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Espoo 2007

α,ω-DIENE FUNCTIONALIZED POLYETHENE PREPARED WITH METALLOCENE CATALYST

Doctoral Dissertation

Pirjo Pietikäinen

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Chemical Technology for public examination and debate in Auditorium E at Helsinki University of Technology (Espoo, Finland) on the 12th of October, 2007, at 12 noon.

Helsinki University of Technology
Department of Chemical Technology
Laboratory of Polymer Technology

Teknillinen korkeakoulu
Kemian tekniikan osasto
Polymeeriteknologian laboratorio

Distribution:
Helsinki University of Technology
Department of Chemical Technology
Laboratory of Polymer Technology
P.O. Box 6100
FI - 02015 TKK
FINLAND
URL: http://polymeeri.tkk.fi/
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ISBN 978-951-22-8955-4
ISBN 978-951-22-8956-1 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)
URL: http://lib.tkk.fi/Diss/2007/isbn9789512289561/

TKK-DISS-2345

Multiprint Oy
Espoo 2007

HELSINKI UNIVERSITY OF TECHNOLOGY
P. O. BOX 1000, FI-02015 TKK
http://www.tkk.fi

ABSTRACT OF DOCTORAL DISSERTATION

Author Pirjo Pietikäinen

Name of the dissertation
α,ω-diene-functionalized polyethene prepared with metallocene catalysts

Date of manuscript 22.5.2007	Date of the dissertation 12.10.2007
☐ Monograph	☒ Article dissertation (summary + original articles)

Department	Chemical Technology
Laboratory	Polymer Technology
Field of research	Polymer Technology
Opponent(s)	
Supervisor	Professor Jukka Seppälä
(Instructor)	Dr. Barbro Löfgren

Abstract

Ethene was copolymerized with linear nonconjugated dienes (1,5-hexadiene (HD), 1,7-octadiene (OD), 7-methyl-1,6-octadiene (MOD)) using homogeneous metallocene catalysts (cyclopentadienylzirconium dichloride, Cp_2ZrCl_2; *rac*-ethylenebis(indenyl)zirconium dichloride, $Et[Ind]_2ZrCl_2$; bis(n-butylcyclopentadienyl)zirconium dichloride, $(n\text{-}BuCp)_2ZrCl_2$; *rac*-ethylenebis(indenyl)hafnium dichloride, $Et[Ind]_2HfCl_2$). The cocatalyst was methylaluminoxane (MAO).

A wide variety of structures can be formed in the copolymerization of ethene and linear non-conjugated dienes. Whether the diene is incorporated in polyethene chain as branches or cyclic structures is determined by the choice of diene, metallocene catalyst, and polymerization conditions. HD is easily cyclized, forming 1,3-cyclopentane rings in the polyethene chain, MOD has a methyl group that prevents its cyclization, and the ability of OD to cyclize depends on the catalyst. In addition, it is important to be able to control the crosslinking, which is effectively diminished by increasing the polymerization temperature.

Polyethenes with modified rheologies can be produced by incorporating long-chain branching (LCB). LCB is desired in metallocene-catalyzed polyethene to enhance processability. The ability of metallocenes to induce LCB *in situ* in ethene polymerization was exploited. Since the formation of LCB is favored by the presence of vinyl groups, copolymerizations with diene offer a useful approach to the formation of LCB. Reasonable amounts of LCB were formed in copolymers of ethene with both HD and OD.

Ethene/diene copolymers were post-polymerization functionalized to reactive silane functional polyethenes (PE-co-SiX, X=Cl, OEt, Ph). These functional polyethenes were able to interact with filler and transfer part of the filler to the rubbery phase of heterophasic polypropene. Significant improvement was thereby achieved in the toughness as compared with unfilled hPP, both below the T_g of PP and at ambient temperature.

Keywords polyethene, linear nonconjugated diene, metallocene, functionalization

ISBN (printed) 978-951-22-8955-4	ISSN (printed) 1795-2239
ISBN (pdf) 978-951-22-8956-1	ISSN (pdf) 1795-4548
ISBN (others)	Number of pages 72 p.+ app. 56 p.

Publisher Helsinki University of Technology, Laboratory of Polymer Technology
Print distribution Helsinki University of Technology, Laboratory of Polymer Technology
☒ The dissertation can be read at http://lib.tkk.fi/Diss/2007/isbn9789512289561

TEKNILLINEN KORKEAKOULU
PL 1000, 02015 TKK
http://www.tkk.fi

VÄITÖSKIRJAN TIIVISTELMÄ

Tekijä Pirjo Pietikäinen

Väitöskirjan nimi

Metalloseenikatalyysillä valmistettu α,ω-dieeneillä funktionalisoitu polyeteeni

Käsikirjoituksen jättämispäivämäärä 22.5.2007

Väitöstilaisuuden ajankohta 12.10.2007

☐ Monografia

☒ Yhdistelmäväitöskirja (yhteenveto + erillisartikkelit)

Osasto	Kemian tekniikan osasto
Laboratorio	Polymeeriteknologian laboratorio
Tutkimusala	Polymeeriteknologia
Vastaväittäjä(t)	
Työn valvoja	Professori Jukka Seppälä
(Työn ohjaaja)	FT Barbro Löfgren

Tiivistelmä

Eteeniä ja lineaarisia, konjugoimattomia α–ω-dieenejä kopolymerointiin käyttäen metalloseenikatalyyttejä. Tutkimuksen dieenit olivat 1,5-heksadieeni (HD), 1,7-oktadieeni (OD) ja 7-metyyli-1,6-oktadieeni (MOD). Käytetyt homogeeniset metalloseenikatalyytit olivat syklopentadienyylizirkoniumdikloridi (Cp_2ZrCl_2), *rac*-etyylibisindenyylizirkoniumdikloridi ($Et[Ind]_2ZrCl_2$), *bis*-n-butyylisyklopentadienyylizirkonium-dikloridi ($(n\text{-}BuCp)_2ZrCl_2$) ja, *rac*-etyylibisindenyylihafniumdikloridi ($Et[Ind]_2HfCl_2$). Metyylialuminoksaani (MAO) oli kokatalyyttinä kaikissa kopolymeroinneissa.

Dieenit voivat polymeroitua polyeteeniketjuun muodostaen monenlaisia rakenteita. 1,2-additio tuottaa lyhyitä haaroja, joiden pituus riippuu dieenistä. 1,2-addition jälkeen voi seurata myös renkaanmuodostusreaktio, johon dieenin reagoimaton kaksoissidos osallistuu. Renkaanmuodostuminen tapahtuu todennäköisimmin kun dieenin pituuden ollessa 6-8 hiiliatomia. Dieenin toisen kaksoissidoksen suojaaminen esimerkiksi metyyliryhmällä estää sekä renkaanmuodostusreaktion, että polymeerin ristisilloittumisen polymerointireaktion aikana.

Lyhyiden haarojen lisäksi metalloseenikatalysoituun polyeteeniin on mahdollista saada myös pitkiä haaroja, jotka parantavat polymeerin työstettävyyttä. Edellytys pitkäketjuhaarautumien muodostumiselle on se että polyeteenissä on riittävästi vinyylisidoksia, joita saadaan polyeteeniin kopolymeroimalla siihen dieenejä. Sekä HD- että OD-komonomeeri muodosti kopolymeeriin merkittäviä määriä pitkäketjuhaaraumia.

Eteni/dieeni-kopolymeeriin muodostuvia kaksoissidoksia voidaan käyttää hyväksi kopolymeerin funktionalisoinnissa. Tässä työssä eteeni/OD kopolymeerin vinyylisidoksia epoksoitiin tai hyrsosilyloitiin. Tutkituissa heterofaasisen polypropeenin ja mikrosilikan seoksissa (hPP/μSi) silyloidut polyeteenit (PE-co-SiX (X=Cl, OEt, Ph)) siirsivät osan täyteaineesta polypropeenin kumifaasiin. Näin murtumismekanismi muuttui ja polypropeenin iskulujuutta saatiin parannettua niin PP:n lasiutumislämpötilan ala- kuin yläpuolellakin. Lisäksi hPP:n lujuus säilyi toisin kuin aikaisempia PE-pohjaisia kompatibilisaattoreita käytettäessä.

Asiasanat polyeteeni, lineaarinen konjugoimaton α–ω-dieeni, metalloseeni, funktionalisointi

ISBN (painettu) 978-951-22-8955-4	ISSN (painettu) 1795-2239
ISBN (pdf) 978-951-22-8956-1	ISSN (pdf) 1795-4548
ISBN (muut)	Sivumäärä 72 s. + liit. 56 s.

Julkaisija Teknillinen korkeakoulu, Polymeeriteknologian laboratorio

Painetun väitöskirjan jakelu Teknillinen korkeakoulu, Polymeeriteknologian laboratorio

☒ Luettavissa verkossa osoitteessa http://lib.tkk.fi/Diss/2007/isbn9789512289561

PREFACE

This work was carried out in the Laboratory of Polymer Technology at Helsinki University of Technology and was partly financed by The Finnish Founding Agency for Technology and Innovation (Tekes).

I am most grateful to my supervisor, Prof. Jukka Seppälä for providing me the opportunity to participate various challenging projects in his laboratory. Dr. Barbro Löfgren is warmly thanked for advice, guidance, and encouragement.

I am greatly indebted to my co-workers, Mrs. Anneli Pakkanen (née Malmberg) and Dr. Esa Kokko from Borealis Polymers, whose contribution to this work has been invaluable. Mr. Sami “Mano” Lipponen, whose expertise and flexibility are unquestioned, is warmly thanked for cooperation and support. The metallocene group of the laboratory assisted by providing a pleasant and fruitful working atmosphere. The whole personnel of the Laboratory of Polymer Technology have contributed a wonderful spirit and unforgettable moments in work as well as leisure. Mr. Jorma Hakala provided invaluable help with library services and Dr. Kathleen Ahonen revised the language of this thesis and the appended publications.

During this project I have had the pleasure of learning from many skilful scientists, all of whom added to the value of this work. Sincere thanks go to all the co-authors and to Dr. Alpo Toivo (Neste Oil Oyj), and to Dr. Eeva-Leena Heino (Borealis Polymers) who assisted me with the polymer analysis.

To my dearest friends Auli, Henna, Merja, and Sirpa, whose comradeship has been essential, my noble thanks. Tuula-Riitta is warmly thanked for her emotional support.

Sincere thanks belong to my parents Riitta and Onni[†] Rautianen for their unwavering trust in me. The grandparents of my children, Iija and Juha Pietikäinen, are thanked for the support they have provided me, also in academic life. Superspecial and dear thanks belong to my wonderful children, Hanna, Mikko, and Kaisa, who have instructed me in the realities of life and kept my mind young (at least I hope so). Mum loves you so much.

Espoo, May 2007,

Pirjo Pietikäinen

CONTENTS

LIST OF PUBLICATIONS

I Pietikäinen, P., Väänänen, T., and Seppälä, J.V., Copolymerization of Ethylene and Non-conjugated Dienes with Cp_2ZrCl_2/MAO Catalyst System, *European Polymer Journal* **35** (1999) 1047-1055.

II Pietikäinen, P., Seppälä, J.V., Ahjopalo, L., and Pietilä, L.-O., Copolymerization of Ethylene and Non-conjugated Dienes with Cp_2ZrCl_2/MAO Catalyst System. The Effect of Polymerization Temperature on the Structure of the Copolymer, *European Polymer Journal* **36** (2000) 183-192.

III Pietikäinen, P., Starck, P., and Seppälä, J.V., Characterization of the Comonomer Distributions Ethylene/Diene Copolymers by ^{13}C NMR, Segregation Fractionation Techinque (SFT) and by DMTA, *J. Pol. Sci. Part A: Polym. Chem.* **37** (1999) 2379-2389.

IV Pietikäinen, P., Malmberg, A., Löfgren, B., and Seppälä, J, Studies on the Properties of Metallocene Catalyzed Copolymers of Ethylene and Linear, Non-conjugated Dienes, in Kaminsky, W. (ed.*), Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler-Natta and Metallocene Investigations*, Springer Verlag, Berlin, Germany, **1999**, pp. 502-508.

V Kokko, E., Pietikäinen, P., Koivunen, J., and Seppälä, J.V., Long-Chain Branched Polyethene by Copolymerization of Ethene and Nonconjugated α,ω-Dienes*, J. Pol.Sci., Part A; Polym. Chem.* **39** (2001) 3805-3817.

VI Lipponen, S., Pietikäinen, P., Vainio, U., Serimaa, R., and Seppälä, J., Silane Functionalized Ethene/Diene Copolymer Modifiers in Composites of Heterophasic Polypropene and Microsilica, *Polymers and Polymer Composites* (2007), accepted.

AUTHOR’S CONTRIBUTION TO THE APPENDED PUBLICATIONS

I Pirjo Pietikäinen planned the experiments, carried out the polymerizations and polymer characterization and was the principal author of the manuscript.

II Pirjo Pietikäinen planned the experiments, carried out the polymerizations and polymer characterizations and was the principal author of the manuscript.

III Pirjo Pietikäinen planned the experiments, carried out the polymerizations and part of the polymer characterizations and prepared the manuscript with the coauthors.

IV Pirjo Pietikäinen planned the experiments, carried out the polymerizations and characterizations of the polymer, except for the rheological measurements, and prepared the manuscript with the coauthors.

V Pirjo Pietikäinen planned and carried out part of the polymerizations, participated in planning and guiding the polymerizations with the coauthor, carried out the NMR characterization of the polymers, and wrote the manuscript with the coauthors.

VI Pirjo Pietikäinen planned and carried out the polymerizations, participated in planning the post-functionalization of the polymer and blending and characterization of the polymers, carried out part of the blending and characterizations, and wrote the manuscript with the coauthors.

