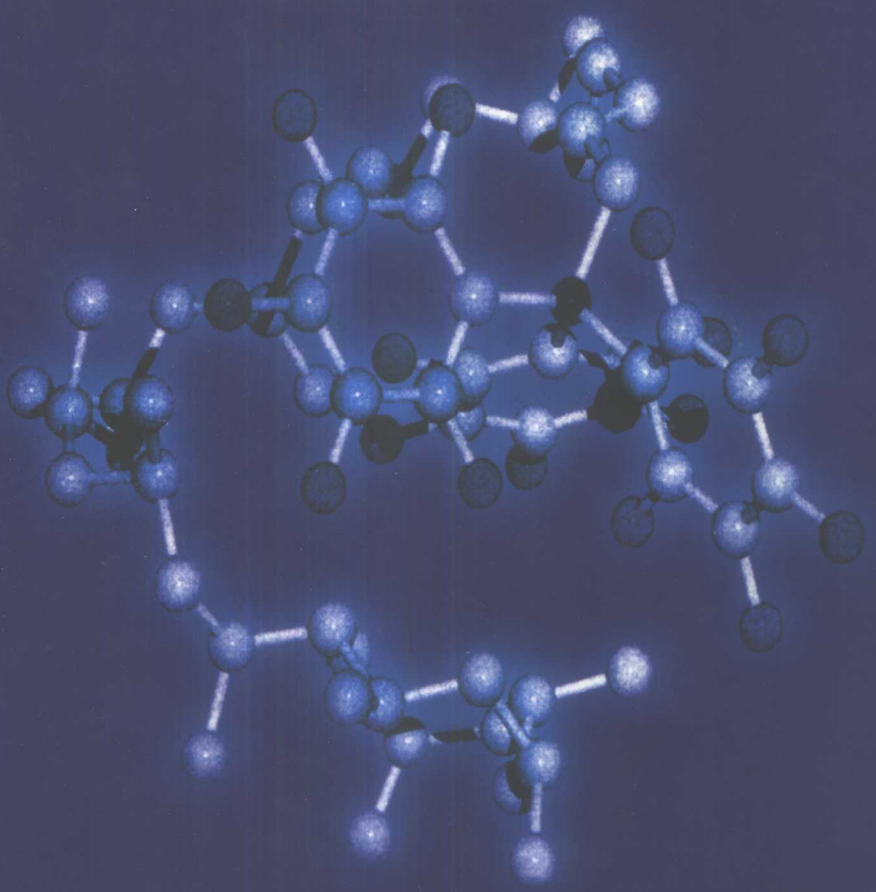
中德金属有机催化剂和烯烃聚合进展

Advances on Organometallic Catalysts and Olefin Polymerization in China and Germany

Edited by

Junquan Sun, Christoph Janiak



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Preface

Since Ziegler's discovery of the polymerization of ethylene with $TiCl_4$-$AlEt_2Cl$ catalyst and shortly after Natta's discovery of the stereo-selective polymerization of propylene in early 1950s, much attractive attentions focused on the improvement of Ziegler-Natta catalyst system and the polymerization process, which led to accelerate polyolefin industrialization all over the world. However unbroken research on Ziegler-Natta catalysts is still most active and exciting area, for the sake of obtaining high catalytic activity and high stereoselectivity. Among the successive progresses, the most important impact on olefin polymerization is extremely high active metallocene methylaluminoxane(MAO) catalysts developed by W.Kaminsky and H. Sinn in late 1970s, which opened new age to design the structure of catalyst and tailor precisely polymer structures.

Modern single-site catalysts based upon metallocene give exact control of molecular weight, stereo-chemistry, end-group compositions, branching, and comonomer incorporation. Syndiotactic, hemiisotactic,stereo-block poly(1-olefins) and cycloaliphatic polyolefins produced by metallocene are now becoming available in commercial quantities. Moreover, the single-site catalyst effectively facilitates elucidation of the basic polymerization mechanism that has remained disputed for long time since discovery of Ziegler-Natta catalysts.

