Macromolecules **2000,** *33,* 1955−1959

Homopolymerizations of α-Olefins with Diastereomeric Metallocene/MAO Catalysts

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Received August 31, 1999; Revised Manuscript Received December 14, 1999

ABSTRACT: 1-Butene and 1-pentene were polymerized with three different metallocenes: dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride [$Me_2Si(2\text{-}Me\text{-}4,5\text{-}BzoInd)_2ZrCl_2$] **(1)**, dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride [$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$] **(2),** and dimethylsilylbis(indenyl)zirconium dichloride [$Me_2Si(Ind)_2ZrCl_2$] **(3)**. The polymerizations were conducted with the *rac*-isomers of the metallocenes and mixtures of the *rac*- and *meso*-systems for **1** and **2** and with the *meso*-form of catalyst **3** combined with MAO. It was shown that the activities in the polymerization of the α-olefins of the *meso*-isomers of **1** and **2** were much higher than those of the *rac*-metallocenes, while a vice versa behavior is observed for catalyst **3**. Additionally, reaction profiles of **1** and **2** were recorded which underline that the stability of their *meso*-compounds is much higher than that of the *rac*-systems for the polymerization of the investigated monomers.

Introduction

Since the discovery of the suitability of the C_2-symmetric *rac*-isomer of the bridged zirconium catalyst $En(H_4\text{-}Ind)_2ZrCl_2$ for the polymerization of olefins, a lot of work has been carried out in order to optimize the ligand environment around the central metal.[1−3] The goal was to produce a polymer in high yield with promising characteristics using the catalyst in combination with a cocatalyst such as MAO (methylaluminoxane).

Two catalysts that showed outstanding success concerning this aim are [$Me_2Si(2\text{-}Me\text{-}4,5\text{-}BzoInd)_2ZrCl_2$] **(1)** and [$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$] **(2)**.

If toluenic solutions of bridged zirconocenes are exposed to daylight, a conversion of the C_2-symmetric *rac*-isomer into the C_s-symmetric *meso*-isomer takes place.[4]

The mechanism of the photoconversion has been observed mostly for titanocenes by Harrigan[5] and by Vitz and Brubaker.[6] Following the explanation given by these authors, the conversion takes place via a homolytic cleavage of the η^5-metal−cyclopentadienyl ring bond (see Scheme 1).

As we reported in a former paper,[4] the conversion of the two diastereomers from one to the other cannot be carried out up to 100%. It reaches a photostationary state that is different for each metallocene. The conversion can be accelerated by irradiation with UV light while the value of the ratio of *rac*- to *meso*-isomer in the photoequilibrium does not differ from the value achieved with daylight irradiation.

This photochemical isomerization has become the subject of scientific interest, and new ways of synthesizing pure *rac*-isomers[7] and polymerization results[8] have been reported in the recent literature.

A mixture of both isomers used in the polymerization with MAO as cocatalyst changes the polymerization properties in comparison to the polymerization with the *rac*-isomer only.

The activity ratio between the *rac*- and *meso*-isomer for dimethylsilylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride for propylene is $rac/meso = 15.6$. Our group found that if higher α-olefins are polymerized, this ratio shows an opposite trend; the activities for the *meso*-diastereomer in the polymerization of 1-pentene, 1-hexene, and 1-octene were higher than those of the *rac*-isomer.[4]

Results and Discussion

In this paper we present the results of our investigations using the above-mentioned two catalysts **1** and **2** as well as the basic system **3** and MAO polymerizing 1-butene and 1-pentene.