ABBREVIATIONS

Bu	butyl
CCD	chemical composition distribution
CGC	constrained-geometry catalyst
Cp	cyclopentadienyl
DCP	dicyclopentadiene
DD	1,9-decadiene
DMO	5,7-dimethyl-1,6-octadiene
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
EBI	Et[Ind]$_2$ZrCl$_2$
ENB	5-ethylene-2-norbornene
EPDM	ethene/propene/diene terpolymer
EPR	ethene/propene rubber
Et	ethyl
Flu	fluorenyl
FTIR	Fourier transform infrared spectroscopy
HD	1,5-hexadiene
1,4-HD	1,4-hexadiene
hPP	heterophasic polypropene
Ind	indenyl
LCB	long-chain branching
MAH	maleic anhydride
MAO	methylaluminoxane
MMD	molar mass distribution
MOD	7-methyl-1,6-octadiene
NMR	nuclear magnetic resonance spectroscopy
OD	1,7-octadiene
PBT	polybutene terephthalate
PE	polyethene
PE-co-SiX	polyethene copolymer containtng SiX group
PE-HD	high-density polyethene
PE-LD	low-density polyethene
PE-LLD	linear low-density polyethene
PP	polypropene
SCB	short-chain branching
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SFT	segregation fractionation technique
SSC	single site catalyst
TCB	trichlorobenzene
TMA	trimethylaluminum
VCH	4-vinyl-1-cyclohexene
PE-VLD	very low-density polyethene
VNB	5-vinyl-2-norbornene
Z-N	Ziegler-Natta

WAXS	wide angle X-ray spectroscopy
μSi	microsilica

ε	molar absorptivity coefficient	[$mm^{-1} \times (mol\%)^{-1}$]
η^*	complex viscosity	[Pa s]
η^0	zero-shear viscosity	[Pa s]
ω	frequency	[rad s^{-1}]
A	absorbance	
d	film thickness	[mm]
E_a	activation energy	[kJ/mol]
G’	storage modulus	[Pa]
G’’	loss modulus	[Pa]
M_e	entanglement molar mass	[g/mol]
M_n	number average molar mass	[g/mol]
M_w	weight average molar mass	[g/mol]
M_w/M_n	polydispersity	
Me	methyl	
T_g	glass transition temperature	[°C]
T_m	melt temperature	[°C]
Tanδ	damping factor, G’’/G’	
S	gel strength	[Pa s]

1 INTRODUCTION

1.1 History and present state of polyethene production

With their wide versatility, low cost, and neutral environmental impact, polyolefins are a major commodity thermoplastic used worldwide. When compared with polar polymers, however, polyolefins suffer from low gas barrier properties, lack of good adhesion, inadequate compatibility, and particularly at high temperatures, poor mechanical properties. They are also difficult to coat. If the applications of polyolefins are to be extended, these disadvantages must be overcome.

The development of polyethene depends heavily on achievements in the field of (coordination) polymerization catalysis. It has been predicted that metallocene catalyst technology will have a highly significant impact on the polymer industry. There has been a veritable explosion of introductions to the market of new products with outstanding properties. On the polymer industry, when we look back over the past century, we can see that the technology has developed step-wise. There have been three phases of development (Figure 1), followed by a long period of evolutionary research, and now we are in the fourth phase.[1]

The first phase in the 1920s, involved the acquirement of a fundamental understanding of the very nature of polymers. The second phase, in the early 1940s, saw the development of commercially viable technologies for low density polyethene (PE-LD) via high pressure free radical polymerization. This was the genesis of polyolefins as we know them today, and of an industry that currently produces more than 90 million tons/year of polyolefins.

The third revolutionary phase in the 1950s, was based on the discoveries of coordination polymerization catalysts by Ziegler, Natta, and others. This was the starting point of isotactic polypropene (PP), high density polyethene (PE-HD), and linear low density polyethene (PE-LLD). [1]

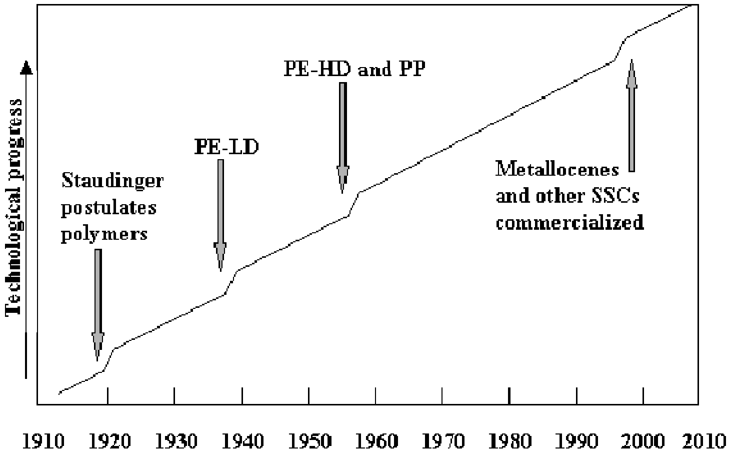


Figure 1. Development of polymer/polyolefin technology.[1]

The fourth ongoing is based on metallocene and other single-site catalyst (SSC) technologies.[1] Metallocene catalysts combined with methylaluminoxane (MAO) as cocatalyst [2,3] deliver remarkable catalytic performances and offer greater versatility and flexibility in the synthesis and structural control of polyolefins than do conventional Ziegler-Natta systems. The importance of metallocenes lies in their high polymerization activity as well as in the breadth of type and level of comonomer that can be incorporated.[4-6] Near random and relatively narrow distribution of the comonomer (CCD) along the polymer chain with narrow molar mass distribution (MMD) is an added advantage of the metallocene-based copolymers.

A metallocene catalyst consists of a group IVB transition metal (most often Zr, Hf, or Ti) sandwiched between two cyclopentadienyl (Cp)-type ligands. As an example of a simple metallocene, the structure of zirconocene is presented in Figure 2.

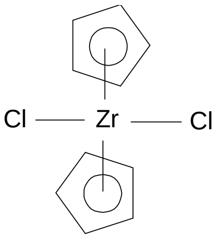


Figure 2. The structure of zirconocene.

The versatility of metallocene catalysts is based on their tunable structure. The presence of Cp-ligands that remain coordinated to the transition metal atom during the polymerization allows control of the behavior of the polymerization and the characteristics of the copolymers. The ligand structures (Cp-rings) can also be substituted with fused ring systems such as indenyl (Ind) or fluorenyl (Flu). In most cases the central metal is bonded to chloride to produce an active site. Alternatively, the two-ring system may be linked by a carbon or silicon atom to form a bridged metallocene structure, which enhances the stereoselectivity of the catalyst. The cocatalyst, MAO, which is a partial hydrolysis product of trimethylaluminum, is oligomeric in nature with a molar mass in the range of 800-1500 g/mol. Though the exact structure of MAO is not known, it can be inferred from the available literature to possesses –Al(Me)-O– repeating units, with tetra-coordinated Al. MAO is always associated with some amount of unhydrolyzed TMA.[7,8]

Table 1 presents the main differences between three types of catalyst used in olefin polymerization.

Table 1. Main features of catalytic systems for ethene/propene (/diene) copolymerization.[6]

	catalytic system based on		
catalyst feature	**metallocenes**	**Vanadium**	**Ziegler-Natta**
catalytic center	single center	single- or multi center	multi- center
catalytic activity	high	Low	high
chemical structure	defined	not defined	not defined

With the aid of metallocene catalysts, polyolefins can for the first time be produced with a property profile that is precisely controllable within wide limits of temperature resistance, hardness, impact strength and transparency. One of the most advantageous features of metallocene/MAO catalytic systems in copolymerization of ethene and dienes is that random copolymers are obtained with minimal amount of chlorine residues relative to vanadium-based catalysts.[9] Moreover, compared with Ziegler-Natta-type catalysts the diene incorporation in ethene copolymerization with metallocenes is highly efficient. This is especially important when the particular diene is less available or more expensive dienes are used.[10]

1.2 Diene-functionalized polyethene

During recent years, goal of many investigations in the field of metallocene and Ziegler-Natta catalysis has been to enhance the chemical and physical properties of polyolefins through their chemical modification.[11-13] Although the lack of polarity of polyethene is often an advantage, it is a disadvantage in applications where adhesion to other materials would be needed, for example in printing. In addition, chemically modified polyethenes have potential as compatibilizors in polyolefin blends and composites.

A common approach to obtain polyethene with improved adhesion properties is to incorporate functional groups in the backbone of the polyethene. Even a small percentage of functionality can dramatically alter the properties of the polyethene. However, the direct copolymerization of ethene with polar comonomer is very difficult with conventional coodination catalysts (Ziegler-Natta catalysts) because of catalyst poisoning by Lewis base components of the comonomers.

The situation is better with metallocene/MAO catalysts, but still, comonomers bearing groups containing nitrogen or oxygen donor atoms (alcohols, amines, carboxylates etc.) are greatly detrimental to the catalytic system. Further more, although these catalysts allow direct copolymerization with functional comonomers,[14-18] they suffer from low catalyst activity and molar masses are low. Methods to diminish the deactivation include copolymerization with protected functional monomer and subsequent modification of the polymer [11,19-24] or post-polymerization modification of appropriate copolymers.[5,25-33] Still another alternative is the use of reactive extrusion, but the disadvantage then is the degradation of polymers at elevated temperatures, especially in the case of polypropene. Finally, high pressure radical polymerization of ethene and, e.g., acrylates must be mentioned.

Linear α,ω-dienes have proven to be suitable comonomers for ethene where the goal is to obtain material for post-polymerization functionalization.[26,28,31,32,34,35] The unsaturation in the diene branch of ethene/diene copolymer can easily be converted to different functional groups through simple organic reactions.

In addition to providing the possibility of post-polymerization functionalization, linear nonconjugated dienes can bring a wide variety of structures to polyethene through their metallocene-based copolymerization with ethene (Figure 3).

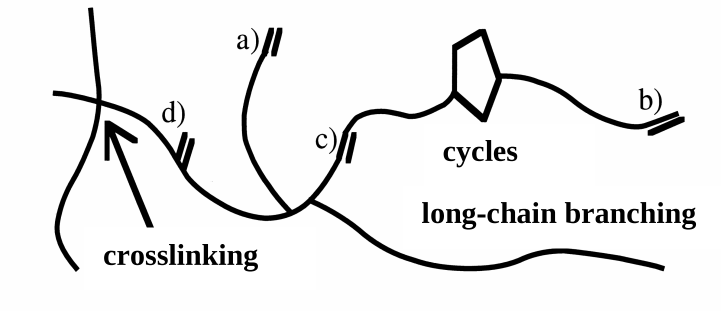


Figure 3. Structures that can be found in an ethene/diene copolymer. Unsaturations in the polyethene chain appear a) at the end of a branch due to the diene comonomer, b) at the end of the chain due to β-elimination, c) in the chain (*trans*-vinyl) and d) in the chain (vinylidene).

The accessible residual unsaturations may be left unaltered in the polymer resin or else reduced by hydrogenation, functionalized, or utilized in post-formation curing to yield a material that behaves much like a thermosetting polymer but retains the processability benefit of a traditional thermoplastic polyolefin.[36] Cyclic structures and long-chain branching (LCB), which also may be formed in ethene/diene copolymerizations, introduce interesting features to the material. During copolymerization reaction of ethene/diene, undesirable side reactions, such as crosslinking, may take place if the polymerization conditions are not optimized.

1.3 Scope of the work

The first objective of the research was to learn to control the structure of ethene/diene copolymer when linear nonconjugated α,ω-dienes are copolymerized with ethene in semi-batch slurry conditions by metallocene catalysts. **I-III,V** The variety of possible structures is wide, and metallocene catalyst technology provides a means to tailor the structure of polyethene via copolymerization. The ability of metallocene to utilize vinyl groups in forming long-chain branching (LCB) during polymerization was then exploited to modify the rheology of polyethene via ethene/diene copolymerization. **IV,V** Finally, the unsaturations of ethene/diene copolymers were post-polymerization functionalized into epoxy groups and various Si-based functionalities via hydrosilylation, and the obtained Si-containing polyethenes were tested as modifiers in composites of heterophasic polypropene and microsilica. **VI**

2 COPOLYMERS OF ETHENE AND LINEAR NONCONJUGATED DIENES

Ethene/propene/diene terpolymers (EPDM) represent the most important use of dienes.[37,38] Most diene copolymers are based on 5-ethylene-2-norbornene (ENB). Other dienes that are used are 5-vinyl-2-norbornene (VNB) and dicyclopentadiene (DCP). In EPDM rubbers, pendant double bonds allow crosslinking during processing. In most EPDM processes, the catalyst systems has been $VOCl_3$ or $VO(OR)_3$ with alkylaluminum chloride as cocatalyst and an organic halogen as promoter. However, both these catalyst systems undergo a drastic loss in catalyst productivity in the presence of diene, and crosslinking easily takes place in the course of terpolymerization.[39] An alternative is be to use coordination catalysts. A serious drawback of Ziegler-Natta catalysts is their low diene comonomer response in polyethene. Homogeneous metallocene/MAO catalysts perform much better in the incorporation of dienes in EPDM.[40]

In addition to effective diene response, metallocene-based catalytic systems enable the production of EPDM without washing or deashing steps. This is thanks to the low chlorine content, the absence of strong acidic sites, and the high catalyst activity. Corrosion problems in the production plant are minimized at the same time. In addition, the formation of gels and indispensable particles is avoided.[6]

Kaminsky and Miri[41] were the first to prepare EPDM using a metallocene catalyst system e.g. $Cp_2Zr(CH_3)_2$/MAO. Exxon has been very active in the field of ethene terpolymerizations. Dienes used with ethene and 1-hexene were 4-vinyl-1-cyclohexene (VCH),[42] 1,4-hexadiene,[42] and 1,5-hexadiene[10] using catalyst (n-buCp)$_2$ZrCl$_2$. Other metallocenes, such as Et[Ind]$_2$ZrCl$_2$ (EBI),[43,44] Et[Ind]$_2$HfCl$_2$,[44] Et[IndH$_4$]$_2$ZrCl$_2$,[43,45] and Me$_2$Si[IndH$_4$]$_2$ZrCl$_2$[45] have since then been used. The most interesting aspect of these zirconocene (and hafnocene)/MAO catalytic systems is the production of random copolymers and higher catalytic activities than for polymers obtained with vanadium compounds.

Linear nonconjugated α,ω-dienes together with metallocene catalyst technology provide the most interesting polyolefin-based elastomer grades today. Already by themselves, unsaturated branches increase the adhesion of polyethene to aluminum and enable structures that can be further functionalized. In addition, diene comonomers make it possible to produce polyethenes with modified rheology by introducing LCB, which is an important feature in processing metallocene-based polyethene. Polyethene possessing a cyclic structure in the main chain may have a high glass transition temperature and excellent transparency.

