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Long-Term Properties of Polyolefins



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Long-Term Properties of Polyolefins

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Preface

We dedicate the current volume entitled “Long-Term Properties of Polyolefins” to Professor Kausch on his 25th anniversary as editor of *Advances in Polymer Science*. Professor Kausch pioneered the work on molecular effects in the fracture of polymers. This is beautifully summarized in his books on polymer fracture. Professor Kausch is also the perfect gentleman – always eager to help newcomers to make their entrance into the scientific community and to assist his colleagues in their work and accomplishments. With his work, Professor Kausch has demonstrated the importance of “source science” – to present new data – and to present reviews of previously published material. This book is presented in the spirit of Professor Kausch, namely showing a good selection of data and explaining what they mean.

The main focus of this book is the relation between structure and properties and the trend towards better quality and reproducibility. The first chapter describes the metallocene polymerisation catalysts and their possibility not only of tailoring polymer properties but also of manufacturing entirely new materials. Due to improved control of microstructure, it will also be possible to produce specialty polyolefins which could compete with non-olefinic polymers. The next chapter shows how in each new development step catalyst and process innovations have gone hand in hand and how the control over polymer structure and the ability to tailor material properties has increased. For a better understanding of properties and behaviour, the basis of morphology is fundamental and is described in chapter three, followed by chapter four about fracture properties and microdeformation behaviour. Promising model systems for the investigations of the relations between crack-tip deformation, fracture and molecular structure are also presented. Chapter five gives an overview of stabilization of polyethylene crucial for long-term properties. Two main approaches have been used; the first advocates the use of biological antioxidants, and the second relies on the use of reactive antioxidants that are chemically attached onto the polymer backbone for greater performance and safety.

Chemiluminescence is presented as a tool for studying the initial stages in oxidative degradation and is explained in chapter six. However, for many years, tailor-made structures specially designed for environmental degradation have also been a reality. One of the key questions for successful development and use

of environmentally degradable polymers is the interaction between the degradation products and nature and this is illustrated in chapter seven. The development of chromatographic methods and use of chromatographic fingerprinting gives not only degradation products but also information about degradation mechanisms as well as interaction between the polymer and different environments. The obstacles and possibilities for recycling of polyolefins are discussed in chapter eight with special emphasis on analytical methods useful in the quality concept. It is also shown how recycled material could be a valuable resource in the future together with renewable resources. Finally, chapter nine gives examples of existing as well as emerging techniques of surface modification of polyethylene.

These chapters together will hopefully inspire to a new generation of polyethylene by mimicking nature and use of new molecular architecture, new morphology and also “activated” additives in microdomains, with even more reproducible properties within narrow limits and with predetermined lifetimes.

January, 2004

Ann-Christine Albertsson

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Specific Structures Enabled by Metallocene Catalysis in Polyethenes

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Abstract This chapter briefly describes the history of metallocene polymerisation catalysts. The behaviour of metallocenes, particularly in copolymerisation of ethene with higher linear α -olefins is discussed. A class of olefin polymerisation catalysts based on siloxy-substituted bis(indenyl) metallocenes is reported. These ligand systems offer efficient opportunities for copolymerisation of ethene with heteroatoms containing monomers and traditional α -olefins. In addition, the formation of long-chain branching, attributed to copolymerisation of vinyl terminated polyethenes, is discussed. Examples of siloxy-substituted bis(indenyls) with high copolymerisation capability and high vinyl selectivity are highlighted.

Keywords Siloxy-substituted metallocenes · Long-chain branching · Rheological properties · Comonomer response · Vinyl selectivity

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1 Introduction

The main benefits of metallocene catalysts in comparison to the conventional Ziegler-Natta catalysts are well-defined microstructures, high activity, narrow molar mass distribution and the possibility of tailor-made polyolefins. The advantages in metallocene catalyst chemistry offer a promising novel

way not only to tailor polymer properties, but also to manufacture entirely new polymeric materials.

The development of metallocene catalysts, also called single-site catalysts, was stimulated by the discovery of highly effective activators. Metallocenes combined with aluminium alkyls for polyolefin polymerisation are not a new discovery. Natta et al. [1] with the homogeneous $\text{Cp}_2\text{TiCl}_2/\text{AlMe}_3$ system and Breslow and Newburg [2] with the $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_2\text{Cl}$ catalyst system conducted almost simultaneously the first metallocene polymerisations in the 1950s. Due to their inferior activity, compared to the heterogeneous TiCl_3 and TiCl_4 Ziegler-Natta catalysts, the time was not right for the metallocenes. Nevertheless, the research on metallocenes continued focusing on polymerisation mechanisms, which was more straightforward in homogeneous catalyst systems.

