Macromolecules **2005,** *38,* 3054−3059

Articles

Alternating Ethene/Propene Copolymers by C_1-Symmetric Metallocene/MAO Catalysts

Björn Heuer and Walter Kaminsky*

Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany

Received September 27, 2004; Revised Manuscript Received February 15, 2005

ABSTRACT: A number of novel C_1-symmetric metallocenes based on substituted fluorenyl and indenyl ligands, [dimethylsilyl(2,7-di-*tert*-butyl-9-η^5-fluorenyl)(1-η^5-indenyl)]zirconium dichloride (**3**), [dimethylsilyl-(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)(1-η^5-indenyl)]zirconium dichloride (**5**), and [dimethylsilyl(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)(2-methyl-1- η^5-indenyl)]zirconium dichloride, and the analogue complexes with a Ph_2Si bridge (**4**, **6**, and **8**) have been synthesized and used for alternating ethene/propene copolymerizations and compared to the unsubstituted complexes **1** and **2**. With growing sterical demand of the substituents, the activities of the catalysts at moderate temperatures decrease strongly, but a very high-temperature stability is achieved. Usage of catalyst species with a Ph_2Si instead of a Me_2Si bridge leads to higher activities and molar masses. The percentages of alternating triads are high for all catalysts and are decreasing with growing polymerization temperature. Surprisingly, the catalysts with the bulky substitution at the fluorene ring (**5**−**8**) yield at 15 and 0 °C copolymers with a lower alternating part than at 30 °C.

Introduction

The development of *ansa*-metallocenes by Brintzinger in 1982[1] in combination with methylalumoxane found by Sinn and Kaminsky[2] opened the door to a variety of stereoregular polymers.[3−8] In the past years, a number of C_1-symmetric metallocenes have been synthesized and used for propene polymerization as well as for alternating ethene/propene copolymerizations.[9,10] In general, two classes of C_1-symmetric complexes can be separated: first, metallocenes with the basic structure $[R_2X(9\text{-}\eta^5\text{-Flu})(3\text{-R}'\text{-}\eta^5\text{-Cp})]ZrCl_2$ (with X = C or Si), producing hemiisotactic−isotactic polypropene[11] and alternating ethene/propene copolymers with a moderate amount of alternating triads[12] and an isotactic structure;[13] second, complexes according to the structure $[R_2X(9\text{-}\eta^5\text{-Flu})(1\text{-}\eta^5\text{-Ind})]ZrCl_2$, which yield moderate isotactic polypropene[14,15] and alternating, atactic ethene/propene copolymers.[16,17] Substitutions at the ligand framework have a strong influence on the polymer microstructure and properties. For example, $[Me_2Si(9\text{-}\eta^5\text{-Flu})(1\text{-}\eta^5\text{-Ind})]ZrCl_2$ (**1**) produces moderate isotactic polypropene and an atactic alternating ethene/propene copolymer with a very low molar mass, whereas $[Me_2Si(9\text{-}\eta^5\text{-Flu})(4,7\text{-Me}_2\text{-}1\text{-}\eta^5\text{-Ind})]ZrCl_2$ yields syndiotactic polypropene and atactic alternating ethene/propene copolymer with a high molar mass.[18] A high number of different substitutions at the indenyl or cyclopentadienyl ligand in these types of metallocenes have been reported in the past years, but to our best knowledge, no polymerization results with C_1-symmetric catalysts with substituted fluorenyl ligands have been published yet. These kinds of substitution patterns are well-known for C_s-symmetric complexes, increasing the syndiotacticity of polypropene in comparison to the unsubstituted species.[19,20]

In this work, we present results of propene homopolymerization and ethene/propene copolymerizations with eight different C_1-symmetric metallocenes. Six of these catalysts (**3**−**8**), with bulky substituents at the fluorenyl ligand, have been synthesized for the first time and compared in their polymerization behavior to the unsubstituted complexes. The used metallocenes are shown in Figure 1.