2.1 Ethene/diene copolymerizations

Nonconjugated α,ω-dienes provide polyethene with many interesting properties. For example the side-chain unsaturation imparts printability and provides reactive functional sites for chemical modification, whereas long-chain branching enhances melt strength and elasticity to facilitate processing of the copolymer. The diversity of possible structures in ethene/diene copolymers has provided an interesting field for research.

In this work, ethene was copolymerized with linear nonconjugated dienes semibatch manner. The reaction medium was either toluene (**I-IV, VI**) or heptane (**V**), and copolymerizations were carried out at temperatures from 20 °C to 90 °C, most usually 80 °C. Dienes selected for the study were 1,5-hexadiene (HD) (**I-V**), 1,7-octadiene (OD) (**I-VI**), and 7-methyl-1,6-octadiene (MOD) (**I-III**). Information about the effect of diene chain length was obtained in a comparison of HD and OD. MOD copolymerizations in turn, provided information on how the methyl group protecting the unsaturation affects the properties of the copolymer. The metallocene catalysts were Cp_2ZrCl_2 (**I-IV**), $(n\text{-}BuCp)_2ZrCl_2$ (**V**), $Et[Ind]_2HfCl_2$ (**V**), and ($Et[Ind]_2ZrCl_2$), (**V,VI**). Methylaluminoxane (MAO) was the cocatalyst in all polymerizations. Study of the effect of polymerization temperature on the structure of the ethene/diene copolymers was carried with the Cp_2ZrCl_2 catalyst. A guideline for selecting the polymerization conditions was the goal of obtaining an uncrosslinked ethene/diene copolymer (**I**). After that it was possible to fine-tune the control of the structure of ethene/diene copolymers.

Compared with the activity in ethene homopolymerizations, the activity of the metallocene catalysts was decreased in all ethene/diene copolymerizations. OD had the strongest deactivating effect and HD the least. Introducing of OD to the reactor caused the catalytic activity to drop because dienes are less reactive than ethene. Relevant to this Koivumäki and Yoon[46,47] found that the catalytic activity for ethene/α-olefin copolymerizations decreases as the chain length of the olefin increases.

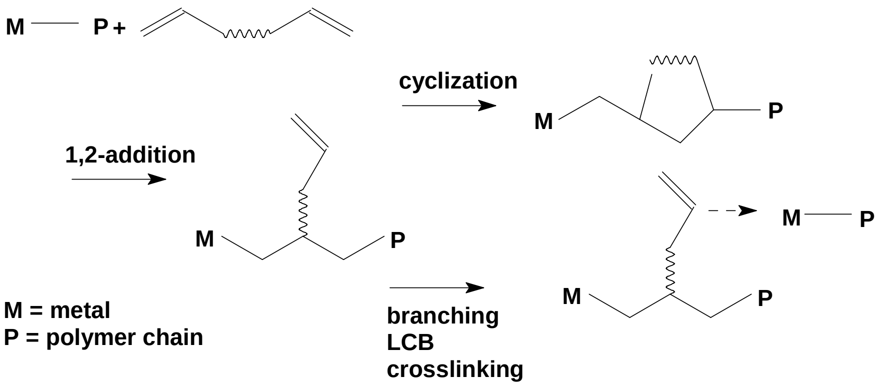
The degree of incorporation of higher olefins, and also dienes, can be enhanced by lowering the copolymerization temperature. Kamisky *et al.*[48] explained this by the different rate constants for monomers inserting in the Zr-C-δ bond. The ratio of the rate constants is temperature dependent and shifts in favor of higher olefins as the polymerization temperature is lowered. In our case, strong crosslinking prevented us from seeing this.

As expected, the molar mass (M_w) of the copolymers increased with decreasing polymerization temperature (**I-VI**). Hydrogen was used to control the molar mass (**V**). Molar mass distribution (MMD) was nearly two when small amounts of dienes were incorporated, and it broadened with increasing incorporation of diene in the polyethene matrix. In some cases, crosslinking was the reason for the broadening (**I-V**). The addition of OD and MOD reduced the molar mass of the polyethene more than did the addition of HD.

2.2 Structure control and analysis of ethene/diene copolymerizations

The copolymerization of olefins with dienes is an emerging area in metallocene-based polymerizations. The type of copolymer naturally depends on the structure of the comonomer. First, there are linear nonconjugated dienes, such as 1,4-hexadiene,[28] 1,5-hexadiene,[49] 3,7-dimethylocta-1,6-diene,[31,50] and 5,7-dimethylocta-1,6-diene.[50-53] The second type of diene comonomer is cyclic ones such as 5-ethylene-2-norbornene (ENB). In addition to ethene/diene copolymerizations, there are terpolymerizations of ethene with higher α-olefins and ENB.[54-56]

Four types of insertions of nonconjugated α,ω-diene into the polyethene chain are illustrated in Scheme 1.[57-59] In the first type of insertion, one end of the diene comonomer reacts in the α-olefin backbone through a simple 1,2-insertion leaving the other end unreacted to provide unsaturated side chains. The second type involves the formation of a 1,3-substituted cycloalkane unit when 1,2-insertion is followed by cyclization. The predominant insertion mechanism is influenced by the selection of diene, polymerization catalyst, and polymerization conditions, and allows tailoring of the properties of the copolymer. In the third possible reaction the unreacted end of 1,2-inserted diene comonomer reacts with a growing polymer chain causing long-chain branches, longer than the α,ω-diene, in a fashion analogous to the branching in low density polyethene (PE-LD).[26] In the fourth case, reaction of the pendant vinyl group with a propagating chain end gives crosslinked-branching or crosslinking.



Scheme 1. Possible insertion reactions of nonconjugated α,ω-dienes into polyethene chain.

In homopolymerizations of HD[60-67] and OD[68] with metallocene catalysts, polymer chains mainly contain five- and seven-membered rings, respectively. In ethene/diene copolymerizations, with all homogeneous metallocene catalysts,[49,59,69-72] HD is preferentially inserted into the backbone as five-membered rings (**I-V**). In the case of OD, the insertion mode is strongly influenced by the catalyst system and polymerization conditions. (**I-V**) [72-75]

2.2.1 Short-chain branches

In this section we look at the short branches of polyethenes that are formed by simple 1,2-insertion of α,ω-dienes. More complicated branch structures are dealt within Sections 2.2.4 and 2.4. As mentioned above, among the dienes of this study HD and OD, can be incorporated into the polyethene chain either as branches or cyclic structures. In the case of MOD, the only possibility is incorporation as branches (**I-III**). Because HD is predominantly incorporated as cyclic structures,[76,77] the structure of ethene/HD is dealt within in more detail in Section 2.2.3.

Branch structures in ethene/diene copolymers are conveniently analyzed by ^{13}C NMR. Figures 4a and 4b show the ^{13}C NMR spectra of (n-BuCp)$_2$ZrCl$_2$- and Et[Ind]$_2$HfCl$_2$-catalyzed ethene/OD copolymers, respectively (**V**). Major differences in the structures of the copolymers can be seen. The copolymer obtained with (n-BuCp)$_2$ZrCl$_2$ (Fig. 4a) contains mainly (ca. 90%) 1-hexenyl branches, whereas that obtained with Et[Ind]$_2$HfCl$_2$ (Fig. 4b) contains equal contents of 1-hexenyl branches and rings. The peak assignments were partially based on literature data (**I**)[78] and the peaks are assigned as follows:

- branch structures (1”) 38.15, (2”) 34.52, (3”) 27.27, (4”) 34.33, (5”) 26.77, (7”) 33.91 ppm
- ring structures (1’) 42.66, (2’) 39.43, (3’) 35.47, (4’) 27.69, (5’) 39.26, (6’) 26.66 ppm.
- saturated chain ends 32.18 and 22.87 ppm.

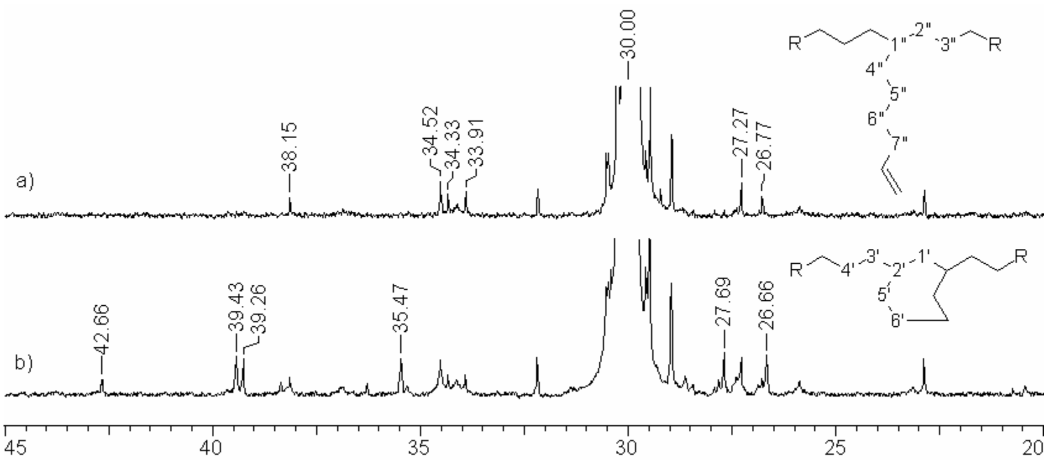


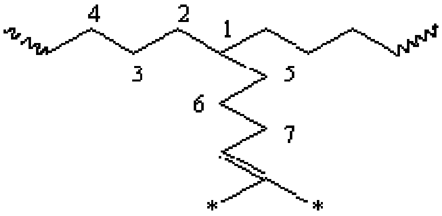
Figure 4. ^{13}C NMR spectra of two ethene/OD copolymers produced with metallocene catalysts at 80 °C and [C_2H_4]=0.4 M. (a) (n-BuCp)$_2$ZrCl$_2$ incorporated OD mainly into branches (ring/branch 8:92). (b) Et[Ind] $_2$HfCl$_2$ produced a copolymer with higher ring formation selectivity (ring/branch 55:45). The shifts are in ppm. (**V**) The spectra were recorded with Varian Gemini 2000XL NMR spectrometer (75 Hz, at 125 °C, in deuterated benzene/1,2,4-trichlorbenzene (10 wt-%/90 wt-%).

Also in copolymers produced with Cp$_2$ZrCl$_2$ catalyst, OD was mainly incorporated as branches. The 1,5-cyclononane structures reported by Sarzzotti *et al.*[79] were not seen in any of our ethene/OD copolymers.

As expected, under our experimental conditions and catalyst system Cp$_2$ZrCl$_2$/MAO, MOD formed only 6-methyl-hexene branches in the polyethene backbone (**I-III**). The branch structure was the same for all copolymers that could be dissolved for the analysis. The methylene group at one end of this diene comonomer effectively prevented the ring formation, which also was shown with modeling (**II**). The structure of the MOD-induced branching in polyethene is depicted in Table 2 with the ^{13}C NMR peak assignments.

Table 2. ^{13}C NMR peak assignments of ethene/MOD copolymer (data from **III**)

Shift, ppm	Carbon in structure
16.0	*
25.8	*
26.3	3
26.6	6
29.0	7
30.6	4
34.3	5
34.7	2
38.1	1



2.2.2 Unsaturations

The unsaturations that may exist in copolymers of ethene and linear nonconjugated α,ω-dienes are illustrated in Figure 5. Vinyl bond content in ethene/diene copolymers is due to butenyl (for HD) or hexenyl (for OD) branches induced by diene insertion (1,2-insertion) and the end of chain unsaturations induced by the chain transfer to the monomer. If every copolymer chain contains an end of chain unsaturation, the diene-induced vinyl bond content can be estimated from the total vinyl bond content by the subtracting of end of chain unsaturation content of the homopolymer.

In addition to vinyl bonds, vinylidene and *trans*-vinyl bonds can be detected in copolymers of ethene and HD or OD. Vinylidene bond is formed in the polymer chain by β-hydrogen abstraction which takes place after diene insertion to the chain. *Trans*-vinyl bonds are formed principally the same way but the monomer insertion of 2,1 type for *trans*-vinyl and 1,2 type for vinylidene bond formation. In these cases both double bonds of the diene are left in the polymer chain; one forms a vinylidene or *trans*-vinyl bond in the polymer chain and the other a chain-end vinyl bond. In the case of MOD, the double bond is of the form $RCH=CMe_2$. Both ^{1}H NMR and FTIR were used for the analysis of unsaturations in ethene/diene copolymers (**I-VI**).

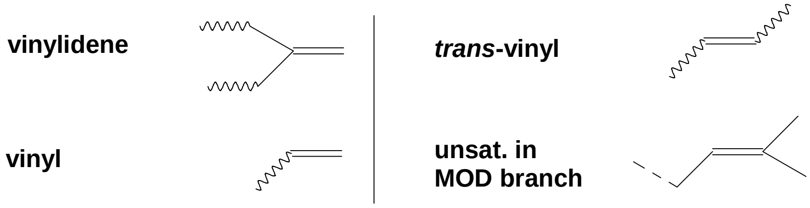


Figure 5. Double bonds in copolymers of ethene and linear nonconjugated dienes.

2.2.2.1 ^{1}H NMR analysis of unsaturations

As can be seen from Figure 6, significant amounts of vinylic chain ends as well as *trans*-vinyl bonds and vinylidene groups were present in the ethene/OD copolymers.(**I**) The vinyl unsaturations are due to the 1-hexenyl branches resulting from OD insertion and the chain-end unsaturations generated during chain termination by chain transfer to monomer after insertion of the diene. β-H elimination is another possible route for the formation of vinyl unsaturations. The lines at 5.9 and 4.9 ppm are assigned to vinyl groups, and those at 4.65 and 5.4 ppm to vinylidene and *trans*-vinyl groups, respectively. The increase in the number of vinyl groups with OD content (**I-V**) indicates that both vinyl groups are polymerized for only a fraction, if any, of the total OD units incorporated.

