

TKK Dissertations 191  
Espoo 2009

**SILANE FUNCTIONALIZED POLYOLEFINS VIA  
METALLOCENE CATALYSIS; SYNTHESIS AND  
USE IN POLYOLEFIN COMPOSITES**

Doctoral Dissertation

**Sami Lipponen**



**Helsinki University of Technology  
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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Chemistry and Materials Sciences for public examination and debate in Auditorium KE2 (Komppa Auditorium) at Helsinki University of Technology (Espoo, Finland) on the 6th of November, 2009, at 12 noon.

**Helsinki University of Technology  
Faculty of Chemistry and Materials Sciences  
Department of Biotechnology and Chemical Technology**

**Teknillinen korkeakoulu  
Kemian ja materiaalitieteiden tiedekunta  
Biotekniikan ja kemian tekniikan laitos**

Distribution:  
Helsinki University of Technology  
Faculty of Chemistry and Materials Sciences  
Department of Biotechnology and Chemical Technology  
P.O. Box 6100 (Kemistintie 1)  
FI - 02015 TKK  
FINLAND  
URL: <http://chemtech.tkk.fi/>  
Tel. +358-9-4511  
E-mail: [sami.lipponen@tkk.fi](mailto:sami.lipponen@tkk.fi)

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ISBN 978-952-248-139-9  
ISBN 978-952-248-140-5 (PDF)  
ISSN 1795-2239  
ISSN 1795-4584 (PDF)  
URL: <http://lib.tkk.fi/Diss/2009/isbn9789522481405/>

TKK-DISS-2664

Multiprint Oy  
Espoo 2009



ABSTRACT OF DOCTORAL DISSERTATION	HELSINKI UNIVERSITY OF TECHNOLOGY P.O. BOX 1000, FI-02015 TKK <a href="http://www.tkk.fi">http://www.tkk.fi</a>
Author Sami Lipponen	
Name of the dissertation Silane functionalized polyolefins via metallocene catalysis; synthesis and use in polyolefin composites	
Manuscript submitted 05.08.2009	Manuscript revised 15.10.2009
Date of the defence 6.11.2009	
<input type="checkbox"/> Monograph	<input checked="" type="checkbox"/> Article dissertation (summary + original articles)
Faculty	Faculty of Chemistry and Materials Sciences
Department	Department of Biotechnology and Chemical Technology
Field of research	Polymer Chemistry
Opponent(s)	Ph.D. John Severn
Supervisor	Professor Jukka Seppälä
Instructor	Professor Jukka Seppälä
<b>Abstract</b> In the first part of this study, olefins (ethylene or propylene) and different kinds of silane monomers were copolymerized with metallocene/MAO catalysts. The copolymerization of 7-octenyldimethylphenylsilane and olefin was conducted with $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ , $\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2/\text{MAO}$ and $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst complexes, and the results (catalyst activity, microstructure of the copolymer) were found to be comparable with the parallel copolymerizations of olefin and 1-alkenes (1-decene, 1-dodecene). In addition, the copolymerization performances of vinyl- and allyltrimethylsilane were studied using $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ . Due to the electronic influence of silicon, these comonomers acted as strong chain transfer agents and the synthesized ethylene/silane copolymers suffered from low molar mass.  Further on, increasing the functionality of polyolefins, the post treatment approach was studied. New routes for silane functionalized polyolefins were developed, where the pendant phenylsilane side groups in the polyolefin-co-7-octenyldimethylphenylsilane (PE-co-SiPh, PP-co-SiPh) copolymer were post treated to fluoro-, chloro-, methoxy- or ethoxysilane moieties. Beside of that, the hydrosilylation reaction was exploited on polyethylene-co-1,7-octadiene, and polyethylene with pendant chloro- or ethoxysilane functionalities were synthesized via that route. As a result, all of these post treatment steps were performed with high conversion and without influencing drastically on the molar mass of the polymers.  In the last part of this thesis, these functionalized polyolefins were tested as reactive compatibilizers in particulate filled polyolefin composites. The properties of these composites, especially the toughness, were influenced with a small amount of the compatibilizer. In addition, the filler/matrix interphase in PE/ATH(aluminumtrihydroxide) composite and a new fracture mechanism in PP/rubber/microsilica ternary composite were discovered. Finally, also the untreated polyolefin-co-7-octenyldimethylphenylsilane (PE-co-SiPh and (PP-co-SiPh) showed high affinity towards microsilica filler. It became clear that the weakly interacting phenylsilane moiety can react in a manner similar to the highly reactive halo- and alcoxysilanes towards the hydroxyl groups at the surface of microsilica filler.	
Keywords Metallocene, Copolymerization, Polyolefin, Phenylsilane, Composite	
ISBN (printed) 978-952-248-139-9	ISSN (printed) 1795-2239
ISBN (pdf) 978-952-248-140-5	ISSN (pdf) 1795-4584
Language English	Number of pages 59 p.+ app. 59 p.
Publisher Helsinki University of Technology, Department of Biotechnology and Chemical Technology	
Print distribution Helsinki University of Technology, Department of Biotechnology and Chemical Technology	
The dissertation can be read at <a href="http://lib.tkk.fi/Diss/2009/isbn9789522481405/">http://lib.tkk.fi/Diss/2009/isbn9789522481405/</a>	





VÄITÖSKIRJAN TIIVISTELMÄ	TEKNILLINEN KORKEAKOULU PL 1000, 02015 TKK <a href="http://www.tkk.fi">http://www.tkk.fi</a>
Tekijä Sami Lipponen	
Väitöskirjan nimi Metalloseenikatalyytti perusteiset silaani funktionalisoidut polyolefiinit; synteesi ja käyttö polyolefiinikomposiiteissa	
Käsikirjoituksen päivämäärä 05.08.2009	Korjatun käsikirjoituksen päivämäärä 15.10.2009
Väitöstilaisuuden ajankohta 6.11.2009	
<input type="checkbox"/> Monografia	<input checked="" type="checkbox"/> Yhdistelmäväitöskirja (yhteenvedo + erillisartikkelit)
Tiedekunta	Kemian ja materiaalitieteiden tiedekunta
Laitos	Biotekniikan ja kemian tekniikan laitos
Tutkimusala	Polymeerikemia
Vastaväittäjä(t)	TkT John Severn
Työn valvoja	Professori Jukka Seppälä
Työn ohjaaja	Professori Jukka Seppälä
<b>Tiivistelmä</b> Tutkimuksen alussa kopolymeroitiin olefiineja (etyleeni tai propyleeni) erilaisten silaanimonomeerien kanssa käyttäen metalloseeni/MAO katalyyttikomplekseja. 7-Oktenyylidimetyyliphenyyilisilaanin ja olefiinien kopolymerointia tutkittiin Et(Ind) <sub>2</sub> ZrCl <sub>2</sub> /MAO, Me <sub>2</sub> Si(2-Me-Ind) <sub>2</sub> ZrCl <sub>2</sub> /MAO ja Me <sub>2</sub> Si(2-Me-4-Ph-1-Ind) <sub>2</sub> ZrCl <sub>2</sub> /MAO katalyyttien avulla, ja tulokset (katalyytin aktiivisuus, kopolymerin mikrorakenne) olivat hyvin yhteneviä vastaaviin olefiini/1-alkeeni kopolymerointeihin. Tämän lisäksi tutkittiin vinyyli- ja allyylitrimetyylisilaanien kopolymerointikykyä kun katalyyttinä käytettiin Et(Ind) <sub>2</sub> ZrCl <sub>2</sub> /MAO kompleksia. Piin elektronisten vuorovaikutusten johdosta nämä komonomeerit toimivat vahvoina ketjunvaihtoaineina, jolloin syntetisoidun kopolymerin moolimassa jäi hyvin alhaiseksi.  Tutkimusta jatkettiin polyolefiinien jälkikäsittelyillä, joissa oli tarkoituksena lisätä niiden reaktiivisuutta. Kehitettiin uusia synteeseireittejä, missä polyolefiini-co-7-oktenyylidimetyylifenyylisilaanin sivuryhmät (PE-co- <b>SiPh</b> , PP-co- <b>SiPh</b> ) voitiin muuttaa erittäin reaktiivisiksi fluori-, kloori-, metoksi- tai etoksisilaaneiksi. Tämän rinnalla tutkittiin hydrosilylointiin perustuvia reaktioita, joiden avulla syntetisoitiin kloori- tai etoksisilaaniryhmiä polyetyleeni-co-1,7-oktadieeniin sivuketjuun. Kaikissa jälkikäsittelyissä saavutettiin hyvä konversio, vaikuttamatta merkittävästi polymeerien moolimassaan.  Tutkimuksen jälkimmäisessä osassa näitä syntetisoituja reaktiivisia polyolefiineja käytettiin kompatibilisaattoreina täyteainestetuissa polyolefiini-komposiiteissa. Jo pienellä määrällä kompatibilisaattoria vaikutettiin merkittävästi komposiittien mekaanisiin ominaisuuksiin, erityisesti sitkeyteen. Tämän lisäksi löydettiin menetelmä millä voitiin analysoida täyteainepartikkelin ja polymeerimatriisin välistä rajafaasia PE/ATH(alumiiniitrihydroksidi) komposiiteissa, sekä määriteltiin uudenlainen murtumismekanismi PP/kumi/mikrosilika kolmifaasikomposiiteille. Työn lopussa havaittiin, että myös jälkikäsittelmättömät polyolefiini-co-7-oktenyylidimetyyliphenyyilisilaanit (PE-co- <b>SiPh</b> ja PP-co- <b>SiPh</b> ) vuorovaikuttivat voimakkaasti mikrosilikan kanssa. Tämän todettiin johtuvan fenyylisilaanin kyvystä reagoida mikrosilikan pinnan hydroksyyli-ryhmien kanssa samalla tavalla kuin halo- ja alkoksisilaanit reagoivat.	
Asiasanat Metalloseeni, Kopolymerointi, Polyolefiini, Fenyylisilaani, Komposiitti	
ISBN (painettu) 978-952-248-139-9	ISSN (painettu) 1795-2239
ISBN (pdf) 978-952-248-140-5	ISSN (pdf) 1795-4584
Kieli Englanti	Sivumäärä 59 s.+ liitteet 59 s.
Julkaisija Teknillinen korkeakoulu, Biotekniikan ja Kemian tekniikan laitos	
Painetun väitöskirjan jakelu Teknillinen korkeakoulu, Biotekniikan ja Kemian tekniikan laitos	
Luettavissa verkossa osoitteessa <a href="http://lib.tkk.fi/Diss/2009/isbn9789522481405/">http://lib.tkk.fi/Diss/2009/isbn9789522481405/</a>	



## PREFACE

This work was carried out in the laboratory of Polymer Technology at Helsinki University of Technology during the years 1999-2009. The main part of the work was performed in the projects funded by the National Technology Agency (TEKES). In addition, the Finnish Cultural Foundation is also gratefully acknowledged for the financial support during the last period of the thesis.

I would like to express my gratitude to Professor Jukka Seppälä for his trust and interest in my work, and for placing the facilities of the laboratory at my disposal. Dr. Barbro Löfgren is warmly thanked for the influence and guidance over the years.

I wish to express my gratitude for the co-authors, Dr. Pirjo Pietikäinen and M.Sc. Mika Lahelin, for giving me the opportunity for co-operation and via that to widen my view in the field of polymer technology.

I am also grateful to the whole personnel of the Laboratory of the Polymer Technology for providing a pleasant working atmosphere. Special thanks for Jorma Hakala for hunting out all the articles I needed, Jaana Rich for revising my written English, Sanna Santamäki&Arto Salminen for the company during the late hours in the laboratory, and Barbro&Pirjo for being the tower of strengths while I was finalizing my thesis.

In the end, my dearest thanks for my parents, Timo and Sirpa, and my sister Taateli for the support, interest, and patience☺

Espoo October 2009

Sami Lipponen



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## LIST OF PUBLICATIONS

**I** Lipponen S., Seppälä J., Functionalization of Polyethylene with Silane Comonomers, *Journal of Polymer Science: Part A: Polymer Chemistry*, 40 (2002) 1303-1308.

**II** Lipponen S., Seppälä J., Functionalization of Polyethylene/Silane Copolymers in Posttreatment Reactions, *Journal of Polymer Science: Part A: Polymer Chemistry*, 42 (2004) 1461-1467.

**III** Lipponen S., Seppälä J., Ethylene/Silane Copolymers Prepared with a Metallocene Catalyst as Polymeric Additives in Polyethylene/Aluminum Trihydroxide Composites, *Journal of Polymer Science: Part A: Polymer Chemistry*, 43 (2005) 5597-5608.

**IV** Lipponen S., Pietikäinen P., Vainio U., Serimaa R., Seppälä J., Silane Functionalized Ethylene/Diene Copolymer Modifiers in Composites of Heterophasic Polypropylene and Microsilica, *Polymer & Polymer Composites*, 15 (2007) 343-355.

**V** Lipponen S., Lahelin M., Seppälä J., Phenylsilane; unreactive group in the metallocene/MAO catalyzed copolymerization of propylene and 7-octenyldimethylphenylsilane, reactive group in melt blending with microsilica filler, *European Polymer Journal*, 45 (2009) 1179-1189.

### The author's contribution in the appended publications

- I** Sami Lipponen is responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript.
- II** Sami Lipponen is responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript.
- III** Sami Lipponen is responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript.
- IV** Sami Lipponen participated in research plan, is responsible for most of the experimental work (excluding all the polymerizations) and interpretation of the results, and wrote the manuscript together with the coauthors.
- V** Sami Lipponen participated in the research plan, and is responsible for the experimental work (excluding all the polymerizations), interpretation of the results and the preparation of the manuscript.

## OTHER RELEVANT PUBLICATIONS

Seppälä J., Löfgren B., Hakala, K., Lipponen, S., Helaja, T., Anttila, U., Functional copolymers by using metallocene catalysis enabling new applications, *Polymeric Materials Science and Engineering*, 84 (2001) 257-258.

Aitola E., Puranen A., Setälä H., Lipponen S., Leskelä, M., Repo T., Copolymerization of vinylcyclohexane with ethene and propene using zirconocene catalysts. *Journal of Polymer Science, Part A: Polymer Chemistry*, 44 (2006) 6569-6574.

## ABBREVIATIONS AND SYMBOLS

ABS	acryl-butadiene-styrene	
ATH	aluminumtrihydroxide	
ATHSA	aluminumtrihydroxide coated with stearic acid	
BA	butylacrylate	
BBN	borabicyclo[3.3.1]nonane	
BDT	brittle to ductile transition point	
Bu	butyl	
Com	compatibilizer	
COOH	carboxylicacid	
Cp	cyclopentadienyl	
d	doublet	
dd	doublet doublet	
ddt	doublet doublet triplet	
DSC	differential scanning calorimetry	
dt	doublet triplet	
EPDM	ethylene/propylene/diene terpolymer	
Et	ethyl	
EtOH	ethanol	
Flu	fluorenyl	
FTIR	fourier transform infrared spectroscopy	
GMA	glycidylmethacrylate	
h-PP	heterophasic polypropylene	
Ind	indenyl	
J	coupling constant	
M	molarity	[mol/L]
MAH	maleic anhydride	
MAO	methylaluminoxane	
Me	methyl	
M <sub>w</sub>	weight average molar mass	[g/mol]

nm	nanometer	
NMR	nuclear magnetic resonance spectroscopy	
PBT	poly(butylene terephthalate)	
PC	polycarbonate	
PD	polydispersity	
PE	polyethylene	
PE-co-SiX	polyethylene copolymer containing pendant SiX group	
PEHD	high-density polyethylene	
PELD	low-density polyethylene	
Ph	phenyl	
PP	polypropylene	
PP-co-SiX	polypropylene copolymer containing pendant SiX group	
ppm	parts per million	
SEM	scanning electron microscopy	
Si(CH <sub>3</sub> ) <sub>3</sub>	trimethylsilane	
t	triplet	
T	temperature	[°C]
T <sub>C</sub>	crystallization temperature	[°C]
T <sub>m</sub>	melting temperature	[°C]
TMA	trimethylaluminum	
Z-N	Ziegler-Natta	
μSi	microsilica	

## 1 INTRODUCTION

Over 50 % of today's synthetic polymers consist of polyolefins and they are the fastest growing polymer family due to their economical and environmental performance and outstanding properties. Among the polyolefins, polyethylene (PE) and polypropylene (PP), are the most cost efficient ones and moreover easiest to produce. Over the decades extensive work has been focused on catalyst and process technologies which have led to significant improvements in production of PE and PP. Today, catalysts are more powerful, products are purer and versatile and productions are simpler and more efficient.[1-4]

The variety of PE and PP grades with different properties is increasing and they are replacing other polymers and traditional materials in many applications. However, to really challenge the engineering plastics (e.g. PC/PBT, PC/ABS, polyamide) and glass fiber-reinforced thermosets, the polyolefins still suffer from several drawbacks, like softness, creeping, and decreased modulus under heating. To overcome these challenges mineral fillers can be added into polyolefin matrix to increase rigidity and heat distortion temperature or as well to bring fire resistance. The required mineral filler concentration may be extremely high (>60 wt-%) and to achieve all the benefits offered by the filler, the filler/matrix interaction must be controlled. This may be problematic in hydrophobic polyolefin matrix where the hydrophilic fillers often remain aggregated and the filler/matrix adhesion is weak. A sophisticated method to reduce the aggregations and increase the filler/matrix interaction is to use small amount of functional/reactive polyolefins as compatibilizers in the host polyolefin matrix. On average, polyolefins containing functional groups show improved adhesive properties, affinity to dyes and printing agents and are more compatible with other polymers and fillers.[2,5-7]

