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**SINGLE-SITE CATALYSTS AND FUNCTIONAL
COMONOMERS IN COORDINATION POLYMERIZATION
OF OLEFINS**

Doctoral Dissertation

Kimmo Hakala



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Department of Chemical Technology
Laboratory of Polymer Technology

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<p>Abstract</p> <p>Three novel transition-metal complexes were studied as catalysts in ethylene polymerization. The aminopyridinato complexes bis(2-benzylaminopyridinato)trichlorotantalum(V) and trichlorobis[2,6-di(phenylamino)pyridinato-N,N']tantalum(V) exhibited moderately high catalytic activities when activated by methylaluminoxane (MAO). The ethylenebis(salicylideneiminato)zirconium dichloride/MAO showed low activity when used as a homogeneous system, but activities were moderate when it was supported on silica. Under industrially relevant conditions all three systems yielded polyethylene with linear structure and moderately high molar mass.</p> <p>Oxygen- and nitrogen-functional alkenes were studied as comonomers in copolymerizations with ethylene and propylene catalyzed by bridged zirconocene/MAO catalysts. The presence of comonomer decreased the activity of the catalyst. The magnitude of the decrease was dependent on the nature of the functional group. Among the oxygen-functional comonomers the alcohols and ethers performed better, whereas the ketone and the less shielded ester had a stronger poisoning effect. Similarly, amines were better tolerated than the corresponding amides. In general, the more shielded comonomers had slightly less negative effect on the catalyst activity.</p> <p>The interactions of several oxygen-functional comonomers with metallocene catalyst components were investigated by NMR. The reactions were found to depend on the nature of the functionality. The alcohols formed aluminum alkoxides with MAO, whereas the ethers remained mainly in the form of free comonomers. Nevertheless, these comonomers behaved in the same way in copolymerizations, which suggests that alkoxide formation is not a prerequisite for copolymerizability.</p> <p>Functionalized polyolefins with reactive alcohol, acid, ester, ether, amine, or amide groups were synthesized. The maximum amount of comonomer in the polymer was 3.6 mol %. NMR and DSC studies indicated that the comonomer was randomly distributed in the polymer chain. The molar masses of the copolymers were lower than those of the corresponding homopolymers. The functionalized polyethylenes were found to act as effective compatibilizers in polyethylene/polyamide 6 blends, increasing both toughness and stiffness.</p>			
Keywords functionalized polyolefin, metallocene, single-site catalyst, ethylene, propylene, copolymerization			
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Työn ohjaaja	Dosentti Barbro Löfgren		
Tiivistelmä Kolmea uutta siirtymämetallikompleksia tutkittiin eteenin polymerointikatalyytteinä. Aminopyridinaattikompleksit bis(2-bentsyyliaminopyridinaatti)triklooritantaali(V) ja triklooribis[2,6-di(fenyyliamino)pyridinaatti-N,N']tantaali(V) olivat aktiivisuudeltaan kohtalaisen korkeita metyyialumiinioksaanilla (MAO) aktivoituina. Etyleenibis(salisylideeni-iminaatti)zirkonium dikloridi/MAO -katalyytin aktiivisuus oli matala homogeenisena, mutta silikalle kiinnitettynä saavutettiin kohtalainen aktiivisuus. Kaikki kolme katalyyttiä tuottivat teollisesti mielekkäissä olosuhteissa rakenteeltaan suoraketjuista polyeteeniä, jolla on kohtalaisen korkea moolimassa. Happi- ja typpifunktionaalisia alkeeneja tutkittiin komonomeereinä kopolymeroinneissa eteenin ja propeenin kanssa käyttäen silloitettua zirkonoseeni/MAO -katalyyttejä. Funktionaalisten komonomeerien havaittiin laskevan katalyytin aktiivisuutta. Aktiivisuuden laskun voimakkuus riippui funktionaalisen ryhmän luonteesta. Happifunktionaalisista komonomeereistä alkoholit ja eetterit toimivat parhaiten, kun taas ketoni ja vähemmän suojattu esteri myrkyttivät katalyyttiä enemmän. Samoin katalyytin havaittiin sietävän amiineja paremmin kuin vastaavia amideja. Yleisesti ottaen paremmin suojatut komonomeerit vaikuttivat katalyytin aktiivisuuteen hieman vähemmän negatiivisesti. Erilaisten happifunktionaalisten komonomeerien vuorovaikutusta metalloseenikatalyyttikomponenttien kanssa tutkittiin NMR:llä. Reaktioiden todettiin riippuvan funktionaalisuuden luonteesta. Alkoholit muodostivat alumiinialkoksiedeja MAO:n kanssa, kun taas eetterit säilyivät pääasiassa vapaina. Siitä huolimatta nämä komonomeerit käyttäytyivät samoin kopolymeroinneissa, mikä viittaa siihen, että alkoksidin muodostus ei ole edellytys kopolymeroitumiselle. Työssä kyettiin valmistamaan funktionaalisia polyolefiineja, jotka sisältävät reaktiivisia alkoholi-, happo-, esteri-, eetteri-, amiini- tai amidiryhmiä. Suurin komonomeeripitoisuus polymeerissä oli 3,6 mol-%. NMR- ja DSC-tutkimusten perusteella komonomeerit olivat satunnaisesti jakautuneina polymeeriketjussa. Kopolymerien moolimassat olivat matalampia kuin vastaavien homopolymeerien. Funktionaalisten polyeteenien havaittiin toimivan tehokkaina kompatibilisaattoreina polyeteeni/polyamidi 6 -seoksissa lisäämällä sekä seoksien sitkeyttä että jäykkyyttä.			
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PREFACE

This thesis is the fruit of research carried out in the Laboratory of Polymer Technology at Helsinki University of Technology between 1995 and 2001. The main part of the work was done under the National Programme for Materials and Structure Research (MATRA), in the project entitled “Design of Novel Polymeric Materials of Next Generation”. The financial support of the Academy of Finland and the Finnish Funding Agency for Technology and Innovation (Tekes) was much appreciated.

I would like to express my gratitude to my supervisor, Head of the Laboratory of Polymer Technology, Prof. Jukka Seppälä, for placing the excellent facilities of the lab at my disposal. I am also greatly indebted to my instructor, Dr. Barbro Löfgren, for her guidance and encouragement during this work. As project leader she was also the hub of the fruitful cooperation with partners of the MATRA research consortium.

All my co-workers at the Polymer Science Centre, in the Laboratory of Polymer Technology, and in the research groups at other universities deserve my warmest thanks for their cooperation and assistance. Deserving of special mention is Dr. Tuulamari Helaja, whose work on the comonomer syntheses and contribution as a coauthor of the joint publications pushed my research forward. I also wish to note the contributions of Dr. Mika Polamo, Dr. Timo Repo, and Dr. Anne-Marja Uusitalo in providing the complexes and catalysts for the polymerization studies. Warm thanks are owed to Dr. Ulla Hippi, who successfully searched for applications for functionalized polyolefin materials.

I am grateful to Jorma Hakala for hunting down the numerous publications and putting them at my disposal. The whole personnel of the Laboratory of Polymer Technology provided help whenever this was needed. Kathleen Ahonen and Cindy Ruuskanen kindly improved the language of the individual publications and this thesis.

Finally, I wish to express my warmest thanks to my family and friends for their support and encouragement.

Helsinki, 17th of March, 2007

Kimmo Hakala

CONTENTS

LIST OF PUBLICATIONS.....	8
AUTHOR’S CONTRIBUTION IN THE APPENDED PUBLICATIONS	9
OTHER RELEVANT PUBLICATIONS AND PATENTS.....	10
ABBREVIATIONS AND SYMBOLS	11
1 INTRODUCTION	13
1.1 Background	13
1.2 Scope of the thesis.....	14
2 EXPERIMENTAL.....	15
2.1 Materials and general methods.....	15
2.2 Polymer synthesis.....	16
2.3 Characterization of polymers	17
2.3.1 Standard methods	17
2.3.2 Gel permeation chromatography	18
2.3.3 Spectroscopic analyses	18
2.3.4 Other analyses	19
3 SINGLE-SITE OLEFIN POLYMERIZATION CATALYSTS.....	20
3.1 The essence of single-site catalysts	20
3.2 Classification of single-site catalysts	21
3.2.1 Metallocenes.....	21
3.2.2 Constrained-geometry catalysts.....	23
3.2.3 Late-transition-metal complexes	24
3.2.4 Other single-site catalysts.....	26
4 NOVEL SINGLE-SITE COMPLEXES IN ETHYLENE POLYMERIZATION	28
4.1 Tantalum(V) aminopyridinato complexes.....	28
4.2 Salen zirconium dichloride.....	31

5	SYNTHETIC ROUTES TO FUNCTIONALIZED POLYOLEFINS.....	36
	5.1 Radical grafting	36
	5.2 High-pressure copolymerization	36
	5.3 Coordination polymerization.....	37
	5.3.1 Direct polymerization of polar monomers.....	37
	5.3.2 Utilization of reactive copolymer intermediates	47
	5.3.3 Terminally functionalized polyolefins.....	48
6	METALLOCENE/MAO-CATALYZED SYNTHESIS OF FUNCTIONALIZED POLYOLEFINS.....	50
	6.1 Comonomers studied in this work.....	50
	6.2 Interaction of functional comonomers with catalyst components.....	53
	6.3 Copolymerization behavior of oxygen-functional alkenes	56
	6.4 Copolymerization behavior of nitrogen-functional alkenes	59
7	PROPERTIES OF METALLOCENE-CATALYZED FUNCTIONAL OLEFIN COPOLYMERS	61
	7.1 Chain structure of copolymers	61
	7.2 Molar mass	64
	7.3 Melting behavior	65
8	POTENTIAL APPLICATIONS FOR FUNCTIONALIZED POLYOLEFINS	67
	8.1 Applications described in the literature.....	67
	8.2 Functionalized polyethylenes as compatibilizers for PE/PA blends	68
9	SUMMARY.....	71
	REFERENCES AND NOTES.....	73
	APPENDIXES Publications I–VII	

LIST OF PUBLICATIONS

This thesis is based on the following appended publications, referred to in the text by Roman numerals **I–VII**.

- I** Hakala, K., Löfgren, B., Polamo, M., and Leskelä, M., Ethylene Polymerizations with Novel Tantalum(V) Aminopyridinato Complex/MAO Systems, *Macromol. Rapid Commun.* **18** (1997) 635–638.
- II** Repo, T., Klinga, M., Pietikäinen, P., Leskelä, M., Uusitalo, A.-M., Pakkanen, T., Hakala, K., Aaltonen, P., and Löfgren, B., Ethylenebis(salicylidene-iminato)zirconium Dichloride: Crystal Structure and Use as a Heterogeneous Catalyst in the Polymerization of Ethylene, *Macromolecules* **30** (1997) 171–175.
- III** Helaja, T., Hakala, K., Helaja, J., and Löfgren, B., Interaction of Oxygen Functionalized Alkenes with a Methylaluminoxane–Zirconocene Catalyst Studied by NMR, *J. Organomet. Chem.* **579** (1999) 164–176.
- IV** Hakala, K., Löfgren, B., and Helaja, T., Copolymerizations of Oxygen-Functionalized Olefins with Propylene Using Metallocene/Methylaluminoxane Catalyst, *Eur. Polym. J.* **34** (1998) 1093–1097.
- V** Hakala, K., Helaja, T., and Löfgren, B., Metallocene/Methylaluminoxane-Catalyzed Copolymerizations of Oxygen-Functionalized Long-Chain Olefins with Ethylene, *J. Polym. Sci., Part A: Polym. Chem.* **38** (2000) 1966–1971.
- VI** Hakala, K., Helaja, T., and Löfgren, B., Synthesis of Nitrogen-Functionalized Polyolefins with Metallocene/Methylaluminoxane Catalysts, *Polym. Bull. (Berlin)* **46** (2001) 123–130.
- VII** Anttila, U., Hakala, K., Helaja, T., Löfgren, B., and Seppälä, J., Compatibilization of Polyethylene/Polyamide 6 Blends with Functionalized Polyethylenes Prepared with Metallocene Catalyst, *J. Polym. Sci., Part A: Polym. Chem.* **37** (1999) 3099–3108.

AUTHOR'S CONTRIBUTION IN THE APPENDED PUBLICATIONS

Publication I: Kimmo Hakala planned and carried out the polymerization tests and polymer characterizations. Kimmo Hakala prepared the manuscript with the assistance of Mika Polamo. Mika Polamo synthesized the complexes.

Publication II: Kimmo Hakala planned the polymerization experiments and carried out the main part of the polymerizations and polymer characterizations. Timo Repo was responsible for the complex synthesis. The heterogenization of the complex and characterization of the supported catalyst were done by Anne-Marja Uusitalo. Kimmo Hakala participated in the interpretation of the results and preparation of the manuscript together with the other authors.

Publication III: Kimmo Hakala participated in the experimental work and assisted in the interpretation of the results. Tuulamari Helaja was in charge of the interpretation of the NMR spectra and the preparation of the manuscript.

Publications IV–VI: Kimmo Hakala planned the polymerization experiments and carried out the polymerizations and the polymer characterizations. Kimmo Hakala interpreted the results and wrote the manuscripts with the assistance of Tuulamari Helaja. Tuulamari Helaja synthesized the functional comonomers.

Publication VII: Kimmo Hakala was responsible for the preparation and characterization of the copolymers. Ulla Hippi (née Anttila) was responsible for the blending experiments and characterization of the blends. Kimmo Hakala and Ulla Hippi jointly interpreted the results and wrote the manuscript.

OTHER RELEVANT PUBLICATIONS AND PATENTS

Other publications and patents relevant to this thesis and containing contributions from Kimmo Hakala:

Polamo, M., Leskelä, M., Hakala, K., and Löfgren, B. (to Borealis), Novel Transition Metal Complexes and Method for Preparing Them, Eur. Pat. EP 0 906 321 B1, Publ. April 9, 2003, 11 p; *Chem. Abstr.* **128** (1998) 48615t.

Rahiala, H., Beurroies, I., Eklund, T., Hakala, K., Gougeon, R., Trens, P., and Rosenholm, J.B., Preparation and Characterization of MCM-41 Supported Metallocene Catalysts for Olefin Polymerization, *J. Catal.* **188** (1999) 14–23.

Uusitalo, A.-M., Pakkanen, T., Kröger-Laukkanen, M., Niinistö, L., Hakala, K., Paavola, S., and Löfgren, B., Heterogenization of Racemic Ethylenebis(1-indenyl)zirconium Dichloride on Trimethylaluminum Vapor Modified Silica Surface, *J. Mol. Cat. A: Chem.* **160** (2000) 343–356.

Britcher, L., Rahiala, H., Hakala, K., Mikkola, P., and Rosenholm, J.B., Preparation, Characterization, and Activity of Silica Supported Metallocene Catalysts, *Chem. Mater.* **16** (2004) 5713–5720.

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Helaja, T., Hakala, K., Helaja, J., Löfgren, B., and Hase, T., Dynamic NMR Study of Tri-*tert*-butylcarbinol and of a Carbinol–Methylaluminoxane Mixture, *Magn. Res. Chem.* **38** (2000) 165–171.

Motha, K., Hippi, U., Hakala, K., Peltonen, M., Ojanperä, V., Löfgren, B., and Seppälä, J., Metallocene-Based Functionalized Polyolefins as Compatibilizers in Polyolefin Nanocomposites, *J. Appl. Polym. Sci.* **94** (2004) 1094–1100.

Motha, K., Hakala, K., Seppälä, J., and Hippi, U. (to Borealis), Polymer Composition Comprising Nanofillers and Functionalized Polyolefins, Eur. Pat. Appl. EP 1 408 077 A1, Publ. April 14, 2004, 9 p; *Chem. Abstr.* **140** (2004) 304726.