2

Milestones in Metallocene Catalysis

Reichert and Meyer [3] were the first to demonstrate in the early 1970s an enhancement in the polymerisation activity upon addition of water to the $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$ catalyst system. Soon thereafter, Long and Breslow [4] reported similar observations for the $\text{Cp}_2\text{TiCl}_2/\text{Me}_2\text{AlCl}$ system, as did Kaminsky and Sinn [5] for the $\text{Cp}_2\text{TiMe}_2/\text{AlMe}_3$ catalyst and Cihlár et al. [6] for the $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$ catalyst. In 1975 Kaminsky and Sinn [7] conducted ethene polymerisation with the catalyst $\text{Cp}_2\text{ZrCl}_2/\text{TEA}$, which can be considered the first effective metallocene catalyst.

The breakthrough in metallocene catalyst development occurred in the early 1980s when a metallocene catalyst, instead of an aluminium alkyl, was combined with methylaluminoxane (MAO) [8, 9, 10]. This catalyst system boosted the activity of metallocene-based catalyst and produced uniform polyethene with the narrow molar mass distribution typical for single-site catalysts. Efforts to polymerise propene failed, however: the product was found to be fully atactic, indicating complete lack of stereospecificity of the catalyst [10].

The synthesis of isotactic polypropene had to wait for sterically rigid catalysts: a group of catalysts in which the movement of the rings is hindered and the angle between the ligands is widened with a bridge. In 1982 Brintzinger et al. [11] synthesised a chiral *ansa*-bis(indenyl) titanocene with C_2 -symmetry. This catalyst, together with MAO, was used by Ewen to first demonstrate the synthesis of isotactic polypropene [12]. This discovery initiated an extensive study in the field of stereospecific polymerisation by varying the composition, structure and the type of symmetry (C_2 , C_1 and C_s) of sterically hindered *ansa* metallocenes. Soon several papers concerning the isospecific [13, 14, 15] and syndiospecific [16] polymers were published. At the same time Ishihara et al. [17] synthesised syndiotactic polystyrene with a half-sandwich titanocene catalyst. The most important characteristic of metallocenes, the type of symmetry, determines the stereospecificity. The *racemic* form of metallocenes with a C_2 -symmetry gives isotactic polymers,

while metallocenes with the C_s -symmetry are used to prepare syndiotactic polymers, and C_1 -symmetry leads to the formation of isotactic, hemiisotactic, and stereoblock polyolefins.

However, the properties of the polypropene produced by the catalysts $\text{Et(Ind)}_2\text{ZrCl}_2$ or $\text{Et(H}_4\text{Ind)}_2\text{ZrCl}_2$ discovered by Kaminsky and Brintzinger were not satisfactory from the industrial point of view as the catalytic selectivity and molar mass of the polymer tended to stay only moderate. The change of the ethene-bridge to a silyl-bridge doubled the molar mass and increased the activity. Addition of a methyl group into the 2(α) position enhanced the catalytic performance further, but the molar mass was still low [18]. After attachment of a phenyl ring to the 4-position, the obtained catalyst *rac*- $\text{Me}_2\text{Si(2-Me-Benzindenyl)}_2\text{ZrCl}_2/\text{MAO}$ showed both high activity and polymer molar mass [19]. The optimisation of the bis(indenyl) catalyst systems lead Spaleck et al. [20] to the silylene-bridged 2-methyl-4-naphthyl-substituted bis(indenyl) zirconium dichloride catalyst, which was an answer to the request of improved isospecific metallocenes. Along the same lines was the first siloxy-substituted bis(indenyl), ethylene bis (2-tert-Butyldimethylsiloxyindenyl)zirconium dichloride reported by Leino et al. [21]. This siloxy-substituted catalyst showed high activity in copolymerisation of ethene with higher α -olefins.

In the early 1990s supported metallocenes were introduced to enable gas phase polymerisation. Also ethene/ α -olefin copolymers with high comonomer content, cycloolefin copolymers and ethene-styrene interpolymers became available. In 1990 Stevens at Dow [22] discovered that titanium cyclopentadienyl amido compounds (constrained geometry catalysts) are very beneficial for the copolymerisation of ethene and long-chain α -olefins.