The most striking result is that if polymerizing α-olefins with the catalysts **1** and **2**, the *meso*-compounds show a higher polymerization activity than the *rac*-forms of the metallocenes. This is remarkable because in the polymerization of propene the reaction rate of the *rac*-compound is higher than that of its *meso*-enantiomer.[9] These results confirm the reported behavior of the dimethylsilylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride in the polymerization of propene and higher α-olefins such as 1-pentene and 1-hexene. The *meso* activities were calculated following this equation:

$$\begin{aligned}&\text{activity } (rac/meso \text{ mixture}) = X \times \\ &\quad \text{activity (pure } rac) + Y \times \text{activity (pure } meso) \rightarrow \\ &\quad\quad \text{activity (pure } meso) \\ &\quad = (\text{activity } (rac/meso \text{ mixture}) - \\ &\quad\quad X \times \text{activity (pure } rac))/Y\end{aligned}$$

where X, Y = percentage of the isomer in the ^{1}H NMR spectrum. Although the toluenic metallocene solutions have to be protected against daylight, the polymerization itself can be carried out without light protection; the results of polymerizations carried out with and without exposure to daylight were identical.

The creation of the active center probably stabilizes the ligand environment, and therefore no interconversion does occur.

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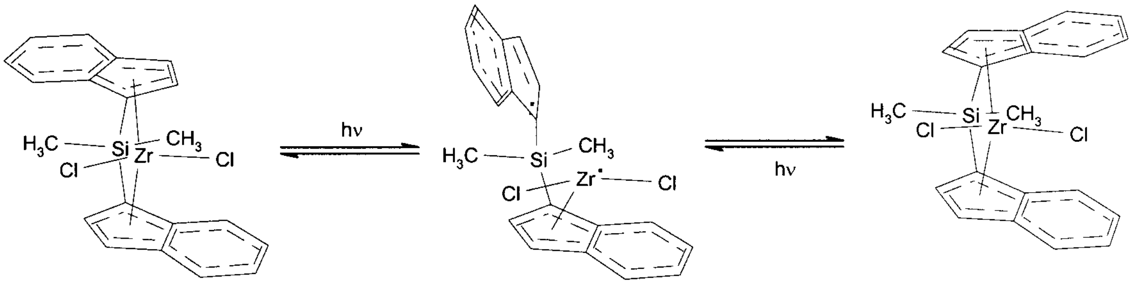
10.1021/ma991498w CCC: $19.00

Scheme 1. Proposed Mechanism of the Photoinduced *Rac/Meso* Interconversion



rac-$[Me_2Si(Ind)_2]ZrCl_2$

meso-$[Me_2Si(Ind)_2]ZrCl_2$

Table 1. Polymerization Results for 1-Butene[a]

catalyst	isomer	activity [kg of PB/(mol of Zr h)]	M_η [kg/mol]	T_m [°C]
1	*rac*	50	290	102
	meso	4200	170	n.d.
2	*rac*	350	300	112
	meso	1850	200	n.d.
3	*rac*	480	130	102
	meso	20	40	n.d.

[a] Polymerization conditions: solvent, 100 mL of toluene; monomer concentration, 0.82 mol/L; catalyst concentration, 1×10^{-5} mol/L; Al/Zr ratio, 6400; temperature, 30 °C; time of polymerization, 10−60 min; turnover, maximum 10%.

Table 2. Polymerization Results for 1-Pentene[a]

catalyst	isomer	acticity [kg of PPe/(mol of Zr h)]	M_η [kg/mol]	T_m [°C]
1	*rac*	100	160	66
	meso	2900	100	n.d.
2	*rac*	75	190	81
	meso	720	30	n.d.
3	*rac*	580	50	83
	meso	120	10	n.d

[a] Polymerization conditions: solvent, 200 mL of toluene; monomer concentration, 1 mol/L; catalyst concentration, 1×10^{-5} mol/L; Al/Z ratio, 6400; temperature, 30 °C; time of polymerization, 10−60 min; turnover, maximum 10%.

The polymers produced with the *meso*-compounds are completely atactic because of the loss of symmetry of the catalysts while the *rac*-forms produce a very highly isotactic polymer.

Polymerization of 1-Butene. Table 1 shows the different activities of the two enantiomers for the polymerization of 1-butene. The *meso*-forms of **1** and **2** are much more active than the corresponding *rac*-isomers. The activity of the *meso*-form of **1**/MAO is more than 80 times higher than the *rac*-component. Nevertheless, the *meso*-catalyst produces a polymer with a smaller molecular weight (170 compared to 290 kg/mol of the isotactic polymer produced with the *rac*-isomer). A melting point is obviously only observable for the isotactic polymer.