ABBREVIATIONS AND SYMBOLS

2D	two-dimensional
acac	acetylacetonate group
acen	<i>N,N'</i> -ethylenebis(acetylacetoneiminato)
ASTM	American Society for Testing and Materials
Bu	butyl group
Bzl	benzyl group
CGC	constrained-geometry catalyst
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl group
Cp*	pentamethylcyclopentadienyl group
DEAC	diethylaluminum chloride
ΔH_m	melting enthalpy (J/g)
DIBAC	diisobutylaluminum chloride
DSC	differential scanning calorimetry
EPDM	ethylene–propylene–diene rubber
EPM	ethylene–propylene rubber
Et	ethyl group or ethylene bridge
Flu	9-fluorenyl group
FTIR	Fourier transform infrared
GPC	gel permeation chromatography
HDPE	high-density polyethylene
Ind	1-indenyl group
IndH ₄	4,5,6,7-tetrahydro-1-indenyl group
iPr	isopropyl group or isopropylene bridge
ISO	International Organization for Standardization
LLDPE	linear low-density polyethylene
MAO	methylaluminoxane
Me	methyl group
[mm]	fraction of isotactic triads from all monomer triads
[mmmm]	fraction of isotactic pentads from all monomer pentads
MMAO	modified methylaluminoxane
M_n	number-average molar mass (g/mol or kg/mol)
M_w	mass-average molar mass (g/mol or kg/mol)
NMR	nuclear magnetic resonance

o.d.	outside diameter
PE	polyethylene
Ph	phenyl group
PP	polypropylene
PS	polystyrene
salen	<i>N,N'</i> -ethylenebis(salicylideneiminato)
SEM	scanning electron microscopy
SHOP	Shell Higher Olefin Process
TCB	1,2,4-trichlorobenzene
TEA	triethylaluminum
THF	tetrahydrofurane
TIBA	triisobutylaluminum
TiCl ₃ AA	titanium trichloride, aluminum activated (TiCl ₃ + AlCl ₃)
T _m	melting temperature (°C)
TMA	trimethylaluminum
TMS	trimethylsilyl group

1 INTRODUCTION

1.1 Background

Polyolefins are the highest consumption polymers today. Most polyethylene (PE) and polypropylene (PP) is produced by low-pressure technologies using Ziegler–Natta catalysts. These transition-metal catalysts, discovered in the 1950s, have been key to the present industrial importance of polyolefins. Beginning in the early 1990s, a new group of catalysts, usually referred to as single-site catalysts, emerged. Market penetration of these new catalysts has proceeded more slowly than was forecast ten years ago. It is estimated that the market share of single-site-catalyzed polymers in 2001 was about 10% for the production of LLDPE and only about 1% for HDPE and PP [1]. In addition, some new types of polyolefins, such as syndiotactic PP, cyclic olefin copolymers, and propylene-based elastomers, have been introduced thanks to single-site catalyst technology.

New single-site catalysts with improved performance are the subject of intensive research within the polyolefins industry and academic laboratories. An impressive number of new transition-metal complexes that are potential catalysts for olefin polymerization have been synthesized in recent years. A review of publications dealing with single-site catalysts for olefin polymerization that appeared during 1997 contained over 500 references [2]. The plenitude of catalysts and different cocatalysts has also led to the implementation of high-throughput screening systems to accelerate research and development in the area of polymerization catalysis [3–5]. These systems include highly automated equipment and data analysis software for rapid ligand synthesis, polymerization, and measurement of polymer properties. The first successful results from high-throughput experimentation in single-site catalyst screening have recently been reported [6–8].

Metallocenes and other single-site catalysts have allowed greater freedom in the selection of comonomers for copolymerization with ethylene and propylene. In addition to simple α -olefins like 1-butene, 1-hexene, and 1-octene, even some cyclic alkenes and dienes are used commercially. A catalyst that could promote the polymerization of functional vinylic comonomers with ethylene and higher α -olefins under low pressures would be of great interest as such a catalyst would make it possible to synthesize functionalized polyolefins with controlled structures. Combining the properties of polyolefins and polar polymers, those polymers could find their way to completely new end applications.

1.2 Scope of the thesis

The objectives of this work were as follows:

- (i) to investigate the behavior of new types of early-transition-metal complexes as single-site olefin polymerization catalysts [**I**, **II**]
- (ii) to study the synthesis of novel functionalized polyolefins by direct, metallocene/MAO-catalyzed copolymerization of functional vinylic comonomers with ethylene and propylene [**III–VI**]
- (iii) to elucidate the chemical structure of prepared copolymers by spectroscopic (NMR, FTIR), chromatographic (GPC), and thermal (DSC) methods [**IV–VI**]
- (iv) to synthesize functional olefin copolymers that can be used as compatibilizers in polymer blends [**VII**]

The following chapters (2–8) give an overview of the subject of the thesis and summarize the major findings presented in Publications **I–VII**.

2 EXPERIMENTAL

2.1 Materials and general methods

rac-Ethylenebis(indenyl)zirconium dichloride [Et(Ind)₂ZrCl₂] and *rac*-dimethylsilylbis(2-methylindenyl)zirconium dichloride [Me₂Si(2-MeInd)₂ZrCl₂], the bridged zirconocenes used as catalysts in the copolymerizations of functional monomers, were obtained from Witco GmbH (Bergkamen, Germany) and Boulder Scientific Company (Mead, CO, USA), respectively. Cocatalyst methylaluminoxane (MAO) was provided as a 10 wt % solution in toluene and was purchased from Witco. Both catalysts and cocatalyst were used as received. Tantalum(V) aminopyridinato complexes were synthesized at the University of Helsinki by Mika Polamo [I, 9, 10]. The salen zirconium complex was synthesized at the University of Helsinki by Timo Repo and deposited onto the silica support at the University of Joensuu by Anne-Marja Uusitalo [II, 11].

Ethylene monomer was grade 3.5 obtained via Oy AGA Ab (Espoo, Finland). Propylene was grade 2.8 from AGA or grade 3.5 from Messer Griesheim (Krefeld, Germany). The gaseous monomers were further purified by being passed through columns filled with 3-Å molecular sieves, BASF R3-11 copper catalyst, and activated Al₂O₃ just before their addition to the reactor. 10-Undecen-1-ol (96%), 5-hexen-1-ol (>97%), 2-methyl-3-buten-2-ol (>97%), and 10-undecenoic acid (97%) were purchased from Fluka, and methyl 9-decenoate was donated by Neste Oy (Porvoo, Finland). Other functional monomers studied in this work were synthesized by Tuulamari Helaja [12]. Toluene (GR grade) and *n*-heptane (p.a. grade) used in polymerization experiments were from Merck (Darmstadt, Germany) and were purified by conducting them through columns filled with molecular sieves (3Å/4Å), BASF R3-11 copper catalyst, and activated Al₂O₃. Toluene used in the experiments described in Publications IV–VI was further purified by refluxing and distilling under nitrogen from sodium benzophenone ketyl.

All manipulations of air-sensitive compounds were carried out under dry nitrogen gas (grade 5.0 from AGA). The catalysts were stored and handled inside a nitrogen-filled glovebox (Vacuum Atmospheres Company, Hawthorne, CA, USA) equipped with a recirculating gas-purification unit. The oxygen content inside the glovebox was monitored continuously and it was below 2 ppm O₂.

2.2 Polymer synthesis

The polymerization experiments were carried out in a 0.5- or 1.0-dm³ stainless steel reactor (Büchi, Uster, Switzerland) equipped with a magnetically driven stirrer. A typical polymerization proceeded in the following way. First, the reactor was evacuated and flushed with nitrogen several times. Polymerization medium (toluene or *n*-heptane), MAO, and comonomer (if any) were then added, and the feed of gaseous monomer was started. Saturation of the reaction medium with gaseous monomer was typically reached in a few minutes. The functional comonomer was allowed to be in contact with MAO for 10, 15, or 30 minutes before the polymerization was initiated by pumping the toluene solution in which the catalyst was dissolved. When nonsoluble catalysts were used [**II**], the catalyst was suspended in toluene and added to the reactor before initiation of the ethylene feed. During polymerization the temperature of the reactor and the partial pressure of the gaseous monomer were maintained constant. The consumption of ethylene or propylene during reaction was monitored with a mass-flow meter connected to a computer.

The polymerization was stopped by degassing the reactor. The product was precipitated with dilute HCl solution in ethanol. The polymer was filtered from the mixture, washed with ethanol and/or acetone, and dried in vacuum to constant weight. The copolymers containing amine functionalities were additionally washed with a 1.0 mol/dm³ NaOH/ethanol solution.

2.3 Characterization of polymers

2.3.1 Standard methods

The procedures of the standard test methods listed in Table 1 were followed when applicable. Short general descriptions of the polymer characterization methods are presented in the next three sections.

Table 1. Standard test methods for characterization of polyolefins relevant to this research [13].

Area	Designation	Name
GPC, general methods	ASTM D 5296-92	Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography
GPC, polyolefins	ASTM D 6474-99 ^a	Determining Molecular Weight Distribution and Molecular Weight Averages of Polyolefins by High Temperature Gel Permeation Chromatography
NMR	ASTM D 5017-96	Determination of Linear Low Density Polyethylene (LLDPE) Composition by Carbon-13 Nuclear Magnetic Resonance
FTIR	ASTM D 5576-94	Standard Practice for Determination of Structural Entities in Polyolefins by Fourier Transform Infrared Spectroscopy (FT-IR)
DSC, ΔH_m	ASTM D 3417-97	Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry (DSC)
DSC, T_m	ASTM D 3418-97	Transition Temperatures of Polymers by Thermal Analysis
Density	ISO 1183- 1987 (E)	Plastics — Methods for Determining the Density and Relative Density of Non-Cellular Plastics
Ash content	ASTM D 5630-94	Ash Content in Thermoplastics

^a The method was first published in 1999.

2.3.2 Gel permeation chromatography

The molar mass distributions and molar mass averages of the polymers were determined by high-temperature gel permeation chromatography (GPC) using a Waters 150C or Waters Alliance GPCV 2000 instrument operating at 135 °C or 140 °C with 1,2,4-trichlorobenzene (TCB) as eluent. The sample solutions (maximum polymer concentration 0.1% wt/vol) were prepared in TCB with an antioxidant (*N*-phenyl-2-naphthylamine or 2,6-di-*tert*-butyl-4-methylphenol). Polymer molecules were separated with a set of cross-linked styrene–divinylbenzene copolymer columns packed with 10- μ m or 20- μ m particles, and the column eluent was monitored with a differential refractometer detector. The column set was calibrated with narrow molar mass distribution PS standards having molar masses from 970 g/mol to 10.2×10^6 g/mol. The molar mass values of polyolefin samples were converted to PE or PP equivalents with use of a universal calibration method. Broad molar mass distribution LLDPE and PP standards were used as references in the selection of the Mark–Houwink parameters, K and α , for the samples.

2.3.3 Spectroscopic analyses

The microstructure and the amount of comonomer incorporated in the copolymer samples were characterized by liquid nuclear magnetic resonance (NMR) spectroscopy. ^1H NMR and ^{13}C NMR spectra were recorded at 120–130 °C on a Varian Gemini 2000 300-MHz or Jeol GSX 400-MHz spectrometer. The samples were dissolved in 1,1,2,2-tetrachloroethane- d_2 , at concentrations of 2 wt % for ^1H and 5 wt % for ^{13}C measurements. The comonomer contents were calculated from ^1H NMR spectra whenever possible because of the better sensitivity of the proton measurements. Signal-to-noise ratios of ^{13}C NMR spectra were improved by using 10-mm-o.d. sample tubes and continuous proton decoupling, which provided enhancements in resonance intensities by nuclear Overhauser effect [14]. The solvent resonances (δ_{H} 5.91 ppm and δ_{C} 74.4 ppm) were used as internal references in the

NMR spectra. Spectra were interpreted on the basis of the spectra of the comonomers and of spectral assignments found in the literature for copolymers of long-chain olefins with ethylene [14,15] and propylene [15]. Fourier transform infrared (FTIR) spectroscopy was used for qualitative analyses of functionalized copolymers. Transmission FTIR spectra were measured with a Nicolet 750 Magna FTIR spectrometer from compression-molded thin polymer films.

2.3.4 Other analyses

Melting temperatures (T_m) and enthalpies (ΔH_m) were determined with a Mettler Toledo DSC 821^o or Perkin-Elmer DSC 7 differential scanning calorimeter. Indium was used for the calibration of the temperature scale. The melting endotherms were measured during reheating of the polymer sample (5 mg) to 150 °C or 160 °C at a heating rate of 10 °C/min. Densities of selected polymers were measured from compression-molded samples by a density-gradient technique according to ISO 1183-1987, method D. Ash contents of selected copolymers of Publication **IV** were determined by a muffle-furnace technique described in standard test method ASTM D 5630-94, procedure A.

3 SINGLE-SITE OLEFIN POLYMERIZATION CATALYSTS

3.1 The essence of single-site catalysts

The mechanism for transition-metal-catalyzed olefin polymerization, originally proposed by Cossee and Arlman [16,17], assumes that the polymerization proceeds in two steps. The first step consists of the coordination of the olefin to the catalytic site and the second of insertion of the coordinated monomer into the metal–carbon bond. During the insertion step the growing polymer chain migrates to the position previously occupied by the coordinated monomer. The exact nature of the catalytic site defines the chain length (i.e., molar mass), stereoregularity, and other fundamental properties of the polymer. Similarly, in copolymerizations the composition of the copolymer is regulated by the relative sensitivity of the active center to incorporate different comonomers.

Several types of active catalyst centers are present in the conventional Ziegler–Natta catalysts, which have been used in industrial polyolefin processes since the 1950s. The multi-site nature of those catalysts makes them difficult to study. Another, more important consequence is that the polymers produced with them are complex mixtures or different kinds of polymer chains.

Single-site catalysts, in sharp contrast to conventional Ziegler–Natta catalysts, possess only one type of active center. This means that the polymers formed by single-site catalysts are uniform — on both intra- and intermolecular basis — in terms of molar mass, microstructure, and chemical composition. The theoretical broadness of the molar mass distribution of single-site-catalyzed polyolefins is $M_w/M_n = 2$, which is significantly narrower than the molar mass distributions of polymers obtained with traditional Ziegler–Natta catalysts. The uniform structure has a direct positive impact on many important polymer properties including mechanical strength and optical and organoleptic properties.

3.2 Classification of single-site catalysts

3.2.1 Metallocenes

The history of metallocenes dates back to the year 1951 when Kealy and Pauson [18] and Miller et al. [19] described the synthesis of dicyclopentadienyliron. Wilkinson and co-workers [20] and Fischer and Pfab [21] soon disclosed that the compound, usually called ferrocene, consists of an iron(II) ion sandwiched between two parallel Cp rings (Figure 1a). Shortly afterwards, Wilkinson et al. [22] reported the synthesis of the first group 4 metallocenes, Cp_2TiBr_2 and Cp_2ZrBr_2 (Figure 1b).

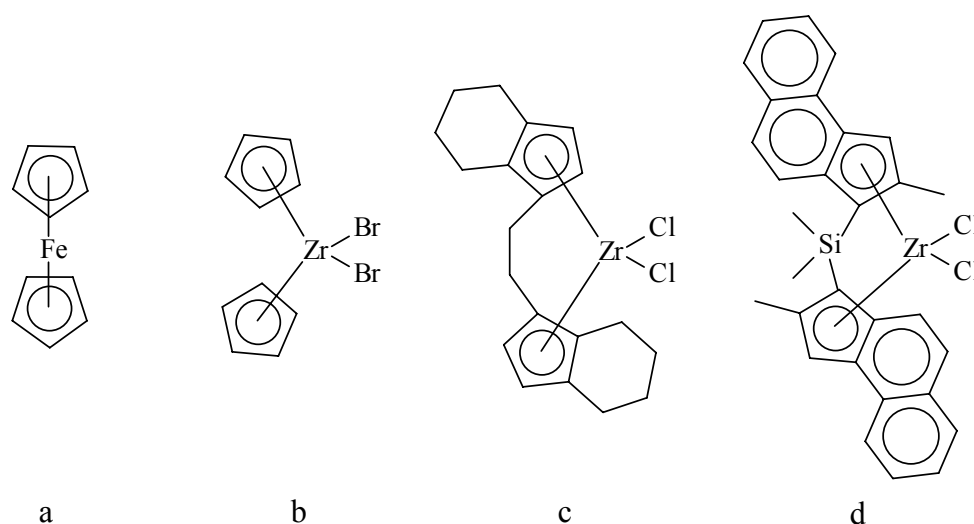


Figure 1. Examples of metallocene structures: a ferrocene (a), a zirconocene dibromide (b), and bridged zirconocene dichlorides (*rac*-isomers) (c, d).

In 1957 Natta et al. [23] and Breslow and Newburg [24] discovered that mixtures of titanocene (Cp_2TiCl_2) with triethylaluminum (TEA) or diethylaluminum chloride (DEAC) catalyze ethylene polymerization. However, the activity of those systems was much less than that of the TiCl_4 - and TiCl_3 -based catalysts developed earlier by Ziegler [25] and Natta [26]. At that time it was also erroneously believed that a solid

surface is required for stereospecificity in the polymerization of α -olefins [27], so soluble metallocenes did not appear of interest for propylene polymerization. For over 20 years the metallocene complexes were considered as little more than useful model compounds for scientific research on mechanisms and kinetics of the commercially important Ziegler–Natta catalysis. For instance, as long ago as the 1960s, Shilov et al. [28,29] showed that the reaction products of the $\text{Cp}_2\text{TiCl}_2/\text{DEAC}$ system include positive ions containing titanium, and that those metallocene cations are the active species in the polymerization of ethylene. The presence of cationic active centers was later generalized to be true for other Ziegler-type olefin polymerization catalysts as well [30].

In the late 1970s it was found that with use of methylaluminoxane (MAO) as cocatalyst in place of aluminum alkyls, the activity of metallocene compounds could be increased dramatically [31–34]. This significant discovery widened the scope of studies on metallocene catalysis within research groups both in academia and in the polyolefin industry. The next milestone in the field was attributable to Ewen [35] and Kaminsky and Brintzinger [36], who used soluble MAO-activated racemic *ansa*-metallocenes (Figure 1c) for the synthesis of isotactic polypropylene. Bridged group 4 metallocenes, especially zirconocenes (Figure 1d), were further developed by the groups of Brintzinger [37] and Spaleck [38] to produce polypropylenes with higher molar masses and higher isotacticities. Meanwhile, metallocenes with different symmetries were synthesized to produce syndiotactic, hemiisotactic, and stereoblock polypropylenes [39]. Other cocatalysts, including perfluoroaryl boranes and trityl and ammonium borates, were developed to replace MAO [40].

