Mechanistic Aspects of the Olefin Polymerization with Metallocene Catalysts

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Abstract: With C_1-, C_2- or C_s-symmetric metallocenes, different intermediates and types of copolymers can be obtained from randomly distributed to alternating structures. Substitution of the Cp-ring in [Me_2C-(tert-Bu Cp)(Flu)]$ZrCl_2$ yields ethene/norbornene copolymers with an alternating structure, because the rigid norbornene can only be inserted from the open side of the metallocene. By variation of the polymerization parameters, copolymers with glass transition temperatures above 180 °C and molecular weights > 100 000 are synthesized. By supporting different metallocenes on a silica/methylaluminoxane (MAO) carrier the deactivation reaction under electron and hydrogen transfer can be suppressed. This is proved for different Al/Zr ratios when trimethylaluminum (TMA) is used as cocatalyst by the lack of methane evolution by metallocenes and by near independence of the polymerization activity on the prereaction time, after reaching maximum activity. Aluminumalkyls and MAO leach Cp_2ZrCl_2 from the carrier, the leached metallocene is only active in polymerization by adding MAO.

INTRODUCTION

Homogeneous catalysts formed by group-4 metallocenes and methylalumoxane (MAO) are of great interest for the olefin poly-

merization. They are able to homo- or copolymerize different
types of olefins, cyclo olefins, and styrene. New classes of
polymeric materials are obtained. The discovery of metallocene
methylalumoxane catalysts has opened a frontier in the area of
organometallic chemistry, polymer synthesis, and processing
(Ref. 1). Based on transition metals such as titanium and zir-
conium atoms sandwiched between ring structures, they have
well defined single catalytic sites and well understood mole-
cular structures.

Stereoselective catalytic sites can polymerize almost any ole-
fin in an exact manner. A great number of symmetric and chiral
zirconocenes have been synthesized to give isotactic, syndio-
tactic, or stereoblock polypropylenes with increased impact
strength and toughness, better melt characteristics or elas-
ticity. Molecular modeling shows that one explanation for the
different regio- and stereospecifity of metallocene catalysts
is attributed to the flexibility of the ligand and electron
transfer processes.

While it is very difficult to polymerize strained cyclic al-
kenes like cyclobutene, cyclopentene, norbornene, dimethanooc-
tahydronaphthalene (DMON) with heterogeneous Ziegler-Natta
catalysts without ring opening, the homogeneous catalysts
formed by group 4-metallocenes and methylalumoxane (MAO) are
able to homo- or copolymerize cyclic olefins only by double
bond opening (Ref. 2, 3). New classes of polymer materials are
obtained. Polycycloolefins are crystalline and show extremely
high melting points over 380 °C.

The polycycloolefins are not processable due to their high
melting points and their insolubility in common organic sol-
vents. By copolymerization of these cyclic olefins with ethene
or α-olefins, cycloolefin copolymers (COC) can be produced,
representing a new class of thermoplastic amorphous materials
(Ref. 4 - 7).

The comonomer distribution may be varied from statistical to
alternating. Statistical copolymers are amorphous if more than
10-15 mol % of cycloolefins are incorporated in the polymer

chain. The glass transition temperature can be varied over a wide range by selection of the cycloolefin and the amount of cycloolefin incorporated into the polymer chain.

While homopolymerization of cyclopentene results in 1,3-en-chainment of the monomer units, isolated cyclopentene units are incorporated into the ethene copolymer chain by 1,2-insertion. Ethene is able to compensate the steric hindrance at the α-carbon of the growing chain after and before the insertion of cyclopentene (Ref. 8).

Supporting of the zirconocenes on silica or alumina give catalysts which produces polypropylenes with different microstructures and show different optimal polymerization parameters (Ref. 9).

RESULTS AND DISCUSSION

Norbornene-ethene copolymers are most interesting for technical uses because of the easily available monomers. Table 1 shows the activity and the incorporation of norbornene in the polymer using different metallocene/MAO catalysts.

