High Molecular Weight Polypropene Elastomers via "Dual-Side" Zirconocene Dichlorides

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Summary: A series of asymmetric *ansa*-zirconocene dichlorides were investigated in propene polymerization reactions with respect to monomer concentration and polymerization temperature. The two different coordination sides of these "dual-side" catalysts allow a precise control of the total amount of randomly distributed isolated stereoerrors along the isotactic polymer chains leading to bulk properties which can be adjusted from flexible, semicrystalline to excellent thermoplastic elastic. The obtained homopolypropenes have a great potential to come into competition with commercialized copolymers for possible industrial applications.

Introduction

The development of new C_2-symmetric metallocenes for the isospecific polymerization of propene increased rapidly since Brintzinger's first introduction of homogeneous *ansa*-metallocene catalysts.[1,2] To a lesser degree, research was focused on asymmetric metallocene species. However, those structures proved to be excellent tools for the design of different polymer properties by introdcution of substitutents in key positions of the ligand framework. Ewen et al.[3] demonstrated with the synthesis of a series of different C_S-symmetric Zr(IV)-complex based on the [2-(9-η^5-fluorenyl)-2-(η^5-cyclopentadienyl)propane]zirconium dichloride that the two different coordination sides available for asymmetric metallocenes customize a broad range of material properties in migratory polyinsertion reactions of propene by modification of the polymer microstructure. So, the stereochemistry of the polymerization reaction can be changed from the production of syndiotactic polypropene to a hemiisotactic form and even to a highly isotactic material by opening or blocking selective and nonselective sides in successive insertion steps. Chien et al.[4] observed at about the same time, that elastic polypropene of narrow molecular weight distribution can be accessed by the asymmetric mono-carbon-bridged titanocene [MeHC(Me$_4$Cp)(Ind)]TiCl$_2$ resulting in increased exertions

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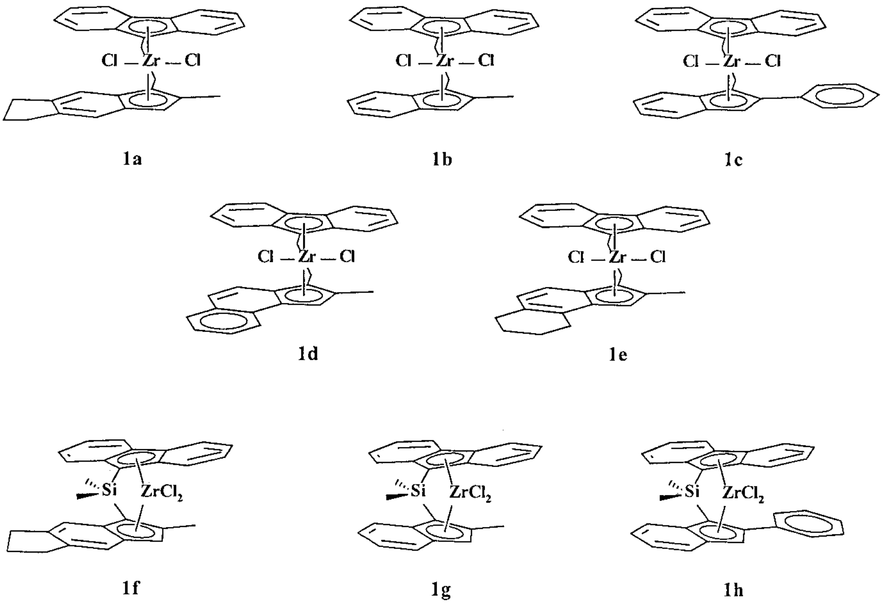
in research on suitable catalysts for the production of elastomeric polypropene.[5,6] The elastic properties were ascribed to arise from blocklike structures composed of isotactic and atactic sequences.[4,7] Our initial forays in the field of asymmetric metallocenes were pointed on the synthesis of the ethylene bridged diastereomeric *rac*-[1-(9-η^5-fluorenyl)-2-(η^5-indenyl)phenylethane]zirconium dichlorides, which contain a bulky phenyl group as bridge substituent to stabilize the conformation of the metallacycles. Therewith we realized that the δ-forward and λ-backward conformers behave completely different with respect to the stereoselectivity of the C-C-bond forming process.[8,9]



1a **1b** **1c**

1d **1e**

1f **1g** **1h**

Figure 1. Summary of complexes used for the propene polymerization reactions.