The commercial utilization of metallocene catalysts has met with many difficulties. Homogeneous catalysts as such are not suitable for most of the modern olefin polymerization processes because they tend to produce fine polymer dust, which leads to fouling and plugging of reactors [41]. Additionally, the use of high excess of MAO,

which is needed for metallocene activation, is a problem in terms of process economics and the cocatalyst residues in product polymers. The answer to these problems is the deposition of the catalyst components on insoluble carriers, for example silica [41]. This decreases the amount of cocatalyst required and enables use of the catalyst in gas-phase, slurry, and bulk-monomer processes. Commercial metallocene-catalyzed production of polyethylene was introduced in 1991 by Exxon in a demonstration plant using the high-pressure process [42]. Since then, metallocene technology has found its way into polyethylene gas-phase and slurry processes, and, beginning in 1995, into polypropylene processes [43,44].

3.2.2 Constrained-geometry catalysts

Homogeneous olefin polymerization catalysts based on group 4 *ansa*-monocyclopentadienyl-amido complexes have received much commercial attention [45]. Originally synthesized by Okuda [46] and researchers at Dow [47] and Exxon [48], these catalysts are usually called constrained-geometry catalysts (CGCs). An illustrative complex of this group is $[\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}t\text{-Bu})]\text{TiCl}_2$ (Figure 2). CGCs can be viewed as analogues of *ansa*-metallocenes. However, because of the more open coordination sphere, they are superior to bridged metallocenes in ethylene copolymerizations incorporating higher α -olefins, cyclic olefins, and styrene [45]. Furthermore, because CGCs retain their activity and ability to produce high-molar-mass polyethylenes at high temperatures (140–180 °C), they are especially suitable for solution polymerization processes [49]. The commercial utilization of constrained-geometry catalysts commenced in 1993, and the product families available today include LLDPE-type plastomers and elastomers, EPDMs, and ethylene–styrene copolymers [49]. Polymerization of propylene with CGCs has met with little success, even though some complexes have been reported to yield isotactic or syndiotactic polypropylenes [50].

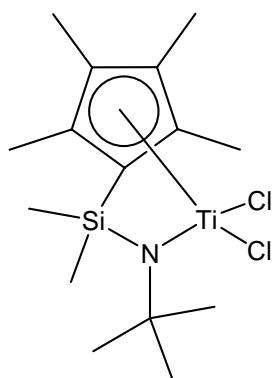


Figure 2. Structure of a typical constrained-geometry Ti complex.

3.2.3 Late-transition-metal complexes

In earlier years, late-transition-metal-catalyzed polymerizations of alkenes received little attention. Ni(II) complexes with chelated P–O ligands are the basis of the Shell Higher Olefin Process (SHOP), which is used for the production of linear α -olefins [51]. In general, late-metal catalysts were considered applicable only to dimerization or oligomerization of ethylene because of rapid chain termination through β -hydride elimination [52]. It was demonstrated in the 1980s that, under suitable conditions, SHOP-type nickel catalysts (Figure 3a) are also able to produce high-molar-mass polyethylene [53], but the real renaissance in late-transition-metal-catalyzed polymerizations did not occur before the late 1990s. Then, the discovery of Ni(II) and Pd(II) α -diimine complexes (Figure 3b) by Brookhart [54] and neutral Ni(II) salicylaldiminato complexes (Figure 3c) by Grubbs [55,56] sparked a growing interest in group 10 metal catalysts. Additionally, highly active iron and cobalt complexes with 2,6-bis(imino)–pyridine tridentate ligands (Figure 3d) were introduced for the polymerization of ethylene [57,58].

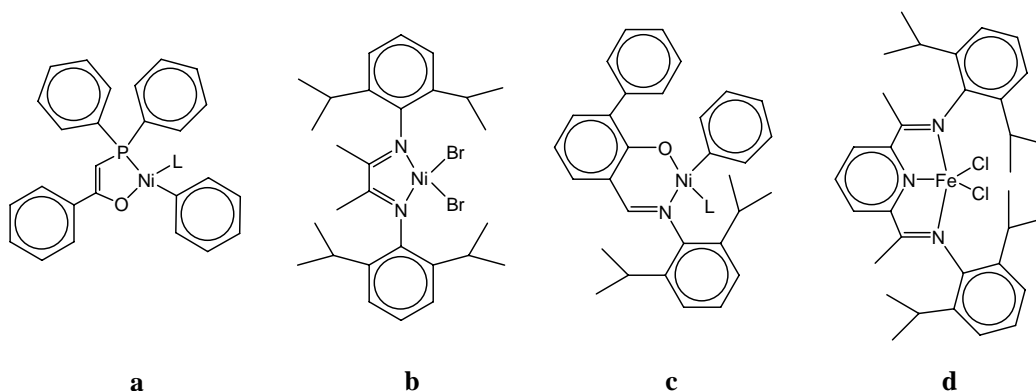


Figure 3. Examples of late-transition-metal-based catalyst precursors, L = PPh₃ or pyridine.

The use of late-transition-metal-based catalysts has provided new types of polyolefins. One example is hyperbranched polyethylenes, which are formed by chain-walking mechanism using Pd(II) α -diimine complexes [59]. These polymers are amorphous and liquid-like even though they have high molar masses [60]. Under certain conditions the same Pd complexes have been reported to catalyze living polymerization of ethylene [61], and related Ni(II) α -diimine catalysts have been used for living polymerization of α -olefins [62]. Additionally, some Ni(II) α -diimine [63] and Fe(II) bis(imino)–pyridine [64] complexes cocatalyzed by MAO can be applied to the highly selective synthesis of linear α -olefins through oligomerization of ethylene.

Even though the main use of the late-transition-metal catalysts has been in ethylene polymerization, some Ni- and Pd-diimine complexes have been reported to produce prevalingly syndiotactic polypropylenes [65,66]. Fe bis(imino)–pyridine catalysts, on the other hand, produce highly regioregular polypropylenes with isotactic structures ([mmmm] = 55–67%) [67]. However, the stereospecificities are far lower than those obtained with bridged zirconocene catalysts.

Pd α -diimine complexes are active catalysts for ethylene and 1-hexene polymerizations even in water [68,69] and supercritical CO₂ [70], which are severe poisons for group 4 metal-based catalysts. This ability is associated with the substantially lower oxophilicity of the late-transition-metal complexes. Thus, late-transition-metal-based complexes have also been intensively explored as potential catalysts for the synthesis of functionalized polyolefins (see Section 5.3).

3.2.4 Other single-site catalysts

Particularly from the mid-1990s onwards, complexes other than ones based on Cp ligands have been extensively explored in both academic and industrial research laboratories [71,72]. The most notable advances have been with complexes based on group 4 metals. Many of those complexes can be seen as mimics of group 4 metallocenes in view of the electrical and sterical resemblances. Some of the complexes that have aroused commercial interest are presented in Figure 4.

Commercial production of polyethylene resins based on single-site catalysts other than metallocenes or CGCs was initiated in 2003 [80]. These ethylene–octene copolymers for film and molding applications feature a combination of excellent mechanical and optical properties together with better processability than other materials prepared with single-site catalysts.

Most non-metallocene single-site complexes are best suited for ethylene homo- and copolymerizations for HDPE or LLDPE production. However, some success has also been achieved in propylene polymerizations. Isotactic ([mm] = 92–96%) propylene homo- and copolymers have been prepared under solution polymerization conditions using Hf pyridyl–amide complexes (Figure 4e) cocatalyzed with an ammonium borate [79]. These Hf-based complexes are used for the production of propylene-based polymers in a high-temperature solution process [81].

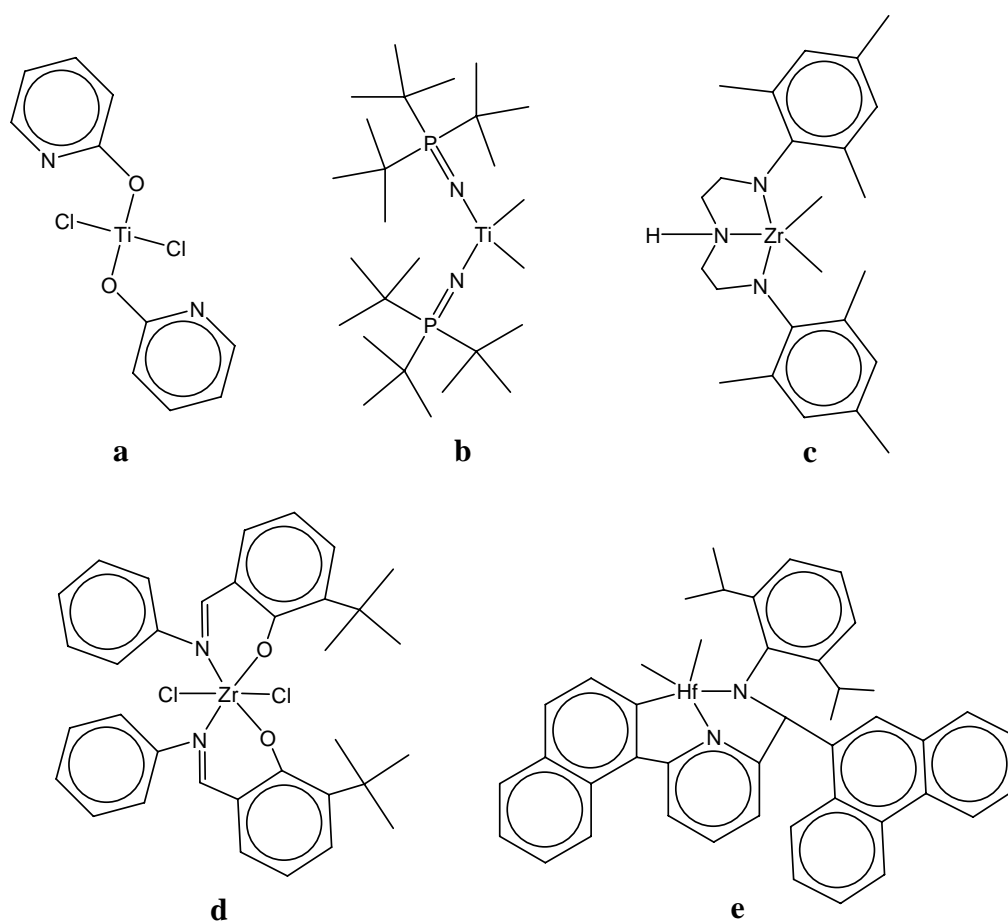


Figure 4. Examples of non-metallocene single-site catalyst precursors: bis(pyridinoxy) Ti (a) [73], bis(phosphinimide) Ti (b) [74,75], bisamide Zr (c) [76], bis(salicylaldiminato) Zr (d) [77,78], and pyridyl–amide Hf (e) [79] complexes.

4 NOVEL SINGLE-SITE COMPLEXES IN ETHYLENE POLYMERIZATION

Sections 4.1 and 4.2 describe the studies on new types of non-metallocene complexes in the polymerization of ethylene (Publications **I** and **II**).

4.1 Tantalum(V) aminopyridinato complexes

A number of vanadium(III) salts have been used as catalysts for olefin polymerizations, especially for ethylene–propylene copolymerization and ethylene–propylene–diene terpolymerization processes [82,83]. Other group 5 elements have not received much attention as catalyst precursors for olefin polymerizations. Among the rare exceptions are Cp*–imido [84] and Cp*–amidinate [85] tantalum(V) complexes, which have been shown to polymerize ethylene with low or moderate activities. Cp*–diene complexes of niobium and tantalum are reported to polymerize ethylene in a living manner in the presence of MAO [86,87]. Some tantalum(V) complexes have also been described as active initiators for homopolymerization of methyl methacrylate [88,89]. Compared with group 4 catalysts, group 5-based complexes are generally presumed to be less active for olefin polymerizations but to have better tolerance toward polar functionalities [88,89].

Amido ligands offer interesting alternatives to Cp ligands as stabilizing components of early-transition-metal ions for complex formation [90]. With its capability to bind to two extra substituents, nitrogen is a more versatile donor atom than oxygen in the formation of well-defined, catalytically active reaction centers. One example of the amido ligands is aminopyridinato, where a pyridine function is located next to the amido group [91]. The presence of two nitrogen atoms in close proximity to each other creates a special character for the chemistry of the aminopyridinato ligand. Additionally, these ligands are easily tailored through the addition of new substituents.

Kempe et al. [92] showed that bridged bisaminopyridinato titanium complexes activated with MAO have some activity as catalysts for ethylene polymerization. Similarly, they have reported that monoaminopyridinato titanium complex polymerizes propylene and 1-butene to atactic, low molar mass polymers [93]. In a publication by Scott et al. [94] some bisaminopyridinato-based zirconium complexes were described as having moderate activity in ethylene polymerization.

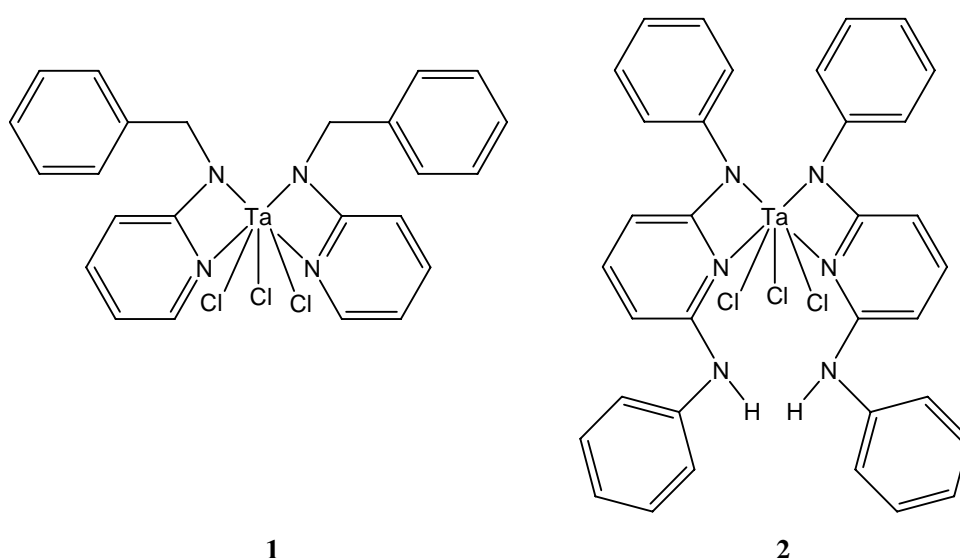


Figure 5. The aminopyridinato complexes: bis(2-benzylaminopyridinato)trichlorotantalum(V) (**1**) and trichlorobis[2,6-di(phenylamino)pyridinato-*N,N'*]tantalum(V) (**2**).

In this work [**I**], two novel aminopyridinato complexes of tantalum (Figure 5) [9,10] were used as catalyst precursors in ethylene polymerizations in toluene medium under partial pressure of ethylene of 5.0 bar. The complexes, provided as toluene solvates, consisted of dark-red crystals, which when dissolved in pure toluene formed solutions of intense blood-red color. MAO was used as a cocatalyst with molar ratio Al/Ta of 2000. The polymerization results are set out in Table 2. Both complexes exhibited relatively high activities [71], the highest activity being 23 900 kg PE/(mol Ta*h) at 80 °C with complex **2**. The activities are higher than reported for any other tantalum-

or niobium-based complexes [71,72]. Furthermore, complexes that most closely resemble the studied complexes have been described as possessing only low polymerization activity [95] or no activity at all [96].

Table 2. Results for polymerization of ethylene with tantalum aminopyridinato complexes **1**/MAO and **2**/MAO.

Complex	T _p °C	Time min	Activity kg PE/(mol _{Ta} ·h)	M _w g/mol	M _w /M _n	T _m °C
1	30	20	800	201 000	2.5	137.7
1	60	7	5000	94 000	2.0	135.4
2	30	30	900	115 000	1.9	136.3
2	60	30	5800	85 000	1.9	135.3
2	60	7	7700	91 000	1.9	134.8
2	80	7	23 900	66 000	1.8	133.9

The catalytic activity of the tantalum complexes was found to increase with polymerization temperature. Activities are good at 60–80 °C which are typical temperatures for commercial polymerization processes. A limiting factor here might be molar masses, which were only moderately high and were lowered along with increasing polymerization temperatures.

The nature of the active species derived from the tantalum-based precursors with MAO activation was not unambiguously identified. Narrow molar mass distributions ($M_w/M_n \approx 2$) of the polymers are indications of single-site behavior with normal chain-termination reactions, in contrast to the living behavior reported for some Ta and Nb complexes [86,87]. On the basis of the melting temperatures (134–138 °C), the polyethylenes are supposed to have linear structure.

