $T_{\text{activation}} = 95$ °C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.60 ($mmmm$), 28.84, 46.42;

S3A6
S3, activated in ethylbenzene

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 95$ °C. $^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.64 ($mmmm$), 28.87, 46.45;

S3A7
S3, activated in toluene/TiCl$_4$, 1:1

Duration: $\Delta t_{\text{activation}} = 90$ min. Temperature: $T_{\text{activation}} = 95$ °C. \textit{Note}: No color change was visible, since TiCl$_4$ itself is yellow.

$^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: $\delta$ 21.61 ($mmmm$), 28.85, 46.42;
S3A8
S3, activated in toluene/TiCl\(_4\), 10:1

Duration: \(\Delta t_{\text{activation}} = 90\ \text{min}\). Temperature: \(T_{\text{activation}} = 95°C\). Note: No color change was visible, since TiCl\(_4\) itself is yellow.

\(^{13}\)C-NMR (TCB/DMSO-\(d_6\), 75.47 MHz) of PP: \(\delta = 21.64\ (mmmm), 28.88, 46.45;\)

6.3.3 Polymerization in the Video Microscope Autoclave

Note: Please refer to Chapter 6.2.2 for a presentation of the VM setup.

Prior to the polymerization, the reactor was thoroughly cleaned, washed with \(n\)-pentane and heated to 70°C. Additionally, high vacuum (< \(1 \cdot 10^{-4}\) mbar) was applied overnight to ensure complete dryness in the reactor chamber. The entire reactor was then transferred into a glove box for loading. A few grains of catalyst S3 were placed on top of the cover slip, located on the steel table. The steel table was then placed into the reactor chamber. A mixture of co-catalyst (1.6 mL of a 1 M TEA-solution in \(n\)-heptane) and external donor (0.4 mL of a 0.2 M DIPS-solution in \(n\)-heptane) was injected into the reactor chamber. The reactor was closed, taken out of the glovebox and attached to the gas supply. After a thorough purge of all connections, propylene was slowly introduced into the reactor until \(p_{\text{propylene}} = 4.00\ \text{bar}\). The digital camera was set to take a micrograph every 30 s. The reactor was then heated and the pressure carefully adjusted to reach 5.00 bar at 70°C. The polymerization was stopped after 20 min (by purging with argon), because no further reaction was visible.

6.4 Novel Method for the Synthesis of Catalyst Supports

6.4.1 Standard Support Precursor Synthesis Procedure

First, anhydrous MgCl\(_2\) was added to the opened 1 L polymerization autoclave. It was then closed and its atmosphere exchanged by applying vacuum (\(\approx 1 \cdot 10^{-2}\) mbar) and recharging with argon 5.0 three times. The third time, vacuum was applied for 15 min. Subsequently, all reactants were added to the autoclave through an opening in the top flange and the manipulations were conducted in a counter current of
argon. 250 mL paraffin oil was introduced with a separatory funnel, the stirrer of the autoclave was set to 400 rpm and the reactor was closed. The short chain alcohol (methanol, ethanol or 1-propanol) was added while shortly opening a valve in the top flange, and after 10 min the autoclave was heated to 70°C. After 2 h, the temperature was decreased to 25°C and the long chain alcohol (1-octanol, 1-decanol) was added, again while shortly opening a valve in the top flange. The autoclave was then heated to 70°C for 1 h. The temperature was then lowered to 25 °C and the binder (PEG-200, PEG-400, PPG-425, PDMS or PolyTHF-250) was added, again while shortly opening a valve in the top flange. The autoclave was then heated to 70 °C. After 30 min the bottom valve was opened and the content quickly released into ≈ 1.2 L of dry n-pentane at −50°C to −40°C in a 2 L Schlenk flask.

The solid support precursor was then filtered off and dried applying Schlenk line vacuum (≈ 1·10⁻² mbar) overnight.

6.4.2 Syntheses of Support Precursors and Catalyst Supports

N5

MgCl₂ (5.0 g, 52.5 mmol), ethanol (6.2 mL, 106.3 mmol), 1-decanol (4.0 mL, 21.0 mmol), PEG-200 (1.0 mL, 5.6 mmol).

N6

Precursor (N5, 2.0 g), n-decane (50 mL). Weight loss: 13.8 %.

N7

Precursor (N5, 2.0 g). Weight loss: 9.5 %.

N8

Precursor (N5, 1.0 g), SiCl₄ (1.5 mL), n-heptane (10 mL). Weight loss: 15.0 %.

N9

Precursor (N5, 3.0 g), ClSi(Me)₃ (4.0 mL), n-heptane (100 mL). Weight loss: 21.3 %.
N10
MgCl$_2$ (2.0 g, 21 mmol), ethanol (2.45 mL, 42 mmol), 1-decanol (4.0 mL, 21 mmol).