Results and Discussion

Influence of the Polymerization Temperature. The polymerization behavior and the polymer properties are primarily dependent on the temperature. In general, the catalyst selectivity is high at low polymerization temperatures, resulting in very stereo- or regioregular polymers, but the activity is moderate. To acquire a complete overview of the performance of the catalysts, alternating copolymers, containing 50 ± 2% propene, were synthesized at different polymerization temperatures in the range from 0 to 60 °C. The complete polymerization results are summarized in Table 1.

The results in Table 1 show clearly a strong decrease of activity with growing sterical demand of the substituents at the ligand framework at low temperatures. Especially the cyclic substitution of catalysts **5**−**8** leads to extremely low activities at 0 or 15 °C but causes on

---

* Corresponding author. E-mail kaminsky@chemie.uni-hamburg.de.

10.1021/ma048009z CCC: $30.25

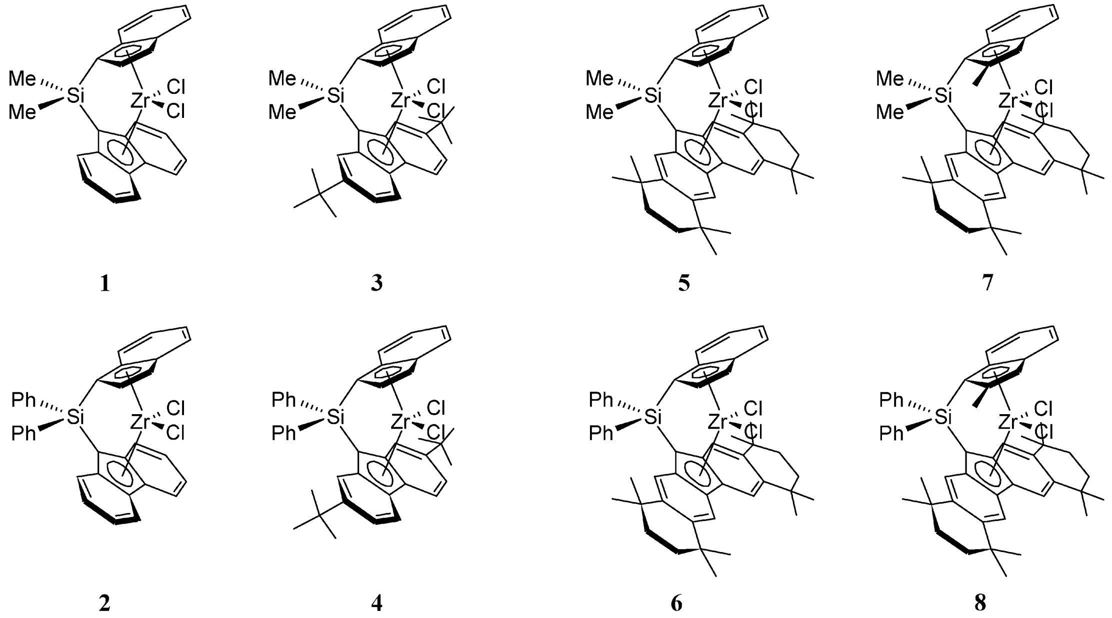

Figure 1. Metallocenes used in this work for propene homopolymerization and ethene/propene copolymerizations.