From Ziegler's discovery of ethylene polymerization under mild conditions to Kaminsky's metallocene methyllalumoxane catalyst, it is very clearly that Germany polymer scientists play key role in innovation of polyolefin technology and stand still on the frontier in the area of polyolefin synthesis and processing. They have made a great contribution to the progress for worldwide polyolefin industry. China polymer scientists have paid much attention to Ziegler-Natta catalysts and have advanced in development of polyolefin technology and industrialization in large scale. In the early 1990s the research on metallocene catalysts has been started under the supports of National Natural Science Foundation of China(NSFC), China Petrochemical Corporation(SINOPEC) and some others. Much progress has been achieved in synthesis of metallocene (and/or) cocatalysts, and in pilot plant.

In recent year, the friendly contacts and the cooperation in research on organometallic catalysts and olefin polymerization between China and Germany become more frequently and actively. Under the efforts of chemists of both countries, China—Germany symposium on organometallic catalysts and olefin polymeriztion was held successfully in Zhejiang University in Hangzhou China from October 9—13, 2000.

The aim of the symposium is to bring together professional chemists and young graduates to exchange and share ideas, discoveries and happiness. The main goals of the symposium are to review and discuss recent advances in the development of metallocene-based catalysts, heterogeneous catalysts, polymerization processes, new materials and deep understanding of reaction mechanism.

During the symposium, we were pleased to receive nearly sixty registration forms and more than 40 abstracts from Germany, UK, Japan, and China.

The symposium would not have been possible without financial support by NSFC, DFG, SINOPEC, and BASF AG. As the organizers we'd like to express our special thanks to all the participants who took part in the discussion and all exchange activities and all the authors who were willing to prepare manuscripts.

We appreciate professor Kaminsky for his personal participating in the symposium and for his valuable presentation and discussion in metallocene catalyst system discovered by him in 1970s.

We are grateful to Prof. Dr. C. Janiak of the Albert-Ludwigs University in Freiburg for close collaboration in symposium organization and for his report with high praise in Nachrichten aus der Chemie in Germany.

It is believed that the publication of this book will strengthen the friendship, and accelerate cooperation between China and Germany. Furthermore it will stimulate more research interesting in China.

Dingyi Hong

Aug. 2001

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1 Engineering Plastics Produced by Metallocene Catalysts

Walter Kaminsky

Institute for Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany
e-mail: kaminsky@chemie.uni-hamburg.de

Abstract

Polymers with special properties can be obtained by a new generation of single site catalysts. Metallocenes and other transition metal compounds are used for the production of precisely designed polyolefins and engineering plastics. The discovery of metallocene methylaluminoxane (MAO) catalysts has opened a frontier in the area of polymer synthesis and pro-cessing. A great number of symmetric and chiral zirconocenes have been synthesized to give isotactic, syndiotactic, isoblock, or stereoblock polymers with increased impact strength and toughness, better melt characteristics or elasticity, and improved clarity in films. Cycloolefin copolymers (COC) and syndiotactic polystyrene can be produced by metallocene catalysts. These are new types of polymers with special properties and a high potential as engineering plastics. Norbornene-ethene copolymers are most interesting for technical uses because of the easily available monomers. Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range and reaches 180℃.

1.1 Introduction

Polyolefins are very important as the most widely used commodity polymers during the last decades[1]. They are known for their low energy demand during polymerization and melt processing. Modern gas phase and liquid pool technologies do not require solvents and polymer purification. New catalysts produce polymers with properties occupied in the past by more sophisticated, expansive and sometime hazardous materials.

Metallocenes in combination with methylaluminoxane or perfluorinated borates as cocatalyst form extremely active catalysts for the polymerization of olefins, cycloolefins, styrene, and butadiene are now used in industrial processes[2–5]. Supporting of the zirconocenes on silica decreases the necessary surplus of MAO and can change the tacticity.

Polyolefins, with different microstructures and characteristics, can be custom-made just by varying the ligands on the metallocene[6–8]. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with narrow molecular weight distributions (M_w/M_n = 2), of syndiotactic polymers and of chemically uniform copolymers has not yet been achieved by conventional Ziegler-Natta heterogeneous catalysts.