Looking at the catalyst system **2**/MAO, the activity difference is not as striking as with catalyst **1**, but in this case the *meso*-form is still about 5 times as active as the *rac*-compound. The molecular weights of the polymers produced with this catalyst system are about the same as with catalyst **1**/MAO.

It is interesting to note that this result, found for the two investigated catalysts **1** and **2** as well as for the zirconocene we reported about before, is not observed for the basic unsubstituted metallocene **3**.

The system **3**/MAO shows a much higher activity for the *rac*-isomer while the activity of the *meso*-compound and MAO is the lowest of all investigated activities in this paper. The molecular weights are significantly lower than those of the polymers produced with the catalyst systems **1**/MAO and **2**/MAO. This behavior follows the same trend as the polymerization of propylene with these catalysts.

The melting point of the polymer made with the *rac*-form of **2** and MAO is 10 °C higher than that of the polymers produced by the other two catalyst systems. This might be due to the crystallization of this polymer in a different modification of poly-1-butene than the other two polymers which seem to crystallize in modification I (T_m = 100 °C).[10]

Polymerization of 1-Pentene. The behavior of the investigated metallocenes in the polymerization of 1-pentene is very similar to that of the polymerization of 1-butene.

The *meso*-compounds of the catalysts **1** and **2** in combination with MAO show a higher activity in the polymerization of this monomer than their *rac*-isomers. The highest activity ratio *meso/rac* can be observed again with catalyst **1** with 29 compared to ∼10 for the combination **2**/MAO.

The trend for the unsubstituted zirconocene **3** is vice versa again; the ratio here is clearly lower than one.

The molecular weights of the polymers produced with the *rac*-isomers are higher than those of the atactic polymers. Interesting is the low molecular weight of the polymer produced with the *meso*-form of **2**/MAO: While the molecular weight of the isotactic material is very similar, the molecular weight of the atactic poly-1-pentene produced with **1** and **2** is not in the same region at all.

Since one side of the zirconocenes is not sterically hindered by the ligand environment in the case of the *meso*-form, chain termination reactions such as hydride eliminations can easily take place here. This could be the reason that, although the activities of the *meso*-compounds of **1** and **2** are much higher than the activities of the *rac*-systems, the molecular weight of the polymers they produce is lower than that of the isotactic material.

The catalyst system **3**/MAO produces the polymer with the lowest molecular weight. This follows the trend observed for the other monomers.

The melting points for the isotactic material produced with the *rac*-zirconocenes **2** and **3** and MAO correspond well with the literature value (81−83 °C).[9] The melting point of the polymer made with **1** and MAO shows a large deviation of 15 °C.