In our present work we compare the polymerization behavior of a series of ethylene and dimethylsilane bridged asymmetric zirconocene dichlorides **1a-h** (Figure 1) and present information regarding the influence of the ligand substitution pattern on the polypropene characteristics with the intention to enable a tayloring of homopolypropene plastomers and elastomers in future approaches. This directive in metallocene chemistry is attributed to the new family of "dual-side" complexes, combining an isoselective side with a less selective side leading predominantly to single stereoerrors within one well defined species.[10] Asymmetric metallocenes serve as a new tool to control the amount of stereoerrors along an isotactic polymer chain allowing to adjust polymers of variable crystallinity with material properties from flexible, semicrystalline to excellent thermoplastic elastic.

Results and Discussion

Propene Polymerizations

Activity. Monomer concentration and temperature variation have proved to be efficient tool to take influence on the polymer microstructure and to achieve defined material properties .[10] Large differences were observed in the polymerization behavior of the examined catalysts by variation of these parameters and the catalyst architecture (Table 1). The highest polymer yields of all asymmetric complexes of the present study could be obtained with the ethylene bridged metallocenes **1a**/MAO (at $T_P = 30$ °C up to 2.9×10^3, at $T_P = 50$ °C up to 12.9×10^3 and at $T_P = 70$ °C up to 31.4 kg of PP (mol of Zr [C_3] h)$^{-1}$). The angular 4,5-substituted metallocenes **1d,e** show lower polymerization activities, which probably result from the enhanced steric encumbrance hindering the incoming propene molecule to coordinate on the active Zr-center. The activity of the complex **1b**/MAO, bearing only the 2-methyl substitution in the ligand framework, is about the same order of magnitude as for the angular complexes **1d,e**/MAO. Interestingly, the propene consumption of the ethylene bridged complexes increases within the first 15–30 minutes of the polymerization experiment (Figure 2, **1a,b**/MAO), indicating a slow activation reaction with MAO, presumably resulting from the sterically demanding substituents around the zirconium center. We found further, that the rate of catalyst activation for this type of asymmetric zirconocenes rises with increasing polymerization temperature (Figure 2, **1a,b**/MAO).[11]

Table 1. Polymerization results of propene with asymmetric complexes **1a-h**/MAO

run	cat.	amount[a]	T_p[b]	$[C_3]$[c]	t_p[d]	yield[e]	activity[f]	M_w[g]	M_w/M_n	[mmmm][h]
1	1a	15	30	1.1	42	31.9	2900	50	1.9	47.8
2	1a	6	30	1.2	73	17.3	2000	55	1.8	42.5
3	1a	3.8	30	3.0	39	18.0	2400	89	1.8	30.3
4	1a	7.5	30	3.9	33	36.9	2300	120	2.0	31.3
5	1a	2.7	30	5.1	30	17.6	2600	125	1.9	27.8
7	1a	5.0	50	0.4	46	13.9	9000	17	1.9	72.1
8	1a	3.8	50	1.1	72	51.4	10200	30	2.2	63.9
9	1a	2.5	50	1.9	50	51.2	12900	34	2.1	59.6
10	1a	2.5	70	1.1	42	60.5	31400	17	2.0	64.0
11	1b	5	30	1.2	72	15.6	2100	62	1.8	17.6
12	1b	5	30	3.0	39	16.7	1700	81	1.9	13.4
13	1b	5	30	5.1	25	16.6	1600	83	1.9	9.7
14	1c	10	30	3.0	27	18,4	1400	62	2.3	98.0
15	1c	10	30	5.1	29	20.3	800	86	2.5	86.0
16	1d	2.5	30	1.1	103	6.1	1300	47	2.9	71.9
17	1d	6.5	30	2.9	43	44.2	3300	60	2.4	69.1
18	1d	2.5	50	0.4	52	4.8	5500	13	1.8	72.6
19	1d	2.5	50	1.1	31	9	6300	27	2.0	74.4
20	1d	2.5	50	1.9	65	40	7800	38	2.0	74.7
21	1d	2.5	70	1.1	53	29.9	12300	23	3.0	66.3
22	1e	2.0	30	1.1	62	2.5	100	33	2.0	69.8
23	1e	12.8	30	2.9	46	58.8	2100	39	1.9	53.7
24	1e	2.0	50	0.4	53	1.9	2100	11	1.8	79.5
25	1e	2.0	50	1.1	29	6.7	5000	15	2.0	78.0
26	1e	2.0	50	1.9	39	17.7	5700	30	1.8	78.4
27	1e	2.0	70	1.1	45	14.4	7000	14	2.0	78.7
28	1f	10	30	1.2	120	12.5	n. d.[i]	103	1.8	61.6
29	1f	10	30	3.0	61	15.2	n. d.	132	1.9	50.6
30	1f	10	30	5.1	30	17.4	n. d.	158	1.9	44.0
31	1f	10	50	1.9	31	11.6	n. d.	64	1.8	68.0
32	1f	10	50	3.0	25	13.2	n. d.	85	1.9	67.4
33	1g	20	30	1.2	106	16.1	n. d.	73	1.8	44.1
34	1g	10	30	3.0	69	15.7	n. d.	81	2.0	39.3
35	1g	10	30	5.1	33	16.4	n. d.	92	2.0	35.3
36	1g	10	50	3.0	65	12.6	n. d.	64	1.9	56.2
37	1h	50	30	1.2	193	8.5	n. d.	32	1.9	70.5
38	1h	30	30	3.0	118	8.9	n. d.	74	1.8	62.2
39	1h	30	30	5.1	125	16.2	n. d.	99	1.8	57.9
40	1h	30	50	3.0	101	5.2	n. d.	31	1.9	71.7