The most convenient way of introducing functional groups in polyolefin chain is the peroxide grafting during the melt processing. PE and PP grafted with acrylic acid, maleic acid, or maleic acid anhydride are widely used as surface modifiers and compatibilizers. One of the major challenges with peroxide grafting is that extensive chain scission and loss in molar mass can occur with some polymers, notably with PP. Also significant homopolymerization of acrylic acid monomer can take place. In parallel with grafted polyolefins, ethylene can directly be

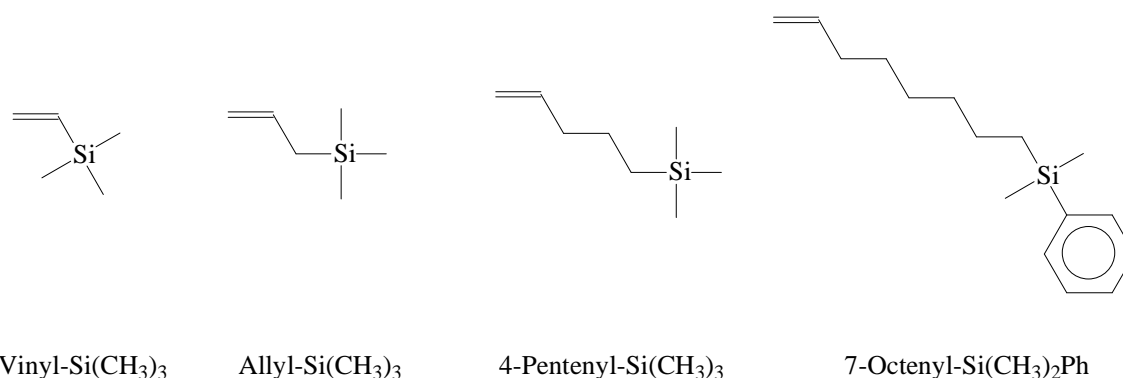
copolymerized with some vinyl monomers (acetates and acrylates) via radical polymerization in pipe line. However, the reaction conditions are rather drastic (>2500 bar, >300 °C) and milder synthesis method are favored.[3,8,9]

The most sophisticated method in producing functional polyolefins would be the controlled copolymerization with co-ordination catalysts. The reaction conditions would be tolerable and the synthesized polymers more homogeneous. Unfortunately most of the polar groups are strong inhibitors of the Ziegler-Natta catalyst. Cationic Group IV metallocene catalysts may provide a solution to these problems as they are found to be less sensitive towards Lewis basic monomers, and the reactivity of weakly interacting monomers (Lewis acids) is outstanding. In addition, metallocenes show overwhelming copolymerization performance (vs. Z-N catalyst) offering several alternative routes to the synthesis of functional polyolefins.[1,10-12]

## 1.1 Scope of the thesis

The thesis summarizes the results of the appended five publications, **I-V**, supported with some unpublished data. The first aim was to study the copolymerization performance of silicon containing monomers (Scheme 1) in metallocene/MAO catalysed polymerization of olefins. In addition, the use of the post treatment approach in the synthesis of halo- or alcoxysilane functionalized polyolefin was studied. Finally, all of the abovementioned functionalized polyolefins were tested as reactive compatibilizers in particulate filled polyolefin composites.

In the first part of the study, the metallocene catalysed copolymerization of 7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph and olefin (ethylene [**I,II**] or propylene [**V**]) was studied, and the results (catalyst activity, the microstructure of copolymer) were compared with the ones obtained in the 1-alkene/olefin copolymerizations. The results in **I** were further supported with the data from the copolymerization of ethylene and 4-pentenyl-Si(CH<sub>3</sub>)<sub>3</sub> [13]. In addition, the literature overview of the polymerization performance of short silane monomers, mentioned briefly also in **I** and **V**, was supplemented with the data from Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO catalysed copolymerizations of ethylene and silane monomer (vinyl-Si(CH<sub>3</sub>)<sub>3</sub>, allyl-Si(CH<sub>3</sub>)<sub>3</sub>) [13].



Scheme 1 The molecular structures of the used silane monomer

The post treatment approach to form highly reactive halo- and alcoxysilanes in the polyolefin pendant chain (PP-co-SiF, PE-co-SiX, X=Cl, F, OEt, OMe) was studied in the publications **II**, **IV**, and **V**. The novel synthetic routes to halo- or alcoxysilanes in polyolefin chain was developed and exploited in **II** and **V**, whereas the conventional hydrosilylation of pendant double bond in polyethylene was studied in **IV**.

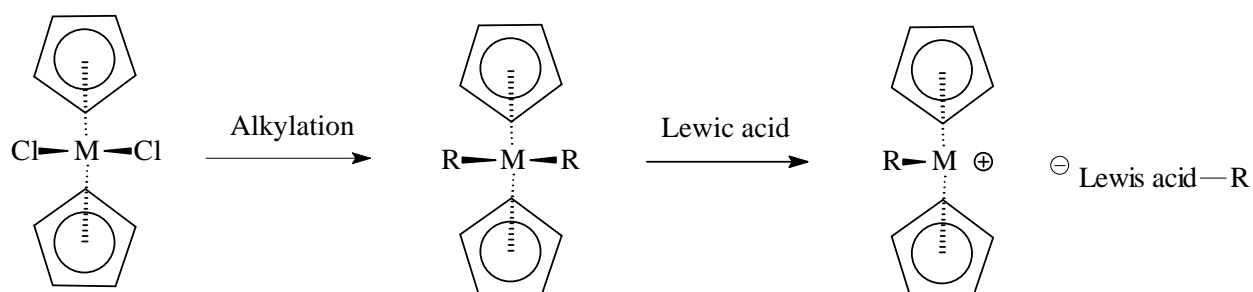
In the final part of the thesis, the functionalized polyethylenes synthesized in **II** and **IV** were tested as reactive compatibilizer in polyethylene/aluminumtrihydroxide (PE/ATH, 40 wt-%) **[III]** and heterophasic polypropylene/microsilica (h-PP/ $\mu$ Si, 30 wt-%) **[IV]** composites. The mechanical properties of the composites were measured, and the fracture surfaces studied in detail by SEM-microscopy.**[III,IV]** The DSC was used to characterize the interphase formation in PE/ATH composites.**[III]** In the last publication**[V]** the affinities of the phenylsilane and halosilane moieties towards microsilica filler were studied. The reactions/interactions of molecular phenyl- or halosilane moieties and the hydroxyl group at the microsilica filler surface was observed with FTIR-spectrometer, whereas the interaction in the PP/ $\mu$ Si/PP-co-SiX ( $\mu$ Si=1-4 wt-%, X=F, Ph) composite was followed by measuring the variations in the crystallization temperature **[V]**. The results in **V** were supported with data obtained from the mechanical testing of PP/ $\mu$ Si/PP-co-SiX and PE/ $\mu$ Si/PE-co-SiX (X=F, Ph) composites containing 30 wt-% of microsilica [14].



## 2 METALLOCENE CATALYST

The group IV metallocenes were discovered already in 1953 [15], but as catalysts for olefin polymerization they remained mainly out of sight until the effective activator, methylaluminoxane (MAO), was discovered (partial hydrolysis of TMA) in the late of 1970 [16,17]. These metallocene/MAO catalyst complexes have then been the base for developing the synthesis of wide variations of polyolefins and their copolymers.[10,18,19]

The basic metallocenes consist of group IV metal coordinated with two cyclopentadienyl ligands and two chloride atoms (Scheme 2). Today it is a widely accepted fact that the active  $14 e^-$  cationic complex of metallocene is generated by alkylation agent and Lewis acid (Scheme 2). As new candidates alongside the ‘unresolved’ MAO [20], the borates and boranes [21,22] have been used as activators to form highly reactive metallocene catalyst complexes. In these cases, however, a separate alkylation step is required, and in practice the MAO is still the prevailing activator as it can act as alkylation agent and Lewis acid at the same time.[10,18]

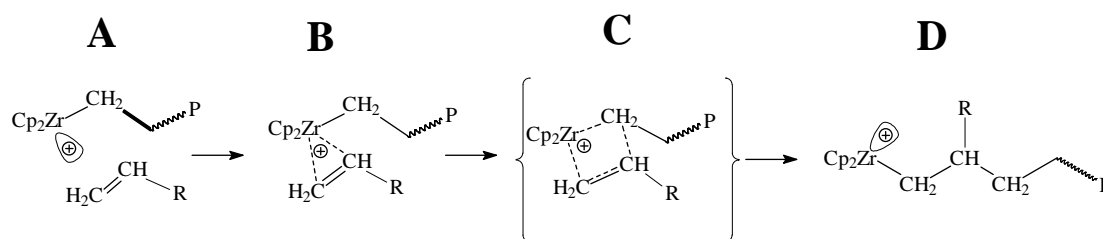


Scheme 2 The activation of the metallocene catalysts, M= Zr, Ti, Hf; R=alkyl group

### 2.1 Monomer insertion mechanisms

The polymerization performance of metallocene catalysts is mainly defined by the insertion (in chain initiation and propagation) and termination mechanisms and their rates. The simplified insertion mechanism is presented in Scheme 3, where the monomer insertion proceeds via planar four centered transition state to final form where the vacant coordination site is replaced at the former position of the polymer chain (scheme 3 A to D). New insertion steps take place extending the polymer chain until a chain termination reaction, normally  $\beta$ -hydrogen

abstraction (uni or bimolecular) or chain transfer to aluminum, occurs.[10,23,24] The monomer insertion mechanism has been the subject of several studies, and in the more detailed studies also the different agostic interactions ( $\alpha$ -,  $\beta$ -,  $\gamma$ -agostic) have been taken into consideration [23-27].



Scheme 3 The simplified monomer insertion route (R=H, alkyl group, etc)

When  $\alpha$ -olefins higher than ethylene are present, the regiospecificity of the insertion has to be taken into account. Due to the steric and electronic effects the insertion proceeds primary through 1,2-mechanism (Scheme 3, R $\neq$ H) but from time to time the secondary 2,1-insertion occurs as well. Especially in propylene homo- and copolymerization the secondary insertion is unwanted because it decreases the propagation rate leading to reduction in molar mass. This has been one of the drawbacks of metallocene catalysts when compared with the highly regiospecific Z-N catalysts.[19,28]

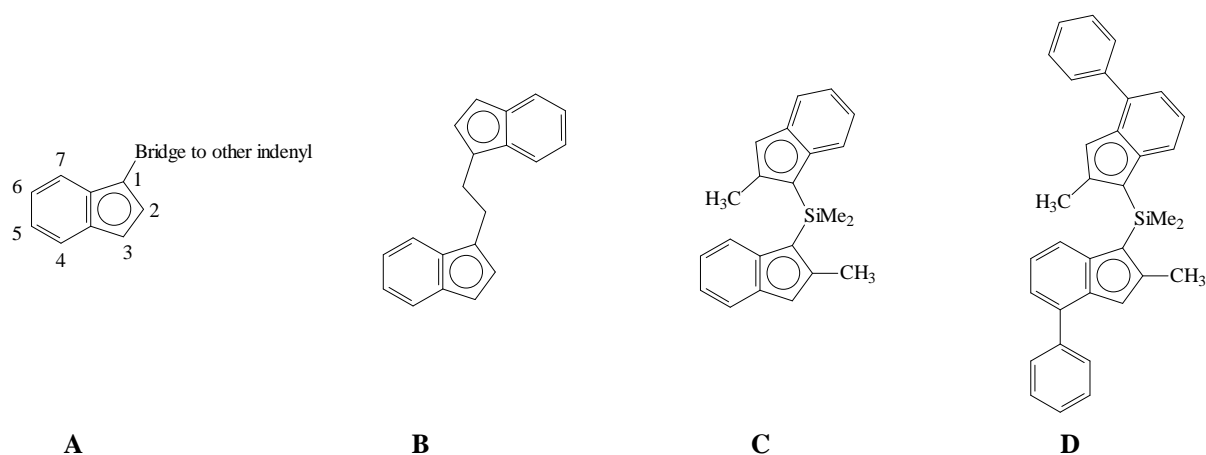
## 2.2 Chain termination mechanisms

The ratio between the rates of chain propagation and chain termination determines the molar mass of the polymer. Several alternative chain growth termination mechanisms have been found for the metallocene catalysed polymerization of  $\alpha$ -olefins. The most common type of termination mechanisms are 1) the  $\beta$ -hydrogen elimination (uni- or bimolecular) after monomer insertion and 2) the chain transfer to aluminum. In the polymerization of propylene also 3) the  $\beta$ -methyl elimination has found to play a significant role. These termination mechanisms determine the end group of the polymer chains as well as the group of the new initiated chain. Each of the chain termination processes has a certain 'finger print' due to the fact that they produce a certain type of groups at the both heads of the polymer chain. This

gives the possibility to estimate the termination mechanism by determining these groups by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR techniques.[10,28,29] The mechanisms will be study more in detail later in the text alongside with the results.

### 2.3 The influence of the catalyst modification

The major advantage of metallocene catalysts is based on their cyclopentadienyl type ligands which can be broadly modified to provide the optimal combination of catalytic activity, molar mass, stereo- and regiospecificity and comonomer uptake. One of the breakthroughs was the development of the bridged ansa type metallocenes [30] (e.g. Scheme 4 A to D) which enhanced the comonomer response without sacrificing the catalyst activity and, more importantly, enabled the stereospecific olefin polymerization [10,31]. Another important development was achieved when the methyl group was placed in 2-positions in metallocene catalyst [32] (Scheme 4 A, C), where after the unwanted 2,1-insertion was sterically shielded and, in addition, the affinity for chain termination via bimolecular  $\beta$ -hydrogen abstraction was reduced. This has been one of the key factors in developing the metallocene catalysts towards high molar mass polypropylene and polypropylene-co-1-alkenes. Finally, the stereospecificity of metallocene catalyst has been further developed, e.g. by placing phenyl ring in the 4-position of indenyl ligand [33] (Scheme 4 A, D) which finally allowed the metallocene to compensate the Z-N catalyst in polymerization of isotactic PP.[19,28,34,35]



Scheme 4 The numbering of the indenyl ring (A), and the structures of the metallocene catalysts B)  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ , C)  $\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2$ , D)  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrCl}_2$  used in this study. The  $\text{ZrCl}_2$  groups are removed for clarity.

### 3 METALLOCENE CATALYSED COPOLYMERIZATIONS

To adjust the properties of the polyolefines the pendant side chains have been added in the polymer chain by copolymerization. The mostly used comonomers are short or long  $\alpha$ -olefins (1-butene, 1-hexene, 1-octene, and 1-decene) which are used to regulate the crystalline properties of the polymer as well as to improve its processability. The heteroatom containing comonomers are usually used to change the hydrophobic nature of the polyolefin to more hydrophilic.

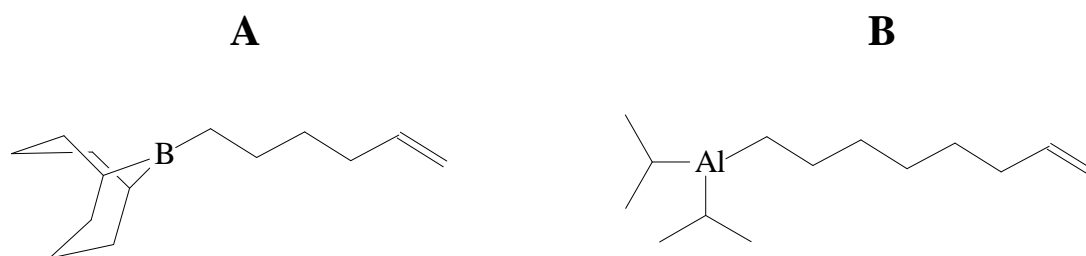
When compared with the Z-N catalysts, the clear advantage of the metallocene catalysts is their extraordinary copolymerization performance as the comonomer is evenly distributed throughout the whole polymer chain and the molar mass region. The metallocenes tolerate also Lewis basic comonomers to some extent, and the polymerization performance of weakly interacting Lewis acidic monomers is often outstanding. In summary, metallocene catalysts give excellent control of molar mass, molar mass distribution, microstructure, comonomer distribution, and comonomer response in copolymerization of reactive polyolefins.[1,10-12]

Still, the use of the different kind of comonomers together with ethylene, or propylene may influence the polymerization mechanisms via electronic or steric interactions. The understanding of these mechanisms and reactions is the base for evolving the catalyst technology and producing a specified polymer. The major variations are often found in monomer insertion and termination mechanisms which mainly determine the catalyst activity, the comonomer uptake and the molar mass of the copolymer. There are also migration mechanisms e.g. acidic [36], allylic activation [36-41] and 'Chain Walking' [29,40,42] that may change the microstructure of the polymer chain.