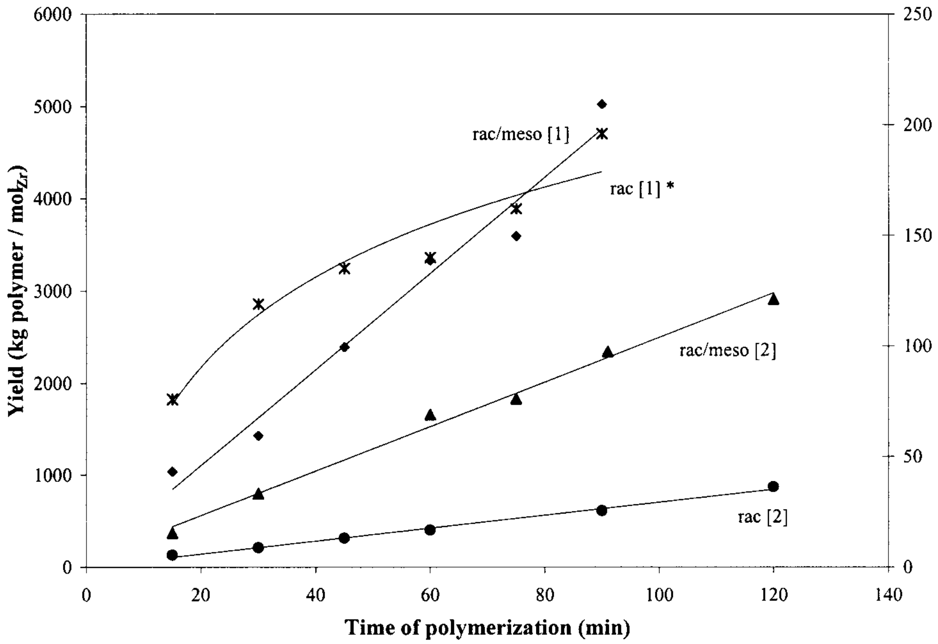


Figure 1. Kinetics of the polymerization of 1-butene. The *y* values of these points* refer to the right (secondary) axis. Polymerization conditions: solvent, 200 mL of toluene; monomer concentration, 0.82 mol/L; catalyst concentration, 1 × 10^{-5} mol/L; Al/Zr ratio, 6400; temperature, 30 °C; turnover, maximum 10%.

Kinetics

If the polymerizations of 1-butene or 1-pentene with the catalyst systems **1**/MAO and **2**/MAO are carried out over a longer period of time, deactivation of the catalyst during the polymerization reaction is observed for some polymerizations with the *rac*-isomers of the catalysts. Therefore, we looked at the kinetic behavior of the polymerization reaction. We carried out reactions with the *rac*-forms of the catalysts **1** and **2** as well as with a mixture of both isomers in the reaction solution. These mixture values are

$$\text{for } \mathbf{1}\text{:} \quad rac{:}meso = 0.6$$

$$\text{for } \mathbf{2}\text{:} \quad rac{:}meso = 0.4$$

In Figure 1 the kinetic behavior of the polymerization of 1-butene with both catalysts is shown. There is a decrease in activity with time for the polymerization with the *rac*-isomer of **1** as the negative deviation from the ideal straight line clearly shows.

The polymerizations carried out with a solution of a *rac*/*meso* mixture of the metallocenes show no deactivation for both catalysts; the yield increases with time in a linear fashion. This is also the case for the polymerization of 1-butene with the *rac*-isomer of catalyst **2**, but the activity is much smaller than that of the polymerization carried out with the catalyst in the mixture.

In Figure 2 the kinetic behavior of the polymerization of 1-pentene with the catalyst complexes of **1**/MAO and **2**/MAO is given. In this case both polymerizations of 1-pentene with the *rac*-forms show deactivation. Compared to the strong activity decrease observed with catatyst **1** polymerizing this monomer, the deactivation of the system **2**/MAO is rather slow.

The other activities seem to be unaffected by increasing time up to even 3 h in the case of the polymerization of 1-pentene with the *rac*/*meso* mixture.

In general, it can be said that the *meso*-isomers not only exhibit higher activities but also seem to be more stable than their *rac*-forms. This stability is of course one of the reasons why the activity over a longer period of time of the *meso*-metallocenes is higher than the activity achieved with *rac*-diastereomers, but it cannot be the primary explanation for *meso* activities which are magnitudes higher than those observed for polymerizations with the corresponding *rac*-compounds.

Conclusion

The two diastereomeric forms of the bridged zirconocene bis(indenyl) compounds **1**, **2**, and **3** show different behavior with respect to the polymerization of 1-butene and 1-pentene.

The *meso*-forms of these substituted metallocenes **1** and **2** exhibit a higher activity in the polymerization while catalyst **3** shows a vice versa performance.

Furthermore, the *meso*-isomers of **1** and **2** are more stable during the polymerization process; a linear dependency of yield on time is observable while the *rac*-compounds seem to undergo deactivation during the reaction.

The molecular weights of the isotactic polymers produced with the C_2-symmetric *rac*-zirconocenes are generally higher than the corresponding polymers produced by their isomers.

The *rac*-isomers of the two metallocenes **1** and **2** are both catalysts developed specifically for the isospecific polymerization of propene. They have been optimized sterically and electronically to render perfect conditions for high activity, high molecular weight, and high isospecifity.