Using metallocene catalyst, it was possible for the first time to produce polyethylenes,

polypropylenes and copolymers with narrow molecular weight distributions[4], syndiotactic polypropylene (in technical scale amounts)[10], syndiotactic polystyrene[11], cyclopolymerisates of 1,5-hexadiene[12], cycloolefin copolymers (COC) with high catalytic activity[13], optically active oligomers [14] and composite materials of biomass, powdered metals with polyolefins[15]. Organic or inorganic particles (starch, cellulose, quartz sand or powdered metal) can be coated with a hydrocarbon soluble metallocene catalyst and in turn, after polymerization, with a polyolefin film of variable thickness[16].

The polymerizations can be controlled precisely by metallocene catalysts. To increase the activity and to make the metallocenes more stable for higher temperatures, $[PhMe_3PenFlu]ZrCl_2$ was synthesized[17]. This zirconocene is more stereorigid and shows high activities for the polymerization of propene and the ethene norbornene copolymerization. A strong dependence of the activity on the propene concentration is observed. The molecular weight of the polypropylene produced is two to four times higher than that synthesized with other C_1-compounds. Isotactic blocks in a hemiisotactic microstructure are observed which are responsible for elastomeric properties.

Metallocene catalysts are particularly important for the polymerization of cycloolefins (cyclopentene, norbornene and their substituted compounds). In this process, only the double bond is opened and not the ring. Crystalline polycycloolefins are rendered, that have extremely high melting points of at least 380℃, sometimes being higher than the decomposition temperature[18].

1.2 Random Cycloolefin Copolymers

While homopolymerization of cyclopentene results in 1,3-enchainment of the monomer units, norbornene is inserted in 1,2-enchainment as usual for olefin polymerization. The problems of processing that arise from the high melting temperatures of the homopolymers can be solved by copolymerizing cycloolefins with ethene[19–21].

The insertion of norbornene units into the growing polymer chain is very easy. As seen by the copolymerization parameter r_1, which is between 2.0 to 3.4 and shows how much faster ethene is inserted than norbornene when the previous insertion was ethene, it is easy to incorporate this huge monomer (Table 1.1).

Table 1.1 Copolymerization parameters r_1 and r_2 of ethene/cycloolefin copolymerizations with different metallocene/MAO catalysts

Cycloolefin	Catalyst	Temp.(℃)	r_1	r_2	$r_1 \cdot r_2$
cyclopentene	$[En(IndH_4)_2]ZrCl_2$	0	1.9	<1	~1
cyclopentene	$[En(IndH_4)_2]ZrCl_2$	25	2.2	<1	~1
norbornene	$[Me_2Si(Ind)_2]ZrCl_2$	30	2.6	<2	~1
norbornene	$[Me_2C(Fluo)(Cp)]ZrCl_2$	30	3.4	0.06	0.2
norbornene	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	0	2.0	0.05	0.1
norbornene	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	30	3.0	0.05	0.15
norbornene	$[Me_2C(Fluo)(t\text{-}BuCp)]ZrCl_2$	30	3.1	0	0
DMON	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	50	7.0	0.02	0.14
DMON	$[Ph_2C(Ind)(Cp)]ZrCl_2$	50	6.4	0.10	0.64
DMON	$[Ph_2C(Fluo)(Cp)]HfCl_2$	50	7.1	0.04	0.28

In most cases the r_1 parameter increases with the temperature and polymers with a statistical structure are obtained.

The cyclopentene ethene copolymers show low molecular weights and low glass transition temperatures. DMON ethene copolymers have a glass transition temperature which is about 20℃ higher than that of analogous norbornene copolymers with the same norbornene content. The structure of the cyclic olefin has a great influence on the properties of the copolymers. Therefore other norbornene derivatives such as 5-butyl-2-norbornene, 5-cyclohexenyl-2-norbornene and 5-methyl-2-norbornene were synthesized and used for the copolymerization of ethene. Table 1.2 shows the copolymerization parameters r_1, when $[Me_2C(Cp)(Flu)]ZrCl_2$/MAO is used as catalyst.