#### 3.1 Weakly interacting polyolefins via metallocene catalysis

The metallocene catalysed polymerizations of Lewis acidic monomers have normally proceeded well if the electronic influence of the heteroatom (B, Si, Al) is diminished by a long spacer. The groups of Chung [42-47] have studied a lot the possibility to combine the co-

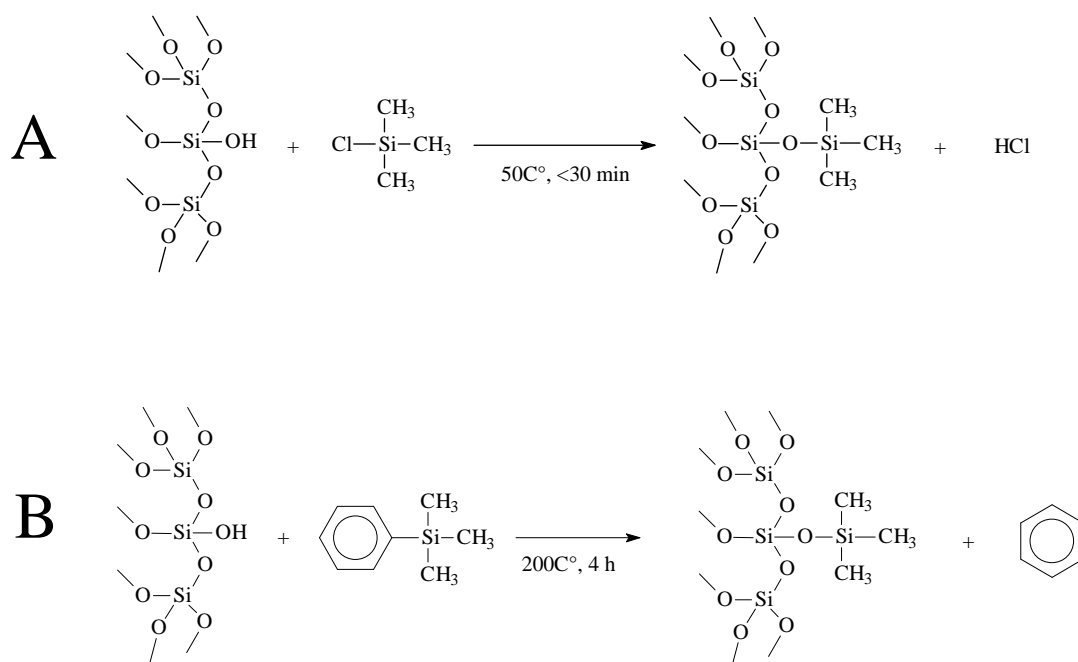
ordiantion catalyst and the chemistry of boranes. In one of their study [45], 5-hexenyl-9-BBN (Scheme 5A) and ethylene were copolymerized with  $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$  catalyst, and the borane monomer acted like any other unfunctional monomer. The borane uptake in polyethylene chain was clearly proportional to the borane concentration in feed, and the ‘positive comonomer effect’ was observed as the catalyst activity increased with the concentration of borane [45].



Scheme 5 The weakly interacting comonomers used in the studies of A) Chung *et al.* [45], and B) Nam *et al.* [48].

Same kind of results were obtained by Nam *et al.* [48] when they copolymerized 7-octenyldiisobutylaluminum (Scheme 5 B) and propylene with two different borate activated metallocenes,  $\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2$  and  $\text{Ph}_2\text{C}[(\text{Cp})(9\text{-Flu})]\text{ZrCl}_2$ . The ‘positive comonomer effect’ was not present, which is the normal situation in propylene copolymerization, but otherwise the copolymerization proceeded smoothly. A disadvantage observed was that the  $\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2/\text{B}(\text{C}_6\text{F}_5)_4$  catalyst complex was sensitive to chain transfer to aluminum, which resulted in decreased molar masses compared to comonomer concentration in the reactor.[48]

In addition to boranes and aluminums, silanes have provided possibilities in the formation of functionalized polyolefines. Especially pendant phenylsilane group in polyolefin chain was considered to be an effective group due to the reactive silicon-benzyl bond [49]. In our study [V] it was found that in some cases the phenylsilane groups can react in a manner similar to how the hydrolysable silanes react with the hydroxyl groups at the filler surface (Scheme 6). Therefore, polyolefins with the pendant phenylsilane groups provide significant possibilities in the polyolefin composite technology.[V]



Scheme 6 The reaction between the free hydroxyl group at the microsilica ( $\mu\text{Si}$ ) surface and A) chlorotrimethylsilane, or B) phenyltrimethylsilane.[V]

### 3.1.1 Copolymerization of ethylene and 7-octenyldimethylphenylsilane

In our first publication [I] the metallocene catalysed copolymerization performance of 7-octenyldimethylphenylsilane (7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph) and ethylene was studied. The phenylsilane moiety was separated from the double bond with six methylene groups and that was expected to be sufficient to hinder the electronic influence of silicon. However, the polymerization performance of phenylsilane containing monomer may raise some questions also from the perspective of the (active)benzyl ring as it has found to interact with the electron deficient metal-centers through the  $\pi$ -aromatic system [50]. Therefore, if any interaction between the phenylsilane moiety and the cationic metal centre is present it would most likely influence the polymerization process. To see the real influence of the phenylsilane containing comonomer the comparable copolymerization was performed with ethylene and 1-decene as well (Table 1).[I]

Table 1 The metallocene/MAO catalysed ethylene/7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph copolymerization results.[I]

Run	Cat.	7-Octenyl-Si(CH <sub>3</sub> ) <sub>2</sub> Ph in feed mM	in polym. mol-%	Cat. activity <sup>B</sup>	M <sub>w</sub> kg/mol	PD
1	<b>1</b>	-	-	21 400	300	3.4
2	<b>1</b>	28	1.5	27 300	230	3.1
3 <sup>A</sup>	<b>1</b>	22	1.3	25 800	230	3.1
4	<b>1</b>	59	2.4	19 100	190	2.9
5	<b>2</b>	-	-	12 500	600	3.3
6	<b>2</b>	19	1.2	18 500	440	3.2
7	<b>2</b>	52	2.6	26 700	320	2.8

Conditions: Catalysts=1 μmol, **1**=Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, **2**=Me<sub>2</sub>Si(Me-2-Ind)<sub>2</sub>ZrCl<sub>2</sub>, Al/Zr=2000, T= 40 °C, t=20 min., ethylene pressure 0.7 bar (84 mM), medium toluene 300ml., stirrer speed=1000 rpm. A) 1-Decene as comonomer. B) Activity as kg<sub>polymer</sub>/mol<sub>cat.</sub>\*P<sub>ethylene</sub>\*h

With both catalysts, the activities were higher in most of the copolymerization than in the homopolymerization (Table 1, Run 1 vs. Run 2, 3<sup>A</sup>; Run 5 vs. Run 6, 7), even though the insertion rates of sterically demanding higher α-olefins are conventionally considered to be slower than that of ethylene.[I] This phenomenon is known as ‘positive comonomer effect’ and it is usually seen with the copolymerization of ethylene with other nonfunctionalized α-olefins. One of the most common explanations has been the increased solubility of the formed copolymer vs. homopolyethylene, which might allow increasing the diffusion of monomers into the catalyst [51-53]. Still, several contrary results are reported where the presence or absence of the ‘comonomer effect’ was influenced by varying the catalyst ligand structure, the metal of the catalyst, or the used cocatalyst [52,54-58]. Based on these results, the observed comonomer effect can not be ascribed directly as a diffusion phenomenon.[I]

When the copolymerizations were compared (Table 1, Run 2 vs. Run 3<sup>A</sup>), both of the comonomers resulted in similar results regarding the catalyst activities, the comonomer uptake, and the reduction in molar mass. To gain more information of the chain termination mechanisms, the microstructures of these copolymers were studied in more detail by observing their <sup>1</sup>H-NMR spectra from the unsaturated area (figure 1).[I]

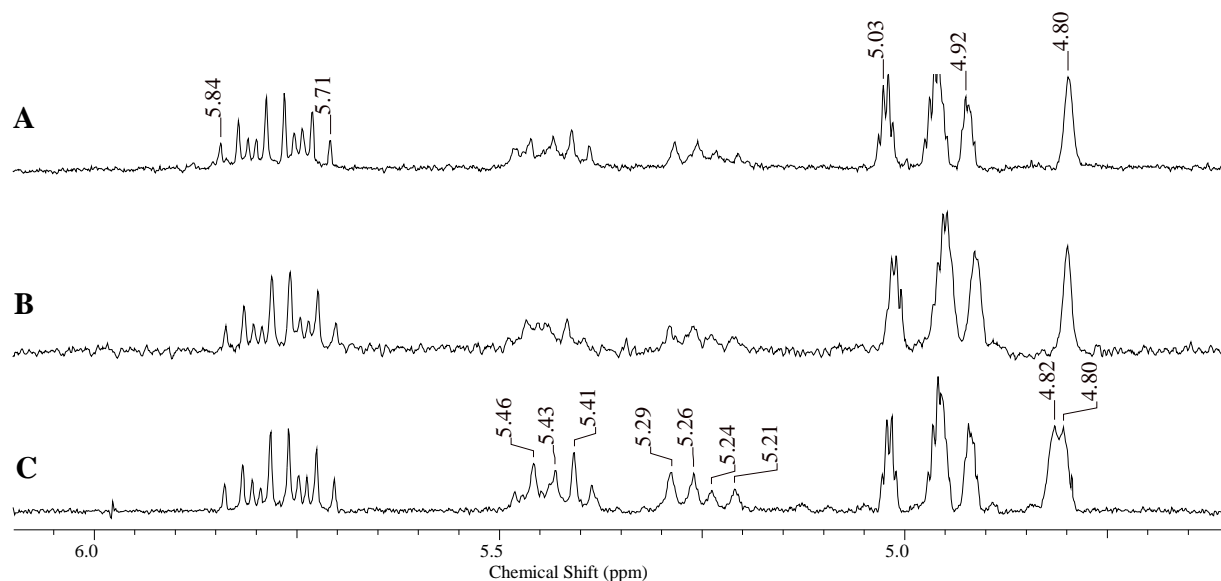


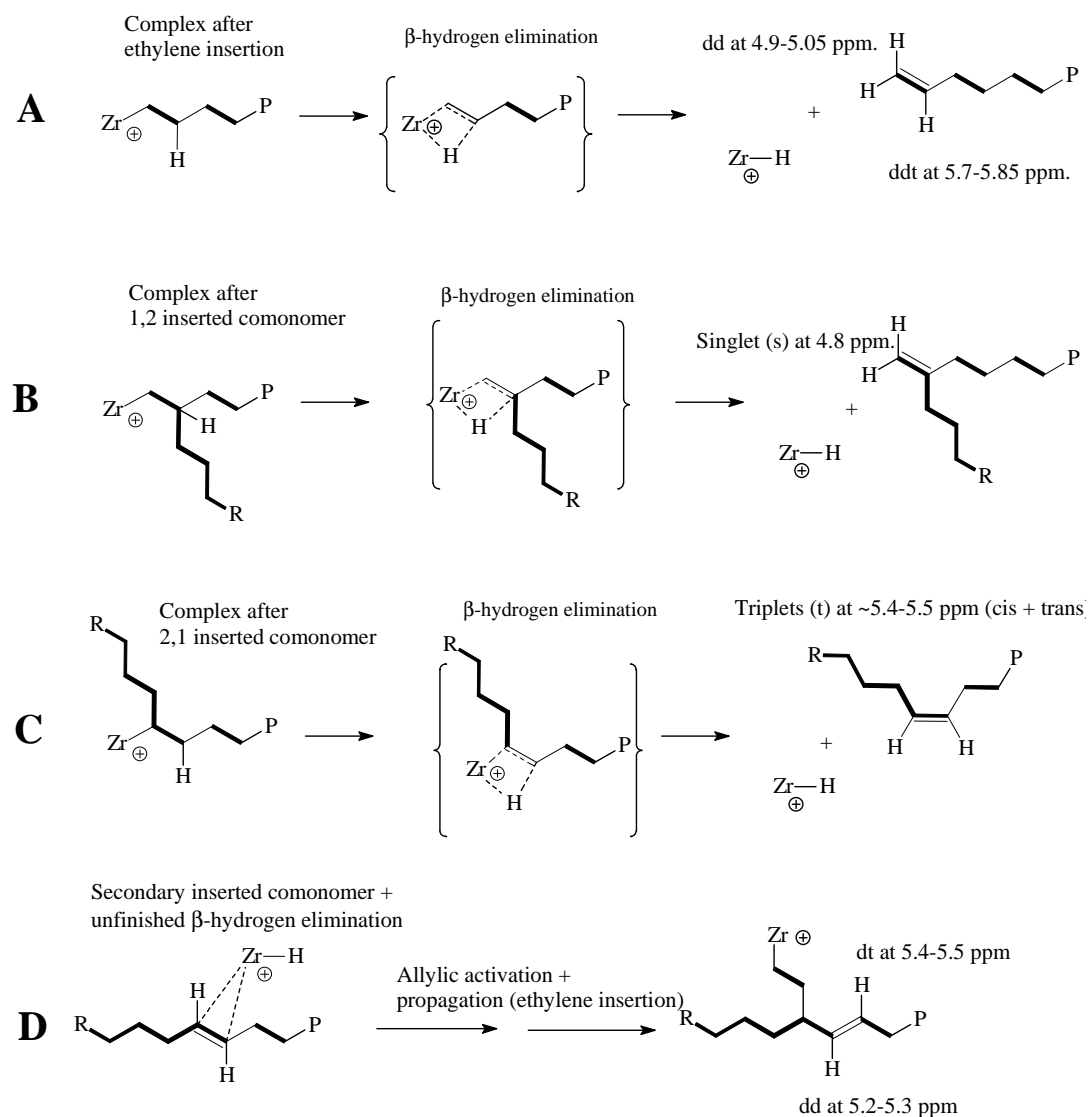
Figure 1 The  $^1\text{H-NMR}$  spectra of A) polyethylene-co-7-octenyl- $\text{Si}(\text{CH}_3)_2\text{Ph}$  (table 1 Run 2) B) polyethylene-co-1-decene (Table 1 Run 3<sup>A</sup>) and C) polyethylene-co-4-pentenyl- $\text{Si}(\text{CH}_3)_3$ . The spectra were run in  $d_8$ -toluene at  $90^\circ\text{C}$ . A and B, data based on [I], C) data based on [13].

When the microstructures of polyethylene-co-7-octenyl- $\text{Si}(\text{CH}_3)_2\text{Ph}$  and polyethylene-co-1-decene were compared (Figure 1 A vs. B), no clear differences were observed. It was obvious that the  $\beta$ -hydrogen chain transfer reaction was the dominating termination mechanism which resulted in vinyl chain end after ethylene insertion (Scheme 7 A vs. Figure 1 multiple resonances at 4.92-5.03 ppm and 5.71-5.84 ppm) and vinylidene chain end after 1,2 inserted comonomer (scheme 7 B vs. Figure 1 singlet at 4.8 ppm). [I] The multiple resonances at 5.4-5.5 ppm. in  $^1\text{H-NMR}$  spectrum has been ordinarily explained by the internal unsaturation formed after chain termination of secondary inserted 1-alkene (Scheme 7 C, cis and/or trans) [41,59]. However, in our case the situation was more complicated due to some undefined resonances at 5.2-5.3 ppm.

In our additional experiments [13], where polyethylene-co-4-pentenyl- $\text{Si}(\text{CH}_3)_3$  was synthesized, these resonances at 5.2-5.5 ppm. appeared more clearly and actually a coupling pattern could be hypothesized (Figure 1 C, two doublets at 5.21-5.28 ppm.,  $J(d)=8\text{ Hz}$ ,  $J(dd)=15\text{ Hz}$ ; and two triplets at 5.41 and 5.46 ppm. ( $J(t)=6\text{ Hz}$ ,  $J(dt)=15\text{ Hz}$ ). This coupling pattern has been assigned to microstructure where the internal trans-vinylidene unsaturation locates next to the branching point [41]. The simple explanation for the formation of this kind



of microstructure would be the allylic activation and propagation after chain termination of 2,1-inserted comonomer unit (Scheme 7 D)[13].



Scheme 7 The mechanisms for different unsaturations in the polyethylene chain, **P**=polyethylene chain, **R**=  $-(\text{CH}_2)_4\text{CH}_3$ ,  $-(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{Ph}$ , or  $-\text{Si}(\text{CH}_3)_3$ . Mechanisms A, B, C based on [59], mechanism D based on [13].

When the copolymerizations of ethylene and 7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph were conducted with Me<sub>2</sub>Si(2-Me-Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO, the results were somewhat different when compared with the results obtained with Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO (Table 1, Run 4 vs. 7). The comonomer incorporation rate was slightly higher which could be explained by the increased co-ordination

gap aperture due to the short Me<sub>2</sub>Si-bridge in the catalyst. When the microstructure was studied, there were no signs of secondary insertion of the 7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph monomer (Figure 2, no resonances at 5.2-5.5 ppm.).[I] This was probably due to the methyl groups in 2-positions in metallocene catalyst which is known to shield the 2,1-insertion mechanism, and in addition diminish the monomer assisted (i.e. bimolecular) β-hydrogen abstraction [19]. This would partly explain the higher molar mass obtained with the Me<sub>2</sub>Si(2-Me-Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst complex (Table 1, Runs 1-4 vs. Runs 5-7).

