THE ROLE OF DORMANT SITES IN PROPENE POLYMERIZATION
USING METHYLALUMOXANE ACTIVATED METALLOCENE
CATALYSTS

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Abstract: Propene polymerization of methylalumoxane (MAO) activated *rac*-Me₂Si(Benz[e]Indenyl)₂ZrCl₂ (**BI**) and *rac*-Me₂Si(2-Me-Benz[e]Indenyl)₂ZrCl₂ (**MBI**) was studied to investigate the influence of the ligand substitution pattern and the role of dormant sites. Poly(propene) end group composition as well as regio- and stereoirregularities were examined by means of ¹H- and ¹³C-NMR spectroscopy. Dormant sites, resulting from 2,1-propene insertion, were reactivated either by β-hydrogen transfer to propene, yielding 2-butenyl end groups, or by 1,2-insertion of propene, yielding regioirregularities. Propene polymerization in the presence of hydrogen gave n-butyl end groups and less regioirregularities as expected for hydrogenolysis of such dormant sites. Methyl substitution in 2-position of the benz[e]indenyl ligand suppressed β-hydrogen transfer to propene, and increased molecular weight with increasing propene concentration. Also, activation energy increased from 30 kJ/mol (**BI**/MAO) to 59 kJ/mol (**MBI**/MAO). For both catalysts activity depended on propene concentration. The order of reaction relative to propene was 1.7.

INTRODUCTION

Variation of the ligand structure of metallocenes is the key to improved catalysts and controlled polymer properties such as tacticity, melting temperature and molecular weight (Ref. 1-4). For instance, benzannellation seems to be critical for high propene polymerization activities, whereas 2-methyl substitution is a prerequisite for high molecular weight and stereoregularity of the poly(propene) produced (Ref. 5, 6). In our research we compare polymerization behavior of MAO-activated *rac*-Me₂Si(Benz[e]Indenyl)₂ZrCl₂ (**BI**) and *rac*-Me₂Si(2-Me-Benz[e]Indenyl)₂ZrCl₂ (**MBI**) (Scheme 1), especially with respect to the influence of propene concentration and temperature.

Scheme 1:

rac-Me₂Si(Benz[e]Indenyl)₂ZrCl₂ (**BI**) and *rac*-Me₂Si(2-Me-Benz[e]Indenyl)₂ZrCl₂ (**MBI**)

RESULTS AND DISCUSSION

Influence of Temperature

Propene polymerization was performed in toluene. A MAO/toluene solution was transferred into the reactor and saturated with propene. The catalyst was prepared by dissolving the metallocene in diluted MAO/toluene. Injection of the metallocene into the thermostated reactor started polymerization. Pressure was maintained by continuously feeding propene. The experimental procedures have been previously described in more detail (Ref. 6, 7).

The effect of temperature on the activity of the two metallocene/MAO catalyst systems at

constant propene concentration is shown in Figure 1 and Table 1. Constant propene concentration is achieved by varying temperature and propene pressure simultaneously according to the calculated solubility of propene in toluene (Ref. 8). At 20°C both catalysts show no deactivation with time. **BI**/MAO polymerizes propene approximately 3 times faster than **MBI**/MAO. At 40°C **BI**/MAO is twice as active as **MBI**/MAO. For **BI**/MAO catalyst activity decreases within 3 hours to the value of **MBI**/MAO that does not show this deactivation. At 60°C both catalysts behave similarly showing an increase in activity within the first 10 to 20 min followed by a pronounced deactivation to 50% of the maximum activity over 3 hours. At 60°C **MBI**/MAO exhibits the higher activity.

Depicted in Figure 2 is the Arrhenius plot for the maximum activities. The activation energy is $E_{act} = 59 \text{ kJ/mol}$ for **MBI**/MAO and $E_{act} = 30 \text{ kJ/mol}$ for **BI**/MAO. It is surprising that **MBI**/MAO shows almost the same catalyst activity as **BI**/MAO although its activation energy is almost twice as high. This large activation energy for **MBI**/MAO is compensated by a

Figure 1. Catalyst activity of **MBI**/MAO (•) and **BI**/MAO (▲) at different temperatures and constant propene concentration $[\text{Pr}] = 0.91 \text{ mol/L}$; $[\text{Zr}] = 1 \times 10^{-6} \text{ mol/L}$, $[\text{Al}]/[\text{Zr}] = 20000$, at 20, 40 and 60°C.