Table 1. Ethene/Propene Copolymerizations at Different Temperatures

entry	metallocene	T_P[a]	yield [g]	activity[b]	$M_W \times 10^3$[c]	T_g[d]	x_P[e]	X_P[f]	% EPE + PEP[g]
1	**1**	0	1.90	1580	20.0	−64.3	0.503	0.98	0.826
2	**1**	15	1.92	6400	19.9	−63.0	0.491	0.965	0.796
3	**1**	30	1.27	25 400	20.9	−61.7	0.507	0.965	0.749
4	**1**	45	1.01	30600	24.8	−61.9	0.481	0.96	0.724
5	**1**	60	0.90	21800	27.1	−61.2	0.486	0.95	0.633
6	**2**	0	2.04	2550	29.8	−59.7	0.496	0.97	0.799
7	**2**	15	1.77	8550	31.7	−59.3	0.496	0.96	0.774
8	**2**	30	2.46	36900	34.5	−57.1	0.497	0.96	0.732
9	**2**	45	2.38	72120	36.8	−57.7	0.492	0.95	0.675
10	**2**	60	1.37	49820	39.3	−58.5	0.491	0.94	0.601
11	**3**	0	0.72	480	14.9	−65.3	0.489	0.98	0.855
12	**3**	15	1.95	3250	15.0	−60.9	0.493	0.97	0.821
13	**3**	30	1.43	9500	15.1	−63.7	0.501	0.97	0.775
14	**3**	45	1.11	22200	18.2	−60.4	0.502	0.96	0.709
15	**3**	60	1.10	40400	19.0	−60.1	0.486	0.94	0.612
16	**4**	0	1.85	1540	22.4	−61.5	0.496	0.965	0.846
17	**4**	15	1.57	10470	24.4	−60.5	0.499	0.965	0.826
18	**4**	30	2.14	42800	25.9	−59.9	0.496	0.96	0.772
19	**4**	45	1.76	107000	32.6	−58.5	0.504	0.95	0.689
20	**4**	60	1.90	139600	35.0	−57.9	0.494	0.93	0.578
21	**5**	0	0.30	18	n.d.[h]	−50.1	0.474	0.985	0.520
22	**5**	15	0.56	112	59.6	−56.7	0.482	0.98	0.658
23	**5**	30	0.92	1150	55.1	−57.7	0.493	0.97	0.705
24	**5**	45	1.85	9250	50.7	−59.4	0.490	0.95	0.666
25	**5**	60	2.20	53330	37.9	−57.3	0.486	0.93	0.543
26	**6**	0	0.30	25	71.7	−57.3	0.486	0.98	0.785
27	**6**	15	0.51	255	65.8	−57.9	0.507	0.98	0.802
28	**6**	30	1.46	3650	76.6	−56.3	0.505	0.965	0.754
29	**6**	45	2.67	40050	79.6	−56.5	0.490	0.94	0.671
30	**6**	60	1.81	131300	77.0	−52.0	0.518	0.93	0.528
31	**7**	0	0.25	3	87.3	−53,5	0.516	0.98	0.620
32	**7**	15	0.80	80	75.3	−58.6	0.509	0.97	0.757
33	**7**	30	1.32	1100	57.7	−58.0	0.506	0.97	0.765
34	**7**	45	1.38	13800	48.6	−58.6	0.495	0.96	0.739
35	**7**	60	1.50	24240	65.8	−58.1	0.505	0.95	0.698
36	**8**	0	0.16	6	152.5	−54.7	0.517	0.98	0.727
37	**8**	15	0.58	193	160.1	−54.8	0.515	0.975	0.749
38	**8**	30	0.76	1900	150.6	−56.9	0.502	0.965	0.750
39	**8**	45	1.11	16820	160.1	−57.2	0.513	0.96	0.740
40	**8**	60	1.13	82180	155.7	−53.8	0.487	0.94	0.681

[a] Polymerization temperature in °C. [b] Activity in $\text{kg}_{\text{polymer}}/(\text{mol}_{\text{Zr}}\ \text{h}\ \text{mol}_{\text{monomer}}/\text{L})$. [c] Molar mass in g/mol measured by high-temperature GPC; polydispersities are for all copolymers in the range of 2. [d] Glass transition temperature in °C measured by DSC. [e] Incorporation rate of propene in the polymer. [f] Percentage of propene in feed. [g] Percentage of alternating triads calculated by Randall's method.[14] [h] Not determined.

the other hand a supreme stability at higher temperatures. For that reason, these species are much more active at 60 °C compared to the unsubstituted metallocenes **1** and **2**. The latter complexes show a decrease