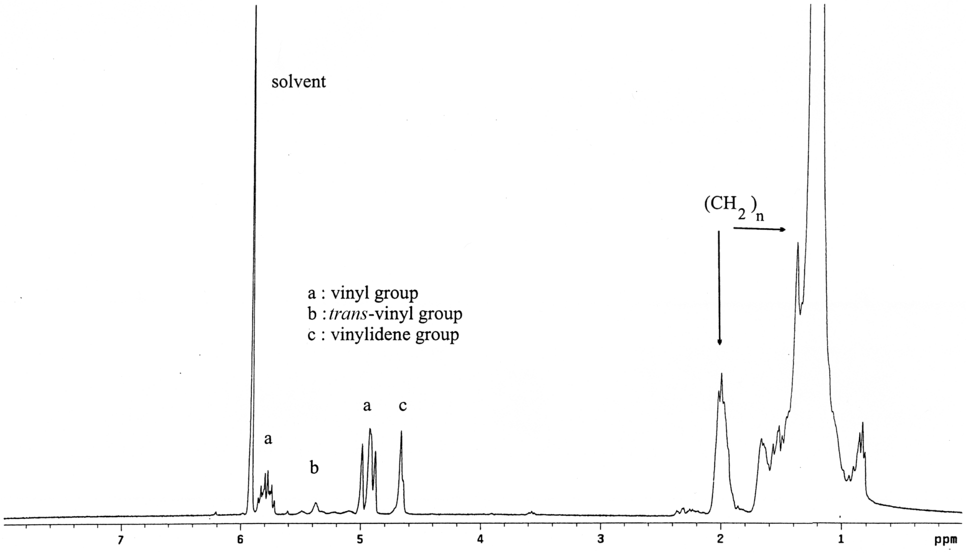


Figure 6. ^{1}H NMR spectrum of ethene/OD copolymer produced at 80 °C by Cp$_2$ZrCl$_2$/MAO catalyst system. (**I**) Spectra were recorded with Varian Gemini 2000XL NMR spectrometer (300 Hz, at 125 °C, in deuterated tetrachloroethane.

Similarly, the structure of ethene/MOD copolymers can be reliably analyzed by ^{1}H NMR. MOD is copolymerized with ethene via its unsubstituted double bond. The branches have an RCH=CMe$_2$ (dimethylvinyl) end, which gives a shift at 5.1 ppm in the ^{1}H NMR spectrum. About 30 to 50% of the double bonds in the ethene/MOD samples were of that kind, the rest being vinyl bonds. The relatively large amount of vinyl bond can be explained by the small amount of MOD incorporated and low molar mass of the copolymer.(**I-III**)

2.2.2.2 FTIR analysis of unsaturations

The appearance of double bonds in ethene/diene copolymers was also studied by FTIR spectroscopy (**I**,**V**), a method that is sensitive even for low double bond concentrations. Preparation of samples is easier for FTIR than NMR as copolymers are merely compressed into films with no need for solvents. FTIR also provides a menas to analyze samples with crosslinking as films can be prepared of samples that no longer dissolve. Wave numbers assigned to the double bonds were 965 cm^{-1} (*trans*-vinyl), 910 cm^{-1} (vinyl) and 888 cm^{-1} (vinylidene)[80]. Figure 7 shows how double bonds appear in the

FTIR spectra of ethene/diene copolymers. The amounts of different double bonds per 1000 carbon atoms were calculated on the basis of FITR absorbances according to Rueda *et al.* [81] and deKock *et al.*[82]

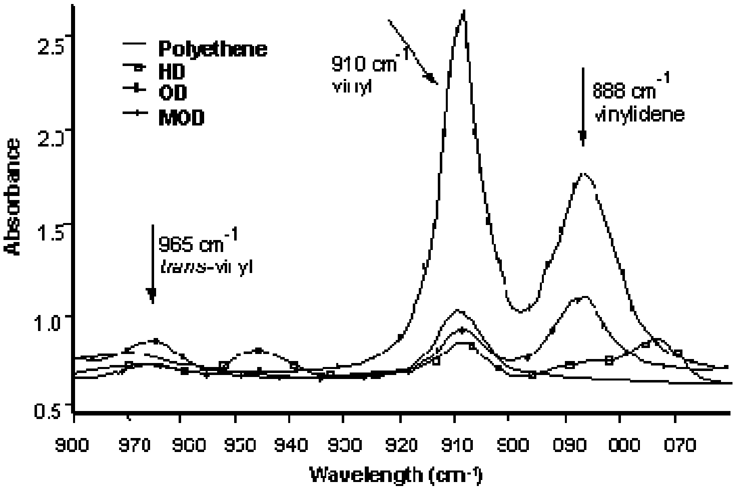


Figure 7. Appearance of double bonds in the FTIR spectra of copolymers of ethene with different dienes (*trans*-vinyl 965 cm^{-1}, vinyl 910 cm^{-1}, and vinylidene 888 cm^{-1}). Samples were prepared with the catalyst system Cp_2ZrCl_2/MAO at 90 °C. HD= 1,5-hexadiene, OD = 1,7-octadiene, MOD = 7-methyl-1,6-octadiene.(**I**)

Like the ^{1}H NMR analysis, the FTIR results showed a clear increase in total double bond amount with OD content in the copolymer.(**I**) The high vinyl bond content is due to the hexene branches formed by OD and also reflects the low molar mass of these products. Increase in the amount of comonomer also increases the amount of vinyl bonds in the product because the probability of primary insertion of the comonomer is very high[83]. The ^{1}H NMR method clearly validates FTIR method, indicating the successful determination of base lines in the FTIR spectra.

Increasing amounts of diene had a minor effect on the double bond concentration in ethene/HD and ethene/MOD copolymers. In both these copolymers the *trans*-vinyl and vinylidene concentrations, but not the vinyl concentration, were increased with the amount of diene in the product. The vinyl bond concentration was decreased with increasing portion of HD in the copolymer because of the efficient ring formation reaction and consumed the free double bonds of the diene. The vinyl bond concentration was lower in the copolymers containing HD and MOD than in homopolyethene produced under the same conditions. In the case of MOD, this can be explained by the change in termination reaction mechanism from β-H elimination to chain transfer to monomer.

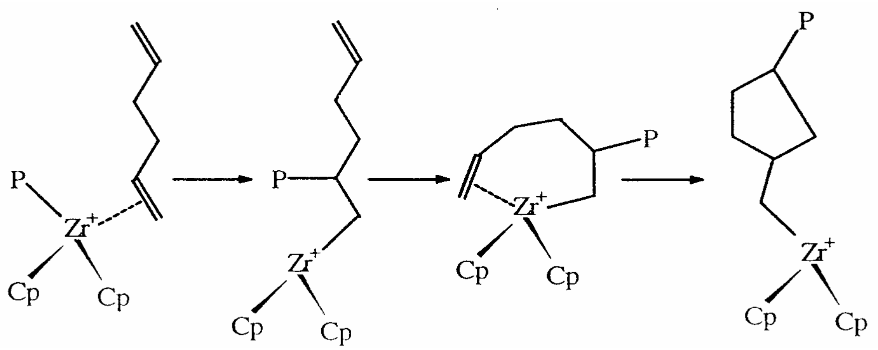
Unlike ^{1}H NMR, FTIR did not provide any additional information on the copolymers containing MOD because the absorbance of the end group of the 6-methyl-hexene branch is overlapped by the peak of the CH_2 oscillation of the polyethene chain at 720 cm^{-1}.

As expected, FTIR revealed a tendency toward decreasing amount of free double bonds with decreasing polymerization temperatures where the product becomes strongly crosslinked.

2.2.3 Cyclic structures

Cyclic structures can be created in polyethene chains with metallocene catalysts by copolymerizing the ethene with cycloalkenes[10,54,84] or bisycloalkenes.[41,55] In addition, a number of nonconjugated dienes are capable of undergoing cyclopolymerization in the presence of a coordination catalyst. Examples of these are 1,5-hexadiene,[49,58,60-62,64,65,67,69,76] 1,7-octadiene,[85] and 2-methyl-1,5-hexadiene[63]. The length of chain of 1,9-decadiene made the ring formation diffilult.[59]

To clarify the formation of rings in ethene/diene copolymers, the structures of HD, OD, and MOD in combination with Cp_2ZrCl_2 catalyst were studied by molecular modeling. Cavallo *et al.*[62] have a mechanism for the ring formation reaction for HD. According to this mechanism, the carbon atoms 2 and 6 in 1-hexadiene have to come into proximity in order to make the ring closure possible. In the B-LYP/DND-optimized structure of the π-complex $Cp_2ZrCH_3(CH_2{=}CH_2)^+$ of the model system for the olefin insertion reaction of metallocene-catalyzed polymerization, the C···C distance of the forming bond was 3.25Å.



Scheme 2. Proposed mechanism for the ring formation reaction for HD.[62]

Possible structures of 1-hexene, 1-octene, and 1-methyl-2-octene were generated using high temperature molecular dynamics and subsequent energy minimization. In the energy minimization the structures converged to a few distinct conformers. In the case of 1-hexene the energies of all conformers were 3.5 kcal/mol or less above the global minimum and, thus, the conformers are easily accessible, especially at elevated temperatures. For one conformer the $C_2 \cdots C_6$ distance was 3.29 Å, i.e. close to the optimum value, while the energy was 2.2 kcal/mol. Superposition of this structure on the π-complexshowed only slight hindrance for the formation of cyclic structure. In 1-octene, conformers having the relevant $C_2 \cdots C_8$ distance of about 3.5 Å have energies about 5.5 kcal/mol higher than the global minimum, which gives them a relatively low population. Some steric hindrance is evident when these conformers are superimposed on the π-complex of the catalyst. The low population and the steric hindrance make the ring formation reaction of the OD comonomer highly improbable. In 1-methyl-2-octene, there are a few conformers in which the relevant $C_3 \cdots C_8$ distance is about 3.7 Å and these have energies 2-3 kcal/mol higher than the global minimum. The ring formation reaction is ruled out by severe steric hindrance, however, as was seen by superimposing these conformers on the π-complex of the catalyst.

These results were in good accordance with those of Welborn *et al.*[10] who state that the six carbon straight-chain diolefin appears to provide the greatest likelihood of backbone incorporation as cyclized species. Less than six or at most seven carbon straight-chained dienes provide good incorporation, the desired levels of residual unsaturation, and minimal cyclization of diene during polymerization. Thus, 1,4-pentadiene and 1,9-decadiene polymerize well without strong cyclization as was seen with 1,5-hexadiene.

Makowski *et al.*[86] already discussed about ring formation of 1,5- and 1,6-dienes in polymerization reactions. They presented a pseudocyclic ring model with which the equilibrium between branch and ring formation in the polymer could be guided. Naga *et al.*[85] studied the cyclopolymerization of OD with various metallocene catalysts. The cyclization specificity was best with isospecific metallocene and decreased in the order aspecific, and syndiospecific metallocenes. Lowering the polymerization temperature and increasing the monomer concentration also decreased the cyclization specificity. When a constrained-geometry catalyst was used, not only 1,3-cycloheptane but also 1,5-disubstituted cyclononane rings were formed[79,87].

The microstructure of ethene/HD copolymers obtained with EBI as catalyst (**V**) is presented in Figure 8. The peaks are assigned as follows:

- *trans*-rings (1”) 39.34, (2”) 39.34, (3”) 37.06, (4”) 28.89, (5”) 33.25 ppm
- *cis*-rings (1’) 41.10, (2’) 40.68, (3’) 37.03, (4’) 28.96; (5’) 32.17 ppm
- branches (1) 37.74; (2) 34.38; (3) 27.20; (4) 33.88; (5) 31.46 ppm.

The assignment of the ring structures is based on our work (**I**), while the assignment of the peaks due to branches is mainly based on a comparison of the chemical shifts of the ethene/HD copolymers with the well-known shifts of ethene/1-hexene copolymers[78]. The integration of peak areas in the spectra at 37.74 : 34.38 : 33.88 : 31.46 : 27.20 gave ratios 1 : 2 : 1 : 1 : 2. The peaks at 34.38 and 27.20 were assigned to the carbons 2 and 3 in the main chain (Fig. 8b). The corresponding peaks were found in ethene/1-hexene copolymers at 34.5 ppm and 27.3 ppm, respectively. The methine carbon of a 1-butenyl branch was concluded to be at 37.74 ppm since the methine carbon of ethene/1-hexene copolymer is at 38.1 ppm. The α-methylene carbon of the branch appears at 34.1 ppm. The double bond at the β-position of the 1-butenyl branch has a weak effect on the chemical shift of the α-methylene, and the α-methylene carbon of the 1-butenyl branch was thus concluded to be at 33.88 ppm. The peak at 31.46 ppm was assigned to the allyl carbon of the 1-butenyl branch. The allyl carbon of the long linear 1-olefin chain has one γ-carbon, and the peak is at 33.9 ppm.

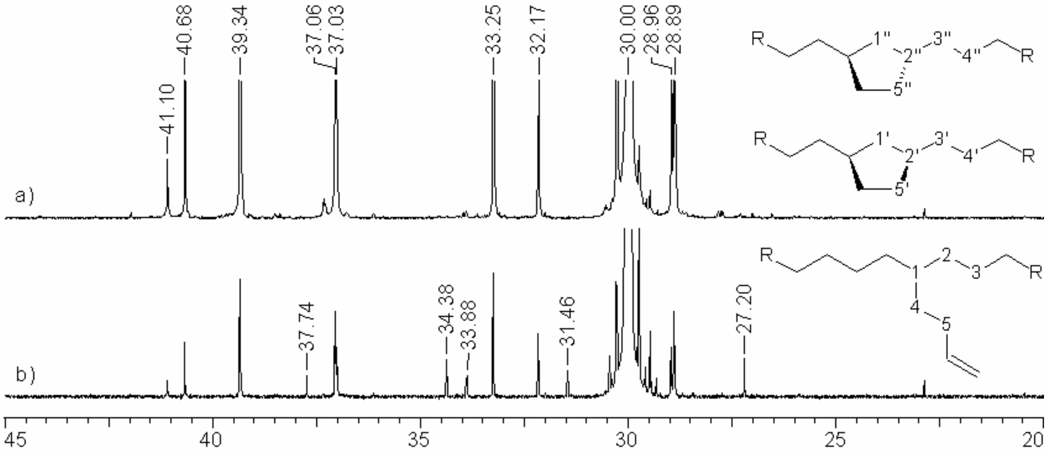


Figure 8. Examples of ^{13}C NMR (300MHz) spectra of ethene/HD copolymers where HD has been incorporated (a) solely as ring structures and (b) as rings and branches. The shifts are in ppm. (**V**) The spectra were recorded with Varian Gemini 2000XL NMR spectrometer (75 Hz, at 125 °C, in deuterated benzene/1,2,4-trichlorbenzene (10 wt-%/90 wt-%).