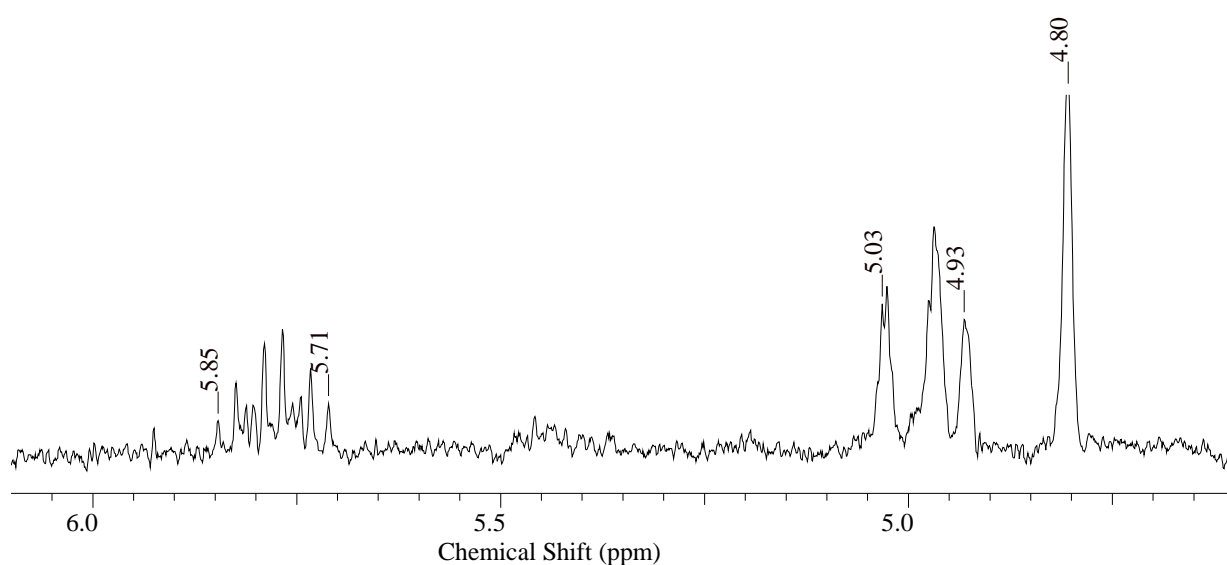


Figure 2 The <sup>1</sup>H-NMR spectra of polyethylene-co-7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph (table 1 Run 7). Spectra was run in d<sub>8</sub>-toluene at 90 °C. Data based on [I]

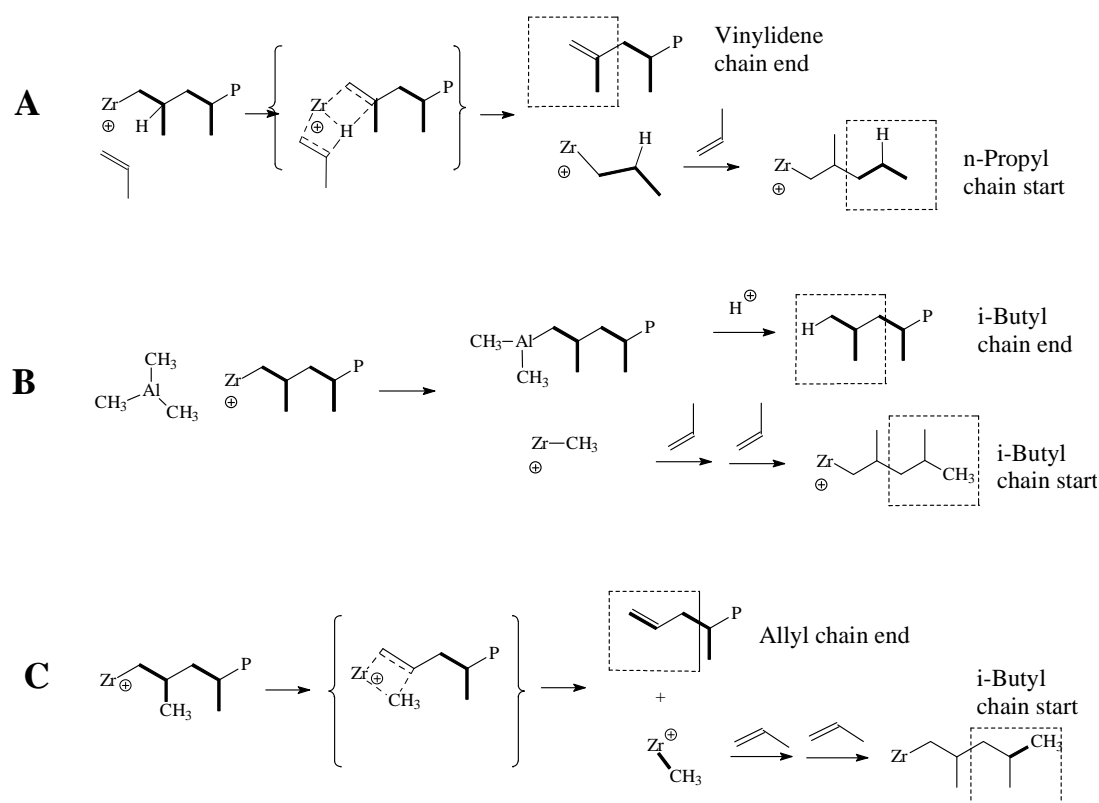
### 3.1.2 Copolymerization of propylene and 7-octenyldimethylphenylsilane

As seen from the results above, no particular influence of phenylsilane monomer in metallocene/MAO catalysed polymerization was observed when the copolymerizations were performed with ethylene.[I] To extend this study, the 7-octenyl Si(CH<sub>3</sub>)<sub>2</sub>Ph was copolymerized with propylene [V], where the more complex structure of the polypropylene allowed detecting with greater sensitivity a possible influence of the used phenylsilane monomer. In this study the polymerization performance of 7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph was compared with that of 1-dodecene, and the results are presented in Table 2.[V]

Table 2 The metallocene/MAO catalysed propylene/7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph copolymerization results.[V]

Run	Propyl. in feed mM	Comon. in		Activity <sup>B</sup>	M <sub>w</sub> *10 <sup>-3</sup> g/mol	Regio + stereo defects		
		feed mM	polym. mol-%			2,1-ins. %	3,1-ins. %	mrrm %
PP 1	205	-	-	317 000	91	0.29	0.09	0.20
PP 2	205	7.1	0.66	160 000	91	0.28	0.08	0.17
PP 3	205	12.7	1.16	112 000	86	0.27	0.08	0.18
PP 4 <sup>A</sup>	205	11.8	1.01	90 000	85	0.29	0.07	0.16
PP 5	205	24.8	2.06	70 000	85	0.27	0.08	0.16
PP 6	410	12.6	0.56	223 000	160	0.33	0.04	0.11
PP 7 <sup>A</sup>	410	12.0	0.62	264 000	155	0.30	0.06	0.11

Conditions: Catalyst (Me<sub>2</sub>Si(2-Me-4-Ph-Ind)<sub>2</sub>ZrCl<sub>2</sub>)=0.2 μmol, Al/Zr=2000, T=60 °C, stirrer speed 1000 rpm. A) 1-dodecene as comonomer, B) Activity as kg<sub>polymer</sub>/mol<sub>cat.</sub>\*P<sub>propylene</sub>\*h



Scheme 8 The characteristic chain heads formed after the dominating chain termination mechanisms in metallocene catalysed propylene polymerizations. A) Bimolecular  $\beta$ -hydrogen abstraction, B) chain transfer to aluminum and C)  $\beta$ -methyl abstraction.[19]

Both of these comonomers were found to decrease the catalyst activity as well to be incorporated in the polypropylene chain almost at the same level (Table 2, PP 3 vs. PP 4<sup>A</sup> and PP 6 vs. PP 7<sup>A</sup>). However, neither of them had any clear influence in the molar mass of the polymer (Table 2, PP 1 vs. PP 2 - PP 5). [V] This was due to the diminished tendency to bimolecular  $\beta$ -hydrogen abstraction (Scheme 8 A) in  $\text{Me}_2\text{Si}(\text{Me-2-Ph-4-Ind})_2\text{ZrCl}_2/\text{MAO}$  catalysed polymerizations [19,60], where after the dominating termination mechanism was found to be the chain transfer to aluminum (Scheme 8 B) [V]. The presence of chain transfer to aluminum was defined by  $^{13}\text{C}$  NMR-spectra (Figure 3) as the characteristic resonances of *i*-butyl chain heads were clearly visible and the resonances for allylic chain heads (e.g. Figure 3, C3 in 41.4 ppm.; due to  $\beta$ -methyl abstraction, Scheme 8 C) were not found at all. This observation correlated well with the results that the molar masses were influenced by the propylene concentration in the feed (Table 2, PP 3 and PP 4<sup>A</sup> vs. PP 6 and PP 7<sup>A</sup>). [V]

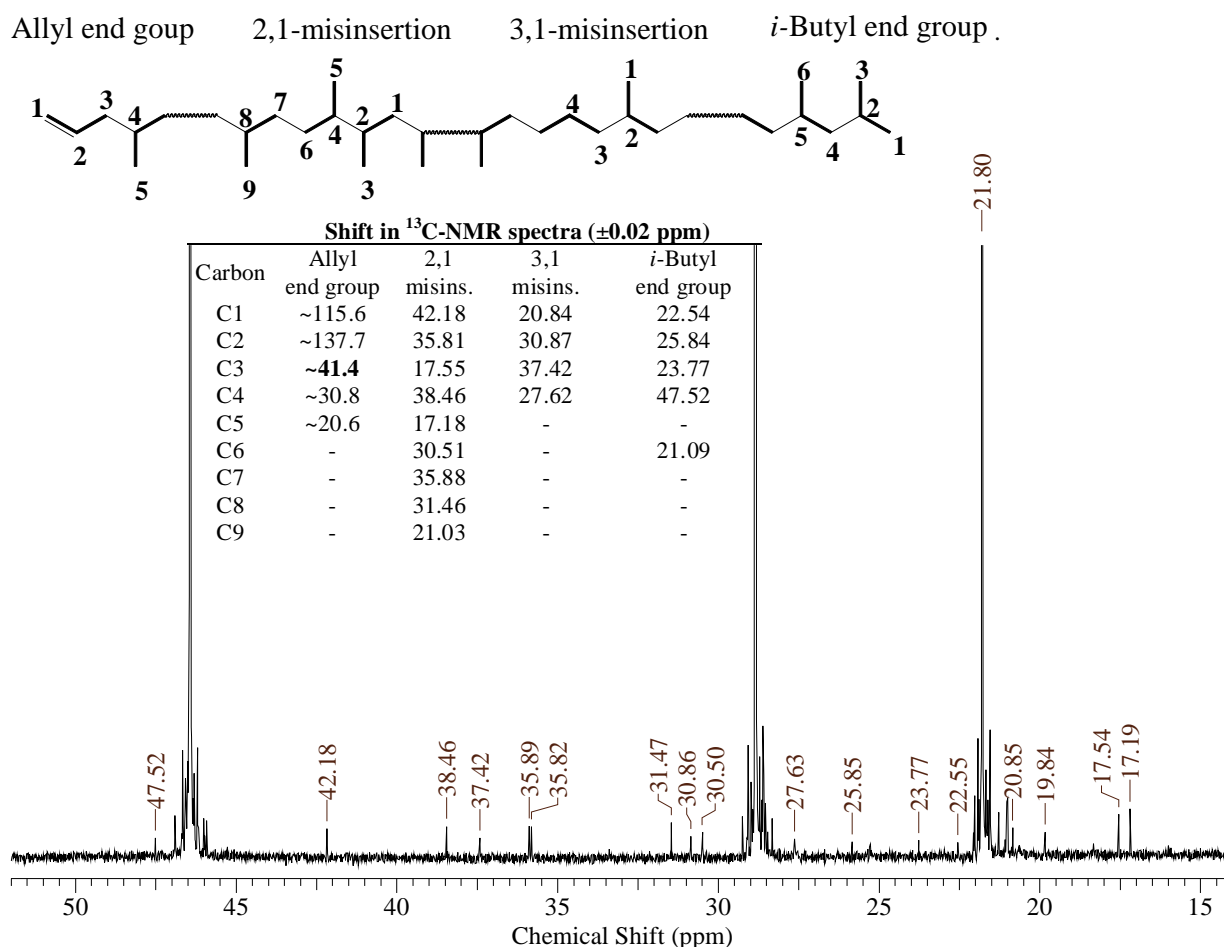


Figure 3 The microstructure of polypropylene determined by  $^{13}\text{C}$ -NMR (Table 2, PP1). [V]

The presence of  $\beta$ -methyl and  $\beta$ -hydrogen abstractions (Scheme 8 A and C) as chain termination mechanisms were later confirmed as the resonances of allyl and vinylidene chain heads were observed in more sensitive  $^1\text{H-NMR}$  spectra (Figure 4). Obviously, all of these termination mechanisms were present in these homo- and copolymerizations, but any kind of influence caused by some of these comonomers were not detected [V]. Additionally to these terminal unsaturations, evidence of the internal vinylidene groups was also found (Figure 4, resonances at 4.86 ppm. and 4.87 ppm.). According to Resconi *et al.* [19], these were formed via allylic activation mechanism after primary inserted propylene.

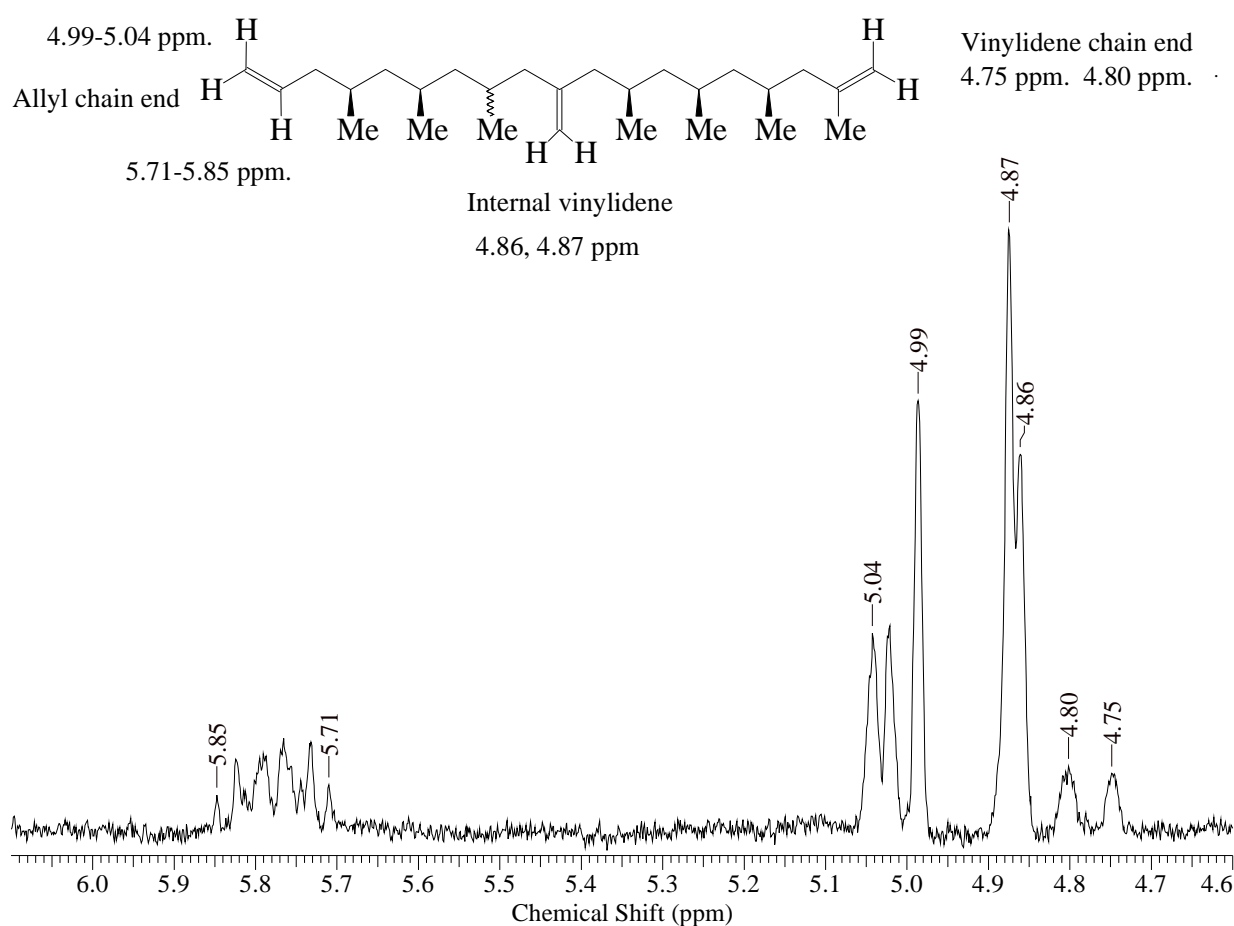
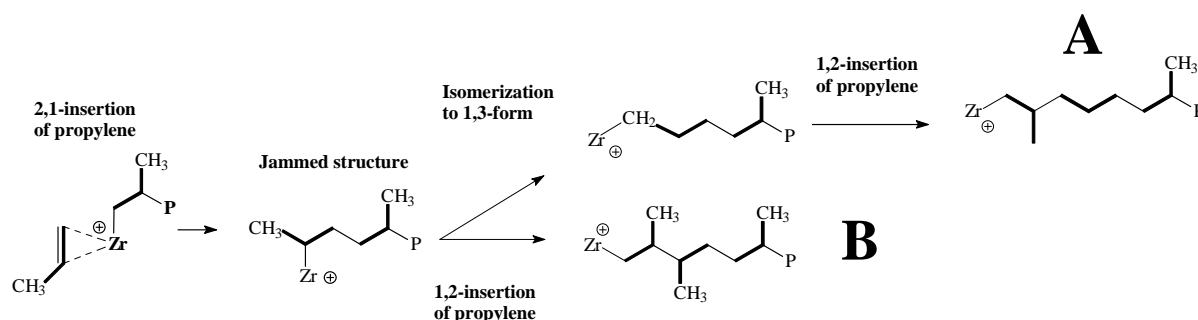


Figure 4 Unsaturated area in  $^1\text{H-NMR}$  spectra of homopolypropylene (Table 2 PP 1). Spectra was run in  $d_8$ -toluene at  $90^\circ\text{C}$ . Data based on V

Finally, the regio and stereo defects in the polymers were detected from the  $^{13}\text{C-NMR}$  spectra, but the slight variations were not resulted from the used comonomer. The total amount of regio defects was around 0.3-0.4 % and the ratio of them (3,1 vs. 2.1) was slightly affected by the

propylene concentration (Table 2, PP 3 vs. PP 6).[V] This can be expected as the 3,1-misinsertion is formed from isomerisation of the 2,1-inserted propylene monomer (Scheme 9 A), and reducing the time for isomerisation (by increasing the propylene concentration in the polymerization reaction) would reduce the degree of 3,1-misinsertion [19].