Table 1.2 Copolymerization of cyclic olefins and ethene by $[Me_2C(Cp)(Flu)]ZrCl_2$/MAO catalyst; zirconocene concentration: $5\times10^{-6}-10^{-7}$ mol/L, MAO: 290 mg in 100 ml toluene

Comonomer	T(℃)	r_1	Activities (kg Poly • (mol M)$^{-1}$ • h^{-1})
5-butylnorbornene	0	3.9	220
	30	3.5	7 600
	60	3.3	15 000
5-cyclohexenylnorbornene	0	6.7	55
	30	7.7	1 500
	60	4.8	11 000
5-methylnorbornene	0	6.2	100
	30	5.6	2 100
	60	4.9	9 200

The copolymerizations were carried out at aluminium:metal ratios of about 10 000 which proved to be the optimum for ethylene norbornene copolymerization. The copolymerization activity of the catalyst increases with the polymerization temperature. With increasing comonomer content in the reaction mixture, the activity of the catalyst decreases. While using only small amount of comonomer, a slightly positive comonomer effect can be observed.

The copolymerization parameters can be obtained by the incorporation rates determined via ^{13}C-NMR spectroscopy. The parameter r_1 vary not uniformly with the polymerization temperature. It is lowest by 60℃ and has a maximum by 0℃ or 30℃. The absolute value of the parameter is strongly dependent on the utilized comonomer. Butylnorbornene can be incorporated faster in the growing polymer chain than methylnorbornene. The r_2 parameter is very small and difficult to be measured. This means that no substituted norbornene blocks are formed.

Melting points (T_m) and glass transition temperatures (T_g) were investigated by DSC, molecular weights(M_w) by GPC. Table 1.3 shows some properties of the synthesized copolymers.

Only copolymers with less than 10 mol% of the comonomer show melting points. The glass transition temperatures increase with the molecular weight of the comonomers and reach with 5-cyclohexenyl-2-norbornene a value of 134℃ by an incorporation of 32 mol%. As usual, the glass transition temperature increases with an increasing comonomer content. The butyl side chain seems

to work as an increasing incorporation of the comonomer. Whereas the copolymers of 5-methyl-2-norbornene are of high molecular weight reaching 510 000, the copolymers of 5-cyclohexenyl-2-norbornene are between 50 000 up to 170 000. The molecular weight distribution (M_w/M_n) is around two. The copolymers are transparent, flexible, and useful as films.

Table 1.3 Properties of copolymers of ethene and substituted cyclic olefins using $[Me_2C(Cp)(Flu)]ZrCl_2$/MAO as catalyst by different temperatures

Comonomer	T(℃)	X^a	T_m(℃)	T_g(℃)	M_w
5-butylnorbornene	0	0	138	—	240 000
	0	0.19		6	140 000
	30	0.22		15	200 000
	60	0.36		53	170 000
5-cyclohexenylnorbornene	0	0.11		40	50 000
	30	0.26		117	170 000
	60	0.32		134	95 000
5-methylnorbornene	0	0.14		32	240 000
	30	0.09	57	6	610 000
	60	0.32		96	180 000

[a] X: comonomer content in molar ratio.

Such materials characteristically have an excellent transparency and a very high continuous service temperature. From cycloolefin insertion rates of 10 mol % upwards, these cycloolefin copolymers (COC) are no longer crystalline but amorphous. They are useful as transparent and flexible films. Since the end of the year 2000, the first industrial plant in Bottrop, Germany produces about 20 000 tons COC a year.

1.3 Alternating Cyclo Olefin Copolymers

In general, metallocenes are more likely to form statistical to alternating copolymers. Alternating copolymers are of special interest because they could form semi-crystalline polymers[22]. Fig. 1.1 shows the types of structures used for the copolymerization of cyclic olefins and ethene[23]. C_1-symmetric metallocenes should produce stereoregular alternating copolymers while meso-compounds should produce atactic alternating copolymers.

The steric demand of the two coordination sites A and B of a C_1-symmetric catalyst was exploited to control the distribution of monomers along the polymer chain and to generate a specific copolymerization mechanism. In this way the formation of alternating copolymers was found. Table 1.4 shows the results of some catalysts in activities of the copolymerization, incorporations of the cyclic olefin, and molecular weights of the copolymers.