In the beginning, the major focus was on the early transition metals such as Ti, Zr and Hf, but today the potential of the late transition metals complexes of Ni, Pd, Co and Fe is well recognised. As the late transition metals are characteristically less oxophilic than the early metals, they are more tolerant towards polar groups. Therefore, it was assumed that with late transition metals catalysts one could produce a wide range of different polymers.

A nickel-based catalyst system, which produces, in the absence of comonomers, highly short-chain branched polyethene was developed by Brookhart et al. [23]. Independently, the groups of Brookhart [24, 25, 26] and Gibson [27, 28, 29, 30] developed efficient iron- and cobalt-based catalyst systems. Nickel or palladium is typically sandwiched between two α -diimine ligands, while iron and cobalt are tridentate complexed with imino and pyridyl ligands.

Grubbs' group [31, 32] developed another type of Ni-based catalyst. This neutral Ni-catalyst, based on salicylaldimine ligands, is active in ethene polymerisation without any co-activator and originated from the Shell higher olefin process (SHOP). Shortly thereafter another active neutral P,O-chelated nickel catalysts for polymerisation of ethene in emulsion was developed by Soula et al. [33, 34, 35]. The historical development of single site catalysts is represented in Fig. 1.

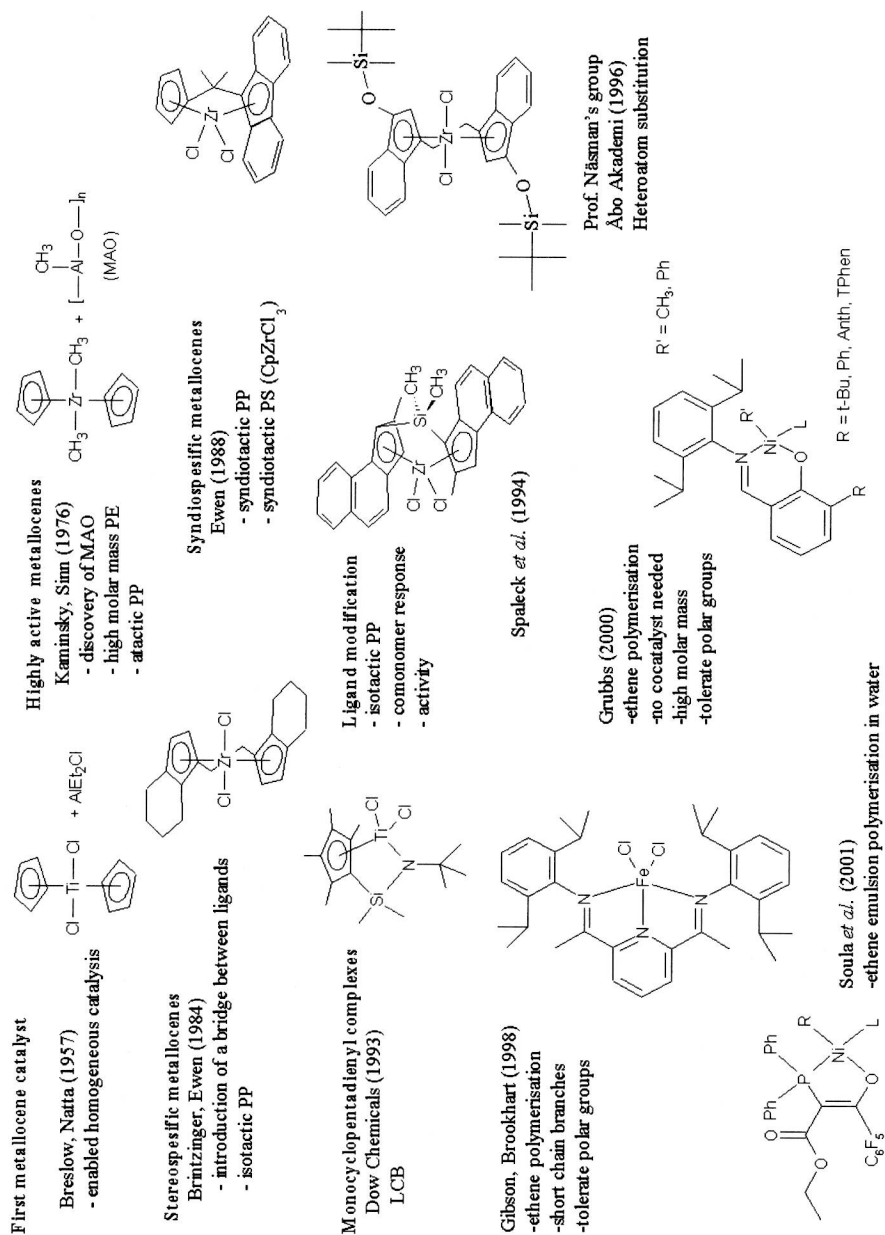


Fig. 1 History of single site polymerisation catalysts

The key to the extremely high activity of single-site catalysts in polymerisation is the activator. MAO is the most common one and it is well recognised that MAO forms cationic alkyl complexes containing a weakly or non-coordinating anion, which is complexed by the MAO molecule. Although MAO is used in industrial processes, a number of other activators have been developed lately. Some boron organic compounds, such as trisphenylmethyl-tetrakis(pentafluorophenyl)borate $[\text{C}(\text{CH}_3)_3]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$, seem to especially fulfil a role as non-coordinating, non-nucleophilic counteranion to the active cationic species [36, 37, 38, 39, 40].

3

Metallocenes with High Activity for Ethene Polymerisation