The decrease in the selectivity for cyclization with increasing HD concentration in the reactor[76,77] was demonstrated by the decrease in the ratio of rings to 1-butenyl branches when the ethene pressure was increased at constant HD concentration (**V**). At low ethene concentration (0.04 M), HD formed only ring structures (Figure 8 a), while ring formation selectivity was reduced to about 90% (Figure 8 b) when copolymerizations were performed with higher ethene concentration (0.40 M).

The ratio of *cis*- to *trans*-conformers of the rings affects the properties of the product. Cyclopentane rings in *cis*-conformation are reported to offer high heat stability.[58,88] The catalyst concentration is one parameter that affects the [*cis*]/[*trans*] ratio of the cyclized HD units.[74] The basic zirconocene catalysts Cp_2ZrCl_2 and bridged metallocene $MeSi(Ind)_2ZrCl_2$ were studied and opposite results were obtained: with Cp_2ZrCl_2 the amount of *cis*-conformer increased with catalyst concentration, and with $MeSi(Ind)_2ZrCl_2$ the opposite was the case.

In the copolymers produced with Cp_2ZrCl_2 catalyst, about 25% of the rings were in *cis*-conformation and about 75% in *trans*-conformation, and the material obtained had significantly lower melt temperatures than homopolyethene produced under the same conditions. Polymerization temperature has no effect on this ratio with the catalyst system.(**II**)

Cyclic structures are principally studied by ^{13}C NMR, but information about them can also be obtained by FTIR (**I**). In a detailed study of the double bond area in the FTIR spectrum of ethene/diene copolymers we found the peaks at 945 cm^{-1} and 875 cm^{-1} to increase with the amount of HD in the polyethene (Figure 9). The same was not found for OD and MOD. Evidently, these peaks are due to the five-membered rings in the polyethene chain: the oscillations of CH_2 bonds on the ring give peaks at these wave numbers. As also is evident from Figure 9, the intensities of the peaks of vinyl, *trans*-vinyl and vinylidene bonds decrease with increasing HD addition.

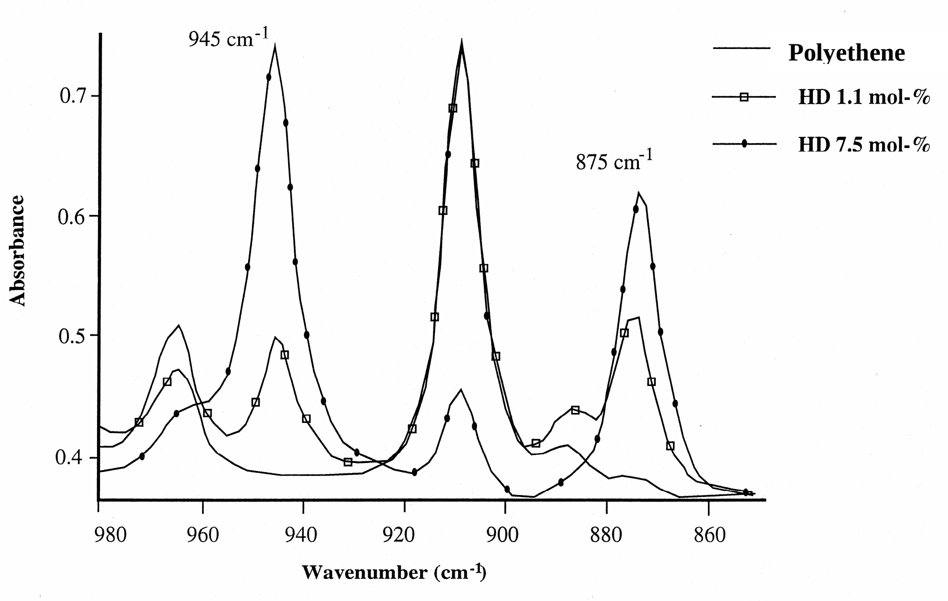


Figure 9. Effect of increasing amount of 1,5-hexadiene (HD) in ethene copolymer on FTIR peaks in the double bond area can be seen as growing peaks at 945 cm^{-1} and 875 cm^{-1} (*trans*-vinyl 965 cm^{-1}, vinyl 910 cm^{-1}, and vinylidene 888 cm^{-1}). Samples were prepared with catalyst system Cp_2ZrCl_2/MAO at 90 °C. (**I**)

The ease of sample preparation for the FTIR measurements encouraged a careful evaluation of the reliability of this method. The match between the results of FTIR and NMR analyzes was investigated for the five-membered rings of copolymers containing HD. Figure 10 shows the correlation between the height of IR absorbance (A) at 945 cm^{-1} divided by the film thickness (*d*) and the ring content calculated from ^{13}C NMR spectra. The slope gives the value of the molar absorptivity coefficient, $\varepsilon=0.084\ mm^{-1} \times (mol\%)^{-1}$, with error margin of about ±4 % (**V**).

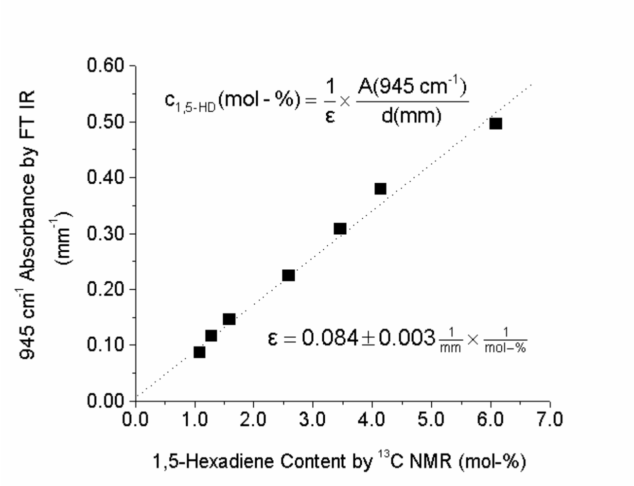


Figure 10. Determination of the ring content in ethene/HD copolymers with an FTIR 945 cm^{-1} absorbance peak. The FTIR data are calibrated against ring content based on ^{13}C NMR spectroscopy (**V**).

2.2.4 Crosslinking

Crosslinking can be either an unwanted side reaction or a desired reaction path in ethene/diene copolymerizations. In most cases the crosslinking is not desired during the polymerization reaction because gelation makes the control of the reaction difficult, or even impossible. The control of crosslinking in the copolymer is a real challenge in the case of α-olefin copolymerization with linear, nonconjugated dienes because of the many free unreacted vinyl groups are available. For the point of view of processing, the material is useful only if the degree of crosslinking is under 2%. Crosslinking also makes the analysis of the polyethene difficult since solubility of the sample is often required.

A chemical crosslink between polyolefin macroradicals can be formed by several alternative methods, including a) recombination of macroradicals, which are generated either chemically or physically, b) addition of a macroradical to a vinyl (vinylidene) bond attached to polyolefin backbone, c) crosslinking via randomly distributed double bonds after abstraction of hydrogen in allyl position, and d) condensation reaction of reactive groups bound to a polymer chain. With α,ω-dienes as comonomer, crosslinkage of the polyethene molecules is highly possible. A copolymer with 2 mol-% of diene has no melting point but may still show rubbery elasticity. Products like these are insoluble in organic solvents and instead swell to more than fivefold their volume. Crosslinking of the polymer was considered as a side reaction during polymerization when ethene was polymerized with linear nonconjugated dienes (**I-VI**). The tendency for crosslinking is dependent on the structure of the diene. Naga[75] has shown that polyethenes with 1,9-decadiene (DD) as comonomer are more strongly crosslinked than polyethene containing OD.

Crosslinking is not a straightforward concept for ethene/diene copolymers because the branched structure in these copolymers can be highly complicated. Longer as well as shorter branches with unsaturated chain ends are able to grow further to form LCB, and linking between the branches may take place leading eventually to crosslinking. In fact, little by little in changing polymerization conditions, entangled long branches begin to act like crosslinked structure, which makes it almost impossible to define a distinct boundary between branching and actual crosslinking. LCB in ethene/diene copolymers is further dealt in Section 2.4.

Measurement of a absolute the degree of crosslinking is difficult. In the early part of this study, a standard measurement based on Soxhlett extraction with decaline or xylene was used (ASTM D-2765-84) to determine the degree of crosslinking of polyethene.(**I-IV**) Despite the fairly large deviations, the results were found to be reliable. Later, the highly branched structures of ethene/diene copolymers were evaluated on the basis of information obtained by SEC and dynamic rheometry.(**VI**,**V**)

2.2.4.1 Degree of crosslinking measured by extraction

Among the dienes of this study, OD as comonomer crosslinked the polyethene most easily (**I-III**). This was as expected since OD has readily polymerizable double bonds at either end. The lesser crosslinking in HD-containing copolymers is due to ring formation, which consumes the vinyl bonds of the diene. In ethene/MOD copolymers the methyl group at one end of MOD effectively prevents this double bond from crosslinking.

Polymerization temperature had a dramatic effect on the degree of crosslinking in the HD- and OD-containing products (**I**). Even very small amounts of HD or OD in the reactor produced high degrees of crosslinking at polymerization temperatures from 20 °C to 50 °C. At 65 °C the degree of crosslinking was decreased with larger diene concentrations in the reactor. At 80 °C the degree of crosslinking was consistently under 10% for all HD and OD concentrations and at 90°C it was less than 2%. Increasing polymerization temperature increases the reactivity of ethene much more than the reactivity of dienes, so that the probability of the diene being polymerized from both ends, i.e. to be crosslinked, decreases, even though the amount of diene in the product increases. It also seemes that higher polymerization temperatures favor ring formation in HD-containing copolymers. This may be understood as follows: a prerequisite for ring formation is that the free end of the butene branch that is first formed in the polyethene chain comes into proximity with the growing chain, and the probability of this happening is increased at higher temperature.

When MOD was used as comonomer the degree of crosslinking did not increase above 40% even for copolymer produced at 20 °C. This was expected, since the methyl group in MOD protects the second double bond, which remains unreacted during the polymerization. For all diene additions, the degree of crosslinking in ethene/MOD copolymers produced at 50 °C was less than 10%, and at 80 °C it was almost 0%.

2.2.4.2 Highly branched structures analyzed by rheometer

The rotation rheometer can be used to assess crosslinking in polyolefins. In a study of melt rheological behavior of ethene/HD copolymers produced with Cp_2ZrCl_2/MAO (**IV**), where increasing amount of diene was incorporated in the polyethene (Figure 11), the yield behavior was that of a partly crosslinked copolymer (P4, estimated diene incorporated 10 mol-%). Although a high degree of crosslinks (>80%), was also measured by extraction method, the sample was still a thermoplastic.

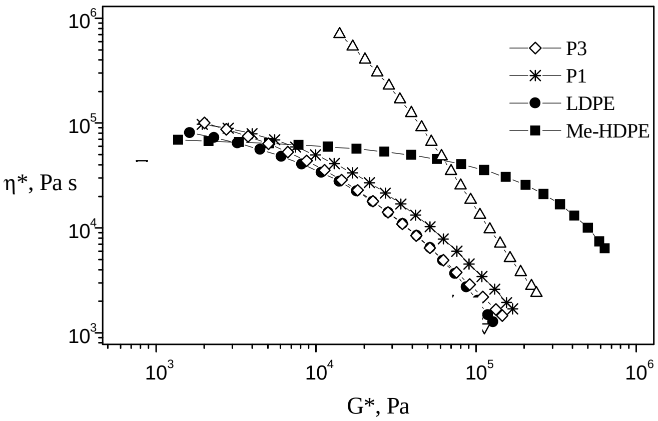


Figure 11. Complex viscosity η* of selected polymer samples (P1-P4 with increasing amount of HD incorporated) as function of complex modulus G* at 170 °C. Reference materials: a broad MMD PE-LD with long-chain branching and a linear, narrow MMD metallocene-catalyzed PE-HD sample (**IV**).

The same kind of behavior was observed in ethene/HD copolymers prepared with $Et[Ind]_2ZrCl_2$ (**V**) (Figure 13 in Section 2.4.2.1). At high diene contents (>2.0 C=C/1000 C atoms), extremely slow relaxation made the rheological measurement impossible.

2.2.4.3 Highly branched structures analyzed by size exclusion chromatography

Indication of crosslinking can be seen in the form of a “shoulder” at high molar mass end of the curves of size exclusion chromatography (SEC). Although no numerical values are obtained for the degree of crosslinking, the method is useful for comparing samples. A limitation of the method is the requirement for the sample to dissolve in an appropriate solvent. Not even at elevated temperatures of 140 °C did samples dissolve in trichlorobenzene (TCB) (**V**). As an example (Figure 12) SEC curves for samples with increasing amount of HD incorporated in the polyethene chain. At higher diene contents (presented as higher vinyl content) polydispersity (M_w/M_n) clearly broadens, and finally a shoulder appears on the high M_w tail, indicating the formation of branches-on-branches structures and eventually crosslinking (**V**).

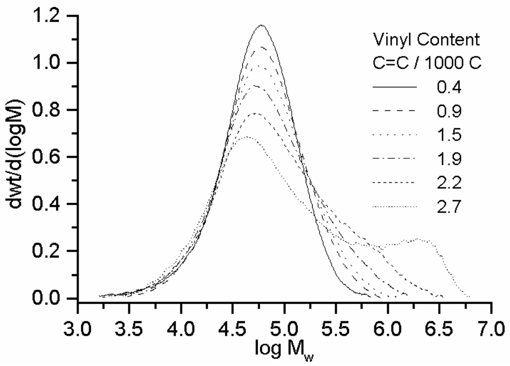


Figure 12. Molar mass distribution curves of ethene/HD copolymers produced at $[C_2H_4]$= 0.24 M with different HD concentrations ($Et[Ind]_2ZrCl_2$/MAO catalyst system). At higher diene contents, a shoulder appears in the high M_w tail, indicating the formation of branches-on-branches structures and eventually crosslinking (**V**).

The similar features seen in $Et[Ind]_2ZrCl_2$/MAO catalyzed homopolyethenes[89] polymerized at low ethene concentrations support the conclusion that increasing amount of vinyl-terminated macromonomers makes M_w/M_n broader. A similar shoulder has been seen by Soares[90] and Sarzzotti et al [79]in the SEC curve of ethene/OD copolymerization with Ti-based CGC.

2.3 Thermal and thermomechanical properties of ethene/α,ω-diene copolymers

Thermal analysis reveals crystallinity and melting temperature and many other features of a polymer sample. The melt behavior is important because polymers are processed in molten stage. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used in this study.