Tab. 1. Copolymerization of norbornene (Nor) and ethene by different metallocene/MAO catalysts by 30 °C; MAO/Zr = 200, [Zr] = $5 \cdot 10^{-6}$ mol/l; ethene pressure = 2 bar; Nor = 0,05 mol/l

Catalyst	Activity kg/mol·h	Incorporation of Nor (%)
1 Cp_2ZrCl_2	1 200	21,4
2 $[En(Ind)_2]ZrCl_2$	9 120	26,1
3 $[Me_2Si(Ind)_2]ZrCl_2$	2 320	28,4
4 $[En(IndH_4)_2]ZrCl_2$	480	28,1
5 $[Me_2C(Flu)(Cp)]ZrCl_2$	7 200	28,9
6 $[Ph_2C(Flu)(Cp)]ZrCl_2$	6 000	27,3
7, $[Ph_2C(Ind)(Cp)]ZrCl_2$	2 960	33,3

Under the selected conditions, Catalyst 2 shows the highest
activity and Catalyst 4 the lowest. Incorporation is highest
with Catalyst 7, a bridged compound with a cyclopentadienyl
and an indenyl ligand, and lowest with the simple Cp_2ZrCl_2.
All other incorporation values are in the same range.

The copolymerization parameter r_1 and r_2 were calculated ac-
cording to the Fineman-Ross method from the rates of incorpo-
ration, determined by ^{13}C-NMR, dependent on the reaction tem-
perature (Ref. 10).

Table 2 shows the temperature dependency of the copolymeri-
zation parameters r_1 and r_2 and of the influence of the cata-
lyst system. Metallocene catalysts show low r_1 values, which

Tab. 2. Copolymerization parameters r_1 and r_2 of ethene/cyclo-
olefin copolymerizations with different metallocene/MAO cata-
lysts. Cycloolefin = Cyc; norbornene = Nor; catalysts see Tab.
1; no. 8 = $[Me_2C(Flu)(t\text{-}BuCp)ZrCl_2$

Cyclo-olefin	Catalyst No.	Temp. (°C)	r_1	r_2	$r_1 \times r_2$
Cyc	4	25	2,2	<1	~ 1
Cyc	3	30	2,6	<2	~ 1
Nor	5	30	3,4	0,06	0,2
Nor	6	30	3,0	0,05	0,15
Nor	8	30	3,1	0	0
DMON	6	50	7,0	0,02	0,14
DMON	7	50	6,4	0,10	0,64

increases with the temperature and allows the easy incorpo-
ration of bulky cycloolefins into the growing polymer chain.
Surprisingly, the copolymerization parameter $r_1 = 1,8 - 3,1$
for cyclopentene and norbornene is considerably lower than
that for the copolymerization of ethene with propene ($r_1 =$
6,6, 37 °C).

The product $r_1 \cdot r_2$ shows if statistical insertion $r_1 \cdot r_2 = 1$
or an alternating one ($r_1 \cdot r_2 = 0$) has occurred. The differ-

ent catalysts produce copolymers with structures that are between statistical and alternating.

Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range that is independent of most of the used catalysts. A copolymer with 50 mol % of the norbornene yields a material with a glass transition point of 145 °C. A Tg of 205 °C can be reached by higher incorporation rates.

As shown in Tab. 2, copolymerization of ethene and norbornene with [Me$_2$C(Flu)(tBuCp)]ZrCl$_2$ leads to a strong alternating structure (Ref. 11, 12). It is impossible to receive copolymers with more than 50 mol % of norbornene.

Using ^{13}C-NMR spectroscopy, it is quite easy to detect the norbornene centered pentads (NENEE, NENEN, EENEE) quantitative because they show different chemical shifts, especially for the bridged carbons (Fig. 1).
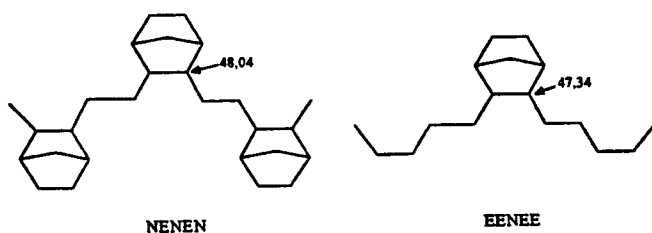

NENEN   EENEE

Fig. 1. Structures of norbornene/ethene copolymers; ^{13}C-NMR spectroscopic shifts

Comparison of the calculated amount to experimental data indicates that using [Me$_2$C(3-tBuCp)(Flu)ZrCl$_2$/MAO at 30 °C in toluene as catalyst results in polymerization by chain migratory insertion. In an alternating fashion insertion of ethene and norbornene takes place at both sides whereas the sterically blocked side is only available for insertion of ethene and the more open side features ethene and norbornene insertion with a "copolymerization parameter" of k_{EE}/K_{EN} = 3.05