Table 1 Influence of Temperature on Propene Polymerization using **MBI**/MAO and **BI**/MAO at constant Propene Concentration ^{a)}

run #	cat.	T _{pol} (°C)	p ^{b)} (bar)	activity ^{c)} (10 ⁶ gPP/(molZr•mol/LPr•h))	M _n (kg/mol)	M _w /M _n	M _{vis} (kg/mol)	T _m (°C)	mmmm (%)	2,1 ^{d)} (%)
106	MBI	60	2.9	109.8	74	1.7	35	149.7	94.4	0.4
82	MBI	40	2.0	29.5	138	1.7	208	155.4	96.6	0.3
108	MBI	20	1.3	6.1	318	2.1	546	161.1	96.9	0.2
110	BI	60	2.9	89.4	18	1.8	27	138.6	90.3	0.7
89	BI	40	2.0	48.0	30	1.6	40	145.6	92.9	0.8
111	BI	20	1.3	20.0	40	1.6	54	146.4	94.5	0.7

a) in toluene with [Zr]=1μmol/L, [Al] = 20 mmol/L;

MBI = Me₂Si(2-Me-Benz[e]Ind)₂ZrCl₂, **BI** = Me₂Si(Benz[e]Ind)₂ZrCl₂

b) p = total pressure = propene partial pressure + toluene partial pressure;

propene concentration = 0.91 mol/L, calculated by BASF AG according to Ref. 8

c) activity = 10⁶gPP/(mol Zr x mol/L Pr x h); maximum activity see Fig. 1

d) by ¹³C-NMR; intensity of signal from meso-2,1-units in % of total methyl intensity

Figure 2. Arrhenius plot for the activity of **MBI**/MAO and **BI**/MAO at constant propene concentration; log(activity) vs 1/temp; [Zr]=1x10⁻⁶mol/L, [Al]/[Zr]=20000.

Figure 3. Arrhenius plot for molecular weight of poly(propene) produced by **MBI**/MAO and **BI**/MAO at constant propene concentration; log(M_n) vs 1/temp; [Zr]=1x10⁻⁶mol/L, [Al]/[Zr]=20000.

much larger frequency factor with respect to that of **BI**/MAO. The frequency factor for **MBI**/MAO is $A=1.8 \cdot 10^{17}$ gPP/(mol Zr x mol/L Pr x h) and for **BI**/MAO $A=5.5 \cdot 10^{12}$ gPP/(mol Zr x mol/L Pr x h) using the following equation : $\text{activity}(T) = A \cdot e^{(-E_{\text{act}}/RT)}$. The 2-methyl group in **MBI** seems to improve the activation entropy of the rate determining step.

The Arrhenius plot for the polymer molecular weight is displayed in Figure 3. In the case of **MBI**/MAO, producing the higher molecular weight poly(propene), one finds a higher difference $E_{\text{act}}(\text{Polym.}) - E_{\text{act}}(\text{Termin.}) = -30$ kJ/mol than for **BI**/MAO with $E_{\text{act}}(\text{Polym.}) - E_{\text{act}}(\text{Termin.}) = -16$ kJ/mol. This corresponds with the higher molecular weight of the polymer produced by **MBI**/MAO.

Influence of Propene Concentration

Plotting the polymerization rate, measured as 10^6 gPP/(mol Zr x h), versus propene concentration on a logarithmic scale (Figure 4) shows the order of reaction with respect to propene concentration to be 1.7 for both catalysts at 40°C. For the simple model of monomer-metal π -complex formation followed by the insertion as the rate determining step one should expect a reaction order of 1.0 as represented by the dotted line. A higher order than 1.0 for the rate of polymerization relative to propene has previously been reported by Fink et. al. (Ref. 9) for metallocene/MAO catalysts (1.2 to 1.4 for $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ and $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$). Siedle et. al. also found higher orders of reaction for the system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/1\text{-hexene}$ (Ref. 10).