4.2 Salen zirconium dichloride

Complexes with Schiff base ligands play an important role as catalysts of chemical reactions, the enantioselective olefin epoxidation catalyzed by chiral Mn(III) salen complexes being the most notable example [97]. Salen-based complexes of early transition metals are described as facily prepared and more easily handled than conventional metallocene complexes. However, in the field of olefin polymerizations Schiff base ligands did not attract much attention during the 1990s. As a rare example, Jordan et al. [98] studied the ethylene polymerization potential of Zr complexes based on acen-type tetradentate ligands (Figure 6a). Those Schiff base ligated complexes were found to function as ethylene polymerization catalysts with low or moderate activity when activated with borate/TIBA. At the same time the first speculations about the usefulness of salicylaldiminato-ligated group 4 metal complexes in olefin polymerizations were presented by Floriani et al. [99].

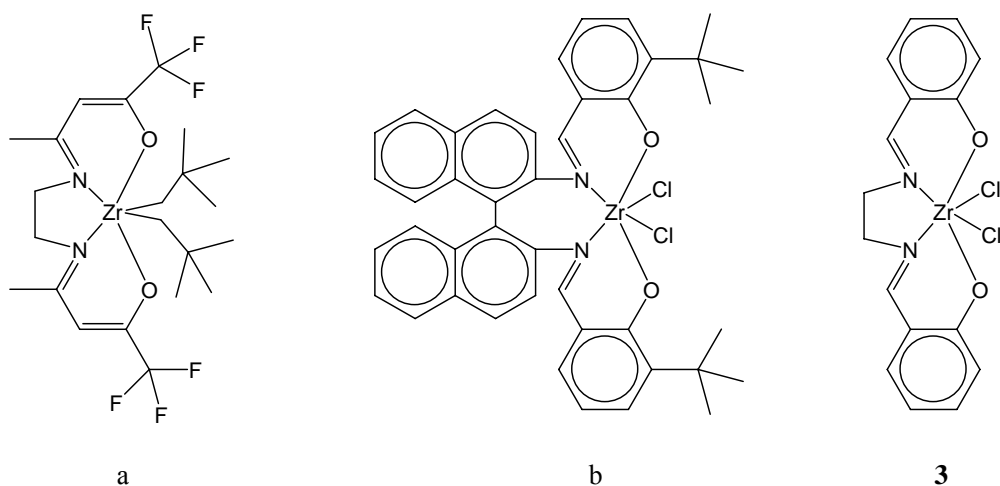


Figure 6. Examples of catalyst precursors containing Schiff base ligands: acen Zr (a), binaphthyl-bridged salen Zr (b), and salen Zr (**3**) complexes.

Salen-type Zr complexes in combination with DEAC are reported to be active in ethylene oligomerization at 150 °C [100]. Recent articles have described the use of salen zirconium derivatives with bulkier cyclohexane [101] or binaphthyl (Figure 6b) [102] bridges, not only as ethylene catalysts but also as capable of producing ethylene-propylene and ethylene-1-hexene copolymers [101], atactic polypropylene [102], and isotactic poly(α -olefins) [102]. In general, interest in imine-based complexes as olefin polymerization catalysts has increased enormously during recent years, ever since the research group of Mitsui found that some phenoxy-imine-based complexes of the group 4 metals (Figure 4d) have very high activities and versatile polymerization capabilities in olefin polymerization [77,78,103–105].

The zirconium salen complex **3** (Figure 6) applied in ethylene polymerization in this work was provided in THF-solvated form $[\text{Zr}(\text{salen})\text{Cl}_2(\text{THF})]$. The pure complex consisted of pale-yellow crystals. The heterogenization of the complex on silica and the characterization of the supported catalysts were made in the Department of Chemistry, University of Joensuu [II, 11]. The spectroscopic characterization of the supported catalysts suggested that the salen complex had reacted with the Si–OH groups of the silica, but the complex had retained its salen ligand. Hence, the active complex is considered a derivative of $\text{Zr}(\text{salen})\text{Cl}_2$, which is a six-coordinated complex. Four supported catalysts differing in Zr content (0.15–0.85 wt %) were studied in polymerization tests.

MAO was used as cocatalyst in the polymerization experiments. According to ^1H NMR experiments, MAO alkylates the salen complex [II, 11]. Thus, the active polymerization catalyst is presumed to be alkyl cation as in the case of group 4 metallocene catalysts. The polymerizations were carried out in toluene or *n*-heptane at 80 °C with ethylene partial pressure of 5.0 bar. The nonsupported complex gave moderate activity of 130 kg PE/(mol_{Zr}*h) when used in toluene medium. Interestingly, under the same conditions the supported catalyst with highest Zr loading (0.85 wt %)

showed about one order of magnitude higher activity, that is, 540–3350 kg PE/(mol_{Zr}*h). The molar masses of the polyethylenes were about 100 000 g/mol. The molar mass curves showed unimodal distribution with $M_w/M_n = 2.3$ –3.7. Particularly, the value $M_w/M_n = 2.3$ obtained with the nonsupported catalyst is characteristic of single-site catalysts where only one type of active species is present.

The silica-supported catalysts were also tested in *n*-heptane medium, which is known to be a worse solvent for both the salen complex and MAO. The activity of the supported catalyst with 0.85 wt % Zr was 70–290 kg PE/(mol_{Zr}*h), that is, on the same level as that of the nonsupported catalyst. When the catalysts with lower Zr loadings were tested under the same conditions, a significant increase was obtained in the activity, the best activity of 3020 kg PE/(mol_{Zr}*h) being found with the catalyst containing only 0.15 wt % Zr. The catalyst activity increased with the Al/Zr ratio, as in the polymerizations carried out in toluene (Figure 7). This behavior is in accordance with earlier findings for silica-supported zirconocenes [106]. The melting temperatures of 133–138 °C and crystallinities of 51–67% illustrated that the formed polyethylenes were linear, that is, of HDPE type.

The higher activity of the silica-supported catalyst than of the nonsupported complex is in contrast to what is usually reported for metallocene complexes immobilized directly on silica without prior aluminum alkyl or MAO treatment [41,106,107]. In a recent patent application [108], the supporting of N,O-ligated phenoxy–imine Zr complexes onto silica pretreated with Al(C₆F₅)₃ was reported to result in moderate polymerization activity, but no comparison was made with nonsupported counterparts. One possible explanation for the positive effect of heterogenization might be that fixation of the complex on silica rules out or slows down the intramolecular reactions of the alkyl salen cations. The reduction reactions of the imine units have been proposed as a reason for the short lifetimes and low activities of salen-based group 4 complexes in olefin polymerizations [109]. An alternative explanation for the better

result with silica support could be that the silica reduces the putative deactivation by dimerization of the MAO-activated complex. Dimerization has been suggested as a possible deactivation mechanism with zirconocene-based catalysts [110].

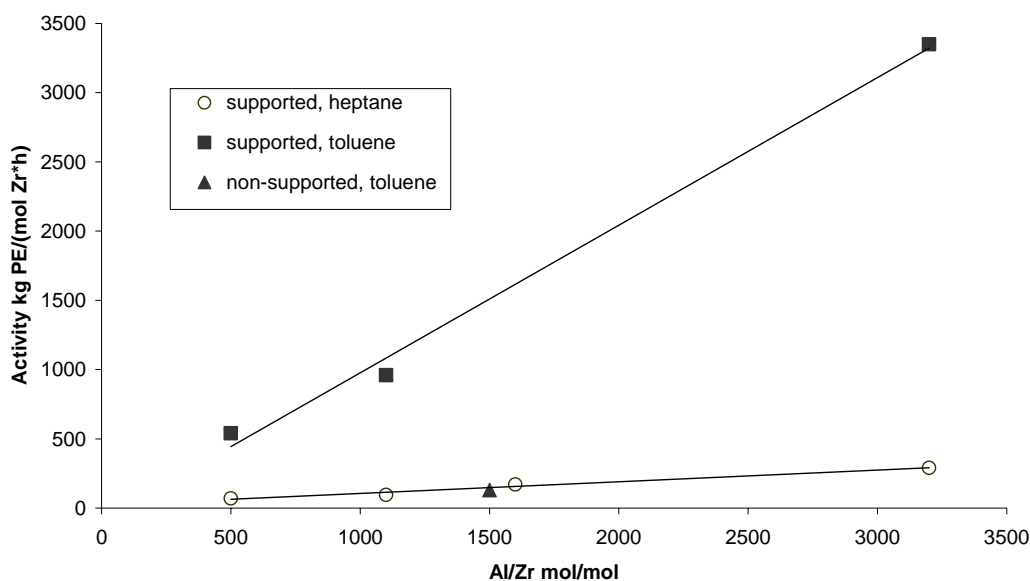


Figure 7. Effect of polymerization medium and Al/Zr on the activity of the Zr salen catalyst. Silica-supported catalyst with 0.85 wt % of Zr, nonsupported catalyst as a reference. Polymerization conditions: 80 °C, $p_{\text{ethylene}} = 5.0$ bar, time = 60 min. [II]

The molar masses of the polymers were clearly higher (ca. 200 000–1 100 000 g/mol) in all the heterogeneous runs performed in *n*-heptane than in those performed in toluene. In particular the polymers produced by catalysts with high Zr content showed bimodal molar mass distributions having a shoulder in the high-molar-mass region. This indicates that the single-site character of the complex is lost in heterogenization and different kinds of active centers are present. The differences in catalyst activity and molar mass of the polyethylene produced in *n*-heptane and toluene might arise from the different solubility of the complex and MAO in the two solvents. It was found that a significant part of the complex was leached out of the support when a

catalyst with very high loading (1.55 wt % Zr) was treated with MAO/toluene solution at 80 °C [II]. It is questionable, therefore, whether the polymerizations in toluene were really heterogeneous. Because of the partial solubility of the polyethylene powder in toluene at 80 °C, the appearance of the polymer did not give a clear indication for or against the support-induced powder morphology.

5 SYNTHETIC ROUTES TO FUNCTIONALIZED POLYOLEFINS

5.1 Radical grafting

Postpolymerization chemical modification of polyolefins by free-radical grafting in melt is a widely studied route to functionalized polyolefins [111,112]. The grafting reactions are usually carried out in extruders, and the process is called reactive extrusion [113]. In the radical-grafting reaction radical-generating species such as peroxides are used to initiate the forming of grafts of an added monomer to the polyolefin backbone. The chain length of the resulting grafts can vary from a single monomer unit to the lengths long enough that the new polymer has physical properties clearly different from those of the original polyolefin [113]. Radical grafting is especially applied to the functionalization of PP, EPM, and EPDM. The monomers that are used include maleic anhydride, acrylic acid, and methyl methacrylate [114]. During reactive extrusion, undesired side reactions such as monomer homopolymerization, polymer degradation, branching, and gel formation compete with the grafting [111]. Hence, reactive extrusion is often difficult to control, and the product is a mixture of different kinds of polymers.

5.2 High-pressure copolymerization

Copolymers of ethylene with vinyl acetate, acrylic acid, or acrylate-type comonomers (e.g., methyl, ethyl, and *n*-butyl acrylate) are made commercially by high-pressure free-radical processes in either tubular or autoclave-type reactors [115]. Ethylene copolymers containing carbon monoxide have also been prepared. A limitation in free-radical polymerizations is that monomers with allylic hydrogens (e.g., propylene) cannot be used because of the rapid chain-transfer reactions. Typically it is possible to prepare ethylene-based copolymers of good compositional uniformity containing up to 20–30 wt % polar comonomer. The copolymers have lower crystallinity than low-

density ethylene homopolymer, and the introduction of polar groups leads to more flexible and tougher products. The major area of application for those copolymers is films [115].

5.3 Coordination polymerization

5.3.1 Direct polymerization of polar monomers

The coordination polymerization by transition-metal catalysts, such as Ziegler–Natta catalysts or metallocenes, is the most versatile method for preparing linear polyolefins under mild and controlled conditions. Unfortunately, attempts at direct incorporation of functional monomers during polymerization run into the problem of catalyst poisoning caused by the interaction of organic functionalities with the catalyst center [116]. Additionally, Ziegler–Natta catalysts may promote the polymerization of polar monomers by cationic, anionic, or radical centers, which in copolymerizations with ethylene or other α -olefins leads to undesired formation of blends of homopolymers [117].

The following methods have been suggested [117] to improve the polymerizability or copolymerizability of polar monomers by Ziegler-type catalysts:

- (i) The polymerizable double bond is isolated from the heteroatom by a spacer, typically consisting of a long sequence of methylene units or a rigid cyclic unit.
- (ii) The heteroatom is shielded by sterically demanding groups.
- (iii) The electron-donating character of the heteroatom is decreased via attachment of electron-withdrawing substituents on or adjacent to it.
- (iv) The polar monomers are precomplexed with a Lewis acid, typically an organo-aluminum compound.

- (v) The catalyst components are chosen so that the deleterious effect of the heteroatom is minimized.

The transition-metal-catalyzed copolymerizations of polar monomers with ethylene and other α -olefins have recently been extensively reviewed [118–121]. Some of the most important references in the field are summarized in Tables 3–5.

Table 3. Examples of polymerizations involving functional monomers, catalyzed by titanium-, vanadium- or chromium-based Ziegler–Natta catalysts.

Catalysts	Functional monomers	α -Olefins	References (year)
TiCl ₃ AA/DEAC	ω -X- α -olefins (X = Cl, Br, I), e.g. 11-chloro-1-undecene	ethylene, propylene, 4-methyl-1-pentene	122 (1965) 123 (1965)
VOCl ₃ or V(acac) ₃ / DIBAC	Mg and Zn salts of 10-undecenoic acid	ethylene, propylene	124 (1966)
TiCl ₃ , VCl ₄ , VOCl ₃ , V(acac) ₃ or Cr(acac) ₃ / DEAC or TIBA	2,6-dimethylphenyl, phenyl and ethyl 10-undecenoates, methyl acrylate	ethylene, propylene	125 (1967)
TiCl ₃ AA/AlR ₂ Cl, TiCl ₃ AA/AlR ₃ , R = C ₂ H ₅ , i-C ₄ H ₉ , 2-methylpentyl	tertiary amine- and silyl ether functional alkenes, e.g. <i>N,N</i> -diisopropyl- 4-pentenylamine, 4-pentenyl trimethylsilyl ether	-	126 (1967) 127 (1968)
VCl ₃ /TIBA, TiCl ₃ AA/DEAC	trifluoromethyl functional α -olefins	linear and branched α -olefins	128 (1969)
TiCl ₃ /DEAC	10-undecen-1-ol, 10-undecenoic acid, 10-undecenamide	propylene, 4-methyl-1-pentene	129 (1970)
TiCl ₃ AA/AlR ₂ Cl, R = C ₂ H ₅ , i-C ₄ H ₉ VOCl ₃ /DEAC	ω -alkenoates, e.g. 2,6-dimethylphenyl 10-undecenoate	ethylene, propylene, longer linear α -olefins	130–133 (1984–89)
TiCl ₃ /DEAC	methyl 10-undecenoate	1-octene	134 (1985) 135,136 (1991)
TiCl ₄ /MgCl ₂ /TEA	silyl-protected alcohols, diols, phenols, and amines	ethylene, propylene, 1-hexene, 1-octene	137 (1988) 138 (1991)
TiCl ₃ /DEAC	10-undecenoic acid, precomplexed with DEAC	propylene	139 (1989)
VCl ₄ /DEAC	norbornene derivatives with active hydrogens, e.g. 5-norbornene-2-methanol	ethylene, propylene	116,140 (1991)
TiCl ₄ /MgCl ₂ /TEA	sterically hindered piperidine and phenol derivatives	propylene	141,142 (1992)

Table 4. Examples of polymerizations involving functional monomers, catalyzed by early-transition-metal metallocene, mono-Cp, or non-metallocene catalysts.