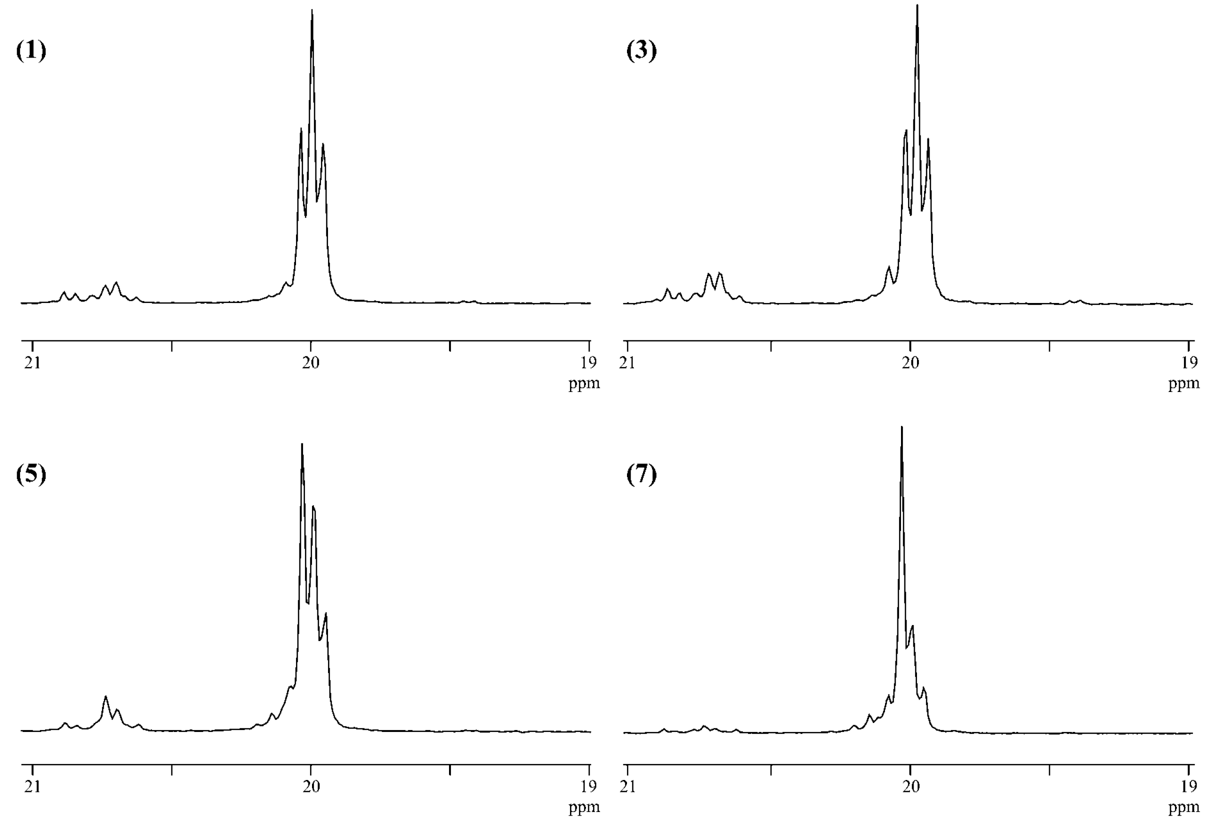

Figure 2. ^{13}C NMR spectra (methyl region) of alternating ethene/propene copolymers, synthesized with metallocenes **1**, **3**, **5**, and **7**.

of activity at polymerization temperatures higher than 45 °C according to a larger amount of irreversible deactivation reactions of the catalyst. The *tert*-butyl substitution of species **3** and **4** enhances the stability of the complexes, but only with the cyclic substituents (metallocenes **5**−**8**) an exponential increase of activity up to 60 °C is observed, indicating that only these catalysts show nearly no deactivation at this temperature. The bridging unit strongly affects the activity; the values reached with catalysts containing the Ph_2Si bridge are up to 4 times higher than the ones achieved with the comparable Me_2Si-bridged species. The temperature stability is not influenced by the bridge.

The molar mass of the alternating copolymers is mainly dependent on the substitution pattern of the ligands, especially the catalysts with the methyl group at the indenyl ligand (**7** and **8**) yield copolymers with a high molar mass. These observations correspond with results by Waymouth, who found a metallocene with methyl substitutions at the indenyl ligand to produce copolymers with high molar mass.[18] Furthermore, it has to be noticed that catalysts with a Ph_2Si bridge lead to polymers with distinctly higher molar masses than the corresponding complexes with a Me_2Si bridge.