[a][μmol] (Al/Zr = 2000). [b][°C]. [c][mol L^{-1}]. [d][min]. [e][g]. [f][kg of PP (mol of Zr [C_3] h)$^{-1}$. [g][kg mol^{-1}]. [h][%]. [i]n. d. = not determined, because of rapid deactivation of the catalyst active species.

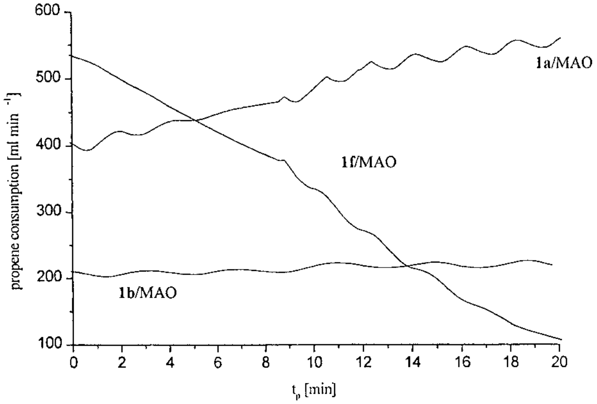


Figure 2. Propene consumption curves obtained with **1a,b,f**/MAO: **1a**/MAO: $T_P = 50$ °C, $[C_3] = 3.0$ mol L^{-1}, $n_{Zr} = 3.8$ µmol and **1f**/MAO: $T_P = 50$ °C, $[C_3] = 3.0$ mol L^{-1}, $n_{Zr} = 10$ µmol; **1b**/MAO: $T_P = 30$ °C, $[C_3] = 3.0$ mol L^{-1}, $n_{Zr} = 5.0$ µmol.

The exchange of the ethylene bridge by a dimethylsilane unit (**1f-h**/MAO) leads to significantly different polymerization properties, especially to a deactivation, resulting in a rapid decline of the propene consumption during the course of the polymerization reaction (Figure 2, **1f**/MAO). Nevertheless, we suppose that also for the dimethylsilane bridged complexes **1f-h**/MAO a slow activation mechanism is present, which however is superimposed in the propene consumption curve by the fast decomposition of the active species.[12] This is in contrast to C_2-symmetric *ansa*-metallocenes that show higher activities for the Si-bridged species due to an enlarged bite-angle of the Cp-ligands in such complexes.[13]

Molecular Weight. In contrast, the Si-bridge strongly increases the polymer molecular weight. In that respect the 5,6-cyclopentyl-substituted complex **1f**/MAO (Table 1, entries 29,30) reached the highest molecular weights under comparable polymerization conditions. Interestingly, the 5,6-cyclopentyl group seems to have generally a beneficial influence on the molecular weight, despite its remote position within the complex relative to the active Zr(IV)-center (Table 1, **1a,f**). We have no genuine explanation for this surprising effect. However, experiments with deuterated propene monomers show, that the 5,6-alkyl substituents suppress effectively a chain end epimerization process (found to be responsible for the formation of stereoerrors in C_2-symmetric catalysts)[14] and hinder at the same time a subsequent chain termination reaction, leading to higher molecular weight products.[10b] Moreover we found a converse effect for the angular zirconocenes **1d,e**/MAO. Both complexes produced polymers with slightly lower molecular weights. Generally, the average polymer chain lengths can be increased by lowering the polymerization temperature (constant monomer concentration) and by enhancing the monomer concentration (constant polymerization temperature).