With using other, sterically more demanding, monomers such as 1-butene and 1-pentene these advantages will be lost because of the sterical interactions between monomer and ligand environment.

It is known that the *rac*-zirconocenes **1** and **2** and MAO polymerize propene much faster than their isomeric *meso*-forms. As shown, a vice versa behavior is observable for higher α-olefins.

In the case of the *rac*-catalysts the usual *alternating mechanism*[11] is proposed, where the position formerly

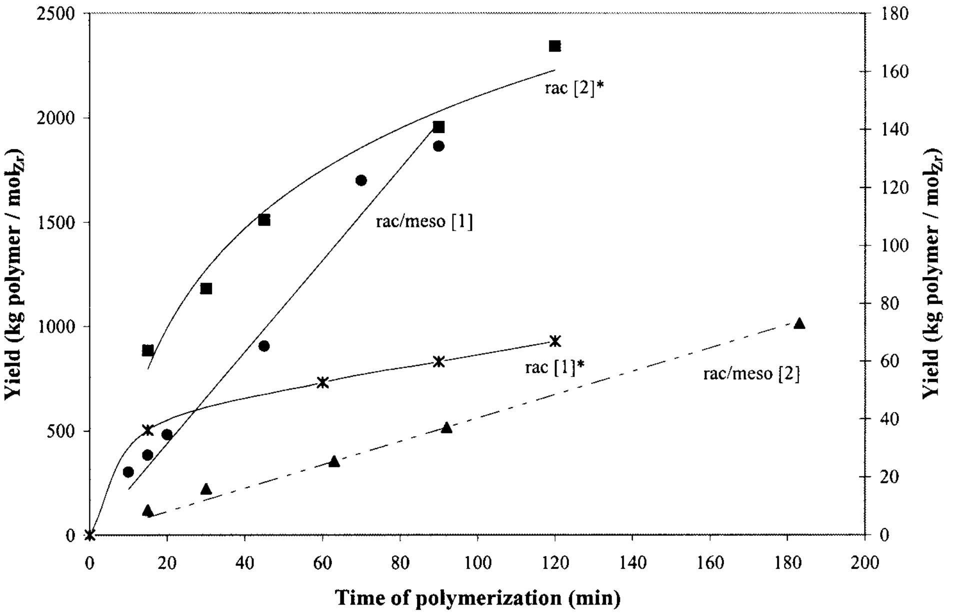


Figure 2. Kinetics of the polymerization of 1-pentene. The *y* values of these points* refer to the right (secondary) axis. Polymerization conditions: solvent, 200 mL of toluene; monomer concentration, 0.82 mol/L; catalyst concentration, 1×10^{-5} mol/L; Al/Zr ratio, 6400; temperature, 30 °C; turnover, maximum 10%.

occupied by the polymer chain is available for the next olefin to approach; the configuration of the metallocene alternates. If this mechanism would apply for the *meso*-forms as well, the observed trend cannot be explained.

Therefore, a change in the mechanism has to be postulated; it is possible that for the *meso*-forms a *retention mechanism*, in which the olefin coordinates to the metal center always from the same side, occurs and that this mechanism becomes favorable for higher α-oelfins compared to the *alternating mechanism* taking place at the *rac*-isomers.

Whether the observed inversion of the relative speed of the diastereomers in the polymerization process can be explained by a change in the mechanism is currently the subject of our investigations.

Experimental Section

Polymerizations were performed at 30 °C in a 1 L Büchi AG glass autoclave for 1-butene or in a 200 mL glass reactor for 1-pentene, which were charged successively with 200 mL of toluene in the autoclave and 100 mL of toluene in the glass reactor, respectively, cocatalyst solution, and monomer. The Al/Zr ratio was 6400, and the monomer concentration was 1 mol/L in the case of the 1-pentene and 0.82 mol/L for the 1-butene.

Since the polymerizations were carried out discontinuously, the turnover value of the monomer was kept under 10%.

They were initiated by injecting the zirconocene and terminated by the addition of ethanol. The products were washed with ethanol/HCl, neutralized, and dried in a vacuum.