The glass transition temperature depends on the amount of propene in the polymer as well as on the percentage of alternating triads. Repeating propene units in the polymer chain increase the glass transition temperature. For that reason, polymers with a high percentage of alternating triads, and therefore less propene diads and triads, show the lowest glass transition temperature. With metallocene **3**, −65 °C was achieved (entry 11), coming close to the value for complete alternating copolymers predicted by Fusco[22] (−69 °C).

Microstructure. The alternating part of the copolymers is at 30 °C comparable for all catalysts; except for **5**, the percentage of alternating triads is about 75%. As one would expect, the selectivity of catalysts **1**−**4** increases at lower polymerization temperatures, resulting in higher values for the alternating triads. Surprisingly, with the cyclic substituted metallocenes **5**−**8**, a decrease is observed when the temperature is below 30 °C. This effect is dramatic for the catalysts with the Me_2-Si bridge (**5** and **7**). A possible explanation for this behavior is the very poor activity these catalysts reach at low temperatures. In these cases, when the insertion reactions are very slow, the backskips are supposed to gain more relevance than at higher temperatures, when the insertions take place more rapidly[17,23−25] (see also Figure 3). With an increased number of backskips compared to insertion reactions, the percentage of alternating triads becomes lower.

At higher temperatures, a decreasing part of alternating triads is observed, according to the lower selectivity of the catalyst. It has to be pointed out that even at 60 °C species **7** and **8** yield copolymers with 70% alternating triads, a remarkably high value.

There are still open questions concerning the alternating polymerization mechanism, but the one specified by Waymouth[17] explains the experimental results very well. Only the insertion at the sterically hindered coordination site is stereospecific;[26] in the case of alternating ethene/propene copolymerizations, ethene is inserted at this site and propene at the other, less sterically hindered coordination site. For that reason, this type of catalyst usually yields atactic ethene/propene copolymers.

Figure 2 shows the EPE triad (methyl region) from the ^{13}C NMR spectra only of the copolymers produced

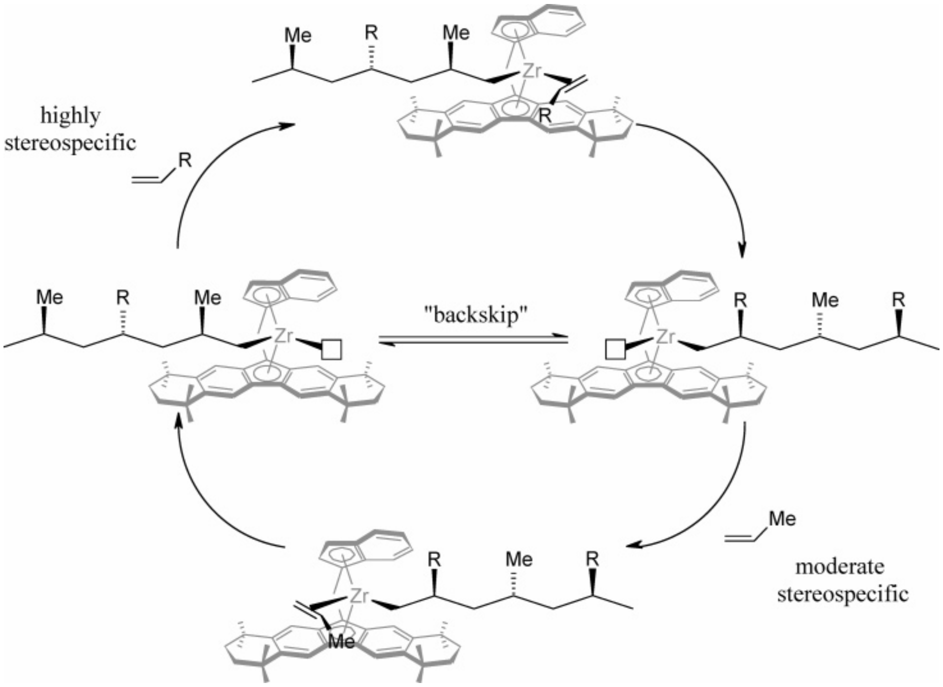

Figure 3. Proposed mechanism for alternating copolymerization (R = H) and propene homopolymerization (R = Me) with bridged indenyl/substituted fluorenyl−zirconium complexes.