In comparison to $[Me_2C(3\text{-}t\text{BuCp})(Flu)]ZrCl_2$ and $[Me_3PhPen(Flu)]ZrCl_2$ the C_1-symmetric catalyst $[Me_2C(3\text{-MeCp})(Flu)]ZrCl_2$ inserted norbornene slightly better. Only isolated and alternating norbornene sequences but no norbornene blocks were performed. Polymers containing more than 40 mol% of norbornene in the copolymer produced by $[Me_2C(3\text{-MeCp})(Flu)]ZrCl_2$

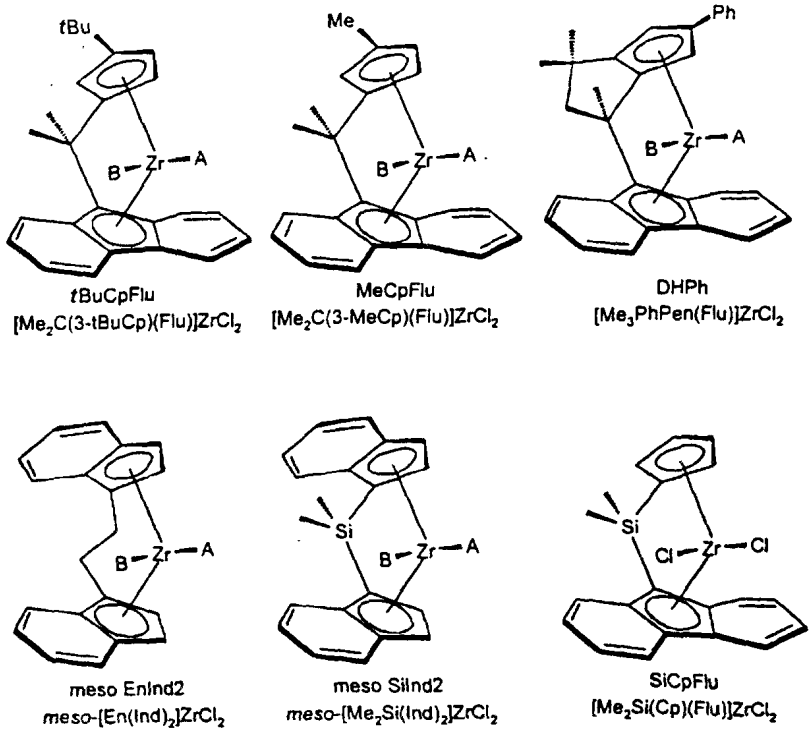

Fig. 1.1 Molecular structure of the used metallocenes and their terms

Table 1.4 Copolymerization of ethene and norbornene with different zirconocenes/MAO catalysts by 30℃ in toluene[a]

Catalyst (see Fig. 1.4)	Norbornene in feed X_N	Norbornene in polymer X_N	Activity (kg Pol • (mol Zr)$^{-1}$ • h^{-1})	Molecular Weight M_w
*t*BuCpFlu	0.23	0.055	1 850	230 000
	0.43	0.080	1 130	159 400
	0.69	0.220	360	89 800
	0.87	0.349	420	94 800
	0.97	0.445	30	
MeCpFlu	0.19	0.073	3 440	145 000
	0.37	0.150	3 270	87 000
	0.77	0.324	4 420	171 000
	0.89	0.407	5 720	252 000
	0.94	0.438	1 600	431 000
meso $SiInd_2$	0.31	0.096	650	12 600
	0.49	0.170	260	200 000
	0.70	0.299	27	222 000
meso $EnInd_2$	0.40	0.041	1 970	221 000
	0.68	0.098	1 080	211 000
	0.90	0.253	180	245 000
DH Ph	0.37	0.094		537 000
SiCpFlu	0.21	0.054	38 900	840 000
	0.57	0.184	30 200	808 000
	0.90	0.407	14 300	1 120 000
	0.99	0.644	430	190 000

[a] [Zr] = 5 μmol/L, MAO = 2.5 g/L, [E] = 0.237 mol/L.