The melting temperature and crystallinity were studied by DSC. Diene incorporation was seen as decrease of the melting temperature of polyethene. This trend can be explained by the decrease in crystallinity due to diene branches in the polyethene. Crosslinking appeared as lower and wider peaks, which disappeared totally in the case of strongly crosslinked copolymers.

Copolymerization of dienes affected the crystallinity of polyethene in different degrees. HD decreased the crystallinity least. The 1,3-disubstituted cyclopentane structure is such a small aberration in the polyethene chain that it was incorporated in crystalline structure of the polyethene (isomorphism).(I-V)[72,91] In a comparison of the crystalline structures of ethene/HD copolymers and copolymers of ethene and cyclopentane, Naga *et al*.[74,92] found a significant difference in the crystalline structures of polyethene due to 1,2-inserted and *cis*- or *trans*-inserted 1,3-inserted cyclopentane groups. Isomorphism did not exist in the case of 1,2-cyclopentane and the *trans*-inserted 1,3-cyclopentane groups.

Branches due to HD, OD, and MOD as well as the cycloheptane unit in the polyethene chain formed by OD, clearly decrease the crystallinity of polyethene (I-VI). Jin and coworkers[72] saw similar effects in their copolymerization of ethene with HD and OD with catalyst (2-MeInd)$_2$ZrCl$_2$. The same trend of strongly decreasing melt temperature and crystallinity with increasing amount of ethene/OD in the copolymer appeared when catalyst system Et[Flu]$_2$ZrCl$_2$ was used in ethene/OD copolymerizations.[93]

More detailed information on the copolymers was obtained using segregation fractionation technique (SFT) with DSC and DMTA, both of which are particularly suitable for semicrystalline polymers.

2.3.1 Segregation fractionation technique

Employing carefully designed thermal cycles in a differential scanning calorimeter thermal fractionation techniques offer quick and practical ways to assess chain heterogenities in semicrystalline thermoplastics. These techniques are particularly useful for studying the degree and distribution of short-chain branches in copolymers of ethene with α-olefins or dienes. Thermal fractionation can replace more time-consuming and complex techniques that require preparative or analytical fractionation in solution. Different procedures can be applied including stepwise isothermal segregation technique,[94] thermal fractionation,[95,96] segregation fractionation technique,[97-99,107] step crystallization,[100] and successive self-nucleation/annealing.[100] The most commonly used techniques today are segregation fractionation technique and successive self nucleation and annealing.[101] Segregation studies involving stepwise annealing with DSC have been applied to various types of metallocene-catalyzed[99,102-106] ethene copolymers.

The use of SFT with DSC, with annealing of the polymer at successively lower temperatures starting just above the melting temperature of the polymer, has been found[97] to provide valuable information about the chemical composition distribution in commercial Ziegler-Natta and metallocene-type commercial PE-LLDs and very low density PEs (PE-VLD). The results reveal differences in the ethene sequence distributions as the polymers are annealed at successively lower temperatures. The multiple endothermic peaks appearing in the melting curves after such treatment correspond to the fraction of segregated molecules that crystallized at a certain temperature. Owing to limitation noted by Hosoda and Lu,[108,109] only qualitative differences in lamellar thickness distribution of the studied copolymers can be discussed.

The annealing temperatures used in the segregation procedure depend on the melting range of the polymer in question. A typical run of our ethene/diene copolymers included successive annealing steps at 122, 116, 110, 104, 98, 92, 86, and 80 °C. The annealing lasted 150 min at each temperature. After cooling of the samples to room temperature, melting curves of the crystallized samples were recorded at heating speed of 5 °C/min.(**III**) These melting curves showed several resolved melting endotherms, due to the separate crystallization of different of copolymer crystallites during the step-wise annealing. The melting curve is a reflection of the lamellar thickness distribution and the comonomer distribution in the copolymers.[95,97,100]

Figure 13 presents the effect of an increasing amount of OD on the lamellar structure of ethene/OD copolymers. OD, incorporated as branches, effectively diminished the crystallinity of polyethene, and the lamellar thickness distribution became broader.

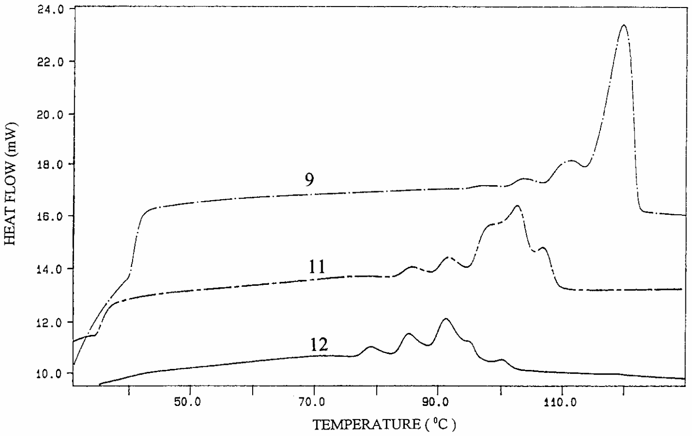


Figure 13. DSC endotherms of ethene/OD samples; polymer **9** (0.6 mol-% OD), polymer **11** (1.9 mol-% OD), and polymer **12** (2.4 mol-% OD) after segregation procedures. (**III**)

The copolymerizations of ethene with different dienes under optimized conditions again showed that the type of diene affects the copolymer structure significantly (Figure 14). The HD comonomer, which was incorporated as ring structures rather than hexane branches, exhibited noticeably different behavior from octadienes.

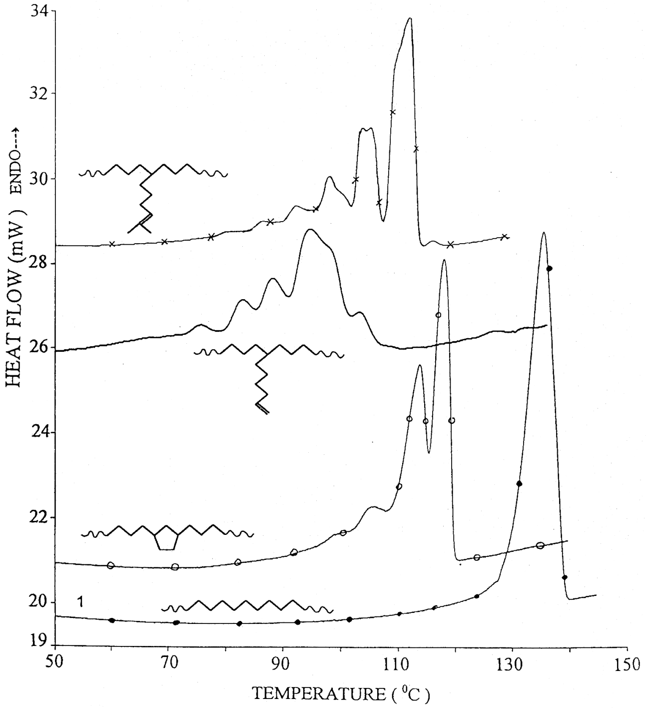


Figure 14. DSC endotherms recorded after segregation of ethene/diene copolymers. PE-HD is used as reference sample (bottom curve). Samples from bottom to top are ethene copolymers with HD, OD, and MOD, respectively (**III**)

The lamellar thickness distributions were narrow for the HD copolymers and broader for the OD and MOD copolymers. Endotherms with several peaks also indicated a distribution of the comonomer along the chain for OD and MOD.

2.3.2 Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) is a very useful tool for characterizing relaxations in both amorphous and semicrystalline copolymers. The influence of structure and morphology on the dynamic mechanical behavior of polyethenes has been discussed in a number of publications.[97,98,104-106,110,111] An understanding of the principles involved is of value in predicting the response of these polymers in product applications. The most interesting transitions seen in the DMTA curves of polyethenes are the α- and β-transitions. The α-peak observed between +20 and 70 °C is highly sensitive to thermal history and is attributed to changes in crystalline phase. The β-relaxation occurs between about +20 and –40 °C depending on the type of polyethene and is ascribed to branched structures[96]. Studies[95-98,100] on ethene/α-olefin copolymers prepared with coordination catalysts have demonstrated a steady decrease of the β-relaxation temperature with increasing comonomer incorporation. Simultaneously, the relaxation intensity, as measured by tan δ peak height, steadily increases with amorphous content. Thus, DMTA technique should be sensitive to the structural heterogeneity of the copolymers of this study.

A study of storage modulus, tan δ curves, and β-relaxations obtained by DMTA (**III**) supported the information obtained from segregation fractionation (and NMR), namely, that there is a significant difference between the incorporations of ODs and HD in the polyethene chain with Cp_2ZrCl_2 metallocene catalyst. The octadiene copolymers showed branched structure, whereas the HD copolymers were linear. Linear in this case means that HD is incorporated in polyethene as five-membered rings. These rings are so small that they do not disturb the crystallization of polyethene. Ethene/diene copolymers with lower comonomer contents showed higher storage modulus, which means greater stiffness and flexural modulus of the product.[111]

2.4 Modification of melt rheological behavior of polyethene

2.4.2 Long-chain branching in ethene/α,ω-diene copolymers

Polyolefins produced with metallocene catalysts are of uniform structure because the catalyst has a single active site. Narrow molar mass distribution is a disadvantage, however, when it comes to processing of the material. Introducing a small amount of long-chain branching offers one solution to this problem. In fact, long-chain branched metallocene polyolefins have remarkable properties, since they combine the good mechanical properties of polyolefins with narrow MMDs (M_w/M_n=2) and the easy processability of branched polyolefins.[112-114] The main feature of long-chain branches is that, contrary to short-chain branches, they improve polymer viscoelastic properties and processability without compromising mechanical properties of the polymer.[115,116] Long branches can be defined as having about the same dimensions as the main chain. It is clear, however, that even branches much shorter than this will affect the properties of the polymer.

Long-chain branching in metallocene-catalyzed ethene homopolymers is suggested to arise from the *in situ* copolymerization of ethene and vinyl-terminated macromonomers.[113,117-120] The probability of macromonomer incorporation is increased with catalysts that have a high selectivity toward vinyl termination and a good ability to incorporate 1-olefins into the polyethene chain. The first example of a single-site catalyst capable of producing LCB *in situ* was the constrained-geometry catalyst (CGC) .[112,116,121] Later on, more hindered dicyclopentadienyl catalysts, e.g. Cp_2ZrCl_2/MAO[122-124] as well as Et$[Ind]_2ZrCl_2$/MAO and other *ansa* metallocenes,[89,117,122,125-127] were successfully used for production of LCB polyethene. Both supported[126] and homogeneous metallocene catalysts[117,124] can be employed. Metallocenes produce LCB polyethene in gas-phase,[125] slurry,[117,124] and solution systems.[128]

The disadvantage of *in situ* formation of long-chain branches is that only a small amount of LCB can be incorporated. An interesting way to promote the formation of LCB (**IV**) [36,58,119] is to copolymerize nonconjugated α,ω-dienes into the polyolefin chain. Even a low α,ω-diene content may facilitate LCB formation by increasing the vinyl bond content or by compensating for the loss of inherent vinyl end-groups due to the chain transfer to hydrogen or aluminum as chain termination reaction. Ethene copolymerization with an α,ω-diene comonomer in the presence of hydrogen may thus provide an effective way to control both the molar mass and branching. In addition to linear α-ω-dienes, cyclic endomethyl-type dienes are among those dienes that are easily polymerized with coordination catalyst.[129,130]

When LCB is desired, conjugated dienes and dienes in which essentially only one of the double bonds is available for coordination polymerization are excluded. These may be useful instead in the preparation of resins where it is desirable to have residual unsaturation in the polymer, and where the dienes preferably have one double bond that is relatively unreactive under the polymer synthesis conditions.[131]

The presently prepared ethene/diene copolymers (**IV, V**) were assumed to consist of both short-chain branched species (ring structures and 1-butenyl or 1-hexenyl branches) and long-chain branched species (two polymer chains connected via the double bonds of a diene comonomer). Some polymer chains were observed to contain branches-on-branches structures. Furthermore, owing to the random nature of the branch formation, branches consisted of different arm lengths. ^{13}C NMR measurements of the ethene/HD and ethene/OD copolymers could not provide unambiguous support for the presence of three- or four-arm structures because peaks were overlapping with those of short diene branches.

2.4.2 Melt rheological properties of ethene/α,ω-diene copolymers

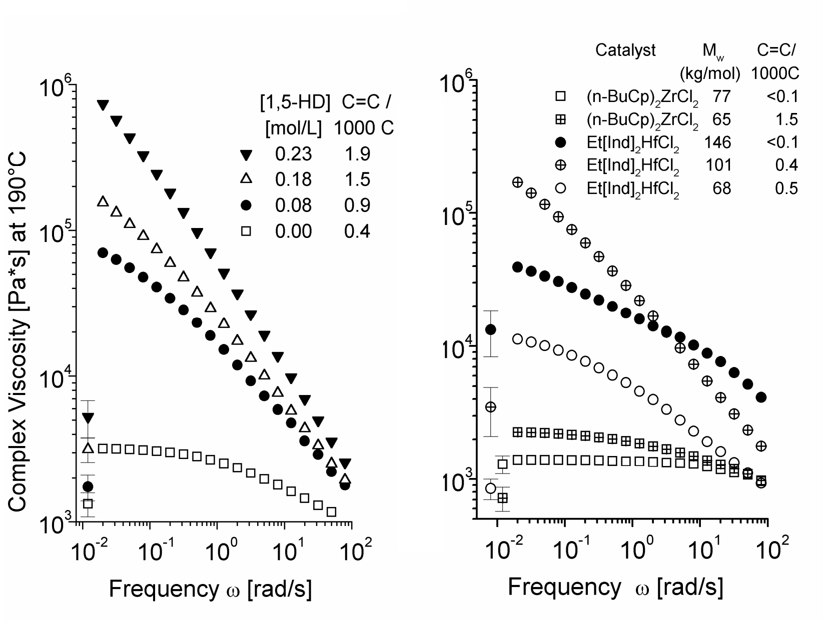
The length of a branch rather than the number of arms has the greatest influence on rheological behavior of branched polyethene, and viscosity has been found to increase exponentially with M_w and arm length.[132-134] Hence, at, metallocene homopolyethenes and ethene/diene copolymers with low branching contents should have similar melt rheological properties. Significant deviation may be expected with high branching content, as more complex, branch-on-branch structures are likely to be present.