Catalysts	Functional monomers	α -Olefins	References (year)
Cp* ₂ ZrMe ₂ /B(C ₆ F ₅) ₃ , Et(IndH ₄) ₂ ZrMe ₂ /B(C ₆ F ₅) ₃	tertiary amine- and silyl ether functional alkenes, e.g. <i>N,N</i> -diisopropyl-4-pentenylamine, 4-pentenyl <i>tert</i> -butyldimethylsilyl ether	-	143 (1992)
Cp ₂ ZrCl ₂ /MAO, Et(IndH ₄) ₂ ZrCl ₂ /MAO, Me ₂ Si(IndH ₄) ₂ ZrCl ₂ /MAO	6- <i>tert</i> -butyl-2-(1,1-dimethyl-6-heptenyl)-4-methylphenol	ethylene, propylene	144 (1994) 145 (1996)
(<i>n</i> -BuCp) ₂ ZrCl ₂ /MAO, (Ind) ₂ ZrCl ₂ /MAO, bridged zirconocenes	10-undecen-1-ol, 5-hexen-1-ol, 10-undecenoic acid, methyl 9-decenoate	ethylene, propylene	146 (1995) 147 (1996) 148 (1997)
Et(Ind) ₂ ZrCl ₂ /MAO	11-chloro-1-undecene	1-hexene, ethylene, propylene	149 (1997)
Me ₂ Si(2-MeBenz[<i>e</i>]-Ind) ₂ ZrCl ₂ /MAO, Me ₂ Si(Ind) ₂ ZrCl ₂ /MAO	<i>N,N</i> -bis(trimethylsilyl)-10-undecenylamine	ethylene, propylene, 1-octene	150,151 (1997)
Cp ₂ ZrCl ₂ /MAO, Me ₂ Si(Ind) ₂ ZrCl ₂ /MAO, Me ₂ Si(Me ₄ Cp)(<i>N-tert</i> -Bu)TiCl ₂ /MAO	9-decenyl-substituted silsesquioxane	ethylene, propylene	152 (1997)
Et[Cp(iPr) ₃]NMe ₂ TiCl ₂ /MAO	5-hexen-1-ol, 5-norbornene-2-carboxaldehyde precomplexed with TEA	ethylene	153 (1997)
bridged and non-bridged zirconocenes/ [HNMe ₂ Ph] ⁺ [B(C ₆ F ₅) ₄] ⁻	tertiary amines, e.g. <i>N,N</i> -diisopropyl-4-pentenylamine	1-hexene, 4-methyl-1-pentene	154 (1998) 155 (1999)
Et(IndH ₄) ₂ ZrMe ₂ / [HNMe ₂ Ph] ⁺ [B(C ₆ F ₅) ₄] ⁻	alkene-substituted alkoxyamine	propylene, 4-methyl-1-pentene	156 (1998)
bridged and non-bridged zirconocenes/MAO	5-norbornene-2-methanol, precomplexed with TMA	ethylene	157 (1998)
Me ₂ Si(Ind) ₂ ZrCl ₂ /MAO, iPr(CpInd)ZrCl ₂ /MAO, iPr(3-RCpInd)ZrCl ₂ /MAO (R = Me, iPr, <i>tert</i> -Bu), homogeneous and on SiO ₂	<i>N,N</i> -diisopropyl-4-pentenylamine, 10-undecen-1-ol, 5-norbornene-2-methanol, their trialkylsilyl ethers, 5-norbornene-2-carboxylic acid, precomplexed with TIBA	ethylene, norbornene	158 (1998) 159 (1999) 160 (2000) 161 (2002) 162 (2004)

Table 4. (continued)

Catalysts	Functional monomers	α-Olefins	References (year)
Et(Ind) ₂ ZrCl ₂ /MAO, (2-MeBenz[<i>e</i>]Ind) ₂ ZrCl ₂ / MAO, Me ₂ Si(Me ₄ Cp)(N- <i>tert</i> -Bu)TiCl ₂ /MAO	10-undecen-1-ol, 5-hexen-1-ol, 10-undecenoic acid, precomplexed with TMA	ethylene, propylene	163 (1999)
bridged and non-bridged zirconocenes activated by MAO or borates	sterically hindered piperidine derivatives	ethylene, propylene, 1-hexene	164 (2000) 165 (2004)
Et(Ind) ₂ ZrCl ₂ /MAO, Me ₂ Si(2-MeBenz[<i>e</i>]- Ind) ₂ ZrCl ₂ /MAO	10-undecen-1-ol, 10-undecenoyl chloride, 10-undecenoic acid, oxazoline functional alkenes	propylene	166 (2000) 167 (2001) 168 (2002)
Ph ₂ C(CpInd)ZrCl ₂ /MAO, Ph ₂ C(CpFlu)ZrCl ₂ /MAO	9-(bicyclo[2.2.1]hept-5-en- 2-ylmethyl)-9 <i>H</i> -carbazole	ethylene	169 (2000)
Et(Ind) ₂ ZrCl ₂ /MAO	9-decen-1-ol fixed on MAO- pretreated glass fiber	propylene	170 (2001)
Et(IndFlu)ZrCl ₂ /MAO, Me ₂ Si(Flu) ₂ ZrCl ₂ /MAO, Me ₂ Si(Ind)ZrCl ₂ /MAO, Me ₂ Si(2-Me-4- PhInd) ₂ ZrCl ₂ /MAO	5-hexen-1-ol, 3-buten-1-ol, allyl alcohol, allyl amine, precomplexed with TMA or TIBA	ethylene, propylene	171 (2001) 172–174 (2004)
Et(Ind) ₂ ZrCl ₂ /MAO	5-hexen-1-ol, 9-decen-1-ol	propylene	175 (2001)
Cp ₂ ZrCl ₂ /MAO	10-undecenoic acid	ethylene	176(2001)
Et(Ind) ₂ ZrCl ₂ /MAO	norbornylene-substituted silsesquioxane	ethylene, propylene	177 (2001)
bridged unsymmetrical metallocenes, e.g. Me ₂ Si(2-MeBenz[<i>e</i>]Ind) (2,7-di- <i>tert</i> BuFlu)ZrCl ₂ / MAO	alcohol, phenol, acid, acid anhydride, aldehyde, ether, epoxy and amine functional long-chain alkenes, allyl alcohol, allyl amine	ethylene, propylene, 1-butene, 1-octene	178 (2001) 179,180 (2002) 181,182 (2003)
phenoxy–, pyrrolide– and indolide–imine complexes of Ti, V, Cr, and Cu with different cocatalysts	alcohol, ester, acid and acid anhydride derivatives of alkenes and norbornene, methyl acrylate, methyl methacrylate	ethylene, propylene	183 (2002)
Me ₂ Si(Me ₄ Cp)(N- <i>tert</i> - Bu)TiCl ₂ /MAO	3-(penten-1-yl)thiophene	ethylene	184 (2002)

Table 4. (continued)

Catalysts	Functional monomers	α-Olefins	References (year)
Me ₂ Si(IndH ₄) ₂ ZrCl ₂ /MAO, IndTiCl ₃ /MAO	α -tocopherol derivative, styrenic sterically hindered phenol and its TMS derivative	ethylene, styrene	185 (2003)
Me ₂ Si(2-Me-4-PhInd) ₂ ZrCl ₂ /MAO, Me ₂ Si(Me ₄ Cp)(N- <i>tert</i> -Bu)TiCl ₂ /MAO	diolefins containing hydrolyzable groups, e.g. 3,9-divinyl-4,6,8,10-tetraoxaspiro[5.5]undecane	ethylene	186 (2003)
mono-Cp Ti ketimide complexes/MAO	10-undecen-1-ol	ethylene	187 (2004)
Me ₂ Si(2-Me-4-PhInd) ₂ ZrCl ₂ /MAO	10-undecen-1-ol precomplexed with MAO and TIBA	propylene	188 (2004) 189 (2005)
Me ₂ Si(Me ₄ Cp)(N- <i>tert</i> -Bu)TiCl ₂ /MMAO, iPr(Ind) ₂ ZrCl ₂ /MAO	N-(vinylphenyl)carbazole	ethylene	190 (2005)
bis(phenoxyimine) and bis(phenoxyketimine) Zr and Ti complexes/MAO, Et(Ind) ₂ ZrCl ₂ /MAO	10-undecen-1-ol, 5-hexen-1-ol, 10-undecenoic acid, precomplexed with TIBA	ethylene	191 (2005) 192 (2007)
Et(Ind) ₂ ZrCl ₂ /MAO	10-undecen-1-ol precomplexed with TMA, TEA and TIBA	ethylene	193 (2005)
Me ₂ Si(2-Me-4-PhInd) ₂ ZrCl ₂ /MAO	allyl ethyl ether, allyl propyl ether, precomplexed with TIBA	ethylene	194 (2006)
Et(Ind) ₂ ZrCl ₂ /MAO supported on montmorillonite	10-undecen-1-ol/TEA	ethylene	195 (2006)

Table 5. Examples of polymerizations involving functional monomers, catalyzed by late-transition-metal catalysts.

Catalysts	Functional monomers	α -Olefins	References (year)
Ni(II) P,O-chelate complexes	various polar monomers with spacer of two or more methylene units	ethylene	196 (1987)
ether adducts or acrylate chelates of Pd(II) α -diimines/ $B[3,5-C_6H_3(CF_3)_2]_4^-$	methyl, <i>tert</i> -butyl, and fluorinated octyl acrylates, methyl vinyl ketone	ethylene, propylene, 1-hexene, 1-dodecene	197 (1996) 198 (1998)
diacetyl-bis(2,6-diisopropylaniline)Pd(methyl)(acetonitrile)/ $B[3,5-C_6H_3(CF_3)_2]_4^-$	methyl acrylate, ethyl 10-undecenoate	ethylene	199 (1999)
Ni(II) α -diimine dibromide complexes/MAO	10-undecen-1-ol, 5-hexen-1-ol, 10-undecenoic acid, precomplexed with TMA	ethylene, propylene	200 (1999) 201 (2005)
bis(benzimidazole) Cu complexes/MAO	<i>tert</i> -butyl and lauryl acrylates, methyl methacrylate, <i>n</i> -butyl vinyl ether	ethylene	202 (1999) 203 (2003)
Ni(II) α -diimine dibromide complex/MAO	acrylamide, ϵ -caprolactam, THF, vinyl acetate, methyl methacrylate, acrylonitrile, methyl vinyl ketone, precomplexed with TMA, TIBA or DEAC	ethylene, propylene	204,205 (2000) 206 (2001)
neutral, single-component salicylaldiminato Ni(II) complexes	alcohol, diol, dioxolane, ester, anhydride and imide derivatives of linear and cyclic alkenes	ethylene, 1-octene	56 (2000) 207 (2002) 208 (2004)
ester chelate of Pd(II) α -diimine/ $[SbF_6]^-$	ω -unsaturated fatty acid methyl esters, e.g. methyl 9-decenoate, methyl acrylate	ethylene	209 (2001)
Ni complexes with bulky phosphino-enolate ligands	methyl methacrylate	ethylene, propylene, 1-hexene	210 (2001)

Table 5. (continued)

Catalysts	Functional monomers	α-Olefins	References (year)
Ni complexes with neutral or monoanionic bidentate P,O- or P,N-ligands, activated with boranes	hexyl, isodecyl, and 2-phenoxyethyl acrylates, methyl methacrylate, ethyl 4-pentenoate, ethyl 10-undecenoate, methyl undecenyl ether	ethylene	211,212 (2001)
Ni(II) α -diimine complex/MAO	5-hexenoic acid, 3-butenic acid, 4-penten-1-ol, 3-buten-1-ol; masked with methylaluminum bisphenoxide derivative	ethylene	213 (2001)
neutral Ni(II) complexes with fluorinated P,O-chelate ligands	10-undecen-1-ol, 10-undecenoic acid, ethyl 10-undecenoate; in emulsion	ethylene	214 (2002)
2,6-bis(imino) pyridine Fe complexes activated with MAO or B(C ₆ F ₅) ₃ /TMA	methyl methacrylate, methyl acrylate, 2-vinyl-1,3-dioxolane; no copolymers were obtained	ethylene	215 (2002)
in situ generated P,O-chelate Pd hydrides	methyl, isopropyl, <i>n</i> -butyl, and <i>tert</i> -butyl acrylates	ethylene	216 (2002)
salicylaldiminate Ni(II) complexes/MAO	methyl methacrylate	ethylene	217 (2002)
Ni(II) complex with a phenacyldi- <i>tert</i> -butylphosphine ligand	methyl 10-undecenoate	ethylene	218 (2002)
ester chelate of Pd(II) α -diimine/ B[3,5-C ₆ H ₃ (CF ₃) ₂] ₄ ⁻	ester, ether, epoxide, and saccharide functional long-chain olefins	ethylene	219 (2003)
Ni(II) α -diimine allyl complexes, phosphine-based neutral and Zwitter-ionic Ni complexes	methyl acrylate, hexyl acrylate	ethylene	220 (2003)
Cu- or Au-based complexes containing ligands with sulfur donors	<i>tert</i> -butyl acrylate	ethylene	221 (2003)

Table 5. (continued)

Catalysts	Functional monomers	α-Olefins	References (year)
neutral Ni complex with N,O-ligand+Ni(cod) ₂	5-norbornen-2-yl acetate, 5-norbornen-2-ol	ethylene	222 (2003) 223 (2004) 224 (2006)
cyclohexyl-substituted salicylaldiminato Ni(II) complex cocatalyzed with Ni(cod) ₂ or TIBA	<i>tert</i> -butyl 10-undecenoate, methyl 10-undecenoate, 4-penten-1-ol	ethylene	225 (2004)
Pd(II) α -diimine chelate/ B[3,5-C ₆ H ₃ (CF ₃) ₂] ₄ ⁻	acrolein dimethyl acetal	ethylene	226 (2004)
neutral Ni complexes with asymmetric β -ketoiminato (N,O) ligands/MMAO	methyl methacrylate	ethylene	227 (2005)
bimetallic and mononuclear salicylaldiminato Ni(II) complexes	2-(methoxycarbonyl)norbornene, 2-(acetoxymethyl)norbornene	ethylene	228 (2005)
Ni(II) complexes with nitro-substituted N,O-chelate ligands/MAO	methyl methacrylate	ethylene	229 (2006)
Pd-allyl complexes with P,O-chelate ligands	hydroxyl- and ester-functional norbornene derivatives	ethylene	230 (2007)

Few papers have appeared on the polymerization of functional comonomers using heterogeneous or homogeneous titanium- or vanadium-based Ziegler–Natta catalysts (Table 3). Particularly infrequent has been the use of supported catalysts, presumably because of the weak ability of supported Ziegler–Natta catalysts to incorporate bulky comonomers. Additionally, in almost all of these studies the functional (co)monomers have been pretreated with aluminum alkyls, in most cases DEAC or TIBA, prior to polymerization.

The last ten years have seen a dramatic increase in the number of publications describing the synthesis of functionalized polyolefins by direct copolymerization. The reason has been the general interest in homogeneous olefin polymerization catalysts,

especially group 4 metallocenes. Many soluble metallocenes, such as bridged zirconocenes, have much better ability to incorporate higher α -olefins than do Ti-based Ziegler–Natta catalysts. This also makes them better suited for copolymerizations involving often very bulky functional comonomers. Just as with the Ziegler–Natta catalysts, papers dealing with supported metallocene complexes are rare [158,159,164].

Late-transition metals are less oxophilic than the early metals. Accordingly, catalysts based on the late-transition metals are believed to be more tolerant of polar groups. The recent scientific and patent literature (Table 5) contains many examples of late-metal-based complexes able to incorporate polar comonomers in copolymerizations with olefins, especially ethylene. The most broadly studied are complexes known as Brookhart's catalysts, that is Ni- and Pd-complexes bearing neutral bidentate α -diimine ligands [52]. Pd α -diimine complexes have even been reported to copolymerize alkyl acrylates [194,195] with ethylene. The incorporation of acrylates is based on the propagation mechanism including isomerization (referred to as chain-walking) [59,216], and the acrylate units are predominantly located in branches or end groups of the copolymer. It has been reported that even though the Pd-based catalysts tolerate polar groups, functionalities with active hydrogens, like hydroxyls, need to be protected, with bulky silyl groups for example [219]. Comonomers with longer spacer groups or blocking quaternary carbons are needed to obtain high-molar-mass copolymers [219]. The presence of a spacer group has also been found crucial for the copolymerizability of functional olefins using neutral salicylaldiminato Ni(II) complexes [208].

New Cu-, Au-, Pd- and Ni-based complexes have been shown to produce true copolymers of ethylene and alkyl acrylates where the ester groups of the acrylate are directly bound to the main chain of the copolymer [202,203,211,212,215,221]. A major problem with these complexes, as well as with Brookhart's Pd-complexes, is

the low productivity [199,203]. Another drawback associated with the use of acrylates as comonomers is the formation of acrylate homopolymers because of free radical polymerization [211,212]. Recently, it was reported that a nickel complex based on N,O-ligand and coactivated with $\text{Ni}(\text{cod})_2$ is capable of catalyzing the quasi-living copolymerization of ethylene with 5-norbornen-2-yl acetate without the addition of Lewis acid cocatalysts [222–224].

In addition to the examples given in Table 5, Ni- and especially Pd-based catalysts are known to catalyze the alternating copolymerization of carbon monoxide with ethylene or higher α -olefins to yield high-molar-mass polyketones with the carbonyl groups directly attached to the polymer backbone [231,232]. The carbonyl groups can be utilized in the further derivatization of those copolymers. The co- and terpolymerizations of oxygen-functional alkenes and allylbenzene derivatives with carbon monoxide and ethylene, propylene, styrene, or other nonfunctional monomers have also been described using Pd(II)-based catalysts [233–237].

5.3.2 Utilization of reactive copolymer intermediates

A fairly new methodology toward functionalized polyolefins is the synthesis of copolymers containing reactive, nonpolar functionalities which are subsequently converted to polar functional groups. The copolymerization of ethylene or propylene with nonconjugated dienes, for example using metallocene catalysts, gives copolymers with pendant double bonds which can be chemically functionalized or cross-linked by post-treatment reactions. However, when symmetrical α,ω -dienes, such as 1,7-octadiene, are used as comonomers, the partial cross-linking or formation of cyclic structures is usually observed [238]. These undesirable side-reactions can be suppressed by utilizing dienes such as 7-methyl-1,6-octadiene [239–241] and 5-vinyl-2-norbornene [242] with two different kinds of double bonds. Derivatization of the olefin–diene copolymers in solution has yielded polymers with, for example, epoxy,

alcohol, phenol, aldehyde, carboxylic acid or halogen functionalities in side chains [242–244]. Side-chain unsaturations provided by diene comonomers have also been used for graft modification to form graft copolymers, for example, poly(propylene-*g*-styrene) [241] suitable for polymer blend compatibilization.