After starting the polymerization, the toluene of the remaining catalyst solution was removed, and the *rac/meso* mixture in the flask was dried under vacuum. For the recording of the NMR spectra it was dissolved in an NMR solvent, and a ^{1}H NMR spectrum was taken.

All procedures were carried out in an argon atmosphere. Toluene was dried over sodium/potassium or by passage through columns with Cu catalyst (BASF R3-11) and a molecular sieve of 4 Å; $CDCl_3$ and 1-pentene (Merck KgaA) were dried over a molecular sieve of 4 Å.

Because of its lacking chirality, the *meso*-isomer produces only atactic polymers, and therefore it should be taken care of that the toluenic solutions are not exposed to daylight.

Rac/*meso* interconversions were examined using a 366 nm DESAGA mercury lamp (75 W) and dry toluene-d_8 or chloroform-d_1 as solvents in sealed glass NMR tubes.

After irradiation the solutions were wrapped in aluminum foil to protect them against further exposure.

Rac/meso proportions were investigated by ^{1}H NMR spectroscopy. Spectra were recorded on an AC 100 Bruker spectrometer.

The zirconocenes were either supplied by the former Hoechst AG **(1, 2)** or synthesized in the group **(3)**.[12] MAO was purchased from Witco.

Viscosimetry was carried out with an Ubbelohde capillary 0a ($K = 0.005$). Measuring conditions were 135 °C/decahydronaphthalene for PP and PB and 30 °C/toluene for PPe. The Mark–Houwink constants ($k = 0.0238$ mL g^{-1}, $a = 0.725$, PP; 0.0062, 0.79, PB; 0.0323, 0.66, PPe) have been reported before.[9,13,14]

Differential scanning calorimetry analyses were performed on a Mettler-Toledo DSC 821e instrument (heating rate 20 °C min^{-1}). The results of the second runs are reported.

Polymer ^{13}C NMR spectra were recorded at 100 °C on a 300 MHz Bruker MSL 300 spectrometer. NMR assignments for the higher poly-α-olefins are reported in the literature.[15]

UV light was produced using a DESAGA mercury lamp with a wavelength of 366 nm.

Acknowledgment. This work has been financially supported by the BMBF and the "Fonds der deutschen chemischen Industrie". We thank the former Hoechst AG for the free sample of catalysts **1** and **2**.

References and Notes

(1) Wild, F. R. W. P.; Zsoluai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.
(2) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.
(3) Spaleck, W.; et al. *New J. Chem.* **1990**, *14*, 499.
(4) Kaminsky, W.; Schauwienold, A.-M.; Freidanck, F. *J. Mol. Catal., Part A: Chem.* **1996**, *112*, 37.
(5) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *81*, 79.
(6) (a) Vitz, E.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1974**, *82*, C16. (b) Vitz, E.; Wagner, P. J.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1976**, *107*, 301.
(7) (a) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030. (b) Könemann, M.; Erker, G.;

Fröhlich, R.; Kotila, S. *Organometallics* **1997**, *16*, 2900. (c) Aulbach, M.; Kühler, F. *Chem. Unserer Zeit* **1994**, *28*, 197.

(8) Naga, N.; Shiono, T.; Ikeda, T. *Macromol. Chem. Phys.* **1999**, *200*, 1587.

(9) Schauwienold, A.-M. PhD Thesis, Hamburg, 1999.

(10) *Ullmann's Encyclopedia of Industrial Chemistry*, 1992; Vol. A21, p 547.

(11) Arndt, M.; Kaminsky, W.; Schauwienold, A.-M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135 and references therein.

(12) Dessenne, S. University of Hamburg, unpublished results.

(13) Scholte, T. G.; Meijerink, N. L. J.; Schoffeleers, H. M.; Brands, A. M. G. *J. Appl. Polym. Sci.* **1984**, *29*, 3763.

(14) Moraglio, G.; Oddo, N. *Chim. Ind.* **1966**, *48*, 224.

(15) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334.

MA991498W