Table 2. Polymerization of Propene by Metallocene 1−8 and MAO as Cocatalyst at 30 °C[a]

metallocene	activity (kg_{PP}/mol_{Zr} h [P])	M_w (g/mol)	T_m (°C)	T_g (°C)
1	720	49 700	143	−10
2	840	125 000	142	−5.6
3	287	26 000		−16.4
4	1150	47 000		−14.4
5	2151	237 000		−7.2
6	310	208 000		−3.9
7	311	299 000		−2.2
8	740	456 000		−1.3

[a] Yield in all runs around 2 g; $M_w/M_n = 2$.

with the Me_2Si-bridged catalysts **1**, **3**, **5**, and **7** because the bridging unit has no influence on the microstructure. The tacticity of the copolymer can be determined by the relation of the *mm*-triad (20.12 ppm), the *mr*- and *rm*-triad (20.08 ppm), and the *rr*-triad (20.04 ppm).[27] Atactic copolymers have a 1:2:1 ratio of the three signals, as can be seen for catalysts **1** and **3** in Figure 2. Catalyst **5** and especially species **7** show a tendency toward isotactic copolymers; the percentage of the *mm*-triad is significantly increased.

This behavior can have two reasons: The first possibility is that the insertion of propene takes place at the sereoselective working, sterically hindered coordination site and the ethene insertion at the other one. Because of the big sterical demand of the cyclic substituents, this seems to be very implausible. The alternative, more likely explanation is that the insertion is stereospecific at both coordination sites. Figure 3 shows the alternating mechanism of the ethene/propene copolymerization and also the steric control for the propene homopolymerization. To confirm this assumption, the microstructures of propene homopolymers were determined at 30 °C. The results are shown in Tables 2 and 3.

Metallocenes **1**−**4** yield propene homopolymers with a slight isotactic structure, as expected for this type of catalyst. With the cyclic substitution at the fluorenyl ligand, the microstructure of the polymer changes from an atactic structure (**5** and **6**) to moderate syndiotactic polypropene (**7** and **8**). This is an evidence for two stereospecific coordination sites at metallocenes **5**−**8**, caused by the cyclic substitution of the fluorenyl ligand and intensified by the methyl substitution at the indenyl ligand.

Influence of Monomer Concentration. To determine the influence of the backskip mechanisms on the microstructure, alternating copolymerizations were carried out at 30 °C under different monomer concentrations. It can be presumed that backskips are the main reason for the formation of nonalternating sequences because the 50/50 copolymers contain besides the alternating triads mainly ethene and propene diads. The insertion of a monomer at the "wrong" coordination site

Table 3. Pentad Distribution of Propene Homopolymers

metallocene	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*rrmr* + *mmrm*	*mrmr*	*rrrr*	*rrrm*	*mrrm*
1	0.310	0.166	0.035	0.157	0.098	0.040	0.036	0.066	0.094
2	0.302	0.160	0.030	0.179	0.091	0.037	0.045	0.066	0.089
3	0.366	0.163	0.024	0.102	0.126	0.046	0.023	0.064	0.086
4	0.317	0.161	0.028	0.117	0.123	0.053	0.028	0.074	0.100
5	0.139	0.127	0.040	0.139	0.162	0.067	0.100	0.137	0.088
6	0.093	0.104	0.040	0.130	0.172	0.068	0.149	0.168	0.076
7	0.040	0.064	0.041	0.127	0.102	0.021	0.383	0.171	0.050
8	0.033	0.056	0.041	0.124	0.116	0.021	0.392	0.173	0.044