Scheme 9 The formation of A) 3,1- and B) 2,1-regio defects in polypropylene chain.[19]

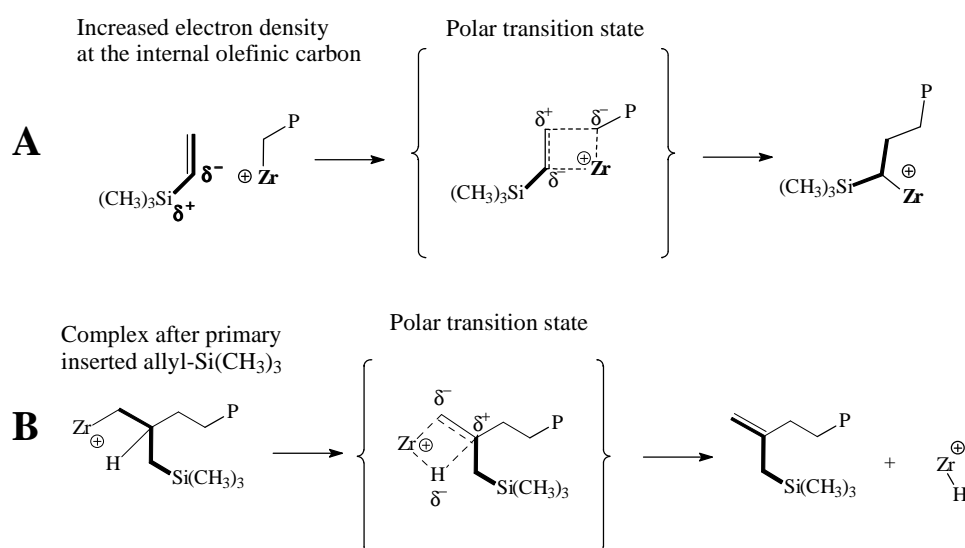
In summary, no influence of phenylsilane was found, as the formed microstructure of the polypropylene (regiospecificity, stereospecificity, chain termination etc.) was independent from the used comonomer (7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph vs. 1-dodecene). It appears that neither the silicon nor the phenyl ring have any influence, good or bad, on the metallocene/MAO catalyst system.[V]

### 3.1.3 Short silane monomers in the metallocene catalysed polymerization

When the weakly interacting (i.e. Lewis acid) monomer contains a heteroatom in the vicinity of the double bond, its behavior at the metallocene cation is altered largely. This was clearly seen in the studies of Guram *et al.* [61,62] where the vinyl-Si(CH<sub>3</sub>)<sub>3</sub> was found to co-ordinate with the cationic metallocene strongly via secondary 2,1-insertion mechanism. This was mainly due to the electropositive nature of silicon, which drives the electron density at the internal olefinic carbon and therefore favors the 2,1-insertion (Scheme 10 A).[61,62]

Contrary to vinyl-Si(CH<sub>3</sub>)<sub>3</sub>, allyl-Si(CH<sub>3</sub>)<sub>3</sub> was found to co-ordinate with metallocene catalyst via the normal primary 1,2-insertion mechanism [61] and several authors have homo- [63,64] and copolymerized [12,65,66] allylsilanes with ethylene by metallocene catalyst. Even though the propagation of allylsilane monomers were rather good they were also sensitive to chain

termination via  $\beta$ -hydrogen abstraction (Scheme 10 B) resulting in low molar mass polymers with allylic silane group in the chain end [65]. This peculiar behavior of allylsilanes (and vinylsilanes) was rationalized on the basis of polar transition state (Scheme 10) which, in this case, was stabilized by the  $\beta$ -effect of silicon [49], and therefore the  $\beta$ -hydrogen abstraction was promoted.[62,65,67,68]



Scheme 10 Polar transition states in the insertion and termination mechanism of short silane monomers, based on [62,65,67,68]

Table 3 The copolymerization results of ethylene and short silane monomers.[13]

Run	Comonomer	in feed mol/mol <sub>ethylene</sub>	in polym mol-%	Activity kg/mol*P*h	M <sub>w</sub> kg/mol	PD
1	-	-	-	10000	450	3.7
2	Vinyl-Si(CH <sub>3</sub> ) <sub>3</sub>	0.25	0.3	4400	<b>92</b>	2.1
3	Vinyl-Si(CH <sub>3</sub> ) <sub>3</sub>	0.50	0.5	2600	<b>63</b>	2.1
4	Vinyl-Si(CH <sub>3</sub> ) <sub>3</sub>	1.0	0.7	1300	<b>39</b>	2.0
5	Allyl-Si(CH <sub>3</sub> ) <sub>3</sub>	0.25	1.4	6100	<b>48</b>	2.0
6	Allyl-Si(CH <sub>3</sub> ) <sub>3</sub>	0.50	2.3	5300	<b>38</b>	2.0
7	Allyl-Si(CH <sub>3</sub> ) <sub>3</sub>	1.0	3.7	1900	<b>25</b>	2.0

Cond. Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> = 1  $\mu$ mol; Al/Zr=2000; P=0.7 bar; T =40 °C; time=25 min.; toluene 300 ml, speed 600 rpm.

In our studies [13] these abovementioned behaviors of short silane monomers were clearly seen (table 3). When ethylene was copolymerized with vinyl-Si(CH<sub>3</sub>)<sub>3</sub> using Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst, the influence of the 2,1-insertion in the polymerization performance was seen in

extremely weak monomer uptake, low molar mass and decreased catalyst activity (Table 3, run 1 vs. 2-4). The propagation of allyl-Si(CH<sub>3</sub>)<sub>3</sub> was clearly better (Table 3, run 5-7) but otherwise the allylsilane acted as chain transfer agent resulting also in low molar mass copolymers.[13]

As an extension to the allylic silane groups in the chain end, a clear indication of internal vinylene unsaturation (Figure 5 A, triplet at 5.19 ppm., J=7.5 Hz; [41]) was found in our polyethylene-co-allyl-Si(CH<sub>3</sub>)<sub>3</sub> synthesized with Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO.[13] Mechanistically this unsaturation can be explained by the allylic activation taking place after the chain termination of primary inserted allyl-Si(CH<sub>3</sub>)<sub>3</sub>. In addition, both of these unsaturations were in allylic position of silicon and were therefore sensitive to electrophilic substitution [49]. This was seen when the normal acidic work-up procedure (after the polymerization step) was extended over night where after most of the allylic silane groups were leached (Figure 5 B). This reactivity may open up new possibilities to use these copolymers as functionalized polyolefins.[13]

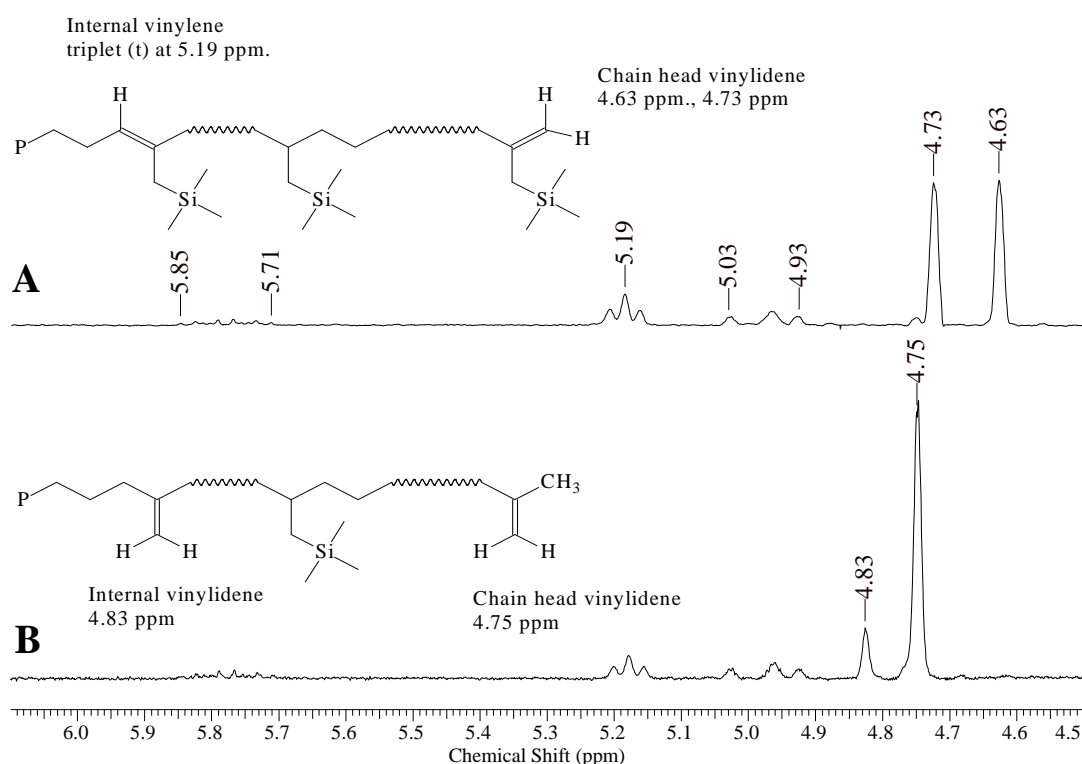


Figure 5 Unsaturated area in <sup>1</sup>H-NMR spectra of polyethylene-co-allyl-Si(CH<sub>3</sub>)<sub>3</sub> (Table 3, Run 6) after 2h in acidic ethanol (normal work-up) A), and after 24 h in acidic ethanol B). Sample run in d<sub>8</sub>-toluene at 90 °C. Data based on [13].



### 3.2 Highly reactive polyolefins via metallocene catalysis

If the functional polyolefin requires stronger reactivity than the Lewis acidic group can provide, the functionalization should be performed with Lewis basic groups. There have been numerous studies where ethylene or propylene is copolymerized with oxygen [69-76] or nitrogen [72,74,77] containing functional monomer using metallocene catalyst. However, the direct copolymerization of Lewis basics is limited by the complex formation between the cationic metal and the free electrons of oxygen or nitrogen. Therefore the results have been often compromises between high functionality content, polymerization activity and molar mass.

The situation is even more complicated if Lewis basic silicon containing monomer are used in metallocene catalysed polymerizations. In addition to the abovementioned cation/free electron complex formation, the high reactivity of these silane groups results in multiple other side reactions, especially when the polymerization is stopped by precipitating in acidic solvent (HCl+Alcohol+some H<sub>2</sub>O as well). This is most likely the reason for the rare reports [73,78,79] found in the current literature concerning the copolymerization of ethylene (or propylene) with monomers containing Si-X (X=O, N, halogen) groups. In the studies of Hakala [73] and Dong [79] the role of the alkylsilane moiety was shielding, and it was actually removed during the acidic work-up.

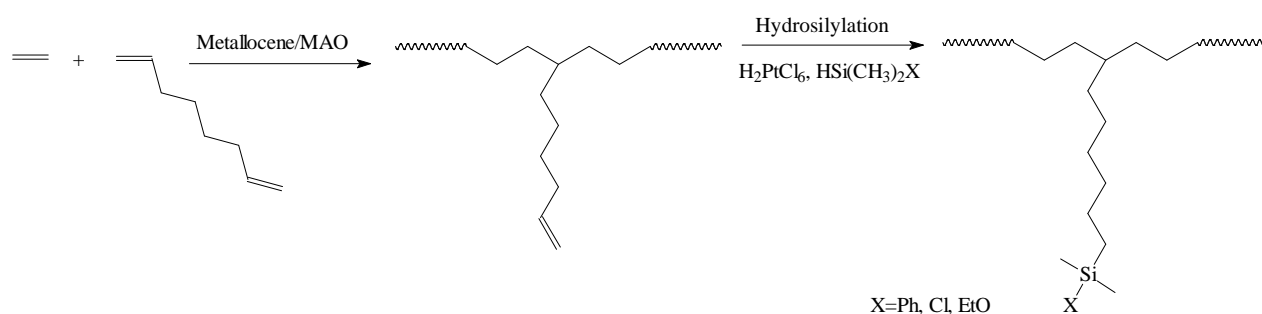
### 3.3 Highly reactive polyolefins via post treatment approach

Because the direct polymerization of Lewis basic monomers is difficult, the functionalization of polyolefins can be performed in two steps. In the first step the olefin (ethylene or propylene) is copolymerized with a suitable long monomer with a weakly reactive group in the other end of the chain. The copolymerization reaction proceeds without catalyst poisoning and a copolymer with high molar mass and high content of pendant reactive groups can be formed. In the second step, these weakly reactive groups are post treated to form a highly reactive pendant group in the polyolefin chain.[12]

The post treatable polyolefins are usually synthesized via the copolymerization of olefins with methylstyrenes [80-83], dienes [45,84-88,**IV**], olefinic boranes [45,47] or olefinic phenylsilanes [**I,II,V**]. Metallocenes are known to tolerate these groups and they are known to be ready for many chemical reactions. When hydrolysable silane functionalities are wanted as the pendant functionality in the polyolefin, the most efficient way is to use polyolefins with pendant double bond [89,**IV**] or phenylsilane moiety [**I,II,V**]. There are some limitations in the polymerization of symmetric dienes (1,5 hexadiene, 1,7-octadiene) as both of the double bonds are alike to react in the polymerization and side reactions are often present. The formation of a suitable polyolefin copolymer with free double bonds (without ring formation or crosslinking) can be achieved with an advanced catalyst and process control [85-87,**IV**].

### 3.3.1 Post treatment of polyethylene-co-1,7-octadiene

The hydrosilylation reaction is a suitable tool for incorporating a wide variety of different kinds of silane functionalities in carbon-carbon double bonds.[89,90] This feature was now utilized to incorporate these groups in polyethylene chain. The hydrosilylation was successfully carried out when dimethylethoxysilane, chlorodimethylsilane, and phenyldimethylsilane were reacted with polyethylene-co-1,7-octadiene (Scheme 11).[**IV**]



Scheme 11 Functionalization of polyethylene-co-1,7-octadiene via hydrosilylation.[**IV**]

As a slight drawback, clear increases in chain extension/cross linking of post treated polymers were observed which were partly due to the moisture sensitivity of chloro- and alcoxysilane. This chain extension can not solely be explained by increased cross linking via siloxane bonds because it was present also with moisture tolerable phenyldimethylsilane groups (figure 6).[**IV**]