Table 2. Polypropene pentad distribution[a] (in %)

run	cat.	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm]+ [rrmr]	[rrrr]	[rrrm]	[mrrm]
1	1a	47.8	16.9	1.0	18.6	3.2	0.8	2.0	9.3
2	1a	42.5	17.5	2.1	19.9	3.4	1.6	2.8	10.2
3	1a	30.3	17.7	2.7	21.3	5.9	4.6	6.6	10.9
4	1a	31.3	17.0	2.9	19.5	7.7	4.6	6.2	10.3
5	1a	27.8	17.7	2.7	22.0	6.6	5.3	7.4	10.5
7	1a	72.1	10.0	-	12.2	2.1	-	-	3.6
8	1a	63.9	12.7	0.3	14.2	1.0	0.3	0.7	6.6
9	1a	59.6	15.9	-	16.5	-	-	-	8.0
10	1a	64.0	14.2	-	12.9	1.2	-	0.9	5.8
11	1b	17.6	16.5	3.8	21.6	20.8	8.9	10.4	11.4
12	1b	13.4	15.6	5.4	22.5	10.3	14.0	11.8	7.0
13	1b	9.7	13.7	5.5	18.5	10.7	15.7	14.8	11.4
14	1c	98.0	2.0	-	-	-	-	-	-
15	1c	86.0	5.4	-	6.3	-	-	-	2.3
28	1f	61.6	15.0	-	16.3	-	-	-	7.1
29	1f	50.6	15.6	1.4	16.8	3.1	1.7	2.5	8.2
30	1f	44.0	16.3	1.8	17.8	4.1	3.0	3.9	9.1
31	1f	68.0	12.0	-	12.4	1.0	-	0.9	5.8
32	1f	67.4	12.6	-	13.0	0.9	-	0.5	5.5
33	1g	44.1	16.7	1.8	18.5	4.0	3.1	3.5	8.3
34	1g	39.3	17.5	2.3	20.6	3.8	3.7	4.8	8.0
35	1g	35.3	17.6	2.4	21.2	4.2	5.4	6.1	7.9
36	1g	56.2	16.4	-	18.0	2.1	-	1.6	5.8
37	1h	70.5	11.8	-	12.6	-	-	-	5.1
38	1h	62.2	12.9	1.1	12.0	2.5	0.9	1.7	5.9
39	1h	57.9	13.9	1.4	12.8	3.2	1.2	2.1	6.2
40	1h	71.7	11.7	-	11.9	-	-	-	4.7

[a] [mrmr] ≤ 1%.

Mechanisms of Stereoerror Formation

Stereoselectivity and temperature. The complexes **1a-h**/MAO gave isotactic polypropenes with variable amount of stereoerrors. In particular the [mmmm]-pentad concentration of the polymers produced with the different C_1-symmetric metallocene catalysts varies over a broad range (10% to 98%) (Tables 1,2; entries 14,15). Generally, the metallocenes **1d,e**/MAO, which show a 4,5-front substitution pattern, gave substantially higher isotactic polypropene products than the side-substituted catalyst **1a**/MAO (Table 2) or the unsubstituted species **1b**/MAO. This behavior can be attributed to the presence of a substituent in the 4-position of the indenyl moiety in **1d,e**, which favors a back-skip of the growing polymer chain before a new monomer inserts on the aspecific side of the complexes. The same effect, compared to the unsubstituted zirconocene **1b,** is also observed, but to a lower degree, for the complexes **1a,f**/MAO bearing the 5,6-cyclopentyl substitution on the indenyl fragment.

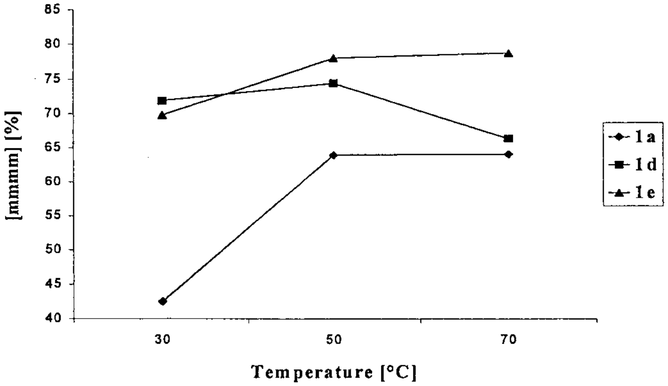


Figure 3. Plot of the propene stereoregularity versus the poylmerization temperature T_P for catalysts **1a,d,e**/MAO at constant monomer concentration ($[C_3]$ = 1.1 mol L^{-1}).

Interestingly, there is no steady decline of the catalysts' stereoselectivities with increasing polymerization temperature (Figure 3) as typically observed for C_2-symmetric metallocenes.[13] The isotacticities of the products prepared with **1e**/MAO at a constant monomer concentration (e.g., 1.1 mol L^{-1}) increase with temperature from 70 (30 °C) to 79% [mmmm] pentads (70 °C). The zirconocene **1d**/MAO gives polypropenes of which the isotacticity goes through a maximum at 50 °C (74% [mmmm]), and the products of **1a**/MAO show an increase of the [mmmm] concentration from 30 °C (48%) to 50 °C (64%), after which it remains constant upon a further increase of the polymerization temperature to 70 °C.