In addition to dienes, comonomers containing boron [245–247], silicon [248,249] or aluminum [250] have been applied in the synthesis of reactive intermediates for functionalized polyolefins. These “weakly interacting comonomers” contain heteroatom functionalities which, when incorporated in copolymers, are precursors for a broad range of functional groups. In a related approach, *p*-methylstyrene as a comonomer in coordination copolymerizations with ethylene [251] or propylene [252] yields copolymers with reactive benzylic protons. Borane- and *p*-methylstyrene-containing copolymers have been described as versatile precursors for graft copolymers [247,253,254]. Additionally, copolymers containing Si–H bonds, poly(propylene-*co*-allylsilane) for example, are easily cross-linked with water, alcohols, or oxygen [255].

5.3.3 Terminally functionalized polyolefins

Chain-transfer reaction to compounds containing heteroatoms is a well-known method to prepare terminally functionalized polyolefins. Chain-transfer agents that cause termination of the chain growth include Al and Zn alkyls [256,257], alkyl and aryl silanes [258,259], and organoboranes [260,261]. In chain-transfer reactions, the heteroatom-containing group is delivered to a chain end of the polymer. If the chain-transfer agent contains a polymerizable double bond, like allyltrimethylsilane [262], allylbenzene [263,264], allyl alcohol [180], allyl amine [181] or styrene derivatives [265,266], they can additionally act as comonomers and be incorporated into the polymer backbone.

When noncopolymerizable chain-transfer agents are used, the amount of functionality is restricted to one functional group per chain at maximum, which may be too low a concentration to have the desired effect on the properties of the polymer. Also, because of the functionalization mechanism the amount of functionality is directly dependent on the molar mass. Nevertheless, the heteroatom–carbon bond is a versatile precursor for functional groups in post-polymerization treatment. In particular, terminally functionalized polyolefins are suitable as precursors for the synthesis of diblock copolymer structures [257,258,261,267].

Terminal functionalization can also be obtained by post-treatment of terminally unsaturated polyolefins. Amino, epoxy, hydroxy, and sulfonic groups are examples of functionalities that can be introduced to metallocene-catalyzed polypropylenes by suitable reactions of terminal double bonds in solution [268,269].

6 METALLOCENE/MAO-CATALYZED SYNTHESIS OF FUNCTIONALIZED POLYOLEFINS

Chapter 6 describes the studies on synthesis of functionalized polyolefins by metallocene-catalyzed direct copolymerization of functional comonomers with ethylene and propylene (Publications **IV–VI**). Additionally, the summary of the study on interaction of functional comonomers with metallocene catalyst components (Publication **III**) is presented here (Section 6.2). The properties of the functionalized polyolefins are discussed in Chapter 7, based on the findings presented in Publications **IV–VI**. Finally, application of functionalized polyolefins as compatibilizers for PE/PA blends (Publication **VII**) is covered in Section 8.2.

6.1 Comonomers studied in this work

The copolymerization of a polar comonomer with nonpolar olefins by coordination polymerization is thought to be possible if the insertion of the polar comonomer takes place on the same active catalyst center as the nonpolar olefin according to the Cossee–Arlman mechanism [16,17]. The prerequisite for this is that the polar comonomer coordinates to the metal center by its C=C double bond rather than by its polar group [52].

Functional long-chain alkene comonomers with different electronic and steric environments were selected for copolymerization experiments (Figures 8 and 9). Most of these comonomers can be considered derivatives of 10-undecenoic acid, which means that they contain a long spacer of methylene carbons between the polymerizable double bond and the polar group. The spacer fades out the direct electronic effect of the polar group on the double bond and makes the chelate formation after comonomer insertion improbable. On this basis it was anticipated that

random-type copolymerization of these comonomers with ethylene and propylene would be possible.

10-Undecenoic acid, as well as its methyl and ethyl esters, are commercially available from several sources. They are manufactured in large scale from castor oil and used, for example, in soaps, cosmetics and perfumes, and as precursors in polyamide 11 production [270,271].

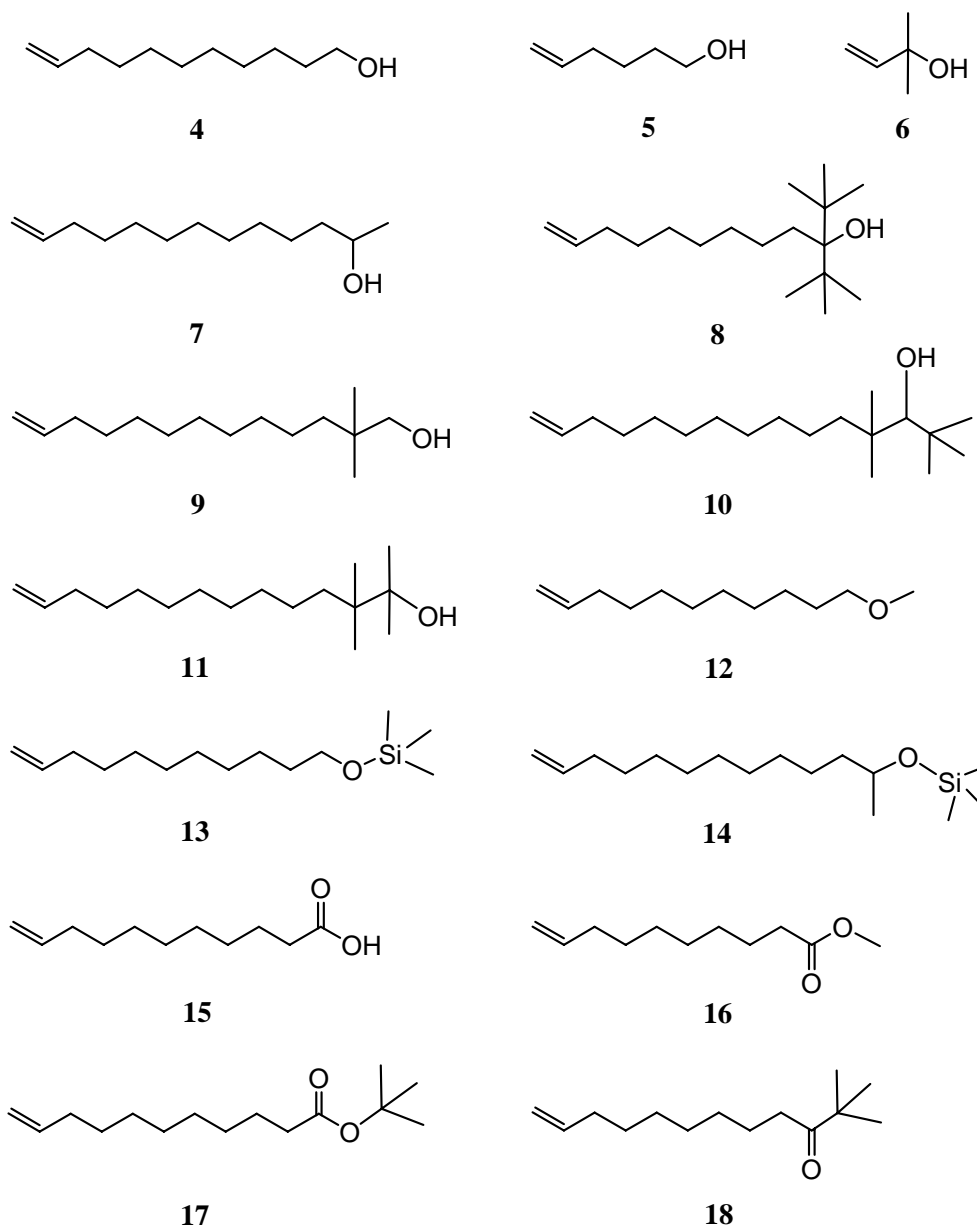


Figure 8. Oxygen-functional comonomers studied in this work: 10-undecen-1-ol (**4**), 5-hexen-1-ol (**5**), 2-methyl-3-buten-2-ol (**6**), 12-tridecen-2-ol (**7**), 2,2-dimethyl-3-(1,1-dimethylethyl)-11-dodecen-3-ol (**8**), 2,2-dimethyl-12-tridecen-1-ol (**9**), 2,2,4,4-tetramethyl-14-pentadecen-3-ol (**10**), 2,3,3-trimethyl-13-tetradecen-2-ol (**11**), 10-undecenyl methyl ether (**12**), 10-undecenyl trimethylsilyl ether (**13**), 12-tridecen-2-yl trimethylsilyl ether (**14**), 10-undecenoic acid (**15**), methyl 9-decenoate (**16**), *tert*-butyl 10-undecenoate (**17**), and 2,2-dimethyl-11-dodecen-3-one (**18**).

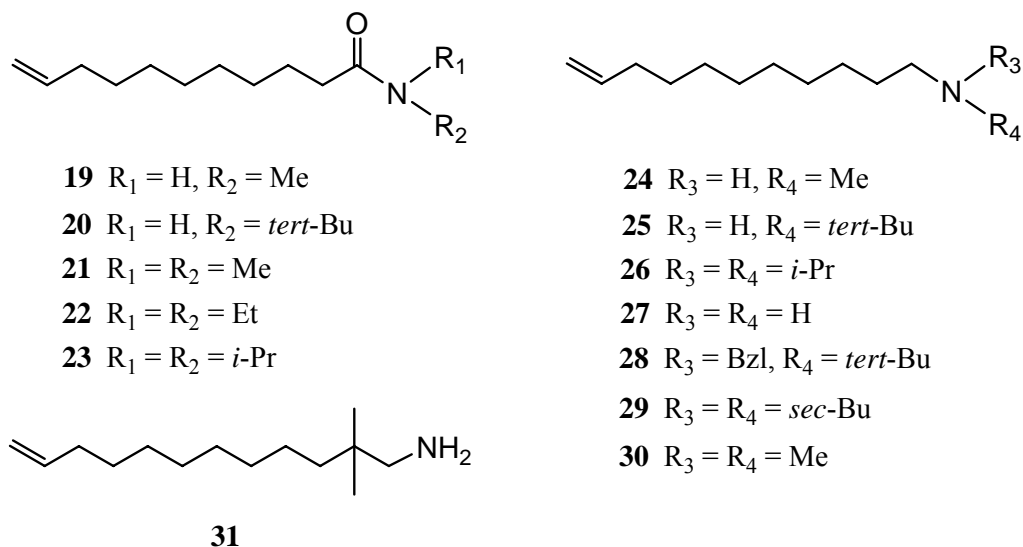


Figure 9. Nitrogen-functional comonomers studied in this work: *N*-methyl-10-undecenamide (**19**), *N-tert*-butyl-10-undecenamide (**20**), *N,N*-dimethyl-10-undecenamide (**21**), *N,N*-diethyl-10-undecenamide (**22**), *N,N*-diisopropyl-10-undecenamide (**23**), *N*-methyl-10-undecenylamine (**24**), *N-tert*-butyl-10-undecenylamine (**25**), *N,N*-diisopropyl-10-undecenylamine (**26**), 10-undecenylamine (**27**), *N*-benzyl-*N-tert*-butyl-10-undecenylamine (**28**), *N,N*-di-*sec*-butyl-10-undecenylamine (**29**), *N,N*-dimethyl-10-undecenylamine (**30**), and 2,2-dimethyl-11-dodecenylamine (**31**).

6.2 Interaction of functional comonomers with catalyst components

The most studied polar comonomers are those containing a functional group directly bound to the olefinic carbon. These include alkyl acrylates, vinyl ethers, and vinyl halides. Recent experimental and computational studies have elucidated the characteristic difficulties in copolymerizations of those comonomers with early- or late-transition-metal catalysts [272–276]. The coordination of the polar comonomers tends to be sterically and electrically unfavorable compared with the coordination of nonpolar olefins, and thus the incorporation rates are slow. An even more severe hindrance to successful copolymerization may be the high barrier to subsequent

monomer insertion after, for example, an inserted methyl acrylate unit, owing to the strong binding of the monomer polar end to the catalyst, i.e. formation of a stable chelate. On the other hand, in investigations of the reactions of vinyl chloride with group 4 metal catalysts [274] and a tantalum hydride model complex [272], 1,2-insertion of the vinyl chloride was found to be followed by selective β -Cl elimination. This means that in copolymerizations with nonpolar olefins, vinyl chloride acts as a chain transfer agent and no chlorine is incorporated into the polymer [277].

The difficulties described above are not encountered with the functional long-chain alkene comonomers studied in this work, or at least the negative effects are weaker. The relatively long distance between the functional group and the double bond makes the chelate formation improbable [278]. Additionally, the effect of the polar groups on the electron density of the double bond is weak over the spacer of many atoms. Hence, the reactions of the polar group and the double bond can be considered as competing but fairly independent of each other. The scientific literature is lacking systematic studies involving the interaction of functionalized long-chain alkenes with olefin polymerization catalyst components [279].

Reactions of the selected functionalized comonomers with MAO and MAO/zirconocene Cp_2ZrCl_2 were examined by ^1H and ^{13}C NMR spectroscopy [III]. 2D NMR techniques were employed as well to identify the intramolecular connectivities in the mixtures. MAO solution in toluene- d_8 was prepared ad hoc by partial hydrolysis of TMA [280]. The mole ratio Al/comonomer in the sample mixtures was 1. The monitored functional comonomers included 11 long-chain alkenes with hydroxyl, ether, and carbonyl functionalities. Most of the comonomers were the same as ones used in the copolymerization experiments.

All five hydroxyl-functional comonomers (**4,7,9–11**) were found to form aluminum alkoxides with MAO. The alkoxide formation has earlier been reported for 10-

undecen-1-ol [281]. The main alkoxide product is assumed to be a product of the reaction of the alkenol with free TMA present in the MAO (Figure 10, Scheme A). In addition to this, minor products were found in the mixtures, perhaps formed in reactions of the main product with structurally different MAO oligomers. The number and relative amount of the minor species varied with the alkenol according to the sterical hindrance, i.e. branching in α - and β -position to the hydroxyl group. Noteworthy, the moderately shielded comonomers **7** and **9** formed several species, but the least shielded **4** and the most shielded ones **10** and **11** a single main species. In contrast to the alcohols, the methyl and TMS ether derivatives **12–14** remained mainly as free comonomers in the presence of MAO. However, indications of complexation of the methyl ether **12** with MAO were seen (Figure 10, Scheme B).

New types of aluminum alkoxides were typically detected in the alcohol/MAO samples containing Cp_2ZrCl_2 as an additional component. The formation of these new species is presumably the result of interaction of the zirconocene with MAO. In the samples of both TMS ether derivatives, the presence of Cp_2ZrCl_2 gave rise to the formation of dimers and methyl-substituted species by reactions of the olefinic parts. Similar types of species were detected with non-functional 1-undecene but not with the methyl ether derivative.

The interaction of methyl ester derivative **16** with MAO had occurred judging by the slightly altered chemical shift values in the spectra. More interestingly, partial decomposition of the *tert*-butyl ester derivative **17** to free acid was found in the mixture containing MAO (Figure 10, Scheme C). Similarly, the *tert*-butyl-substituted ketone **18** had been reduced to a new vinyl ether species by reaction with MAO (Figure 10, Scheme D). Introduction of Cp_2ZrCl_2 as a third component to carbonyl functional comonomer/MAO mixtures had no significant effect on those reactions.

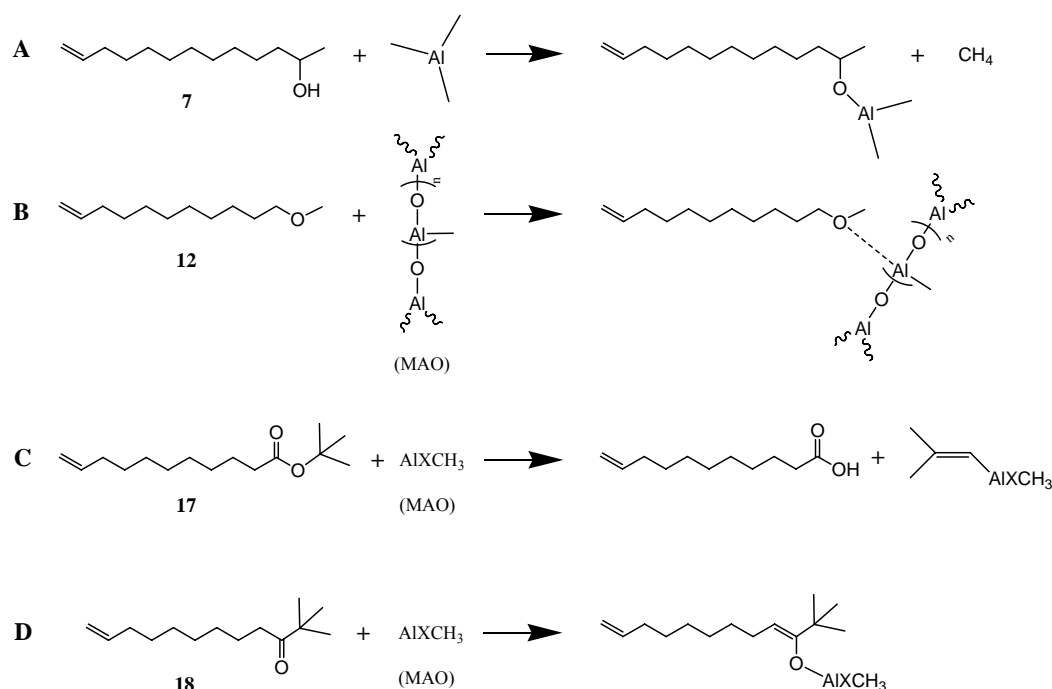


Figure 10. Examples of interaction between different oxygen-functionalized alkenes and MAO revealed in the NMR measurements.