To explain the observed order of reaction of 1.7 relative to propene concentration for both metallocene catalyst systems **MBI**/MAO and **BI**/MAO one can assume two propene molecules to participate in the rate determining step as proposed for some heterogeneous (Ref. 11) and homogeneous catalysts (Ref. 12). This seems difficult to imagine for these metallocenes with sterically demanding ligands. Alternatively, propene might influence an equilibrium involving dormant and active catalyst sites, thus increasing the concentration of active sites.

Propene concentration has a remarkable effect on poly(propene) molecular weight only for

Figure 4. Rate of polymerization for **MBI/MAO** and **BI/MAO** at different propene concentrations; logarithmic plot; $[\text{Zr}] = 1 \times 10^{-6} \text{ mol/L}$, $[\text{Al}]/[\text{Zr}] = 20000$, 40°C , pressure 0.5-6 bar, $r_p = k'[\text{propene}]^m$; $\log(r_p) = m \cdot \log([\text{propene}]) + \log(k')$; the order of reaction is the slope $m = 1.7$ for **MBI/MAO** and **BI/MAO**; the dotted line with a slope of $m=1$ is plotted for comparison.

Figure 5. Dependence of poly(propene) molecular weight on propene concentration for **MBI/MAO** and **BI/MAO**, $[\text{Zr}] = 1 \times 10^{-6} \text{ mol/L}$, $[\text{Al}]/[\text{Zr}] = 20000$, 40°C , total pressure 0.5-6 bar.

the catalyst **MBI**/MAO as displayed in Figure 5. Molecular weights of polymer produced with **BI**/MAO are almost independent of propene concentration. These findings indicate that propene is involved in the mechanism of chain transfer for **BI**/MAO. Since propene participates in the propagation as well as in the chain termination step, the degree of polymerization, reflecting the rate ratio of these two steps, becomes independent of propene concentration.

Studying the ^1H -NMR spectra of the poly(propenes) produced by **BI**/MAO one can identify three types of olefinic signals (Figure 6). The signals at 4.74 and 4.66ppm due to the vinylidene end group are well known for poly(propene) produced with metallocenes such as $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ or $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$ (Ref. 13). The more intense signal at 5.45ppm is attributed to a 2-butenyl end group ($\text{MeHC}=\text{CH}-\text{CH}_2-$), which results from 2,1-propene insertion followed by β -H-elimination. The corresponding ^{13}C -NMR signals of the olefinic carbons at 129.4 and 124.3ppm could be detected (Ref. 14). Either at lower propene concentration or higher temperature, a third type of end group was detected by means of ^1H -NMR spectroscopy. The signal at 5.18ppm was assigned to a $\text{Me}_2\text{C}=\text{CH}-$ end group arising from an isomerization of the vinylidene end group forming the thermodynamically favored vinylenic group with internal double bond (Ref. 15).

Figure 6. 300MHz ^1H -NMR-spectrum (region of olefinic end groups) of poly(propene) prepared with $\text{Me}_2\text{Si}(\text{Benz}[\text{e}]\text{Ind})_2\text{ZrCl}_2/\text{MAO}$, $[\text{Zr}]=1 \times 10^{-6} \text{ mol/L}$, $[\text{Al}]/[\text{Zr}]=20000$, toluene, 2 bar, 60°C , signals marked with "solv." are due to impurities of the solvent $\text{C}_2\text{D}_2\text{Cl}_4$

The intensity of the ^1H -NMR signal of the 2-butenyl end group relative to the aliphatic signal increases with propene concentration in the case of poly(propene) produced with **BI**/MAO. This indicates that the 2-butenyl end group is in mechanistic connection with the observed independence of molecular weight on propene concentration using **BI**/MAO. Most likely, the low molecular weight poly(propene) is formed with **BI**/MAO by termination via a 2,1-insertion followed by β -hydride transfer to a coordinated propene.