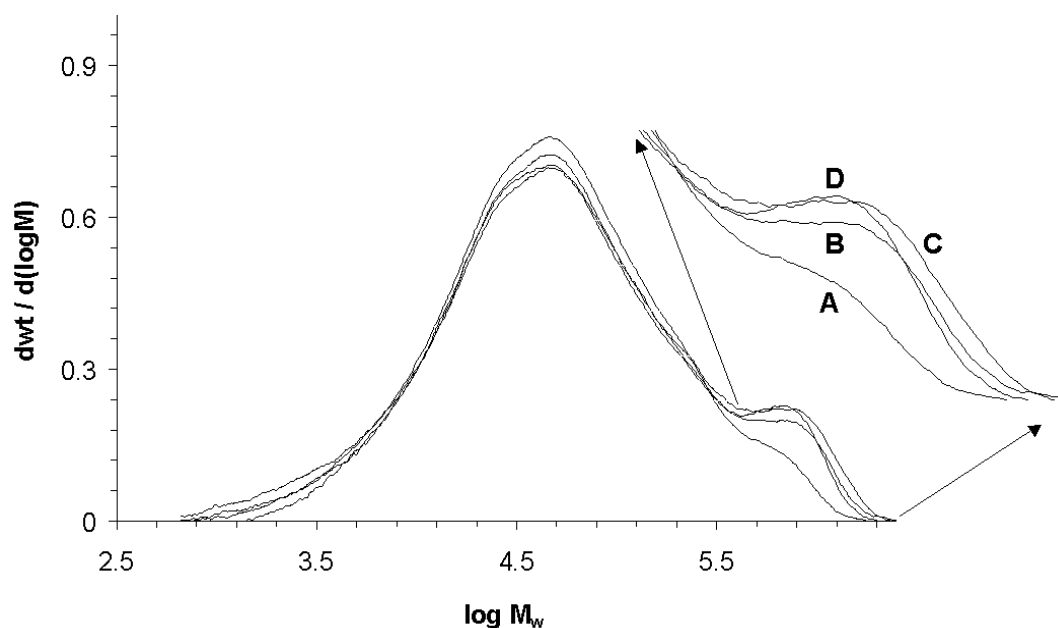


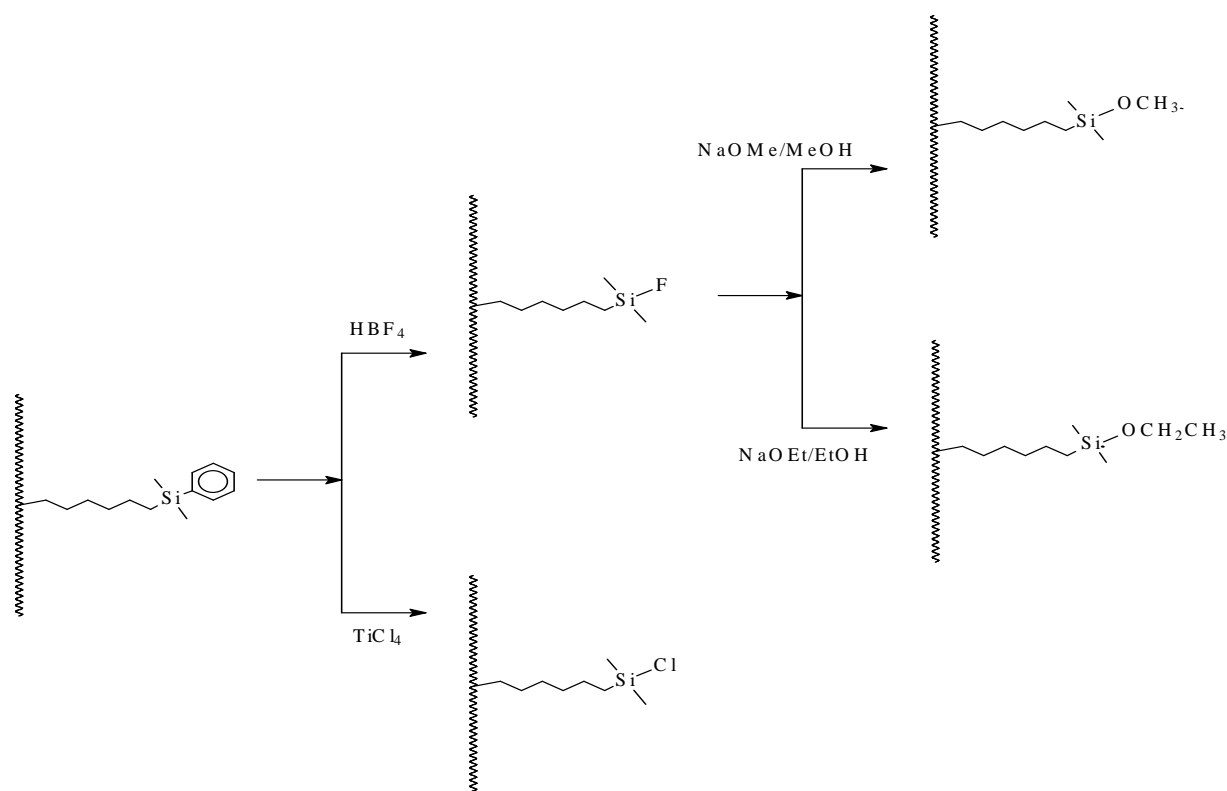
Figure 6 The molar mass curve of the untreated PE-co-1,7-octadiene (A) and the curves after hydrosilylation to PE-co-SiPh (B), PE-co-SiOEt (C) and PE-co-SiCl (D).[IV]

### 3.3.2 Post treatment of pendant phenylsilane in polyolefin

One of our goals was to study the possibilities to post treat the synthesized polyolefin-co-7-octenyl-Si(CH<sub>3</sub>)<sub>2</sub>Ph and, indeed, new alternative routes for different functionalities were developed (Scheme 12). The formation of fluorosilane groups in pendant polyolefin chains with the help of HBF<sub>4</sub> was a simple and quick reaction resulting in nearby 100 % conversion. The only problem was that the HBF<sub>4</sub> may also react with the glassy reaction vessel which may result in some residues in the polymer. Contrary to the synthesis of fluorosilanes, the formation of chlorosilane pendant groups in polyethylene chain with the help of TiCl<sub>4</sub> was rather sluggish and to obtain conversions above 90 %, reaction times over 40 h at elevated temperature was required. These long reaction times resulted in slight degradation of the polyethylene and therefore these post treatments were often shortened at the cost of conversion.[II,V]

It was not possible to synthesize alcoxysilanes directly from the phenylsilane but it was easily done by reacting the pendant fluorosilane moiety with the desired alcohol (Scheme 12). The

equilibrium of the reaction was still strongly on the left side and therefore the alcohol corresponding sodium alcoxide was required to drive the equilibrium to the right. This is how the conversion of alcoxilation was increased to nearly 100 %.[II]



Scheme 12 The reaction pathway for different silane functionalities in polyolefin pendant side chains. Data based on II and V

Even though these silane functionalities were moisture sensitive and the reactions were performed at elevated temperature and even without antioxidant in the case of polypropylene, the damages on the post treated polymers were minor. The long reaction time needed for the formation of chlorosilane, resulted in slight degradation of the polyethylene chain, whereas the alcoxilation with wet ethanol (1300 ppm. of  $\text{H}_2\text{O}$  in EtOH) resulted in minor cross-linking of the polymer.[II,V]

#### 4 POLYOLEFIN COMPOSITES

The advantages of polyolefines are unquestioned and they are one of the commercially most important filled polymers. The market for filled polyolefin grades will grow fast and these composites are widely used in many fields of applications. With proper filler choice properties of the composites such as the stiffness, toughness, the dielectric loss, heat resistance etc. can be influenced.[2,5,6,7]

The fillers used in polyolefin composites are usually inorganic materials with polar hydrophilic surfaces. These particles are attracting each other by van der Waals forces and mechanical energy is required to break the filler aggregates. To hinder the filler reagglomeration during the melt blending the polymer phase should have high affinity for the filler surface. This complicates the compounding in the case of hydrophobic non-polar polyolefins, especially when high filler loadings or submicron size fillers are used. If any form of aggregates remains in the polymer matrix, they can act as flaws (crack) resulting in a drastic decrease in toughness of the composite. In addition, most of the fillers are less than optimally bonded with the non-polar polyolefin matrix. Still, the strong adhesion strength between these phases is usually required to ensure adequate mechanical properties of the composites.[7,9,91]

Normally, the filler/matrix adhesion strength increases when functional polyolefin is blended in the composite. The long polymer chain entangles with the host matrix while the functional group reacts with the hydroxyl groups on filler surface. The type of the formed filler/matrix bond depends strongly on the type of the functional group in the compatibilizer. E.g. the acids, esters or alcohols form weak acid-base, dipole-dipole, or hydrogen bonds, whereas strong covalent bonds can be formed in the reaction with the hydrolysable halo- or alcoxysilanes [92-95].

In this research, we focused on different kind of particulate filled polyolefin composites where a small amount of functionalized polyolefins were used as compatibilizer. The aim was to study their influence on composites properties by increasing the filler/matrix adhesion strength in polyolefin/filler composites [III,V]. On the other hand, in ternary PP/rubber/filler

composites [IV] the compatibilizers were used to change the morphology of the composite. When functional PP was blended in this composite the fillers favored the PP matrix where as the addition of functional PE resulted in filler encapsulation in the rubbery phase [IV].

When the functional polyolefins were blended in the particulate filled polyolefin composites a wide range of the properties of the composites were altered. In addition to the mechanical properties (yield strength, toughness), also the weak dispersion forces appearing at the filler/matrix boundary layer were influenced. The scale of the influence was varied by the strength of the filler/matrix interaction, normally defined by the functional group in the compatibilizer, as well by the crystallinity/stiffness of the compatibilizer.[III-V] Therefore, the individual properties of the used functional polyolefins are gathered in the table 4, and they will be referred later in the text as their code (Com-1 to Com-7).

Table 4 The properties of the selected functional polyolefins used in this study (X=Cl, F, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub>.[14,III-IV])

Origin	Code	Study	Functionality	mol-%	$\Delta H$ (J/g)
Commercial	Com-1	III	PE-co-BA	1.5	<b>75</b>
Metallocene	Com-2	III	PE-co-SiX	0.15	<b>150</b>
Metallocene	Com-3	Continuation for III	PE-co-SiF	0.64	<b>135</b>
Metallocene	Com-4	Continuation for III	PE-co-SiF	0.15	<b>60</b>
Commercial	Com-5	IV	PE-co-GMA	1.6	<b>80</b>
Metallocene	Com-6	IV, 14	PE-co-SiF	1.0	<b>125</b>
Metallocene	Com-7	14	PE-co-SiPh	1.0	<b>123</b>

#### 4.1 Weak filler/matrix interactions in polyolefin composites

Despite the lack of reactive groups in polyolefin matrix, hydrophilic fillers have a strong ability to interact with the melted polyolefin and influence its crystallization during cooling. The results of this interaction can be seen in the form of nucleation phenomenon as well as in the formation of polymeric interphase between the filler and the matrix. This ability of controlling the crystallization of the polymer segments is a consequence of the free surface energy of the filler. If the surface energy of the filler is reduced e.g. by coating, the intensities of these effects are clearly decreased.[7,9,96,97]

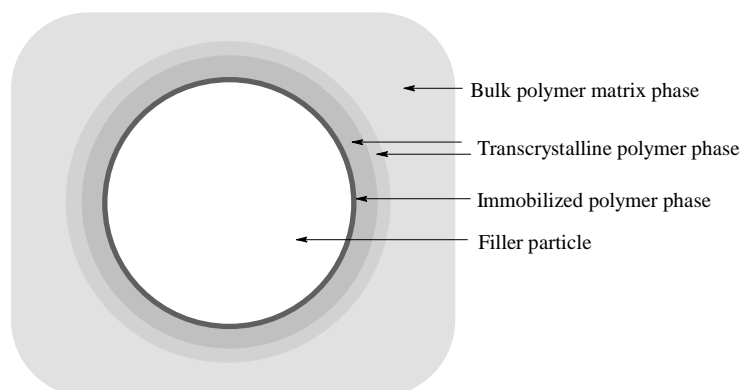
#### 4.1.1 Nucleation effect of fillers

Polyolefins tend to super cool before crystallization and therefore they are very prone to the nucleating agents which have an ability to organize molecules to a conformation that facilitates rapid crystallization. In polyolefin composites several fillers have been found to act as nucleating agents, and especially in particulate filled polypropylene composites the nucleation phenomenon can be seen in faster crystallization rate and smaller spherulite size.[7,9,96] In addition, when functional PP's were blended in these composites, the filler matrix interaction was enhanced and the crystallization rate was increased even more due to the stronger nucleation effect [98,99,IV,V].

The nucleation effect of the fillers in PE-based composites is not very clear and can be observed more clearly in HDPE than in LDPE matrix.[96] That was also seen in **III** where the nucleation of the ATH filler resulted merely in widening the crystallization temperature area of the LDPE matrix. In these composites the influence of the filler was seen more clearly in the formation of the interphase at the filler/matrix boundary layer [**III**].

#### 4.1.2 Filler/matrix interphase formation

The polymeric interphase formed at filler/matrix boundary layer consists of two specified phases, called immobilized phase and transcrystalline phase (Scheme 13). The immobilized phase is formed when the van der Waals dispersion forces of the filler surface drive the polymer segments to organize in very compact form (immobilized phase). The dispersion forces are strong only in the vicinity of the filler surface and therefore the immobilized phase is very thin (1-50 nm). Beyond this phase the dispersion forces weaken rapidly but they can still orientate the polymer chains to form a transcrystalline phase. The range of this phase is reported to reach up to 150 nm, but the actual border is undetermined as the transcrystalline phase changes little by little in the form of bulk phase.[7,9,100]



Scheme 13 The different phases existing in most of the polymer/filler composites

In most cases the influence of the interphase in the polymer composites has been overlooked because it becomes important only with high filler loading or nano sized filler particles. In addition, its observation with analytical methods is rather difficult because the thickness of the formed interphase is usually in the nanometer scale.[97] In PE/ATH composite [III] the interphase (or solely the immobilized phase) was, however, discovered by studying the DSC-curve more precisely beside the primary crystallization peak (Figure 7, inset). A secondary crystalline region,  $T_{C2}$ , was found which crystallized (and melted) at clearly higher temperature than the bulk matrix (Figure 7 C;  $T_{C2}$  at 125 °C vs.  $T_{C1}$  at 103 °C). To promote the correlation to the filler/matrix interphase, this secondary crystalline region was absent in unfilled PE or when stearic acid coated ATH (ATHSA) were used (Figure 7 A and B).[III]

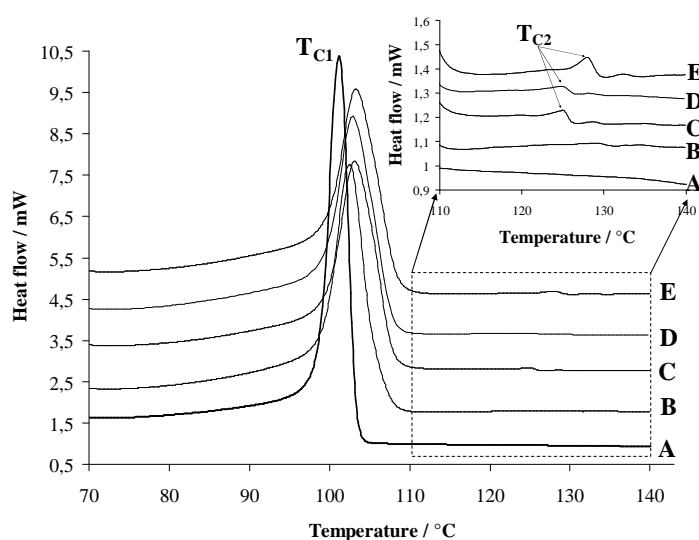


Figure 7 DSC-exotherms of the studied composites, A) PE, B) PE/ATHSA, C) PE/ATH, D) PE/ATH + 3.0 wt-% Com-1, and E) PE/ATH+ 0.5 wt-% Com-2.[III]



When different functional polyethylenes were used in these PE/ATH composites (to promote the filler/matrix interaction) their influence in the interphase was quite different. The soft commercial PE-co-**BA**, Com-1, resulted only in slight decrease in the intensity of this secondary crystallization peak (figure 7 C vs. D), whereas a clearer distinction was observed with highly crystalline PE-co-Si(CH<sub>3</sub>)<sub>2</sub>**X**, Com-2. In that case, the addition of 0.5 wt-% was enough to increase ~3-4 °C the crystallization temperature of the T<sub>C2</sub> (Figure 7 C vs. 7 E, inset).[III]

## 4.2 Mechanical properties of polyolefin composites

Fundamentally, the crucial factors determining the macro scale mechanical properties of the composites are the sum of micromechanical-energy-consuming deformation processes and the volumes of these deformations. The prediction of the mechanical properties of polyolefin composites is rather difficult because of the several micromechanical mechanisms that contribute in semicrystalline polymers. Especially, when reaching the yield point, i.e. the point where the elastic reversible deformations change to plastic irreversible deformation, is not so straightforward. Around the yield point there are several different deformation mechanisms that can take place, e.g. multiple crazing, shear yielding, particle debonding [101], or cavitation of amorphous phase [102-104]. In addition, the preferred deformation mechanism is influenced by the deformation rate [105], temperature, and the crystalline nature of the polymer matrix. Therefore, e.g. the overall toughness of polyolefins and their composites may be expressed in the brittle or the ductile manner depending on whether the deformation rate is below, or the temperature is above so-called brittle to ductile transition point (BDT).[106-108]

### 4.2.1 Tensile properties

The addition of rigid fillers into polyolefin matrix increases the stiffness and that increase is rather straightforward to estimate. The strength of interfacial adhesion between these faces should have no influence on the modulus, and the theoretical modulus of a composite can be calculated e.g. by extended Kerner equation [109] by knowing the characteristic moduli of the filler and the matrix as well the volume ratio between these phases.[7,110,IV]

The situation was, however, more complex in study **IV**, where the morphology of the ternary PP/rubber/filler composite was modified by reactive compatibilizers. When functional polypropylene (PP-g-COOH) was used, the modulus was increased indicating that the filler concentration in the PP phase was enhanced (Table 5, Run 4 vs. Run 5). On the contrary, the use of functional PE resulted in increased filler dispersion in the rubbery phase, and the modulus of the composite was finally lower than that of the unfilled h-PP (Table 5, Run 6 vs. Run 1). The decrease in the modulus of these rubber modified composites was unwanted, but the functional PE's were required to adjust the impact strengths of these composites. The decrease in stiffness was controllable to some extent by choosing the rigid metallocene based PE-co-SiF, Com-6, over the soft commercial PE-co-GMA, Com-5 (Table 5, Run 7 vs. Run 6, respectively). [IV]

Table 5 Tensile properties of h-PP/ $\mu$ Si composites.[IV]

Run	Composition	Modulus MPa	Yield	
			strain %	strength MPa
1	h-PP	770 $\pm$ 20	9.9 $\pm$ 0.2	25.6 $\pm$ 0.2
2	+10 wt-% $\mu$ Si	880 $\pm$ 20	7.3 $\pm$ 0.2	24.3 $\pm$ 0.3
3	+20 wt-% $\mu$ Si	1000 $\pm$ 30	5.5 $\pm$ 0.3	23.6 $\pm$ 0.2
4	+30 wt-% $\mu$ Si	1090 $\pm$ 30	4.6 $\pm$ 0.1	23.6 $\pm$ 0.2
5	h-PP/ $\mu$ Si (30 wt-%) + 2 wt-% PP-g-COOH	1140 $\pm$ 20	4.7 $\pm$ 0.1	23.8 $\pm$ 0.3
6	+ 2 wt-% PE-co-GMA, Com-5	710 $\pm$ 20	13.8 $\pm$ 0.4	24.9 $\pm$ 0.4
7	+ 2 wt-% PE-co-SiF, Com-6	960 $\pm$ 30	7.4 $\pm$ 0.1	24.2 $\pm$ 0.4

As mentioned previously, it is not so straightforward to estimate the strength of the plastic deformation (e.g. tensile stress at yield in **III**, yield strength in **IV**) in polyolefin composites. Normally the yield strength decreases in parallel with the filler content because the filler debonding is the dominating plastic deformation mechanism in most of the particulate filled composites.[97] This was seen also in our study **IV** even though the decrease was not so clear (table 5, Runs 1-4). However, the situation may also be vice versa, like in **III** where the tensile stress was clearly higher in PE/ATH composite than in the plane polyethylene (~19 MPa vs ~13 MPa, respectively). The particular reason for this in **III** was unclear, but the dominating plastic deformation mechanism was probably something else than the normal particle debonding (e.g. shear yielding, cavitation of amorphous phase). This hypothesis was supported

by the fact that the use of reactive compatibilizers in PE/ATH composites did not have any clear influence on the strength of the tensile stress at the yield [III].