N11
MgCl$_2$ (3.0 g, 31.5 mmol), ethanol (3.68 mL, 63.1 mmol), PEG-200 (1.0 mL, 5.6 mmol).

N12
MgCl$_2$ (0.5 g, 5.3 mmol), ethanol (0.6 mL, 10.3 mmol), 1-decanol (0.3 mL, 1.6 mmol), PEG-200 (0.1 mL, 0.6 mmol).

N13
MgCl$_2$ (0.5 g, 5.3 mmol), ethanol (0.6 mL, 10.3 mmol), 1-decanol (0.5 mL, 2.6 mmol), PEG-200 (0.1 mL, 0.6 mmol).

N14
MgCl$_2$ (0.5 g, 5.3 mmol), ethanol (0.6 mL, 10.3 mmol), 1-decanol (0.3 mL, 1.6 mmol), PEG-200 (0.05 mL, 0.3 mmol).

N15
MgCl$_2$ (0.5 g, 5.3 mmol), ethanol (0.6 mL, 10.3 mmol), 1-decanol (0.3 mL, 1.6 mmol), PEG-200 (0.2 mL, 1.1 mmol).

N16
MgCl$_2$ (5.0 g, 52.5 mmol), ethanol (6.2 mL, 106.3 mmol), 1-decanol (4.0 mL, 21.0 mmol), PEG-200 (1.0 mL, 5.6 mmol).

N17
MgCl$_2$ (5.0 g, 52.5 mmol), ethanol (6.2 mL, 106.3 mmol), 1-octanol (4.0 mL, 25.5 mmol), PEG-200 (1.0 mL, 5.6 mmol).

N18
MgCl$_2$ (0.5 g, 5.3 mmol), methanol (0.42 mL, 10.4 mmol), 1-decanol (0.99 mL, 5.2 mmol).
N19
MgCl$_2$ (0.5 g, 5.3 mmol), ethanol (0.6 mL, 10.3 mmol), 1-decanol (0.6 mL, 3.1 mmol), PEG-400 (0.1 mL, 0.3 mmol).

N20
MgCl$_2$ (5.0 g, 52.5 mmol), ethanol (6.2 mL, 106.3 mmol), 1-decanol (4.0 mL, 21.0 mmol), PPG-425 (2.0 mL, 4.7 mmol).

N21
MgCl$_2$ (5.0 g, 52.5 mmol), 1-propanol (7.9 mL, 105.0 mmol), 1-decanol (4.0 mL, 21.0 mmol), PEG-200 (1.0 mL, 5.6 mmol).

N22
MgCl$_2$ (5.0 g, 52.5 mmol), 1-propanol (7.9 mL, 105.0 mmol), 1-decanol (4.0 mL, 21.0 mmol), PDMS (2.0 mL).

N23
MgCl$_2$ (5.0 g, 52.5 mmol), 1-propanol (7.9 mL, 105.0 mmol), 1-decanol (4.0 mL, 21.0 mmol), PolyTHF-250 (4.0 mL).

N24
Precursor (N5, 0.52 g), TiCl$_4$ (10.0 mL), mixture (2.0 mL TiCl$_4$, 10.0 mL n-decane), DIBP (0.1 mL). Yield: 0.59 g.

N25
Support (N8, 1.0 g), n-heptane (10 mL), TiCl$_4$ (2.0 mL), mixture (4.0 mL TiCl$_4$, 15.0 mL n-decane), DIBP (0.1 mL). Yield: 0.9 g.

N26
Support (N8, 4.31 g), n-heptane (10 mL), TiCl$_4$ (4.0 mL), mixture (1.0 mL TiCl$_4$, 10.0 mL n-decane). Yield: 0.9 g.
6.4.3 Polymerizations

*Note:* The $^{13}$C-NMR data corresponds to polypropylene, synthesized with the respective catalyst. See Chapter 6.1.4 for a detailed description of the polymerization procedure.

**N27**

$^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: δ 20.88 (mmrr, 1.0%), 21.42 (mmmr, 2.7%), 21.64 (mmmm, 96.3%), 28.88, 46.45.

**N28**

$^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: δ 20.16 (rrrr, 1.1%), 20.88 (mmrr, 2.9%), 21.43 (mmmr, 4.1%), 21.66 (mmmm, 91.9%), 28.90, 46.47.

**N29**

$^{13}$C-NMR (TCB/DMSO-$d_6$, 75.47 MHz) of PP: δ 20.20 (rrrr, 0.9%), 20.90 (mmrr, 2.0%), 21.45 (mmmr, 3.3%), 21.67 (mmmm, 93.8%), 28.92, 46.50.
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Figure 6.5: In front of the house where Karl Ziegler was born (Helsa/Germany).