Figure 7. 75MHz ^{13}C -NMR-spectra of poly(propene) prepared in the absence (a) and presence (b,c) of hydrogen; region of methyl carbons; for $\text{Me}_2\text{Si}(\text{Benz}[\text{e}]\text{Ind})_2\text{ZrCl}_2/\text{MAO}$; $[\text{Zr}] = 1 \times 10^{-6} \text{ mol/L}$, $[\text{Al}]/[\text{Zr}] = 20000$, toluene, 40°C , 2 bar propene; a) without H_2 , b) with 0.35 bar H_2 , c) with 1.0 bar H_2 . P1, P2, P5 : n-propyl end group signals; B1, B2, B6 : n-butyl end group signals; m-2,1 : signals due to meso-2,1-units

The large content of these poly(propene) end groups resulting from elimination following a 2,1-insertion makes it probable that a substantial portion of active sites are rendered dormant after 2,1-insertion has occurred. Addition of hydrogen to the polymerizations with **MBI**/MAO and **BI**/MAO reduces poly(propene) molecular weight and the amount of 2,1-units in the polymer. As the incorporation of 2,1-units in the polymer decreases, formation of n-butyl end groups increases as can be seen from the ^{13}C -NMR spectra in Figure 7. The n-butyl groups result from the hydrogenolysis of Zr-2,1-units.

The NMR signals of n-propyl and n-butyl polymer end groups have almost the same intensity, while isopropyl end groups could hardly be detected within the limits of the ^{13}C -NMR measurement (Ref. 16). This shows that most metallocenes have a 2,1-inserted propene as the last unit of the polymer chain, with the assumption that the rates of chain transfer to H_2 from a Zr-2,1-unit and a Zr-1,2-unit are of the same magnitude. This seems to be realistic for the small hydrogen molecule (Ref. 17, 18). The subsequent 1,2-insertion of propene into a Zr-2,1-unit seems to be slower than the 2,1-insertion leading to the formation of dormant catalyst sites upon 2,1-insertion. Formation of dormant sites by 2,1-insertion has been observed for heterogeneous catalysts (Ref. 19) as well as for zirconocene/MAO/propene systems (Ref. 14, 17) by end group analysis of poly(propenes) formed in the presence of hydrogen.

CONCLUSION

Propene concentration has been shown to be an important parameter for MAO activated homogeneous catalysts based on the metallocenes **BI** and **MBI**, influencing catalyst activity, polymer molecular weight and polymer end groups. The reaction order of the rate of polymerization in toluene at 40°C is found to be significantly larger than 1 with respect to propene for both metallocene catalysts.

For **BI**/MAO chain transfer to propene from a Zr-2,1-unit controls the molecular weight of the polymer, leading to $\text{MeHC}=\text{CHCH}_2$ - end groups. The methyl group in the 2-position of the benz[e]indenyl ligand for **MBI**/MAO seems to suppress this chain transfer pathway causing **MBI**/MAO to produce higher polymer molecular weights increasing with increasing propene concentration.

Addition of hydrogen to polymerizations with **BI**/MAO and **MBI**/MAO reduces the incorporation of 2,1-inserted propene units into the polymer and leads to n-butyl and n-propyl end groups (Scheme 2). This indicates that a substantial portion of the metallocene sites are rendered dormant when 2,1-insertion occurs.

Scheme 2 : reaction pathways following a 2,1-insertion

Since catalyst activity and polymer molecular weights depend on propene concentration and propene solubility in toluene depends on temperature it is important to study the effect of temperature on these catalyst system properties at constant propene concentration.

The 2-methyl substitution in **MBI**/MAO accounts for a higher polymerization activation energy and an increased frequency factor, resulting from a favorable activation entropy with respect to that of **BI**/MAO.

The difference between the activation energies of chain propagation and termination is larger for **MBI**/MAO when compared to **BI**/MAO. This is in accord with the higher molecular weight poly(propene) produced by **MBI**/MAO.