#### **4.2.2 Toughness**

In general, the neat PE and PP are considered as tough and ductile materials at ambient temperature. The external impact energy is distributed over a wide area in the polyolefin phase where the stress is dissipated in different kind of plastic deformation mechanisms, dominantly via shear yielding in PE-phase and via multiple crazing in PP-phases. However, whenever the external energy is high enough to produce an actual crack in the polyolefin, the residual stress will concentrate at the crack-tip. If this stress at the crack-tip is not delocalized and dissipated e.g. by rubbery phase, the crack proceeds through the rest of polymer phase almost without resistance in a brittle manner.[106-108,111]

The addition of rigid fillers in polyolefin matrix often leads to unwanted decrease in toughness. Contrary to the unfilled polymer, the external impact energy in the composites is concentrated via the filler to the matrix nearby. The detrimental stress level is locally rapidly reached which results in early stage crack initiation. In addition, from the crack propagation point of view, the weak filler/matrix boundary layer offers an easy way for the crack to proceed in the composite (i.e. particle debonding, adhesion failure).[5-7,107]

##### **4.2.2.1 Compatibilizer in polyethylene composites**

The major deformation mechanism in particulate filled polyethylene based composites is the debonding of the fillers which results in brittle fracture of the composite. This becomes problematic especially in composites with high filler loadings. The most convenient way of reducing the filler debonding, and increasing the toughness was obtained by using functional polyethylenes as compatibilizers in these composites. With increasing amount of functional PE a steady increase of toughness was achieved, until a kind of maximum toughness value, a plateau region, was reached.[112-114]

In parallel with the normal mechanical testing, Hippi *et al.* [114] studied also the fracture surfaces of the cryo fractured PE/Filler composite samples. These results clearly indicated that with increasing amount of functional PE in the composite, the pure adhesion failure mechanism (particle debonding) of the plane PE/Filler composite gradually changed to total cohesion failure. This total change in the failure mechanism explained also the observed maximum toughness obtained for these composites.[114]

Similar results was obtained in our study [III] where 3 wt-% of commercial grade PE-co-BA (Com-1) in PE/ATH composite was sufficient to obtain the maximum toughness (Figure 8). In addition, the observed fracture surfaces revealed the mechanism suggested by Hippi *et al.*[114]. The adhesion failure of PE/ATH composite was obtained as the loosely bonded particles detached from the matrix and remained visible (Figure 9 A), whereas in the cohesion failure the fracture surface was clearly smoother (Figure 9 B) due to the strong particle/matrix adhesion strength.[III]

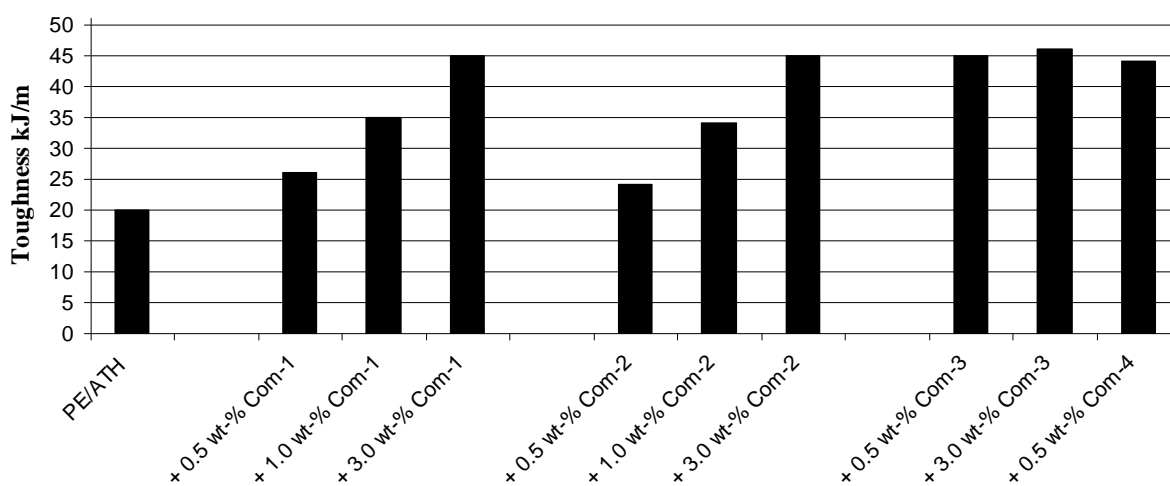


Figure 8 The toughness of the PE/ATH composites. Data based on III + some additional data

In parallel with PE-co-BA, the metallocene based PE-co-SiX (Com-2, X=Cl, F, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub>,) resulted in comparable toughening results (Figure 8). However, in this case the deformation mechanism of the cryo fractured samples did not match with the mechanism obtained in PE-co-BA toughened composites (Figures 9 C vs. B). In addition, some kind of droplet formation at the matrix phase was dominating (Figure 9 D) which we were not able to explain.[III]

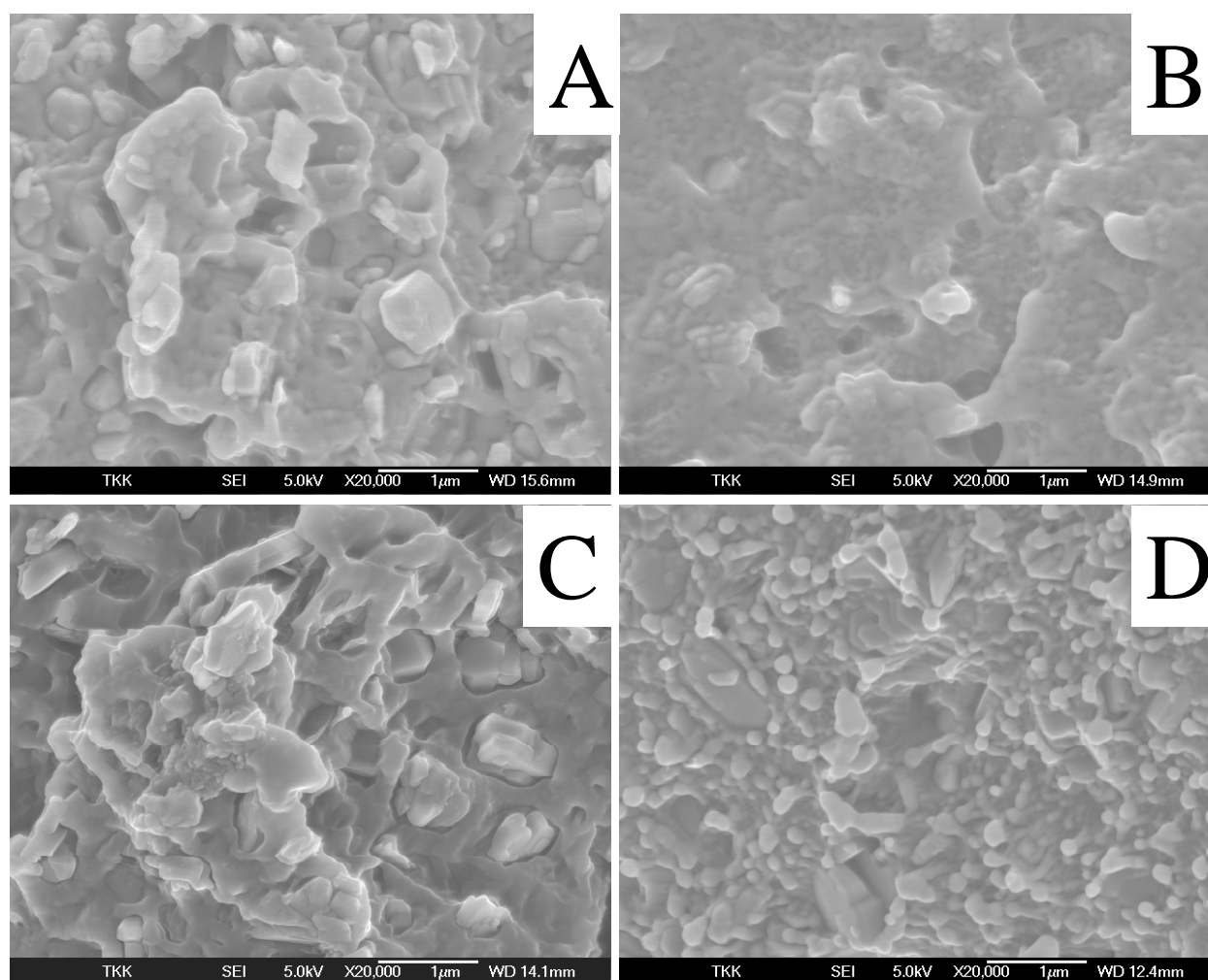


Figure 9 The SEM-micrographs of cryo fracture surfaces of A) PE/ATH, B) PE/ATH + 1 wt-% Com-1, C) PE/ATH + 1 wt-% Com-2, and D) PE/ATH + 3 wt-% Com-2. Data based on **III**

Slightly unexpectedly, the used compatibilizers (Com-1 vs. Com-2) resulted in parallel toughening effect despite the highly reactive halo- and alcoxysilane functionalized polyethylenes, Com-2, were expected to be more efficient. However, their outstanding coupling performance became clearer when their less crystalline grades, Com-3 and Com-4, were used. In these experiments the maximum toughness of PE/ATH composite was achieved already with the addition of 0.5 wt-% compatibilizer (Figure 8). The influence of the compatibilizers has been often studied from the functionality point of view (OH vs. COOH vs. MAH etc.) but, as now clearly seen, the crystalline nature (soft vs. rigid) of the functional polyethylene played also a major role.

#### 4.2.2.2 Compatibilizer in heterophasic polypropylene composites

The mechanical property profile of polypropylene is relatively close to that of some engineering thermoplastics, but its usefulness is limited by poor notch toughness and decreased impact strength at low temperatures. The most convenient way to increase the brittle toughness of polypropylene is to blend in rubber particles. They are able to induce multiple crazing and/or shear yielding at the surrounding PP phase as well increase the crack-tip dissipation. The increase in toughness is, however, performed at the cost of stiffness and therefore filler particles are often added together with the rubber modification.[107,108,115]

As the fillers usually bring brittleness to the composite, the methods to increase stiffness and toughness simultaneously have generated much interest. The prediction of the toughness of these ternary PP/elastomer/filler composites is difficult because their phase structure can vary widely. The fillers may be dispersed separately in the matrix, or the filler particles can be embedded in the elastomeric phase (i.e. encapsulation, core-shell structure). In practice, the phase structure lies somewhere between these two morphologies as the filler dispersion is primarily affected by thermodynamics. Therefore a separated structure is obtained only when one of the polymeric phases in the composite contains some functionality. However, it is unclear whether one of these morphologies is preferred in the sense of toughness as the results have, indeed, been contradictory.[110,116-123]

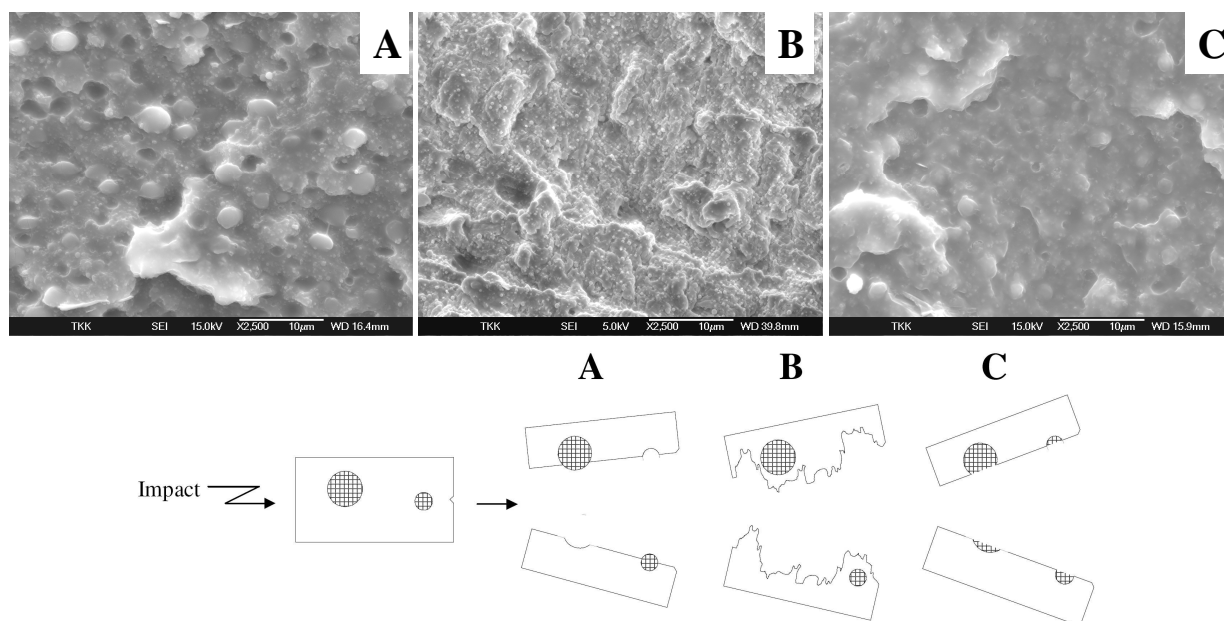
One of the reasons for these contradictory results was that in some cases [110,121,123] the fillers acted as toughening agents in the composite. The same was seen in our study [IV] where microsilica filler was compounded with heterophasic polypropylene (h-PP, i.e. reactor grade of rubber modified PP) and a clear increase in toughness was obtained (Table 6, run 1 vs. 2). Whereas the unfilled h-PP fractured in a brittle manner (Scheme 14 A), the plane h-PP/ $\mu$ Si composites fractured in a ductile manner (Scheme 14 B). Unfortunately, this filler toughening was not present at lower temperatures and the unmodified h-PP/ $\mu$ Si composites fractured in the brittle manner at -20 °C. The filler toughening was also absent at ambient temperature if even a small amount of any functionalized PP or PE (Table 6, Run 2 vs. runs 3, 4, and 7) was used as

a compatibilizer in these composite. The fracture mechanism of these modified composites was the same brittle mechanism observed for the unfilled composite.[IV]

Table 6 Charpy impact strengths of h-PP and h-PP/ $\mu$ Si composites with and without compatibilizer. The strengths of composites injection molded at of 80 °C rather than the normal 40 °C are presented in parenthesis.[IV]

Run	Composition	Impact strength (kJ/m <sup>2</sup> )	
		at 25 °C	at -20 °C
1	h-PP	11.6 ± 1.6 (11.7 ± 0.8)	6.0 ± 0.4 (5.9 ± 1.0)
2	+ 30 wt-% $\mu$ Si	38.4 ± 4.1 (15.6 ± 3.4)	4.6 ± 0.2 (4.6 ± 0.8)
3	h-PP/ $\mu$ Si (30 wt-%) + 2 wt-% PP-g-COOH	10.0 ± 1.1	2.8 ± 0.1
4	+ 0.5 wt-% PE-co-GMA (Com-5)	10.7 ± 0.8	6.0 ± 0.5
5	+ 1 wt-% PE-co-GMA (Com-5)	15.2 ± 0.4	6.4 ± 0.4
6	+ 2 wt-% PE-co-GMA (Com-5)	20.6 ± 0.8	7.7 ± 0.6
7	+ 1 wt-% PE-co-SiF (Com-6)	10.1 ± 0.5	4.8 ± 0.2
8	+ 2 wt-% PE-co-SiF (Com-6)	17.8 ± 3.7	7.4 ± 0.7

When the concentration of functional PE in the h-PP/ $\mu$ Si composite was increased further (Table 6, Run 4 vs. Runs 5 and 6; Run 7 vs. Run 8) the toughness started to increase again. The explanation for this odd behavior was found when a third fracture mechanism, called semibrittle, was discovered. In this mechanism the crack was now able to penetrate to the tough rubbery phase as well (Scheme 14 C), as previously the crack exceeded via PP/rubbery boundary layer (brittle), or solely in PP matrix (ductile). This semibrittle fracture mechanism became possible when the filler encapsulation was increased enough. In the unmodified composite the filler distribution was quite equally distributed, but with the help of functional polyethylene the filler started to concentrate in the rubbery phase. The semibrittle mechanism of the modified h-PP/ $\mu$ Si composites was dominating also at below room temperature which resulted in slight increase in strengths at -20 °C (Table 6, Runs 6 and 8 vs. Run 2).[IV]