The lowest isotacticities are observed for the non-substituted complex **1b**/MAO with the lowest steric demand reducing the rate of the growing polymer chain to undergo a chain backskip reaction (c.f. Scheme 1). This temperature dependence of the isotacticity on the polymerization temperature indicates that the stereoerror formation at higher temperatures is based on two different pathways. The stereoerror formation of asymmetric complexes originates predominantly from the kinetic competition between chain back-skip, that increasingly takes place with rising temperatures and monomer coordination at the aspecific side of the catalyst structure. As a result, we observe initially an increase of the [mmmm] pentads at elevated temperatures. The most conspicuous effect of the Si-bridged *ansa*-metallocenes **1f,g**/MAO is the distinct ascent of the isotacticity compared with their ethylene bridged counterparts **1a,b**/MAO. The series of propene polymerizations applying the 2-phenyl substituted complexes **1c**/MAO has produced polymers with the highest isotacticities (e.g **1c**: [mmmm] = 98%, Table 2, entry 14). Exchange of the C_2H_4-bridge by a Me_2Si-unit (**1h**) results in a strong decrease of the isotacticity of the polypropene products (e.g. Table 2, entries 37-40), while for both complexes the same influence of the monomer concentration on the stereoselectivity is observed (Table 2, **1c**: entries 14, 15; **1h**: entries 37-40), suggesting that a mechanism like the one depicted in Scheme 3 might still be active. Generally, 2-phenyl substitution leads to a strong decrease in polymerization activity, while the molecular weight is not essentially altered.

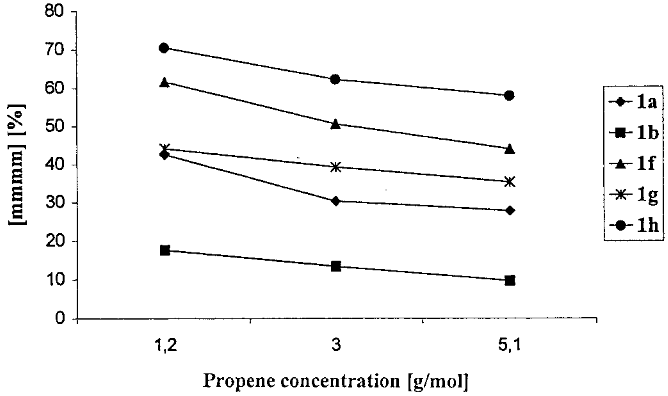


Figure 4. Plot of the propene streoregularity versus the monomer concentration for catalysts **1a,b,f-h**/MAO at constant polymerization temperature (T_P = 30 °C).

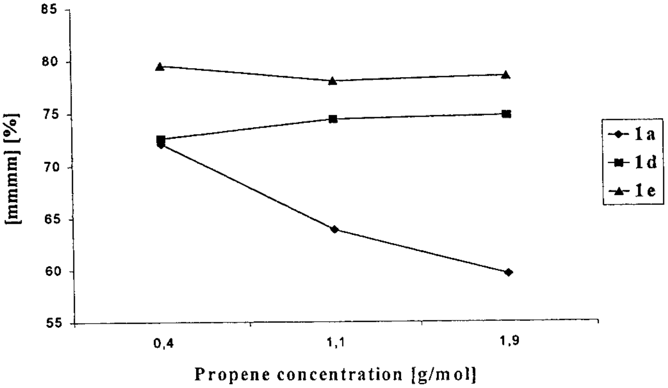
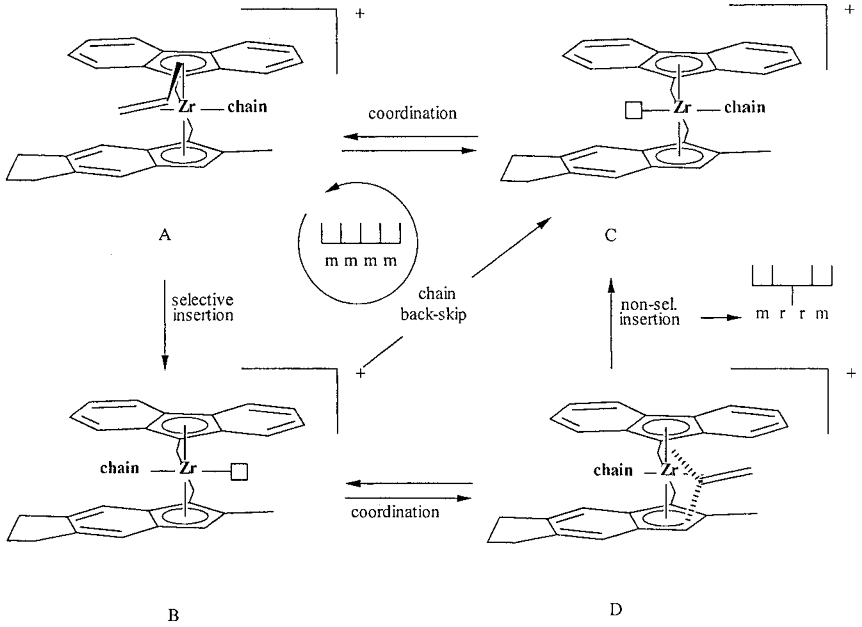