Unbridged, bridged, substituted and half-sandwich complexes have been used as catalysts for ethene polymerisation. In the series of various *ansa* cyclopentadienyl, indenyl and fluorenyl derivatives of metallocene complexes, the bridged indenyl complexes show the highest activities as homogeneous ethene polymerisation catalysts. In general, zirconium catalysts are more active than the hafnium or titanium systems. These metallocene catalyst systems provided a unique opportunity for new tailor-made polymers and increased the range of comonomers that could be used. An interesting peculiarity of metallocene systems is that the difference in the reactivities of ethene, propene and higher α -olefins is markedly less compared to the conventional Ziegler-Natta catalysts [41]. This opens many new possibilities for the synthesis of copolymers.

3.1

Copolymerisation Behaviour

3.1.1

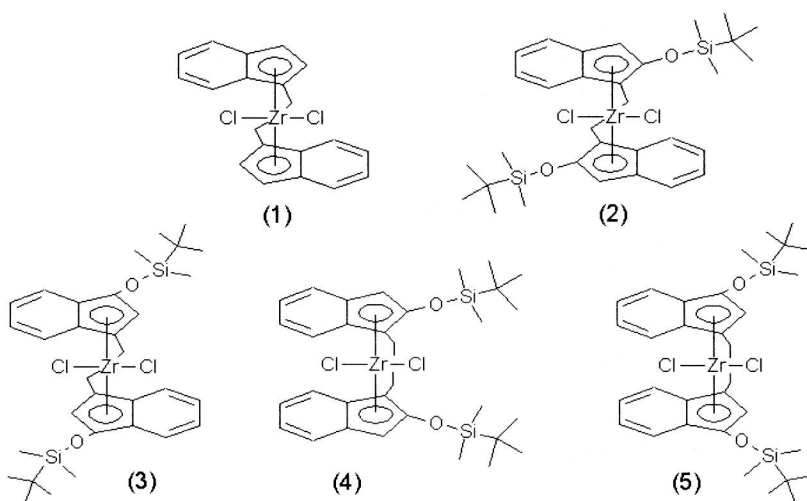
α -Olefin Comonomer Response

Ethene copolymers of higher α -olefins such as 1-butene, 1-hexene and 1-octene are industrially important materials. In contrast to Ziegler-Natta catalysts, metallocene catalyst systems offer several advantages. Metallocenes give, as already earlier has been mentioned, narrow molar mass distribution and high comonomer incorporation and, in addition, even compositional distribution. Copolymerisation of ethene with α -olefins, ranging from C_3 - C_{18} , has been reported by us [42, 43, 44] and by several other groups [45, 46, 47, 48, 49, 50, 51, 52, 53, 54]. We have studied incorporation of comonomers as a function of ligand substitution pattern and interannular bridge. Some general observations about the influence of the ligand structure on the polymer structure have been made [55, 56], although the details are not known of how both electronic and steric effects, in combination with each other, determine the reactivities of reactants.

Generally, *ansa*-metallocenes with bridges between the ligands incorporate α -olefin comonomers better than unbridged ones. It has also been shown that benzannulation of bridged indenyl ligands increases reactivity toward α -olefins.

The transition metal has, in addition to ligand substitution and interanular bridge, a distinctive effect on the copolymerisation behaviour. Hafnium-based metallocenes are considered to exhibit higher comonomer response than zirconium based ones [45].