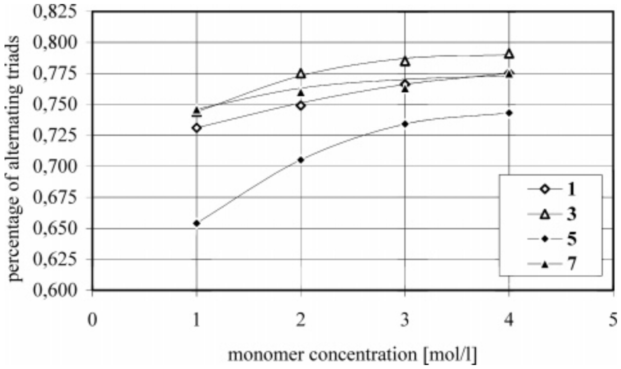

Figure 4. Influence of the monomer concentration on the percentage of alternating triads.

(e.g., propene at the right site in Figure 3) leads to the corresponding triad in the polymer when otherwise "normal" insertions are assumed. The absence of ethene and propene triads indicates that these kinds of misinsertions are rare. Because the backskip is not dependent on the monomer concentration, a variation alters the ratio of backskip to insertion and should therefore have an influence on the percentage of alternating triads. Figure 4 shows this dependency for the Me_2Si-bridged catalysts; the corresponding species with the Ph_2Si bridge possess no significant differences.

It can be seen clearly that with decreasing monomer concentration the percentages of alternating triads become lower for all catalysts. As Rieger found for propene homopolymerization,[25] the increase of isotacticity with decreasing monomer concentration, this behavior is another clear example for the influence of backskips on the polymer microstructure.

Conclusions

All examined catalysts produce highly alternating ethene/propene copolymers; an increase of the percentage of alternating triads in comparison to the unsubstituted reference catalysts is only possible with the *tert*-butyl-substituted species **3** and **4**. The substitution pattern of metallocenes **5**−**8** primary alters the activity. These systems have a very low activity at temperatures below 30 °C but show on the other hand a remarkable temperature stability. Especially catalysts **7** and **8** are very active at 60 °C and yield in addition copolymers with the highest percentage of alternating triads observed at this temperature. The molar masses achieved with catalyst **8** are furthermore with 150 000 g/mol an order of magnitude higher than for the reference system **1**. The cyclic substitution of metallocenes **5**−**8** leads to ethene/propene copolymers and propene homopolymers with an exceptional microstructure. The copolymers show a tendency toward isotactic structures; the homopolymers are slightly syndiotactic, indicating that both coordination sites are stereoselective. The backskip mechanism is the main reason for the nonalternating sequences in the copolymer chains, as can be concluded by the decrease of the percentage of alternating triads at low monomer concentrations.

Experimental Section

General Remarks. Catalyst synthesis were performed under standard Schlenk and glovebox techniques, and only dried solvents were used. The fluorene derivatives were synthesized according to the literature procedures: Kajihaeshi's method[29] for 2,7-di-*tert*-butylfluorene and the method from Kagechika[30] and Bercaw[31] for 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]fluorene. Metallocenes were synthesized according to Alt,[32] and the reactions leading to the ligands containing a Ph_2Si bridge were monitored by ^1H NMR spectroscopy because the reaction times strongly differ from those of the Me_2Si bridged species. Methylalumoxane (MAO) was purchased from Crompton as a solution in toluene containing trimethylaluminum (TMA). The solution was filtered, the solvent condensed, and the residue dried in vacuo yielding solid, TMA-free MAO.

Ethene/Propene Copolymerizations. The copolymerizations were performed in a 500 mL glass autoclave in 200 mL of toluene. MAO was added to the toluene, and the solution was cooled or heated to the required temperature. The mixture was saturated with propene and subsequent with ethene before the polymerization was started by addition of the metallocene complex solution. The monomer incorporation was monitored by a mass flow controller and the reaction terminated after a consumption of about 5% by addition of 10 mL of ethanol. The polymer solution was stirred overnight in 300 mL of diluted hydrochloric acid; the organic layer was separated and washed several times with water before the solvent was removed in vacuo. The polymers were dried under reduced pressure at 40 °C overnight (example polymerization with metallocene complex **8**, polymerization temperature 30 °C, propene pressure 2.60 bar = 1.93 mol/L, ethene pressure 0.60 bar = 0.07 mol/L, 0.2×10^{-6} mol of **8**, 200 mg (3.45 mmol of Al) MAO; Al:Zr = 17 250, polymerization time 1 h, yield 0.76 g [see Table 1]).