(Fig. 2). Preliminary investigations on [Me$_2$C(3-iPrCp)(Flu)]-ZrCl$_2$ in turn indicated alternating copolymers with an even better incorporation of norbornene. The geometry of this "open" site in these metallocenes is similar to that of [Me$_2$C(Cp)(Flu)]ZrCl$_2$ which gives at similar conditions a copolymerization parameter of $k_{EE}/k_{EN} = 4,15$ ($k_{NN}/k_{NE} = 0,033$).
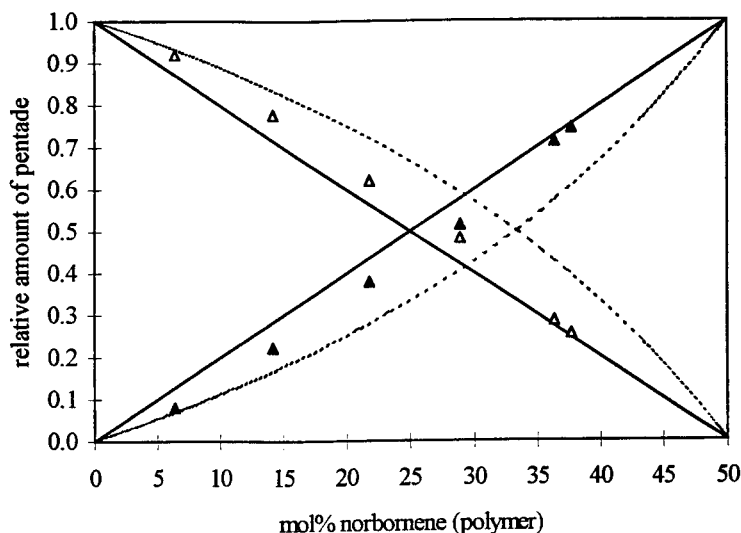

Fig. 2. Fraction of isolated [0,5 NENEE + EENEE ($\sqsupset$)] and alternating [o,5 NENEE + NENEN (■)] norbornene units as a function of norbornene incorporation for ethene/norbornene copolymers produced by [Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$ in toluene at 30 °C, [ethene] = 0,237 mol/l; [Zr] = $5 \cdot 10^{-6}$ mol/l; Al/Zr = 7800 compared to pentade fractions according to the chain migratory (solid lines) and chain stationary model (dashed lines)

An alternating structure with high amounts of ENEN-pentades is given, if the starting monomer mixture is a low ethene and a high norbornene concentration. Because of the low copolymerization parameter of 3 norbornene inserts always in the more open side feature of the catalyst. In the blocked side only ethene can insert even when its concentration is low. The alternating copolymer of ethene and norbornene is partially crystalline and shows melting points up to 320 °C (Fig. 3).
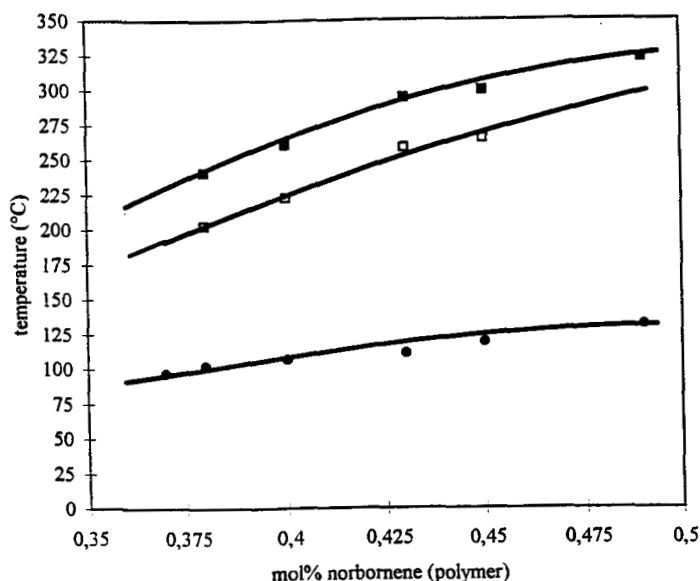
Fig. 3. Melting points (■) and crystallization temperature (□) and glass transition temperature (•) of ethene/norbornene copolymers containing alternating sequences

Supporting of the zirconocenes on silica are shown in Fig. 4.