Recent developments in catalyst design have offered more sophisticated catalyst structures with even better copolymerisation ability. $\text{Me}_2\text{Si}(\text{Me-Benz(e)Ind})_2\text{ZrCl}_2$ is an example of such a catalyst [57, 58]. This catalyst, as mentioned earlier, was originally designed for polymerisation of isotactic polypropylene, but it also shows a very high comonomer response in ethene polymerisation [51].



Catalyst	1	2	3	4	5	Comment
r_{Ethene}	48 ± 4	55 ± 3	19 ± 4			at 80°C
$r_{1\text{-Hexene}}$	<0.02	0.005	0.006			
r_{Ethene}		36 ± 3	16 ± 1	11 ± 1	10 ± 1	at 40°C
$r_{1\text{-Hexene}}$		0.003	0.005	0.005	0.001	

Fig. 2 Comonomer response of siloxy-substituted metallocene catalyst in copolymerisation of ethene with 1-hexene. The catalysts are: (1) *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$; (2) *rac*- $\text{Et}(2\text{-tert-BuSiMe}_2\text{OInd})_2\text{ZrCl}_2$; (3) *rac*- $\text{Et}(3\text{-tert-BuSiMe}_2\text{OInd})_2\text{ZrCl}_2$; (4) *meso*- $\text{Et}(2\text{-tert-BuSiMe}_2\text{OInd})_2\text{ZrCl}_2$; (5) *meso*- $\text{Et}(3\text{-tert-BuSiMe}_2\text{OInd})_2\text{ZrCl}_2$

The use of heteroatoms, such as N, O, S and P, as ligand substituents has resulted in new catalyst families with improved comonomer response. For example, *rac*-Et(3-*tert*-BuSiMe₂O Ind)₂ZrCl₂ gives an almost threefold increase in comonomer response compared to *rac*-Et(Ind)₂ZrCl₂ catalyst (see Fig. 2). The siloxy-substituted single-site catalysts also have some other advantages over conventional metallocenes. Siloxy-substituted bridged bis(indenyl) metallocenes also exhibit, except for high 1-hexene response, high vinyl end group selectivity. In addition, the siloxy groups are beneficial when the metallocene is heterogenised to suit industrial purposes better.

Figure 2 presents examples of some siloxy-substituted metallocene catalysts (2–5) and, for comparison, an ordinary bis(indenyl) catalyst (1). The relative reactivity in ethene/1-hexene was investigated [44, 59, 60, 61, 62] in order to predict their copolymerisation ability compared with the conventional bis(indenyl) catalyst (1).

The comonomer response (compare *rac*-catalysts 2 and 3 with the corresponding *meso*-catalysts 4 and 5 in Fig. 2) can be improved by using *meso*-isomers of C₂ symmetric metallocenes [60]. In copolymerisation of ethene with 1-hexene the reactivity ratios of siloxy-substituted *meso*-isomers, catalysts 4 and 5, are comparable with those of Me₂Si(2-Me-Benz(e)Ind)₂ZrCl₂ [52], which is considered to be a highly efficient copolymerisation catalyst.

3.1.2

Copolymerisation of Functional Monomers with Ethene

Incorporation of functional groups into polyolefins has long been a scientifically interesting and technologically important subject. Metallocene catalysts have opened new perspectives in this area, through direct copolymerisation of ethenes with functional monomers [63, 64, 65, 66, 67, 68, 69, 70, 71, 72]. The direct copolymerisation of ethene with oxygen- or nitrogen-containing comonomers is, however, in general accompanied by a great loss in activity of the catalyst. Our recent studies [73] show that a siloxy-substituted catalyst is superior to the ethylene bis(indenyl) zirconocene catalyst and can successfully copolymerise ethene with 10-undecen-1-ol (see Table 1). The activity in copolymerisation of the siloxy-substituted catalyst is almost tenfold the ordinary bis(indenyl) catalyst.

Table 1 Effect of the catalyst on copolymerisation of ethene with 10-undecen-1-ol

Catalyst	Comonomer in feed	Activity	MW	Comonomer in polymer
	mmol L ⁻¹	kg (mol Zr ⁴⁺ h) ⁻¹	g mol ⁻¹	wt%
Et(Ind) ₂ ZrCl ₂	-	90,000	130,000	-
Et(Ind) ₂ ZrCl ₂	25	3,000	75,000	5.9
Et(3- <i>tert</i> -BuSiMe ₂ Oind) ₂ ZrCl ₂	-	250,000	130,000	-
Et(3- <i>tert</i> -BuSiMe ₂ Oind) ₂ ZrCl ₂	25	25,000	80,000	4.7