In rheology, side branches are considered to be long when they are long enough to form entanglements of their own. Chain length long enough to influence rheology is considered to be two to three times M_e which is the chain length for entanglements. M_e for polyethene is 1300 g/mol,[135] which means that branches longer than 250 carbon atoms should significantly influence rheological behavior.

Rheological parameters respond to changes in the molecular structure in different ways: 1) complex viscosity (η^*) is influenced by the M_w and LCB, 2) dynamic melt elasticity (storage modulus (G') vs. loss modulus (G") by M_w/M_n and LCB, and 3) flow activation energy (E_a) solely by LCB.[117,127,136] In ethene polymers (with low amounts of linear comonomer), the flow activation energy (E_a) is sensitive to the presence of long-chain branches, growing with increasing content of increased length of the long branches.[133,137] Thus an Arrhenius-type flow activation energy E_a of 59 kJ/mol was obtained for long-chain branched PE-LD, and 28 kJ/mol the linear PE-HD sample.

Differences in the structures of the studied ethene/diene copolymers (cycles, short branches, LCB) (**I-V**) were reflected in the melt rheological behavior of the copolymers. To investigate the effect of the ring structure in ethene/HD copolymers on the polymer melt flow behavior, the study was made of the dynamic rheological properties of ethene/HD copolymers prepared with Cp_2ZrCl_2/MAO.(**IV**). An increasing content of ring structures in polyethene chain increased the shear sensitivity in the same manner as do high molar masses. The copolymer with ca. 10 mol-% HD incorporated clearly showed the yield behavior of a crosslinked material. LCB seemed to mask effectively the effect of ring structures.

Figure 15A shows the η^* of selected samples from copolymerization of ethene and HD carried out with $Et[Ind]_2ZrCl_2$ as a function of the oscillation frequency (ω) and illustrates the relationship between the measured η^* at low shear rate and the calculated value of zero-shear viscosity (η_0) (**V**).



A **B**

Figure 15. The complex viscosity (η*)curves of ethene/HD and ethene/OD copolymers. Single points shown at the left side of the graphs are calculated η_0 values corresponding to the SEC-based M_w and assuming the linear structure. The increasing differnece between the calculated and measured values suggests an increasing amount of branching. (data from **V**). **A**) The η*-curves of ethene/HD obtained with different HD concentrations and catalyst Et[Ind]$_2$ZrCl$_2$ **B**) The η* of ethene/OD copolymers produced with Et[Ind]$_2$HfCl$_2$ or (n-BuCp)$_2$ZrCl$_2$.

The η_0 has been calculated from the M_w data obtained by SEC with the equation $\eta_0 = 3.4\times10^{-15}\times M_w^{3.6}$ [Pa×s] provided by Raju *et al.*[135] The equation is based on the correlation between the M_w and η_0 of linear very narrow M_w/M_n polyethenes. A difference between the calculated and measured values suggests the presence of LCB. Figure 15A shows a clearly increasing difference between η* and η_0 with the increasing double bond content in the copolymer. The measured η*(0.02 rad/s) value of the Et[Ind]$_2$ZrCl$_2$/MAO-catalyzed homopolymer was slightly higher than expected, but the measured η*(0.02 rad/s) values of the diene copolymers were 40 to 140 times higher than the calculated values.

The flow activation energy (E_a) of both Cp$_2$ZrCl$_2$ (**IV**) and Et[Ind]$_2$ZrCl$_2$ (**V**) ethene/HD copolymers increased (up to 55 kJ/mol) with the diene content indicating the presence of significant amounts of LCB. The E_a was also found to depend on ω, too, which is typical for polyethene containing LCB.[138,139] Linear polyethenes have E_a values less than 30 kJ/mol.[138,140] Short-chain branching (SCB) also has some influence on the value of E_a,[140] and ethene/1-olefin copolymers may have E_a values from 30 to 40 kJ/mol depending on the comonomer content. However, small amounts of SCB have not been found to increase the value of the storage modulus (G').[127] The copolymers studied here had clearly elevated G' values, indicating the presence of LCB structures.

It was found in ethene/HD copolymerizations with Et[Ind]$_2$ZrCl$_2$ (**V**) that when the ethene pressure (concentration) was decreased, no gelation occurred even at high diene content. Most likely this was due to the reduced tendency for vinyl bond formation, which decreased the probability of LCB formation. The complex rheological behavior of the copolymers with ≈100% ring formation selectivity is partly explained by the fact that Et[Ind]$_2$ZrCl$_2$ at low ethene concentration is capable of producing LCB without the comonomer.[122]

The introduction of a low double bond content via OD incorporation to (n-BuCp)$_2$ZrCl$_2$-catalyzed polyethenes had a modest impact on the rheological properties (**V**). In contrast, the rheological properties of Et[Ind]$_2$HfCl$_2$-catalyzed copolymers were significantly altered even at much lower double bond content, indicating higher LCB content. Figure 15 B shows η^* as a function of the oscillation frequency (ω). The η^* vs. η_0 of the polymers increased slightly with the diene content when (n-BuCp)$_2$ZrCl$_2$ was used as catalyst, but the increase was dramatic for Et[Ind]$_2$HfCl$_2$-catalyzed polymers. The Et[Ind]$_2$HfCl$_2$-catalyzed copolymers also had very high E_a values. The (n-BuCp)$_2$ZrCl$_2$-catalyzed homopolymer had an η^* value at low ω very close to that expected for linear polymers of this M_w. With this catalyst only the copolymer with high diene content exhibit slightly elevated η^*(0.02 rad/s) value relative to that expected on the basis of its M_w. Although the E_a value of 33 kJ/mol obtained for the (n-BuCp)$_2$ZrCl$_2$-catalyzed copolymer may result from a very small amount of LCB the presence of LCB cannot be unambiguously shown because of the presence of SCB.

Since the boundary between LCB and crosslinking is blured and control of the structure is important, LCB has been studied theoretically as well. Both the population balance model using the method of moments[141] and the polynominal approximation method using lading moments of the distribution[90] led to the conclusion that increasing diene content and polymerization time increases the LCB content of these polymers up to the point where gel formation is apparent.

3 FUNCTIONALIZED ETHENE/DIENE COPOLYMERS

3.1 Post-polymerization functionalization of ethene/diene copolymers

The lack of functional groups in polyethene restricts its compatibility with many materials. Achieving satisfactory adhesion between polyethene and various substrates (e.g. paints) usually requires surface pretreatment of the polyethene. An alternative approach is the production of functional polyethenes, either by direct polymerization or by post-polymerization modification of appropriate copolymers of polyethene. The copolymerization of ethene and α,ω-dienes is of considerable commercial interest because of the possibility of producing distinct polymer products, including the formation of side chains with terminal unsaturation, allowing the further introduction of functional groups.

The possibility of using copolymers of ethene and nonconjugated dienes prepared with metallocene catalysts for post-polymerization functionalization was noted in Section 1.2.

3.1.1 Chemical modification of unsaturations in ethene/diene copolymers

Post-functionalized polyethene in this work means ethene/diene copolymers that are functionalized after the polymerization reaction itself. The reactions were carried out in solution [142](**VI**). The poor solubility of polyethene forced us to use high temperatures (just below the boiling temperature of reagents). Another possibility would have been to carry out the reactions in molten polymer without solvents, but even in this case the temperature is above 150 °C.

The availability of unsaturations in polyolefins can be exploited in reactions such as hydrosilylation, hydroboration, or epoxidation. Various functionalities have been obtained by applying simple organic chemistry to diene copolymers of polyethene. Both straight chained (symmetrical and unsymmetrical) and cyclic dienes are appropriate comonomers for ethene where the aim is to produce functionalized polyethenes via the post-functionalization method. Yanjarppa[8] compiled the following list of dienes that have been used in functionalization of polyolefins:

- **Symmetrical dienes** (1,3-butadiene, HD, OD, DD)
- **Bicyclic dienes** (2,5-norbornadiene (NBD))
- **Unsymmetrical dienes** (VCH, 6-phenyl-1,5-hexadiene, MOD, *R*(+)-5,7-dimethyl-1,6-octadiene (isocitrollene), VNB, ENB, dicyclopentadiene, 1,4-hexadiene)

Table 3 shows the functionalities that have been inserted into polyethenes copolymerized with dienes using metallocene catalysts.

Table 3. Functionalities inserted into ethene/diene copolymers by post-polymerization functionalization.

diene	Reaction	Final functionality	Reference
1,4-HD	hydroboration	-Br_2, -OH, -NH_2, -$OSi(CH_3)_3$	21,27
VCH	hydroboration	OH	29
DCP		epoxy	25
ENB	hydroboration	-OH, -NH_2, -COOH, -I, Br, -$OSiI(OH)_3$	144
DMO	hydrochlorination	phenol	35

There is also an example where polyethene containing unsaturations was first hydroxylated and then treated with n-BuLi in order to make graft copolymerization with ε-caprolactone possible.[21] In some cases, crosslinking of the material is a desired reaction. Peroxide crosslinking is effective but difficult to control when total crosslinking is not desired.

In this work, ethene/OD copolymers containing 1 mol-% of OD were post-polymerization functionalized by epoxidation and hydrosilylation reactions.

3.1.2 Epoxidation of ethene/1,7-octadiene copolymer

Blending of thermoplastics is a useful and relatively cost-effective way to produce new materials with desired property combinations. Polyolefins are characterized by good moisture stability, good processability, and low cost. Engineering plastics, on the other hand, have good thermal and mechanical properties. However, most thermoplastic blends of polyolefins and engineering plastics are immiscible and exhibit unstable morphology and poor interfacial adhesion, and inferior mechanical properties as a consequence.

Blends of polyolefins and PBT (polybutene terephthalate) offer an interesting combination of properties for applications in the electronics industry. Compatibilizers that contain epoxy groups have shown potential in these blends. Epoxy functionality cannot be polymerized into polyolefins even with metallocenes, but post-polymerization functionalization of ethene/diene copolymers offers an indirect route to their preparation.

In this work,[142] epoxidation of ethene/OD copolymer was first performed in chloroform suspension (at RT), but the conversion did not rise above 50 % even at reaction times up to 70 h. Nearly 100 % conversion of vinyl bonds to epoxy groups was later achieved with toluene as solvent (3h, 70 °C). These results indicate the importance of solubility of the polymer material. The higher temperatures required for total dissolution of polyethene could not be used due to the heat sensibility of epoxidation reagents. Characterization of the structure of the copolymer was carried out by ^{1}H NMR technique (Figure 16).[142]

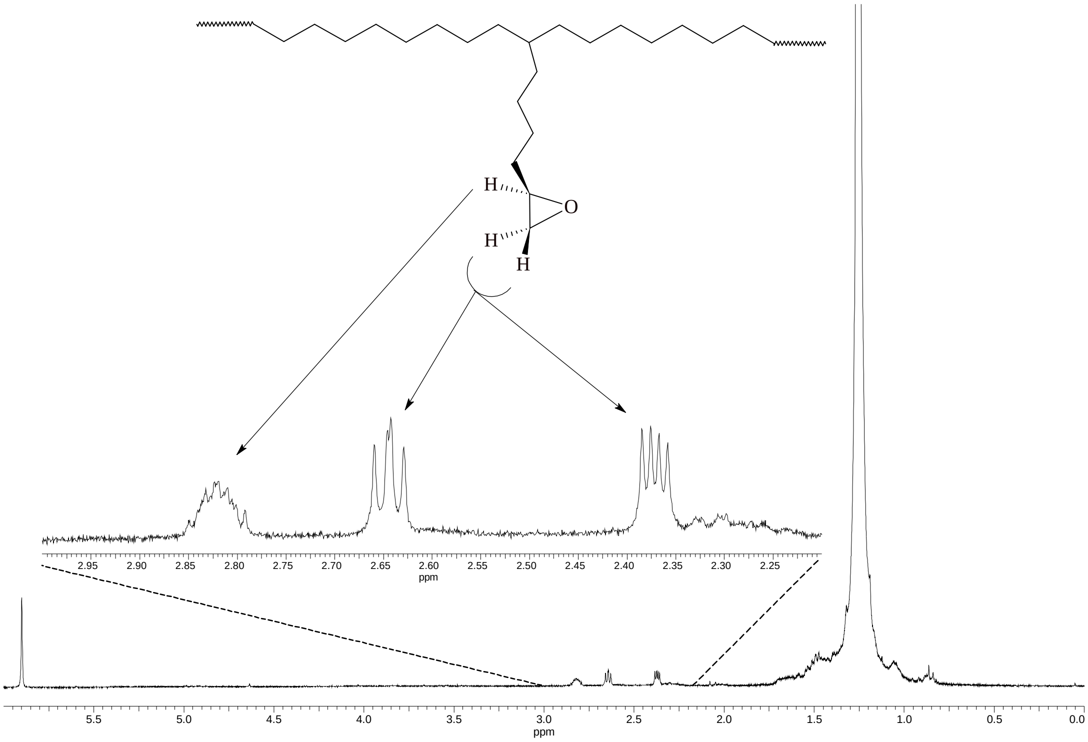


Figure 16. ^{1}H NMR spectra of an epoxidized ethene/1,7-octadiene copolymer. Shifts are in ppm.[142] The spectra were recorded with Varian Gemini 2000XL NMR spectrometer (300 Hz, at 125 °C, in deuterated toluene.

3.1.3 Silane-functionalization of ethene/1,7-octadiene copolymer

In this work, several silane functional polyethenes were prepared via a hydrosilylation reaction (**VI**). Ethene/OD copolymer was prepared using metallocene catalyst system Et[Ind]$_2$ZrCl$_2$/MAO and post-treated into silicon-containing polyethene (PE-co-SiX, X=Cl, OEt, Ph) via hydrosilylation (in toluene at 100 °C) (see Figure 17). The hydrosilylation reaction of ethene/OD copolymers was carried out in extremely dry conditions, as the chloro- and ethoxysilane groups are still moisture-sensitive after hydrosilylation, and moisture could lead to crosslinking of the copolymer. The hydrosilylation reactions were successfully carried out with dimethylethoxysilane, chlorodimethylsilane, and phenyldimethylsilane, and a total conversion of vinyl bonds to different Si-functionalities was achieved.