Scheme 14 The schematic presentation of crack propagation mechanisms, and the corresponding SEM-micrographs of the fracture surface, in brittle A), ductile B), and semibrittle C) fracture of microsilica filled h-PP. The fillers are removed for clarity. Data based on **IV**

#### 4.2.2.3 Filler toughening mechanism

As mentioned in the paragraph above, the recent studies [110,124-131] have shown that several fillers can act as toughening agents in the polyolefin matrixes. This phenomenon is studied widely and usually explained by two slightly different mechanisms, namely ‘critical ligament thickness’ and ‘particle debonding’. According to these hypotheses, the filler separation from the matrix is the crucial factor in both of the mechanisms. When the filler is debonded from the matrix, the debonding creates voids, and in some cases these voids can mimic a rubber toughening mechanism.[132-135] These mechanisms were supported by the observations where the increased filler/matrix adhesion strength hindered the filler debonding and thereby the filler toughening was vanished.[121,125,126,135]

Contrary results have also been reported where the filler toughening have been observed without any clear signs of the filler delamination/debonding [128,129,136]. That was also the case in **IV** where the microsilica fillers were observed to act as toughening agents in heterophasic polypropylene (Figure 10 A vs. B). As mentioned, this filler toughening mechanism was not stable, and the addition of functionalized PP or the functionalized PE



decreased the toughness drastically. In addition, the change in the mould temperature from 40 °C to 80 °C (table 6, Run 2) in the injection moulding of h-PP/ $\mu$ Si composite had the same detrimental influence on the toughness. These results together with the SEM-micrographs (Figure 10 A, no indication of filler debonding) suggested that the filler toughening mechanism is rather complicated and can not be explained solely by the filler debonding/cavitation from the matrix.[IV]

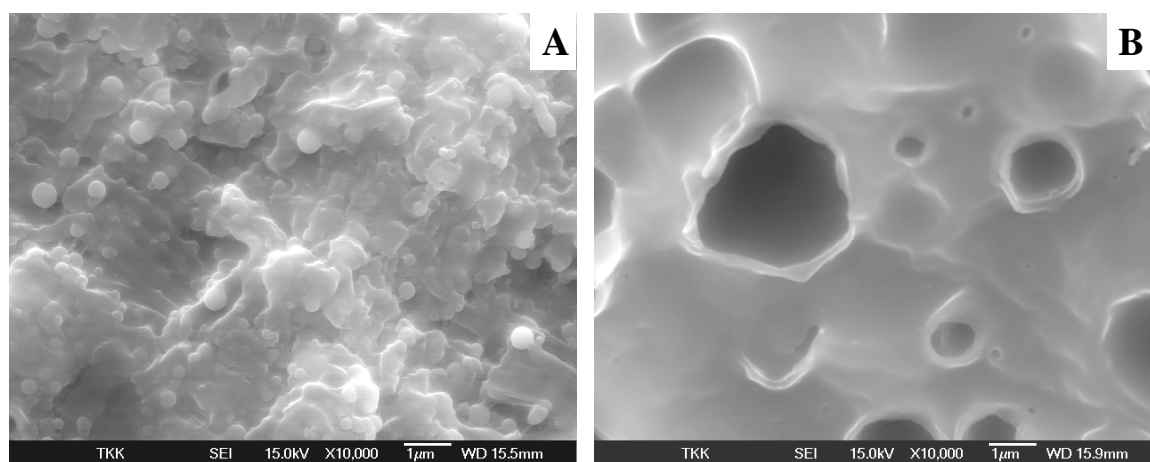


Figure 10 The SEM-micrographs of fracture surfaces of A) ductile h-PP/ $\mu$ Si and of B) brittle plane h-PP. The rubbery phase is leached by xylene. Data based on IV

### 4.3 The reactivity of phenylsilane functionality in particulate filled composites

The polyolefin composites are usually modified by compatibilizer that contains some Lewis basic reactive groups. However, in our study [V] we found that the molecular trimethylphenylsilane (Lewis acid) reacted with the microsilica filler as well, and the same reaction was exploited now in some polyolefin composites. When polypropylene with pendant phenylsilane groups (PP-co-SiPh) was used as compatibilizer in PP/ $\mu$ Si composite, an improved interaction between matrix and filler was created which lead to a stronger nucleation effect (Figure 11 A vs. B vs. C) [V].

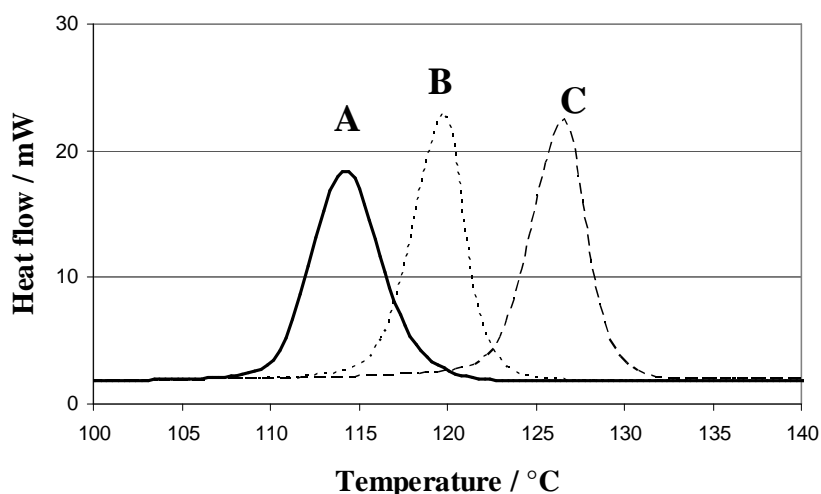


Figure 11 The DSC-cooling curves of **A)** PP, **B)** PP/ $\mu$ Si-composite (4 wt-% of  $\mu$ Si) and **C)** PP/ $\mu$ Si/PP-co-SiPh composite (4 wt-% of  $\mu$ Si and 0.4 wt-% of compatibilizer).[V]

Even though the phenylsilane functionality was found to react with the microsilica in PP based composites [V], the situation was slightly different in rubber toughened polypropylene [IV]. For some reason, the PE-co-SiPh had no influence on the mechanical properties of the h-PP/ $\mu$ Si composites, even though the influences of the other functional PE grades were obvious [IV]. When the phenylsilane functionalized compatibilizer was used in PE/ATH composite there were, indeed, some minor marks of influenced interaction at the filler/matrix boundary layer, but the toughness was not improved above the plane PE/ATH composite [III].

The influence of phenylsilane functionalized compatibilizer was further studied in microsilica filled polyolefin composites.[14] As an extension in the study V, the microsilica concentration was increased (from 4 wt-% to 30 wt-%), where after the influence of the functional polypropylene was seen in the mechanical properties as well. The influence of the commercial PP-g-COOH was minor (Table 7, Run 7 vs. Run 6), which was likely due to the acidic nature of the microsilica, but the phenylsilane, as well the fluorosilane functionalized polypropylenes (PP-co-SiPh and PP-co-SiF) were able to equally increase the yield and tensile values of the composites (Table 7, Runs 8 and 9 vs. Run 6). This was a clear indication of the formation of a stronger bond between the filler and the matrix, as the particle debonding was considered to be one of the plastic deformation mechanisms.[14]

Table 7 The tensile properties of PP/ $\mu$ Si composites modified by functional PP. [V,14]

Run	Composition	Modulus Mpa	Yield		Tensile	
			strain %	strength MPa	strain %	strength MPa
1 <sup>V</sup>	PP	860±30	12.8±0.3	29.1±0.2	>1500	~50
2 <sup>V</sup>	PP/ $\mu$ Si (4 wt-%)	930±30	11.7±0.3	30.0±0.3	-	-
3	PP/ $\mu$ Si (10 wt-%)	990±40	10.1±0.3	30.0±0.5	1140±20	~43
4	PP/ $\mu$ Si (15 wt-%)	1060±20	8.8±0.2	28.8±0.1	1030±30	~41
5	PP/ $\mu$ Si (20 wt-%)	1110±30	7.2±0.1	28.1±0.4	830±80	~30
6	PP/ $\mu$ Si (30 wt-%)	1260±30	5.2±0.1	28.1±0.1	500±110	~26
7	PP/ $\mu$ Si (30 wt-%) +3 wt-% PP-g-COOH	1220±40	5.6±0.1	28.2±0.1	420±120	~26
8	+1.5 wt-% PP-co-SiPh	1250±20	7.9±0.2	31.9±0.2	740 ± 30	~34
9	+1.5 wt-% PP-co-SiF	1240±10	8.2±0.1	32.3±0.3	750 ± 30	~35

Similar results were observed when microsilica was compounded with polyethylene. The toughness of PE/ $\mu$ Si composite was increased from 20 kJ/m<sup>2</sup> to 45 kJ/m<sup>2</sup> when the PE-co-SiPh (Com-7) or PE-co-SiF (Com-6) was used as compatibilizer (Figure 12).[14] This correlated well with the results of **III** where the toughness of particulate filled polyethylenes was improved by increasing the filler/matrix adhesion strength.

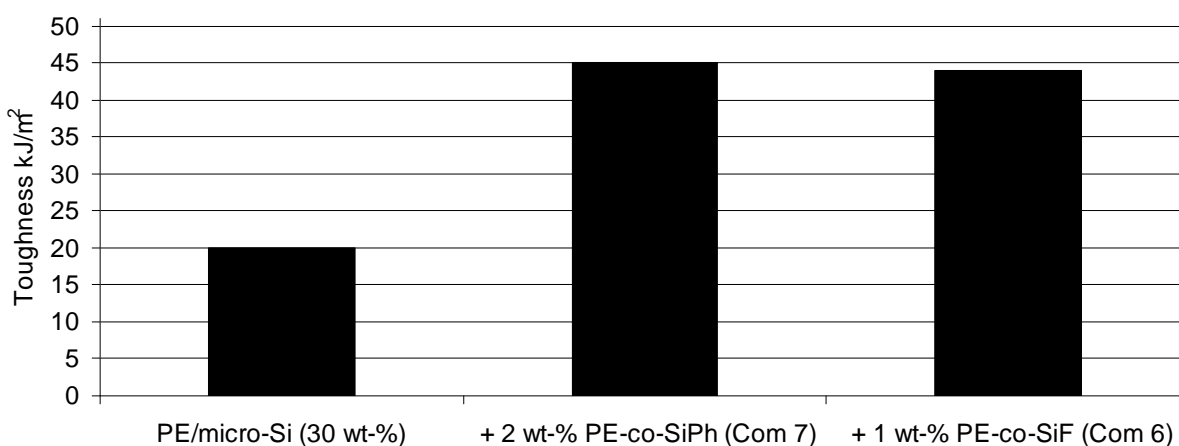


Figure 12 The Charpy toughness of the PE/ $\mu$ Si composites (notched samples).[14] The materials (PE, microsilica) correlate with the ones used in **III**, **IV**.

## 5 CONCLUSIONS

Polyolefins are relatively inert materials which limits some of their end usages, especially in the field of particulate filled polyolefin composites. Therefore, increasing the reactivity of polyolefins has long been an important research subject. A widely studied area has been the metallocene catalysed copolymerization of olefins with functional comonomers.

Despite the fact that the metallocenes tolerate Lewis acidic monomers, the electronic influence of the heteroatom can be seen as well. The  $\text{Et(Ind)}_2\text{ZrCl}_2/\text{MAO}$  catalysed copolymerization of short trialkylsilane monomers (vinyl- $\text{Si}(\text{CH}_3)_3$  and allyl- $\text{Si}(\text{CH}_3)_3$ ) suffered from electronic influence of silicon which resulted in poor polymerization performance, especially in the sense of molar mass. In these cases, however, the chain end of the synthesized polyethylene-co-allyl- $\text{Si}(\text{CH}_3)_3$  consisted of reactive allylic silane groups and therefore functionality/reactivity of these copolymers was higher than the weakly interacting trimethylsilane moiety can solely provide.

In addition to allylic silane chain ends, especially phenylsilane group in polyolefin pendant chain was found to be an effective group and offered new possibilities to functionalization. Therefore, the metallocene catalysed copolymerization performance of 7-octenyl- $\text{Si}(\text{CH}_3)_2\text{Ph}$  was studied in detail and compared with that of long 1-alkenes. As a result, the catalyst activities as well the microstructure of the formed polyolefin-co-7-octenyl- $\text{Si}(\text{CH}_3)_2\text{Ph}$  was comparable with those one obtained for polyolefin-co-1-alkene. It appeared that neither the silicon nor the silicon activated phenyl ring had any influence on the metallocene/MAO catalyst system, whenever the phenylsilane moiety was separated from the double bond with a long enough spacer to hinder the electronic influence of silicon.

When the reactivity of the weakly interacting polyolefin was not enough, it was effectively enhanced by post treatment approach. The hydrosilylation of polyethylene-co-1,7-octadiene, and protodesilylation/alcoxylation of polyolefin-co-7-octenyl- $\text{Si}(\text{CH}_3)_2\text{Ph}$  were found to be efficient routes to synthesize polyolefins with highly reactive halo- or alcoxysilanes. In addition, these functionalized polyolefins were found to act as effective compatibilizers in

different kind of particulate filled polyolefin composites. The toughness of PE/filler composites was increased with a small amount of the synthesized compatibilizer, and the impact strengths (at 25 and -20°C) of h-PP/ $\mu$ Si composite were effectively adjusted by functional polyethylenes. In addition to these, the rarely obtained interphase of polyolefin composites was found spectroscopically in PE/ATH composites, and a new fracture mechanism, called semibrittle, was discovered in h-PP/ $\mu$ Si composites.

Finally, the untreated pendant phenylsilane functionality in polyolefin was also found to react in a manner similar to how the abovementioned halo- and alcoxysilanes reacted with the hydroxyl groups at the microsilica surface. The affinity of phenylsilanes towards inorganic fillers can offer new possibilities in the polyolefin composite technology by enabling the soft synthesis of reactive compatibilizer directly via metallocene catalysed copolymerization.

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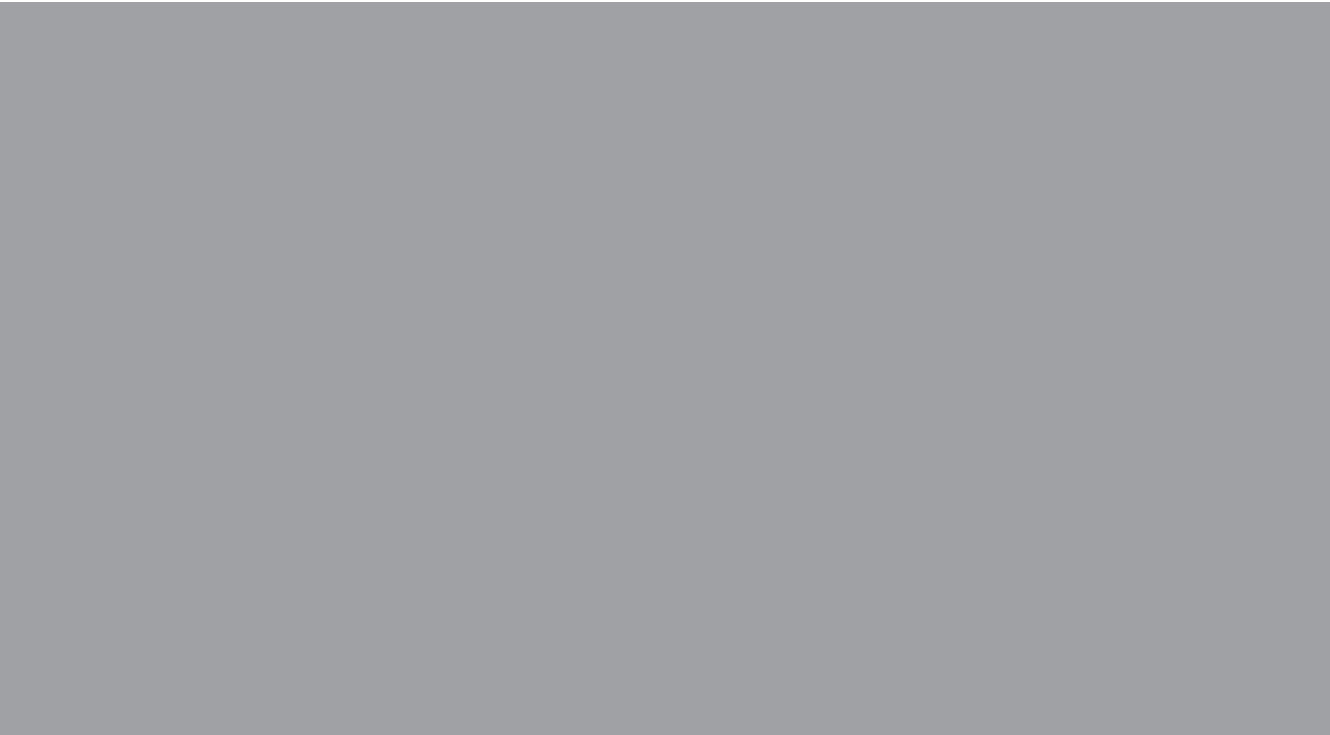


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ISBN 978-952-248-139-9  
ISBN 978-952-248-140-5 (PDF)  
ISSN 1795-2239  
ISSN 1795-4584 (PDF)