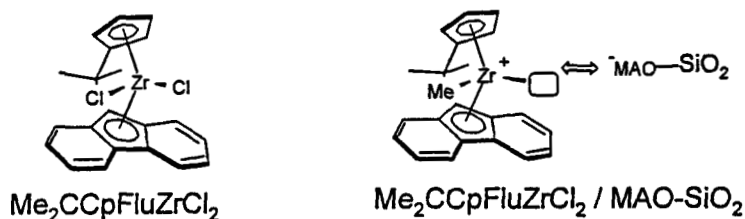Me$_2$CCpFluZrCl$_2$ Me$_2$CCpFluZrCl$_2$ / MAO-SiO$_2$

Fig. 4. Zirconocene supported on silica

Supported and unsupported zirconocene catalysts decreases the necessary surplus of MAO (Tab. 3). There is a good activity given by a ratio of Al (MAO) : Zr = 300. If triisobutyl aluminum (TIBA) is used as scavanger, the optimum (TIBA : Zr) is about 500 (Ref. 13).

Tab. 3. Polymerization of propene with silica supported zirco-
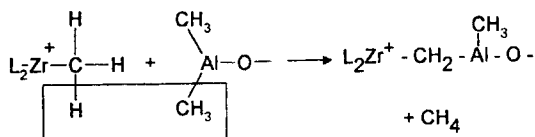nocene catalysts in dependence of the amount of cocatalyst

Al(MAO):Zr [ ]	$Me_2CCpFluZrCl_2$/MAO-SiO$_2$ Activity [kg sPP/(mol Zr*h*c$_{mon}$)]
30	47
100	352
300	708
1000	1034

[TIBA]:[Zr] [ ]	$Me_2CCpFluZrCl_2$/MAO-SiO$_2$ Activity [kg sPP/(mol Zr*h*c$_{mon}$)]
1000	470
500	708
100	331
10	94

The filtrate of the supported catalyst is inactive for the
propene polymerization if TIBA is used as scavanger. But if
the catalyst is washed with MAO, a lot of activity is given in
the filtrate. The supported catalyst shows an increase of the
isotacticity with a growing propene concentration while the
homogeneous catalyst is more indepentent. Similar results are
found for the molecular weight of the resulting polypropylene,
showing the influence of electron transfer processes on the
growing polymer chain.

The deactivation reactions under hydrogen transfer can be sup-
pressed, too.

$$L_2Zr^+-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \; + \; \underset{CH_3}{\overset{CH_3}{\diagdown}}Al-O- \; \longrightarrow \; L_2Zr^+-CH_2-\underset{\overset{|}{CH_3}}{Al}-O- \; + \; CH_4$$

The homogeneous catalyst shows a much higher rate of the pro-
duction of methane than the supported one. If different Al/Zr
ratios for trimethylaluminum as cocatalysts are used, the pro-

duced methane decreased with the alkyl concentration. The polymerization activity is near independent on the prereaction time after reaching a maximum. The inactive Zr-Ch$_2$-Hl structure can be reactivated by an excess of MAO.

REFERENCES

1. W. Kaminsky, *Macromol. Chem. Phys.* **197**, 3907 (1996)
2. W. Kaminsky, R. Spiehl, *Makromol. Chem.* **190**, 515 (1989)
3. W. Kaminsky, A. Noll, *Polym. Bull.* **31**, 175 (1993)
4. W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* **47**, 83 (1991)
5. H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chem.* **223**, 121 (1994)
6. N. Herfert, G. Fink, *Makromol. Chem. Macromol. Symp.* **66**, 157 (1993)
7. G.M. Benedikt, B.L. Goodall, N.S. Marchant, L.F. Rhodes, *New J. Chem.* **18**, 105 (1994)
8. S. Collins, W.M. Kelly, *Macromolecules* **25**, 233 (1992)
9. K. Soga, M. Kaminaka, *Macromol. Chem. Rapid Commun.* **13**, 221 (1992)
10. M. Arndt, W. Kaminsky, *Macromol. Symp.* **95**, 167 (1995)
11. M.-J. Brekner, F. Osan, J. Rohrmann, M. Antberg, EP 503422 Al (1992) to Hoechst AG
12. M. Arndt, I. Beulich, Poster, Catalysis Symposium Friedrichroda, 20-23 March, 1996
13. H. Winkelbach, Dissertation, University of Hamburg 1997