Figure 5. Plot of the propene streoregularity versus the monomer concentration for catalysts **1a,d,e**/MAO at constant polymerization temperature (T_P = 50 °C).

Stereoselectivity and monomer concentration. The [mmmm] pentad content declines continuously with increasing monomer concentration (Figure 4 and Figure 5). This is a exceptional behavior that distinguishes our catalysts entirely from the polymerization properties of common C_2-symmetric metallocenes. The decrease of isotactic sequences is attributed to the existence of two different coordination sides in our type of asymmetric metallocene complexes. We assume that the two sides differ distinctly in their stereoselectivity toward the propene insertion reaction, a hypothesis, that was supported by Guerra et al. in a comprehensive theoretical study.[15] Isotactic sequences are formed by a reaction path, which involves repeated migratory insertion of the growing polymer chain into the propene monomer, coordinated between the sterically demanding fluorenyl-indenyl moieties, (Scheme 1, A → B) and a consecutive back-skip of the chain to the sterically less encumbered side (B → C). At low monomer concentrations, the chain moves back to the previous position (C → A), because the sterically less encumbered side of complex structure is energetically favored by the bulky polymer chain, resulting in consecutive insertion reactions of propene molecules at the sterically more hindered coordination side (A → B). Increasing the monomer concentration leads to a higher probability for monomer coordination and insertion at the less hindered side before a back-skip of the growing chain can occur.[15] Migratory insertion of the chain to the free side results in a non-selective insertion of the monomer (D → C). The next insertion from (A → B) is again stereoselective,[16] leading - after a back-skip of the polymer chain - to an isolated [mrrm]-error pentad.



Scheme 1. Monomer concentration as a tool for the formation of stereoerrors in high molecular weight polypropenes with “dual-side” systems as presented in the present study.

At the same time as higher monomer concentrations result in a decline of the polymer isotacticity, all pentads being characteristic for an isolated stereoerror increase distinctively with monomer concentration. Figure 6 and Figure 7 show a fingerprint of the polymerization mechanism and point out that the proposed polymerization mechanism is independent of the bridging unit. For these catalysts the ratio of the rate of back-skip of the chain to the rate of monomer concentration at the free side can be understood to determine to a large extent the amount of isolated stereoerrors formed during the polymerization reaction. The amount of stereoerrors increases with the monomer concentration (c.f. Table 2, entry 1-6), because the rate of monomer coordination at the free side (B → D) depends on C_3-coordination while the rate of back-skip of the chain (B → C) is an intramolecular reaction.[17]

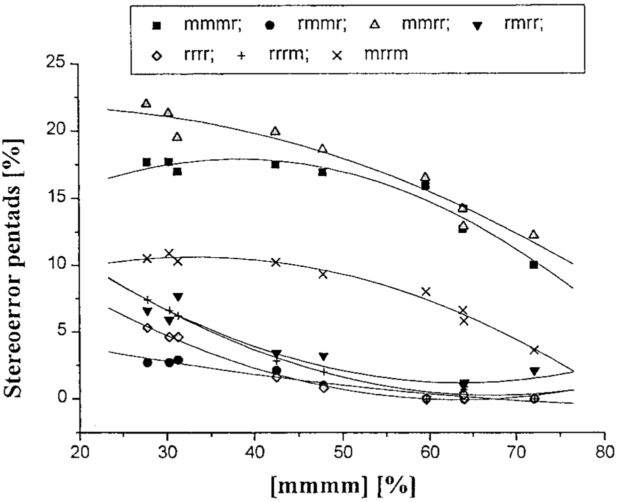


Figure 6. 1a/MAO: Variation of stereoerrors in polypropenes with reduced isotacticity as a fingerprint for the polymerization mechanism.