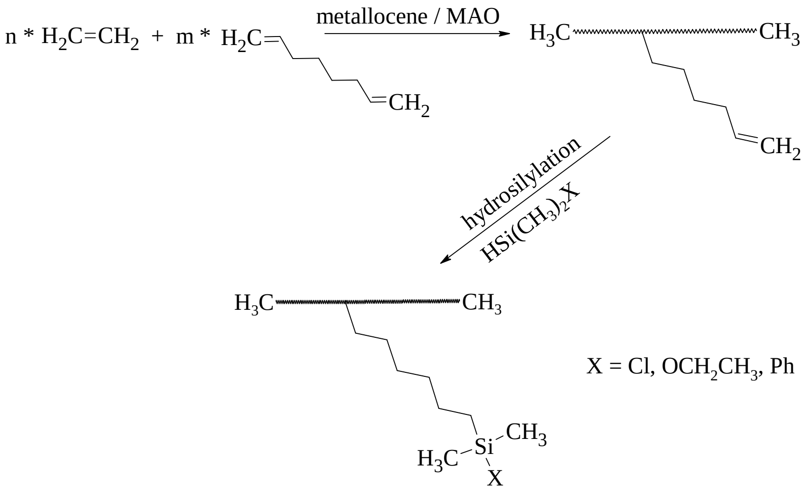


Figure 17. Functional polyethenes prepared via hydrosilylation reaction.(**VI**)

The properties of the ethene/diene copolymer were slightly altered during the hydrosilylation. This can be seen in the DSC measurements, as the area of thicker lamellae was diminished. SEC measurements showed a shoulder at the high molar mass end of the curve, which was an indication of chain extension.(**V**)

3.2 Functionalized ethene/diene copolymers in composites

3.2.1 Overcoming incompatibility of polypropene composites

New materials can be created by adding fillers to polyolefins or by blending two different polymers. However, homogeneity of the structure is essential to creating synergistic properties in these multiphase materials.

The challenge, especially for polyolefins, is to overcome the poor adhesion and chemical incompatibility of the components, which otherwise result in poorly dispersed and attached phases. The technology created to solve these problems employs additives, modifiers, and compatibilizers, which facilitate the functioning together of poorly compatible components of a composite or blend so that they act as a single material with precise properties.

Polyolefins modified by the introduction of polar groups have significant potential as modifiers and blending agents in composite applications. The most widely used commercial compatibilizers are copolymers of polyolefins, or elastomers with maleic anhydride (MAH), epoxy, or carboxyl functionality. Functionalized polyolefins obtained with metallocene catalysts have successfully been used as modifiers in various polymer blends and composites.[145-149] As an example, in an earlier study of our group[150] polyethene-based halosilane and alkoxysilane-functionalized polymers were found to be highly effective adhesion promoters in polyethene-based composites leading to improvements in mechanical properties. Interaction was even found between less reactive phenylsilane-functionalized polyethene and filler.

Impact strength appears to be the weakest link in the otherwise competitive properties of polypropene. Major challenges are encountered in attempts to improve the impact strength. Thus, when rubber toughening is used to enhance impact strength the stiffness of the material decreases and fillers that improve stiffness is added, the polypropene (PP) matrix loses its impact strength.[151]

Methods to increase stiffness and toughness simultaneously have generated much interest. A balance between these mechanical properties is often sought by simultaneous addition of filler and elastomer to the PP matrix, where the final morphology defines the mechanical properties. Functionalized polypropene has been used as modifier to attach the filler to the PP matrix, preventing the filler from dispersing into the rubbery phase.[152] The so-called core-shell structure is often considered a requirement for increased toughness in these ternary composites.[153] Core-shell structure can be obtained by addition of a functionalized rubbery phase e.g. EPR-g-MAH (ethene/propene rubber grafted with maleic anhydride). As an extension of the idea of a core-shell structure, the toughness of a composite might be correlated with the interaction achieved between filler and matrix. Recent studies have shown that fillers can act as toughening agents in the polypropene matrix.[151,154-156]

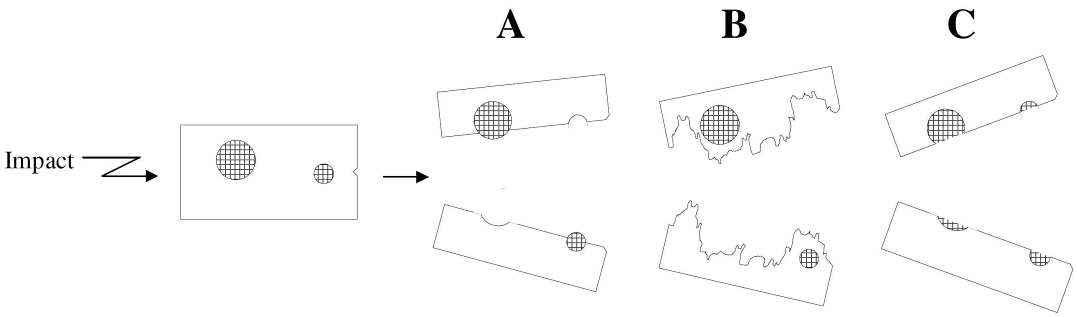
The increase in impact resistance after addition of submicron-size filler particles (<1 μm) to the PP matrix is usually explained by the separation of the filler from the matrix. Instead of crazing, the small cavities that are formed allow shear yielding to take place, after which the voids act like rubber particles and the fracture mechanism changes from brittle to ductile. With this explanation, the increase in toughness would be lost if the shear yielding or debonding was prevented.

In addition to filler/matrix interaction, the size, shape, and quality of the filler and the microstructure of the matrix at the boundary layers between different phases can all influence the toughness of composites.[151,155,157] Basically, the crucial factors determining toughness are the prevailing micromechanical energy-consuming deformation process and the volume of this deformation.

3.2.2 Silane-functionalized ethene/1,7-octadiene copolymer in PP/elastomer/μSi composite

Increased stiffness of heterophasic polypropene (hPP) without loss of toughness can be generated by blending in submicron-size silica fillers (μSi). The achieved increase in toughness is sensitive and easily lost, however, e.g. at temperatures below T_g of PP. In this work, silane functionalized modifiers (PE-co-SiX, X=Cl, OEt, Ph, F) were applied to these composites to alter the morphology and find a way to increase impact strength of hPP especially at lower temperatures. Glycidylmetacrylate-grafted polyethene (PE-co-GMA) was used as a reference.(**VI**)

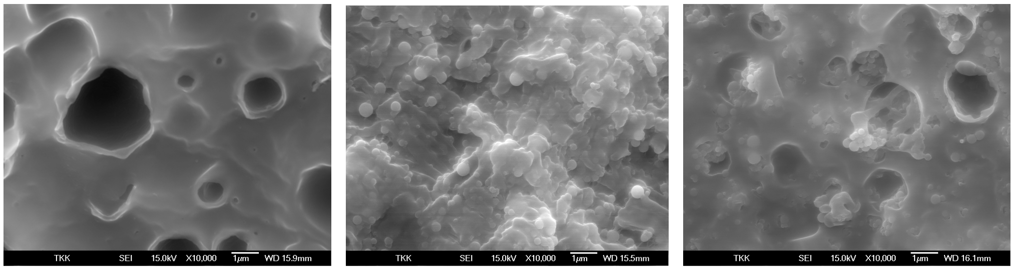
The mechanical properties of the hPP/μSi composites varied with on the composition(**VI**). In a SEM study, the toughness was found mainly to correlate with the dominating fracture behavior of the composite, and three different mechanisms were observed to operate during the impact (Figure 18). A schematic presentation of crack propagation in brittle (hPP), ductile (hPP+μSi), and semibrittle (hPP+μSi+modifier) fracture mechanisms is shown in Scheme 4. SEM micrographs of the composites can be seen in Figure 18, and the mechanical properties of selected samples are collected in Table 5.



Scheme 4. Schematic presentation of the crack propagation in brittle (A), ductile (B), and semibrittle (C) fracture mechanisms. Top view, the notch is on the right side and the impact comes from the left. The rubbery phase is gridded. The filler particles are removed for clarity.(**VI**)

The fracture mechanism in hPP is a brittle one. The crack proceeds linearly and smoothly in the PP matrix before striking the rubber particles, and then continues by winding around them via the rubber/matrix interphase (Scheme 4 A; Figure 18 SEM micrograph A). The addition of 30 wt-% μSi to hPP changed the fracture mechanism to ductile. In the ductile fracture mechanism the crack proceeds mainly in the hPP matrix, avoiding the rubber and rubber/matrix interphase (Scheme 4 B; Figure 18 SEM micrograph B). The long route of the propagating crack is seen as a rough fracture surface. However, the fracture mechanism of this hPP/μSi composite was again brittle when the temperature was below T_g of hPP, and the toughness decreased below the value of plain hPP (Table 5, Run 2 vs. Run 1).

The demonstrated[153] usefulness of the core-shell structure encouraged us to study the capability of our Si-functionalized PE in moving the filler into the rubbery phase of hPP. Use of Si-functionalized PE as a modifier (addition 2 wt-%) changed the fracture mechanism to somewhere between brittle and ductile. In this case the fracture surface was smooth, as in brittle fracture, but the crack was now able to pass through the rubber particles rather than winding around via the rubber/matrix interphase (Scheme 4 C; Figure 18 SEM micrograph C). The ability of the rubbery phase to carry a larger amount of the impact energy than the rubber/matrix interphase was exploited in this “semibrittle” mechanism. This led to higher impact strength of our hPP/μSi composite compared to the unfilled hPP, also below -20°C (Table 5, Run 1 vs. Run 5).



A **B** **C**

Figure 18. SEM micrographs (*10 000) of the fracture fields of samples fractured at ambient temperature. hPP (A); hPP/μSi (B); hPP/μSi + 2 wt-% of PE-co-GMA (C). The rubber phase has been leached away with xylene. (data from **VI**)

Table 5. Tensile properties and toughness of hPP/μSi composites (with and without modifiers). The values of modulus and yield strain are results with draw speed 1 mm/min. Toughness of hPP and hPP/ μSi composites was measured above and below the T_g of PP. Impact strength values are for notched specimens. (data form **VI**)

Run	**Composite**	**Modulus** MPa	**Yield Strain** %	**Impact strength** at 25 °C, kJ/m^2	**Impact strength** at -20 °C, kJ/m^2
1	**hPP**	770 ± 20	9.9 ± 2.2	11.6 ± 1.6	6.0 ± 0.4
2	+30 wt% μSi	1090± 30	4.6 ± 0.1	38.4 ± 4.1	4.6 ± 0.2
	hPP+30 wt-% μSi				
3	+2.0wt% PE-co-GMA	710 ± 20	13.8 ± 0.4	20.6 ± 0.8	7.7 ± 0.6
4	+2.0wt% PE-co-SiOEt	890 ± 30	7.8 ± 0.1	15.5 ± 2.2	7.1 ± 0.3
5	+2.0wt% PE-co-SiF	960 ± 30	7.4 ± 0.1	17.8 ± 3.7	7.4 ± 0.7

The SEM micrographs show that the filler particles were effectively dispersed in the rubbery phase. A large concentration of filler particles in the rubbery phase fulfills the requirement for a semibrittle fracture mechanism. Unlike the ductile fracture mechanism, the semibrittle one is maintained at –20 °C, and the toughness of the composite is higher than that of hPP. Commercial PE-co-GMA increased the toughness most, but it also resulted in loss of the stiffness achieved through the addition of μSi. When PE-co-SiOEt or PE-co-SiF was the modifier, almost the same increase in toughness was achieved as with the commercial PE-co-GMA, but now with only a moderate decrease in the stiffness (e.g. Run 3 vs. Run 5). This can be explained by the more controlled and rigid structure of polyethenes made with metallocenes. After reaction of the modifier with the filler, the ability of the filler to act as stiffening agent was largely maintained.

4 CONCLUSIONS

The following conclusions can be drawn from the studies described in this summary and in publications **I-VI**:

Nonconjugated α,ω-dienes can effectively be copolymerized by metallocene catalysts. Used as comonomers these dienes induce a wide variety of interesting structures in polyethene; even the rheological properties can be modified. The structure of the copolymers can be tailored through choice of diene, metallocene catalyst, and polymerization conditions. Linear nonconjugated dienes can be incorporated as branches or cyclic structures. A catalyst with good comonomer response readily forms long-chain branched structures via intermolecular bonding even at low α,ω-diene content. The amount of vinyl bonds induced by α,ω-diene addition can be controlled by the monomer concentration and ring formation selectivity. Polymerization temperature plays an important role in controlling crosslinking in copolymerization.

The rheological behavior of the ethene/α,ω-diene copolymers studied in this work is similar to that of metallocene-catalyzed LCB homopolyethenes. An increasing vinyl content leads to the formation of branches-on-branches structures and eventually to crosslinking. The rheological parameters (dynamic viscosity (η^*), storage modulus vs. loss modulus, and gel strength) together with the M_w/M_n can be used to evaluate the degree of branching. The difference between η^* and η_0 and the increased activation energy (E_a) values with the increasing double bond content in the copolymer clearly point to the existence of LCB in both ethene/1,5-hexadiene and ethene/1,7-octadiene copolymers.

The unreacted vinyl bonds of ethene/diene copolymers can effectively be used for post-polymerization functionalization of the material by methods of conventional organic chemistry. This is important, since many functionalities are difficult if not impossible to insert into polyolefins in coordination catalyzed polymerizations and even reactive extrusion has its limitations. In epoxidation reaction of ethene/1,7-octadiene copolymer, 70% conversion was achieved. The hydrosilylation of ethene/1,7-octadiene copolymers to polyethenes containing reactive silane functionalities (PE-co-SiX, X=Cl, OEt, Ph), in turn, was be carried out with 100% conversion of vinyl groups.

Si-functionalized polyethenes were applied as effective modifiers in hPP/μSi composites. Just 0.5-2 wt-% of copolymer containing 1 mol-% of functional group effected notable changes in properties of these composites. The Si-functionalized polyethenes were able to interact with the filler and transfer part of the filler to the rubbery phase of heterophasic polypropene. This provided an effective way to guide a propagating crack into the rubbery phase instead of its going around via the PP matrix/rubber interlayer and significant improvement was achieved in the toughness compared with that of unfilled hPP, below the T_g of PP as well as at ambient temperature. Addition of this functional PE grade made it possible to maintain the stiffness as well.

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ISBN 978-951-22-8955-4
ISBN 978-951-22-8956-1 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)