6.3 Copolymerization behavior of oxygen-functional alkenes

Several alcohol-, ether-, acid-, ester- and ketone-functional alkenes were tested as comonomers in polymerization experiments [IV,V]. A bridged zirconocene complex $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (Figure 11, **32**) was selected as catalyst for the studies because it is a relatively good copolymerization catalyst and capable for both ethylene and propylene polymerizations. MAO was used as cocatalyst. MAO and the comonomers were precontacted for 15 min in the reactor just before start of the polymerization.

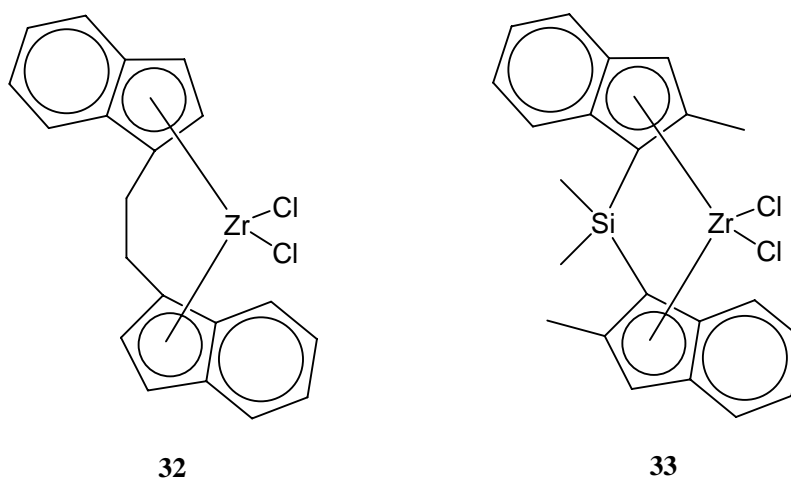


Figure 11. The metallocene catalyst precursors used in the studies of polymerizations involving functional comonomers: $\text{Et(Ind)}_2\text{ZrCl}_2$ (**32**) and $\text{Me}_2\text{Si(2-MeInd)}_2\text{ZrCl}_2$ (**33**).

The catalyst activity dropped significantly in the presence of every one of the oxygen-functional comonomers. As depicted in Figure 12, among the different alcohols the more shielded ones (**6,8**) induced the least decrease in activity in propylene copolymerizations. The length of the spacer between the alcohol group and the double bond had no effect on the decline in activity. Comparison of the alcohol- and ether-functional comonomers (**4** vs **12** and **13**) in ethylene copolymerization shows that the catalyst activity is on the same level for all three comonomers. This means that methyl and trimethylsilyl groups are not good protecting groups for oxygen atom. Among the carbonyl-containing comonomers, the carboxylic acid **15** and the more shielded ester **17** performed best in terms of catalyst activity, whereas the ketone comonomer **18** almost completely killed the catalyst.

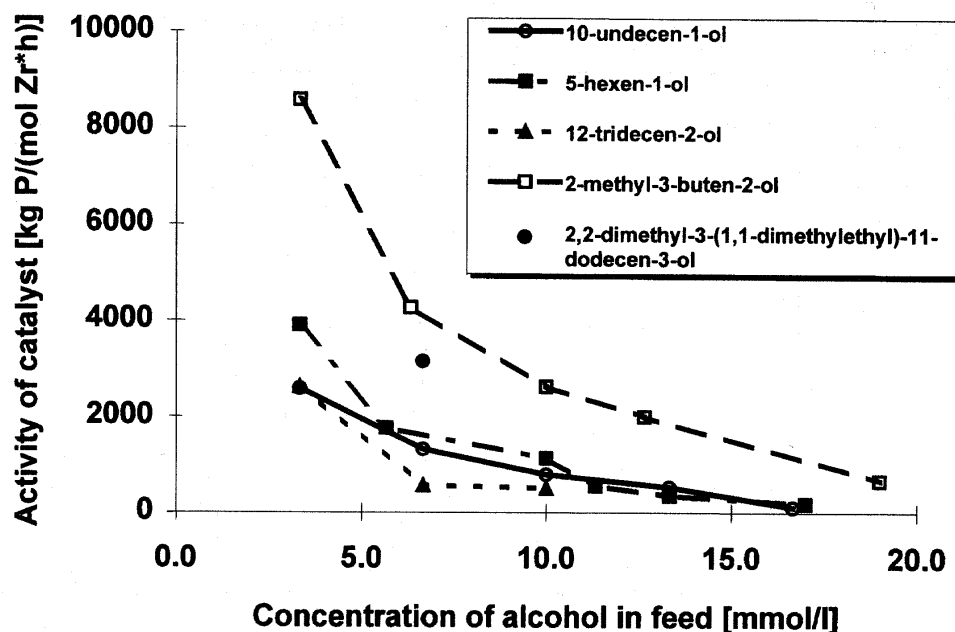


Figure 12. Effect of different alcohol comonomers on the activity of the catalyst **32**/MAO in propylene copolymerizations. Polymerization conditions: $T_p = 30\text{ }^{\circ}\text{C}$, $p_{\text{propylene}} = 3.0\text{ bar}$, $\text{Al/Zr} = 4000\text{ mol/mol}$. **[IV]**

In the studies of copolymerizations with propylene **[IV]** it was found that a longer spacer favors the copolymerizability of the oxygen-functional comonomer. Double the amount of 10-undecen-1-ol **4** was incorporated into the polymer chain compared with the amount of 5-hexen-1-ol **5**. The comonomer **6** with methyl branches at α -position to the vinyl group did not copolymerize at all. The reactivities of carbonyl-functional comonomers **15** and **17** were about the same or slightly higher than the reactivity of 10-undecen-1-ol. A similar trend was found in the ethylene copolymerizations, where ether comonomers were incorporated to about the same degree as 10-undecen-1-ol (Figure 13) **[V]**. From the different reactions of those comonomers with MAO known from the NMR studies **[III]**, it can be concluded that the formation of aluminum alkoxides is not crucial for comonomer incorporation. However, non-functional 1-undecene exhibited the highest relative reactivity, which could be inferred to derive

from the smaller size of the comonomer which does not react with aluminum-containing cocatalyst species.

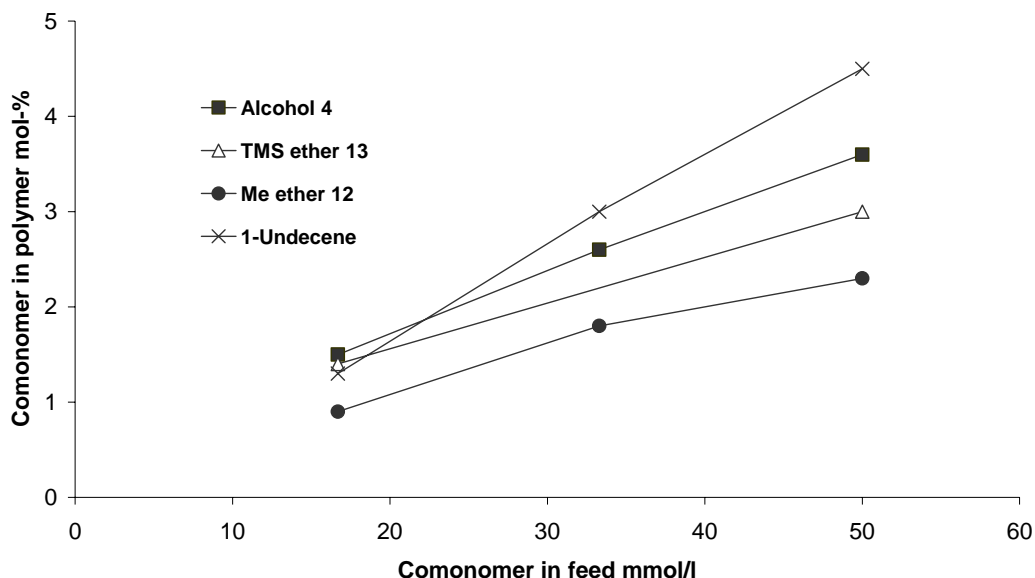


Figure 13. Reactivity of different comonomers in copolymerizations with ethylene. Polymerization conditions: $T_p = 60\text{ }^{\circ}\text{C}$, $p_{\text{ethylene}} = 1.5\text{ bar}$, $\text{Al/comonomer} = 4.0\text{ mol/mol}$. [V]

6.4 Copolymerization behavior of nitrogen-functional alkenes

Thirteen differently substituted long-chain amide- and amine-functional comonomers (Figure 9) were studied in ethylene and propylene copolymerizations carried out with catalyst **32** (for ethylene) or **33** (for propylene) [VI]. As for the oxygen-functional comonomers, MAO was used as cocatalyst. Amide-functional comonomers were found to depress the catalyst activity even with high excess of MAO (Al/comonomer 40–80 mol/mol). Slightly less poisonous were monomers **19** and **20**, which contain active hydrogens and thus are capable of reacting with TMA or MAO. No significant differences were observed in the dimethyl-, diethyl-, and diisopropyl-substituted amides.

Compared with the amides, the amine comonomers **24–31** were much better tolerated by the catalyst system. In ethylene copolymerizations the catalyst activity remained at a moderate level, that is, 1000–3000 kg polymer/(mol_{Zr}*h), when Al/comonomer ratios were 4–10 mol/mol. In the comparison of different amines, the increased bulkiness around nitrogen was found slightly to favor the catalyst activity.

Despite the low catalyst activity, all studied amides **19–23** formed copolymers with ethylene and propylene. The maximum amount of amide incorporated was 1.3 mol % with ethylene and 0.96 mol % with propylene. In the copolymerizations of amines with ethylene, the highest comonomer contents were on the same level (1.2 mol %) even though much higher comonomer concentrations could be used in the polymerizations. It seems that when the functional comonomers are better masked by the cocatalyst the reactivities are at the same time decreased. Nonetheless, even the unhindered primary and secondary amines with acidic hydrogens were incorporated in the polymer chain. In this respect, amines behave much like the alcohols and ethers studied in Publications **IV** and **V**, whereas amides resemble the less shielded esters.

7 PROPERTIES OF METALLOCENE-CATALYZED FUNCTIONAL OLEFIN COPOLYMERS

7.1 Chain structure of copolymers

Since the functionalized copolymers targeted in this work were to contain only small amounts of functional groups, it was important to study carefully the amount and type of functionalities obtained in the copolymers. The best method of analysis for this purpose is liquid NMR. The relatively low molar masses, and in the case of propylene copolymers also the low isotacticities, increased the solubility of the copolymers and facilitated the recording of high-resolution NMR spectra.

The formation of true copolymers was confirmed in all copolymers studied by ^{13}C NMR. The comonomers were present as isolated units arising from random-type incorporation of the comonomers. No consecutive comonomer units were detected by NMR, which means either that the concentration of comonomer dyads was below the sensitivity of the ^{13}C NMR measurements or that formation of the dyads was suppressed. In copolymerizations of ethylene and higher α -olefins, the bridged bis-indenyl-type metallocene catalysts, such as $\text{Et}(\text{Ind})_2\text{ZrCl}_2$, have tendency to form slightly alternating structures because of the lower relative reactivity of the bulkier comonomer at the comonomer propagating end [282].

The NMR and FTIR investigations revealed that in most cases the functional group in the copolymer was the same as that in the comonomer before polymerization. An example is the secondary amine **24** shown in Figure 14. The absence of resonances from the free comonomer shows that it has been effectively removed by the washing procedure. As an exception, the trimethylsilyl ether functionality of comonomer **13** has been converted to the corresponding alcohol, as is clear from the FTIR (Figure 15) and NMR spectra.

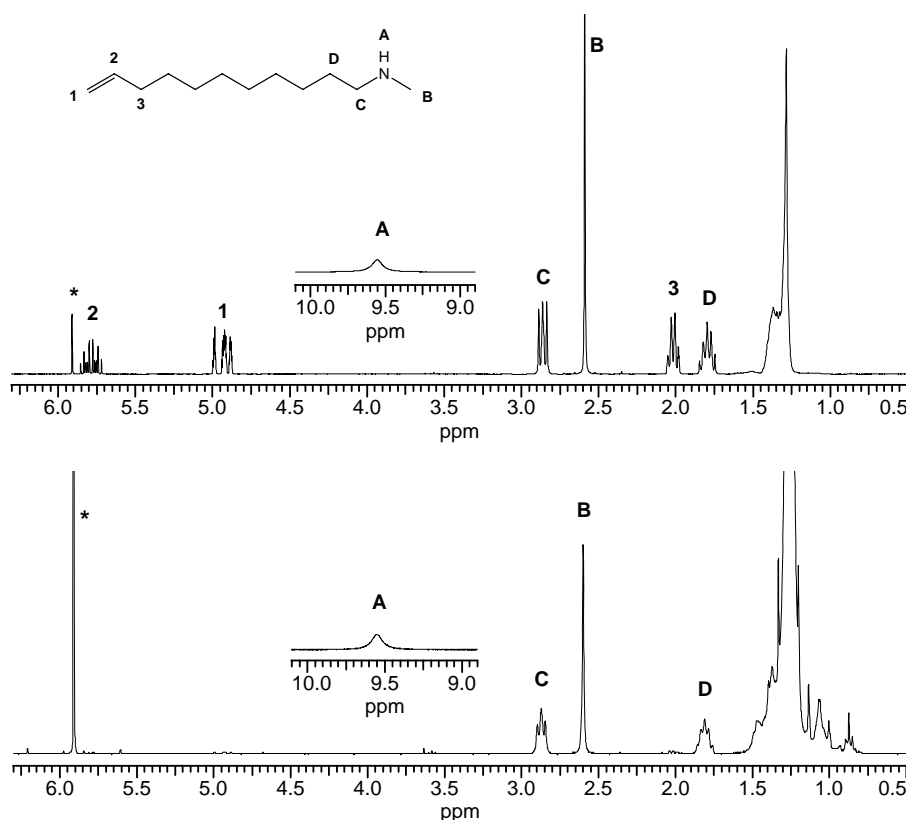


Figure 14. ^1H NMR spectra of amine **24** (above) and poly(ethylene-co-**24**) containing 1.3 mol % of amine units (below). The asterisk denotes a solvent resonance. [VI]

The NMR studies of copolymers containing amide comonomer revealed some peculiarities. In all amide copolymers the amount of saturated end groups was higher than the amount of double bonds. Termination by chain transfer to aluminum results in the polymer chains having Al–C bonds, which normally undergo hydrolysis to saturated end groups during the polymer workup [283]. It has been reported that transfer to aluminum, which normally is a minor chain termination mechanism in metallocene-mediated polymerizations, may become dominant if the monomer insertion is delayed, as it is in cyclopolymerization of 1,5-hexadiene [284] and ethylene copolymerization with allylbenzene [263,264]. In the ^1H NMR spectra of ethylene–amide copolymers there was also a triplet signal at δ 3.5 ppm, typical of

primary alcohols. The presence of hydroxymethylene groups in these copolymers was confirmed by ^{13}C NMR spectroscopy (Figure 16). A reasonable explanation of the emergence of the hydroxyl groups is as follows: since the polymer slurry was brought into contact with air a few minutes before the acidic ethanol was added, a fraction of the Al-functional chain ends may have been oxidized by oxygen and subsequently converted to hydroxyl groups by alcoholysis [284,285]. However, this cannot explain the trace amounts of similar types of hydroxyl groups seen in ^1H NMR spectra of some of the propylene–amide copolymers. On this basis it seems probable that a fraction of the amide functionalities was reduced to primary alcohol groups during either the polymerization or the acidic workup [286]. In ethylene–amide copolymers where the amount of hydroxyl groups was higher, it is not possible by NMR to differentiate between the hydroxyl groups at polymer chain ends and at the end of comonomer side chains.