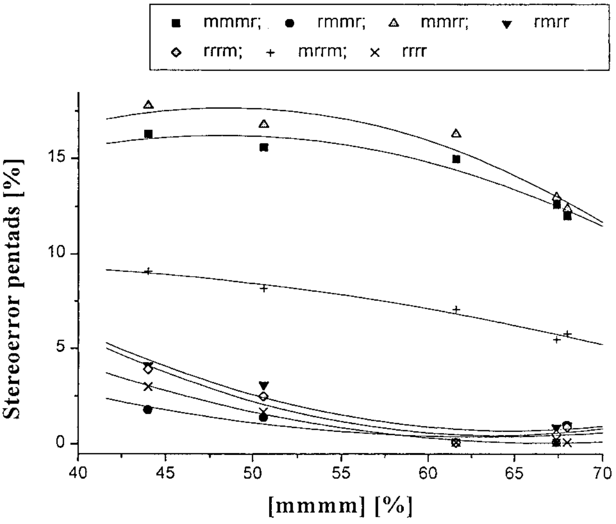


Figure 7. 1f/MAO: Variation of stereoerrors in polypropenes with reduced isotacticity as a fingerprint for the polymerization mechanism.

The Design of Material Properties

The linear, ethylene bridged, 5,6-cyclopentyl substituted system **1a**/MAO reflects the best balance between the formation of stereoerrors with respect to monomer concentration, a high molecular weight (up to 125 × 10^3 g Mol^{-1}, Table 1, entries 5) and an optimized activity for the production of a wide variety of polypropene materials. The exact setting of isotacticity and molecular weight allow a fine-tuning of the materials by adjusting the polymerization conditions, so that polypropenes with properties ranging from crystalline thermoplastic (Figure 8, entries 8, 28, 31, 35) to thermoplastic elastic (Figure 8, entry 4 and 33) can be achieved. The length of the isotactic segments is - at increased [mmmm] pentad concentrations (higher temperatures, lower [C_3]) - long enough to afford a higher degree of crystallinity so that these materials display the behavior of tough thermoplastic plastomers with relatively high melting temperatures.[18] Interestingly, our simple homopolypropenes can compete with more complicated copolymers, like Engage (Figure 8, entry 43) and even Kraton (Figure 8, entry 42) which might point to a variety of applications.

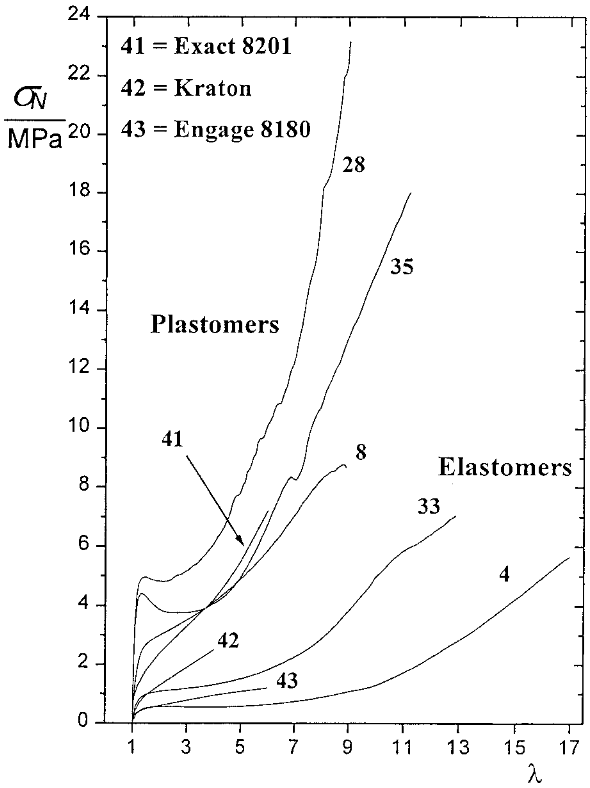


Figure 8. Typical stress-strain curves of selected polymers prepared with the zirconocenes **1a,f,h**/ MAO in comparison with the tensile behavior of commercial polymer samples (entries 41-43).

The maximal elongations, λ_{max}, of these partly crystalline polymers depend – besides the catalysts structure itself - on both the isotacticity and the molecular weight of the samples. Reduction of the isotacticity leads to the formation of highly elastic materials with λ_{max} = 17-20 times the original length.