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REFERENCES AND NOTES

- (1) a) A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.-J. Vollmer, *Angew. Chem.*, **88**, 689 (1976), *Angew. Chem. Int. Ed. Engl.* **15**, 630 (1976)
 b) W. Kaminsky, K. Külper, H.-H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.* **97**, 507 (1985), *Angew. Chem. Int. Ed. Engl.* **24**, 507 (1985)
 c) K. Heiland, W. Kaminsky, *Makromol. Chem.* **193**, 601 (1992)
 d) W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, R. Rohrmann, *Makromol. Chem.* **193**, 1643 (1992)
 e) W. Kaminsky, A. Noll, *Polym. Bull.* **31**, 175 (1993)
- (2) a) P. Burger, K. Hortmann, H.-H. Brintzinger, *Makromol. Chem. Macromol. Symp.* **66**, 127 (1993)
 b) W. Röhl, H.-H. Brintzinger, B. Rieger, R. Zolk, *Angew. Chem.* **102**, 339 (1990), *Angew. Chem. Int. Ed. Engl.* **29**, 279 (1990)
 c) F. R. W. P. Wild, L. Zsolnai, G. Huttner, H.-H. Brintzinger, *J. Organomet. Chem.* **232**, 233 (1982)
- (3) a) J. A. Ewen, *J. Am. Chem. Soc.* **106**, 6355 (1984)
 b) J. A. Ewen, "Catalytic Polymerization of Olefins", T. Keii, K. Soga, (Eds.), Elsevier, Kodansha, Tokyo, 1986, p. 271
 c) J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Atwood, S. G. Bott, K. Robinson, *Makromol. Chem. Macromol. Symp.* **48/49**, 253 (1991)
 d) J. A. Ewen, M. J. Elder, *Makromol. Chem. Macromol. Symp.* **66**, 179 (1993)
- (4) a) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, *Organometallics* **9**, 3098 (1990)
 b) S. Collins, W. J. Gauthier, D. A. Holden, B. A. Kuntz, N. J. Taylor, D. G. Ward, *Organometallics* **10**, 2061 (1991)
 c) I. K. Lee, W. J. Gauthier, J. M. Ball, B. Iyengar, S. Collins, *Organometallics*, **11**, 2115 (1992)
- (5) a) W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W. A. Herrmann, *Angew. Chem.* **104**, 1373 (1992); *Angew. Chem., Int. Ed. Engl.* **31**, 1347 (1992)

- b) W. Spaleck, F. Kuber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E. F. Paulus, *Organometallics* **13**, 954 (1994)
- (6) U. Stehling, J. Diebold, R. Kirsten, W. Röhl, H.-H. Brintzinger, S. Jüngling, R. Mülhaupt, F. Langhauser, *Organometallics* **13**, 964 (1994)
- (7) a) D. Fischer, R. Mülhaupt, *J. Organomet. Chem.* **417**, C7 (1991)
b) D. Fischer, Ph.D. thesis, University of Freiburg, 1992
- (8) U. Plöcker, H. Knapp, J. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* **17**, 324 (1978)
- (9) N. Herfert, G. Fink, *Makromol. Chem.* **193**, 1359 (1992)
- (10) A. R. Siedle, W. M. Lamanna, J. M. Olofson, B. A. Nerad, R. A. Newmark, "Selectivity in Catalysis", M. E. Davis, S. L. Suib, (Eds.), ACS Symposium Series **517**, Washington, 1993, p. 156
- (11) M. Ystenes, *Makromol. Chem. Macromol. Symp.* **66**, 71 (1993)
- (12) G. Hidalgo-Llinas, A. Munoz-Escalona, poster #54, Milano, STEPOL 1994
- (13) a) A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, *Macromolecules* **21**, 617 (1988)
b) H. N. Cheng, J. A. Ewen, *Makromol. Chem.* **190**, 1931 (1989)
c) B. Rieger, X. Mu, D. T. Mallin, M. D. Rausch, J. C. W. Chien, *Macromolecules* **23**, 3559 (1990)
d) T. Shiono, H. Kurosawa, O. Ishida, K. Soga, *Macromolecules* **26**, 2085 (1993)
- (14) T. Tsutsui, N. Kashiwa, A. Mizuno, *Makromol. Chem. Rap. Com.* **11**, 565 (1990)
- (15) B. Rieger, A. Reinmuth, W. Röhl, H.-H. Brintzinger, *J. Mol. Catal.* **82**, 67 (1993)
- (16) Due to the low intensity of the polymer end group signals an isopropyl end group concentration of less than 10% relative to the observed n-butyl end group would not be detectable by ^{13}C -NMR spectroscopy.
- (17) V. Busico, R. Cipullo, P. Corradini, *Makromol. Chem. Rap. Com.* **14**, 97 (1993)
- (18) A. B. de Carvalho, P. E. Gloor, A. E. Hamielec, *Polymer* **30**, 280 (1989)
- (19) a) V. Busico, R. Cipullo, P. Corradini, *Makromol. Chem. Phys.* **194**, 1079 (1993)
b) J. C. Chadwick, A. Miedema, O. Sudmeijer, *Makromol. Chem. Phys.* **195**, 167 (1994)