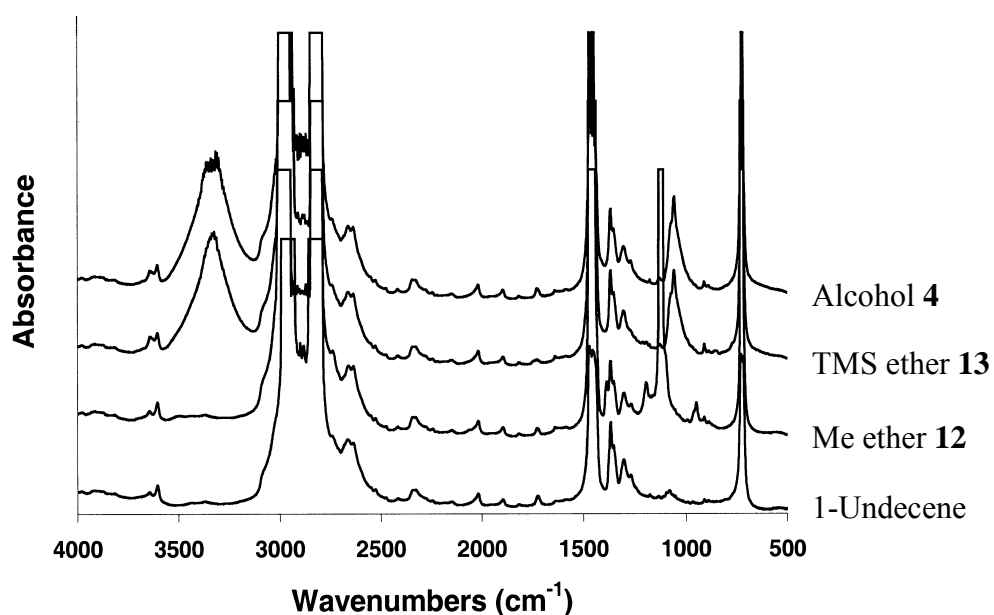


Figure 15. IR spectra of the ethylene copolymers with 1.3–1.8 mol % of functional units. Comonomers: alcohol **4**, trimethylsilyl ether **13**, methyl ether **12**, and 1-undecene. [V]

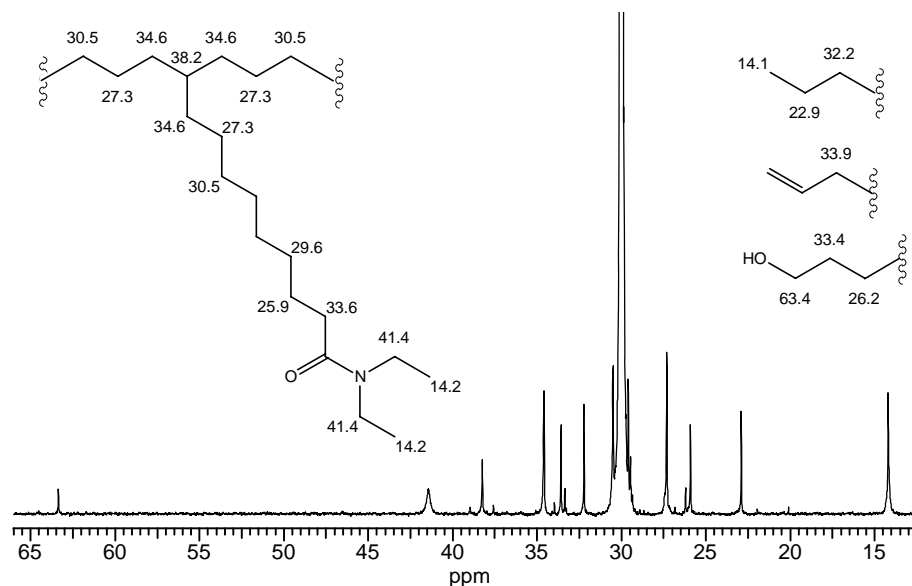


Figure 16. ^{13}C NMR spectrum of poly(ethylene-co-22) with 1.3 mol % of amide units. [VI]

7.2 Molar mass

Molar mass distributions of the prepared copolymers were measured by GPC. Relative to the molar masses of the corresponding homopolymers, the molar masses of the functionalized copolymers were always decreased. This argues in favor of the ability of the functional comonomers to terminate the propagation of the polymer chain. The decreasing effect on the molar mass was most prominent with amides and amines. In general, the functional comonomers had a greater lowering effect on molar masses in the ethylene polymerizations. However, the molar masses of propylene copolymers were also low because the complexes that were used are not capable of forming high-molar-mass polypropylene.

As discussed above, NMR studies suggested that chain transfer to aluminum is an important chain-transfer mechanism especially in the copolymerizations involving

amides or amines as comonomers. A comparison with the non-functional 1-undecene also demonstrates that the functional comonomers have a greater effect on the molar masses than do simple α -olefins [V]. In all cases the molar mass distributions remained narrow, as is typical for single-site catalysts. This finding is contradictory to the results reported for ethylene–10-undecen-1-ol copolymerizations carried out with non-bridged zirconocene/MAO, where significant broadening of the molar mass distributions was observed [146].

7.3 Melting behavior

Polyethylene and polypropylene homopolymers are semicrystalline polymers. The melting point of PE is slightly affected by molar mass and the possible presence of branching. The melting point of isotactic PP is additionally dependent on the stereo- and regioregularity of the chains. The amount of stereo- and regiodefects, which is characteristic for each metallocene complex, also depends on the polymerization conditions (temperature, monomer concentration) [110].

The melting points of the homopolyethylenes prepared with the metallocene catalyst **32** were measured by DSC to be 135–137 °C. Incorporation of functional comonomer as side chains to the polyethylene chain resulted in a decrease in the melting temperatures of the copolymer, as illustrated in Figure 17. The lower heat of fusion values with the increasing comonomer content provide additional support for lowering of the polymer crystallinity due to side chains. In a comparison with the non-functional comonomer 1-undecene [V], the change in the melting points with functional comonomers was found to follow approximately the same trend. This demonstrates that the incorporation of functional comonomers is random, and the chain structure of the functionalized copolymers is similar to that of ethylene– α -olefin copolymers prepared with single-site catalysts.

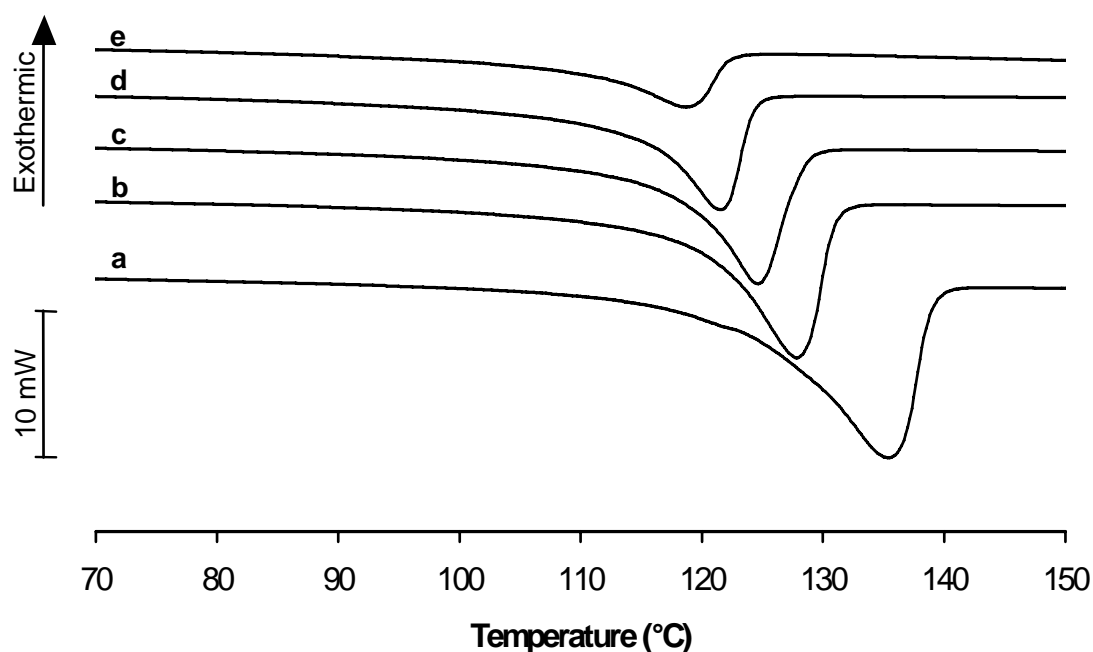


Figure 17. DSC melting curves of ethylene homopolymer (a) and ethylene/10-undecen-1-ol copolymers containing 0.7 mol % (b), 1.4 mol % (c), 2.6 mol % (d), and 3.6 mol % (e) of 10-undecen-1-ol. Data from the second heating are presented, heating rate 10 °C/min.

The melting points of the propylene homopolymers synthesized by zirconocene catalysts **32** and **33** were 138 °C and 148 °C, respectively. These values are significantly lower than the value for conventional highly isotactic Ziegler–Natta PP, which is about 165 °C. The reason for the low melting temperatures is the high content of stereo- and regioerrors. As for the ethylene copolymers, the melting points of the propylene copolymers decreased with increasing incorporation of functional comonomer. In the case of amide **23**, a 12-degree lowering of T_m was obtained with incorporation of 1 mol % comonomer. All copolymers exhibited just one melting transition, which once again is an indication of homogeneous structure.

8 POTENTIAL APPLICATIONS FOR FUNCTIONALIZED POLYOLEFINS

8.1 Applications described in the literature

Functionalized copolymers prepared by coordination copolymerization have many advantages over the functionalized polyolefins prepared by radical polymerization or grafting. Coordination polymerization gives access to stereocontrol as well as to precise control of composition, crystallinity, molar mass, and their distribution. Copolymers prepared in this way can thus be applied to a great variety of different end uses, as is well illustrated in the literature, and particularly in the patent literature.

Many useful properties can be imparted to polyolefins by incorporating a small percentage of functional comonomer. It has been demonstrated, for example, that isotactic copolymers of propylene with allyl or diallyl amines (less than 1 mol %) have good color uptake in dyeing, whereas the corresponding PP homopolymer remains undyed [138]. Relative to the homopolymer, a five-fold increase in the tensile adhesion strength to aluminum was observed in functionalized ethylene copolymers containing 1.7 mol % copolymerized 10-undecenoic acid units [287]. A similarly great improvement of adhesion between glass and PP film was found in laminates when poly(propylene-*co*-5-hexen-1-ol) was used as an interfacial adhesion promoter [288]. Recently, examples have been presented of the use of metallocene-catalyzed anhydride-functionalized PP as a compatibilizer in PP/PA blends and as an adhesion promoter in PP composites [179]. Furthermore, nitrogen- or oxygen-functionalized olefin copolymers can be used as viscosity improvers and dispersants in lubricating oils and hydrocarbon fuels [134–136,289,290], and hydroxylated polypropylenes are applicable as catalyst supports in cationic [291] and metallocene-catalyzed polymerizations [292].

Polyolefins with a low content of chemically bound sterically hindered phenol or amine functionalities have been prepared with use of Ziegler–Natta and metallocene catalysts [293,294]. The copolymers show enhanced light and heat stability. In contrast to this, it has been proposed that hydrolytically degradable polyolefins could be synthesized by copolymerization of olefins with diolefin comonomers containing hydrolyzable functional groups, for instance cyclic diketenes [186]. A drawback of this approach is that relatively high levels of hydrolytically cleavable linkages are needed, so that the content of functional comonomer in the copolymer should be at least 20 mol %.

8.2 Functionalized polyethylenes as compatibilizers for PE/PA blends

Polymer–polymer blends are finding extensive application in the development of new materials. As an example, immiscible blends of polyolefins and engineering plastics offer novel types of polymers which synergistically combine the properties of their components [295]. Key to the physical properties of these blends is their morphology, i.e. the size and shape of the dispersed phase [296]. The phase morphology and its stability are largely controlled by interfacial adhesion.

One way to control the blend morphology is to apply a compatibilizer, which acts as an interfacial agent promoting adhesion between the phases [297]. The compatibilizers are usually block, graft, or random copolymers, which often contain constituents identical with blend components [114]. Because of the importance of polyolefin-based blends, the use of functionalized polyolefins as interfacial agents in polymer–polymer blends is a major application. Among agents widely used are maleic anhydride- or acrylic acid-grafted polyolefin homo- and copolymers [298].

In this work [VII] the novel functionalized ethylene copolymers synthesized by methods presented in the preceding chapters were investigated as compatibilizers in

blends of commercial low-density polyethylene (40 wt %) and polyamide 6 (60 wt %). The compatibilizers differed in comonomer type (10-undecen-1-ol, 10-undecenoic acid, *N*-methyl-10-undecenylamine) and amount (0.2–1.2 mol %) as well as in molar mass (M_w 11–136 kg/mol) and crystallinity (ΔH_m 106–190 J/g). Blends containing 5 or 10 wt % of the compatibilizer were prepared by melt mixing of the polymers in a small-scale twin-screw extruder. The performance of the compatibilizers was assessed on the basis of mechanical and thermal properties and morphology of the blends.

Blends containing 10 wt % of metallocene-based copolymer were found to be significantly tougher and stiffer than the uncompatibilized blend. This is a clear indication of the presence of the functionalized copolymer at the PE/PA interface, which lowers the interfacial tension. Higher values of elongation at break for the compatibilized blends provide support for enhanced adhesion between the phases. The improved compatibility was also seen in the SEM micrographs as much finer morphology and a more ragged interface between the phases in the compatibilized blends. In the blends containing hydroxyl- or carboxyl-functional polyethylenes, higher molar mass of the compatibilizer was found to be advantageous in terms of mechanical properties. This can be explained by enhanced entanglement formation with the polyethylene phase at higher molar mass [299,300]. On the other hand, the *N*-methylamino-functional compatibilizer also gave a substantial increase in stiffness and toughness even though it had the lowest molar mass of all compatibilizers.

Chemical linkage formation among the functional groups of the functionalized polyethylenes and the terminal groups of the polyamide was verified by studying the IR spectra of the blends after dissolving the pure polyamide part with formic acid. Ester groups were found in blends containing hydroxyl-functional polyethylenes, indicating a grafting reaction between the hydroxyl groups and carboxyl end groups of polyamide. Similarly, in blends containing *N*-methylamino-functional polyethylene, the presence of amide groups arising from the reaction of the secondary amino groups

with the carboxyl groups of the polyamide was evidence of graft copolymer formation. Carboxyl functionalities of acid-functional polyethylenes are assumed to form amide linkages with the amine end groups of the polyamide, though it was not possible to obtain clear evidence of that by the IR measurements because of the overlapping peaks from polyamide. It is also known that interfacial interactions can be substantially enhanced by the formation of hydrogen bonds between the blend components, so that covalent bonding is not a prerequisite for efficient compatibilization [301].

The results show that the functionalized copolymers prepared with metallocene catalysts possess increased compatibility with polyamide and they can be applied as compatibilizers in PE/PA blends. Further studies by Seppälä and co-workers have demonstrated the applicability of these types of copolymers as coupling agents in polyethylene-based composites [302,303] and nanocomposites [304,305] as well as the efficiency of the corresponding functionalized polypropylenes in PP/PA 6 blends [306]. Recently, related functionalized metallocene polyethylenes have been reported as compatibilizers in PE/polyaniline [307], PE/starch, and PE/dextran [308] blends.

9 SUMMARY

Two new classes of transition-metal complexes were successfully utilized as catalysts in ethylene polymerization. Aminopyridinato-ligated tantalum(V) complexes **1** and **2** activated by MAO exhibited higher activities than reported for any other tantalum- or niobium-based single-site complexes [71,72]. Zr(salen)Cl₂/MAO showed low catalytical activity when used as a homogeneous system, but moderate ethylene polymerization activities were obtained when it was supported on porous silica. Zirconium salen complex **3** was one of the first olefin polymerization catalysts published in the class of phenoxy–imine type single-site complexes, which have been an object of intensive research in recent years [104,105]. All complexes **1–3** yielded polyethylene with linear structure and molar masses on a level relevant for commercial applications.

The difficulty in using functional comonomers in transition-metal-catalyzed polymerizations is associated with their tendency to poison the Lewis acidic catalyst centers by strong coordination. In NMR studies of the oxygen-functional comonomers, clear correlations were discovered between the nature (type, sterical hindrance) of the functional groups and their interaction with MAO and zirconocene. Alkenols formed different kinds of aluminum alkoxides, whereas ethers remained mainly as free comonomers. In a comparison of these findings with the behavior of the same comonomers in ethylene copolymerizations it became clear that the formation of aluminum alkoxides is not a prerequisite for polymerizability of the functional comonomer. As a matter of fact, 10-undecen-1-ol and its ether derivatives performed in a similar way in terms of both catalyst poisoning and comonomer incorporation rate. In the group of nitrogen-functional comonomers, amines exhibited behavior comparable to that of the alcohols, whereas with amides much higher excess of MAO was needed to keep the catalyst active.

The structure of the functionalized copolymers, investigated by NMR and DSC, was interpreted to consist of randomly distributed comonomer units in the polyolefin chains. Copolymers with free alcohol, acid, ester, ether, amine, or amide groups were synthesized, judging from the spectroscopic characterization of the copolymers. Molar masses of the comonomers were lower than those of polyethylene and polypropylene homopolymers prepared under the same polymerization conditions. Chain transfer to aluminum was recognized as an important chain-termination mechanism especially with amine- and amide-functional comonomers.

The metallocene-catalyzed ethylene copolymers containing hydroxyl, carboxyl, or methylamino functionalities were found to function as effective compatibilizers in polyethylene/polyamide 6 blends. The toughness of the blends was clearly increased with 5 or 10 wt % of functionalized copolymer as compatibilizer. Interestingly, the strength and stiffness of the blends were also improved. The improved compatibility of the blend components was also seen in SEM micrographs. The IR studies indicated that the functional groups of the copolymers had reacted with the terminal groups of the polyamide.

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