It is important to point out that the elastic properties of the polypropene polymers obtained with our asymmetric complexes are not ascribed to chain entanglements as reported for high molecular weight, atactic polymers. For our homopolypropenes the interesting elastic property profile results obviously from a strengthening of the amorphous phase by a crystalline network, which can be adjusted by regulating the isotactic block length. The position and length of the elastic plateau of these materials can be tailored together with the initial force to stretch the polymers so that a continuous change of mechanical properties from elastic to thermoplastic can be achieved (Figure 8).

Conclusion

In the present study, we provided access to a wide variety of new polypropene materials resulting from a new family of asymmetric metallocene complexes. As a new tool, the C_1-symmetry of these "dual-side" catalysts allows to place single stereoerrors along an isotactic chain leading to a broad range of isotactic polypropene microstructures that can be accurately adjusted by variation of the monomer concentration and the polymerization temperature. A controlled tailoring of the properties of the polymer products from highly elastic to crystalline thermoplastic is enabled by varying the catalyst structure and the polymerization conditions. The interesting elastic property profile results from a reinforcement of the amorphous phase by a crystalline network, which is validated in preliminary scanning force microscopy studies giving a first insight into the crystallite size and the their distribution needed for the formation of a stable three dimensional network. Interestingly, the 5,6-cyclopentyl substitution on the indenyl moiety of the ethylene bridged species was found to play an important role in obtaining a good balance between optimized activity, increased molecular weight and a sufficient amount of stereoerrors for the design of thermoplastic elastomers. Detailed mechanistical studies support the 5,6-substitution to act as key position in the formation of stereoerrors, that originates predominantly from the kinetic competition between chain back-skip and monomer coordination at the aspecific side of the catalyst structure.[10] In contrast to most of the known catalyst systems for the production of elastic PP, of which structure variations are not possible or lead to non-elastic products, our complexes have a variable structure possessing unlimited possibilities for the design of new polypropenes. It will be interesting to see up to what extent this new family of high molecular weight, isotactic polypropenes can proceed in the resolute competition of commercialization.

Experimental Section

Complex synthesis: The syntheses of the complexes **1a-h** have been previously described in literature and were prepared according to these literature recipes.[10,19,20] Methylalumoxane and triisobutylaluminum were purchased from Witco and toluene for the polymerization reactions from Merck.

Propene Polymerization Reactions: The polymerization reactions were performed in a 1 L Büchi steel reactor at constant pressure and temperature. The autoclave was charged with 300 mL of toluene and with the desired amount of MAO. Subsequently, the polymerization temperature was adjusted, the reactor was charged with propene up to the desired partial pressure and the preactivated catalyst solution (Al:Zr = 100:1) was injected into the autoclave via a pressure burette. The monomer consumption was measured by the use of a calibrated gas flow meter (Bronkhorst F-111C-HA-33P), and the pressure was kept constant during the entire polymerization period (Bronkhorst pressure controller P-602C-EA-33P). Pressure, temperature and consumption of propene were monitored and recorded online. The polymerization reactions were stopped and treated as described above.

Polymer Analysis: ^{13}C NMR spectra were recorded on a Varian GEMINI 2000 spectrometer ($C_2D_2Cl_4$, 100 °C, 75 MHz, 10 mm probe), or on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 80 °C, 125 MHz, 5 mm probe) in the inverse gated decoupling mode with a 3 s pulse delay and a 45° pulse to attain conditions close to the maximum signal-to-noise ratio. The number of transients accumulated was between 5–15 K. The spectra were analyzed by known methods.[21] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 150 C ALC, 135 °C in 1,2,4-trichlorobenzene) relative to polystyrene and polypropene standards. Mechanical measurements were performed on a Zwick 1445 tensile apparatus at room temperature with an extension rate of 10 mm min^{-1}. All samples were prepared under identical conditions by pressing the polymer melt (170 °C) in vacuo to 10- × 5- × 0.1-cm specimens, which were cooled to ambient temperature over 20 min.

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[11] Figure 2 shows only a small digest of all propene consumption curves; the given tendencies are valid for all complexes.

[12] First experiments of the corresponding dimethyl complex *rac*-[(9-η5-fluorenyl)-(2-methyl-1-η5-indenyl)dimethylsilane]zirconium dimethyl using borates as cocatalyst support these considerations.

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[15] For theoretical calculations on the occurrence of back-skip of the growing chain in the case of asymmetric metallocenes, see: Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1996**, 29, 4834.

[16] Monomer misinsertion from A → B after D → C will result in [mrmr]-error pentads, the concentration of which is however close to zero in polypropenes obtained with asymmetric catalysts of the type studied here.

[17] For a detailed discussion of the polymerization mechanism see: Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, 121, 4348.

[18] The following melting temperatures were observed: entry 8: Tm = 96.0 °C; entry 28: 104.1 °C; entry 35: 72.6 °C.

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