Propene Homopolymerizations. The propene polymerizations were performed in a 500 mL glass autoclave in 200 mL of toluene at 30 °C with a monomer pressure of 2.67 bar (propene concentration = 2.0 mol/L). The reaction vessel was charged with solid MAO, toluene, and propene, and the reaction was started after complete saturation by addition of the metallocene complex solution and terminated after 1 h by addition of 10 mL of ethanol. The reaction mixture was stirred with diluted hydrochloric acid overnight; the organic layer was separated and washed several times with water. The solvent was removed in vacuo and the polymer dried under reduced pressure at 40 °C overnight (example polymerization with metallocene complex **8**, polymerization temperature 30 °C, propene pressure 2.67 bar = 2.00 mol/L, 0.5×10^{-6} mol of **8**, 200 mg (3.45 mol of Al) of MAO, Al:Zr = 6900, polymerization time 2.5 h, yield 1.85 g [see Table 2]).

Metallocene Complex. The synthesized precatalysts were examined by ^1H NMR spectroscopy and elemental analysis. The unsubstituted species **1** and **2** have already been described.[21] The spectra have been recorded at 400 MHz in $CDCl_3$ as solvent; chemical shifts are given in ppm.

[Dimethylsilyl-(1-η^5-indenyl)(2,7-di-*tert*-butyl-9-η^5-fluorenyl)]-zirconium dichloride (**3**). ^1H NMR: 0.02 (s, 3H), 0.61 (s, 3H), 1.16 (s, 9H), 1.24 (s, 9H), 5.88 (d, J = 3.1 Hz, 1H), 6.08 (d, J = 3.1 Hz, 1H), 6.65 (s, 1H), 7.11 (m, 2H), 7.15 (s, 1H), 7.23 (m, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H). Elemental analysis: C: 62.98% (exp 62.92%), H: 6.03% (exp 5.94%).

[Diphenylsilyl-(1-η^5-indenyl)(2,7-di-*tert*-butyl-9-η^5-fluorenyl)]-zirconium dichloride (**4**). ^1H NMR: 0.99 (m, 18H), 6.00 (d, J = 3.3 Hz, 1H), 6.69 (m, 1H), 6.72 (s, 1H), 6.85 (d, J = 3.3 Hz, 1H), 7.11 (m, 1H), 7.18 (s, 1H), 7.22 (m, 1H), 7.30 (m, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.54−7.62 (m, 6H), 7.82 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 8.20 (m, 2H), 8.34 (m, 2H). Elemental analysis: C: 68.60% (exp 68.63%), H: 5.55% (exp 5.49%).

[Dimethylsilyl-(1-η^5-indenyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)]-zirconium dichloride (**5**). ^1H NMR: 1.11 (s, 3H), 1.19 (s, 3H), 1.25 (s, 3H), 1.33 (s, 9H), 1.37 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 1.52 (s, 3H), 1.64 (m, 4H), 1.74 (m, 4H), 5.77 (d, J = 3.1 Hz, 1H), 6.70 (d, J = 3.1 Hz, 1H), 6.84 (dd, J = 7.6 Hz, 1H), 7.11 (dd, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.50 (s, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.82 (s, 1H), 7.92 (s, 1H). Elemental analysis: C: 66.84% (exp 66.82%), H: 6.93% (exp 6.73%).

[Diphenylsilyl-(1-η^5-indenyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)]zirconium dichloride (**6**). ^{1}H NMR: 0.74 (s, 3H), 0.80 (s, 3H), 0.86 (s, 3H), 1.06 (s, 3H), 1.31 (s, 3H), 1.33 (s, 3H), 1.37 (s, 3H), 1.47 (s, 3H), 1.56−1.66 (m, 8H), 5.95 (d, $J = 3.2$ Hz, 1H), 6.57 (s, 1H), 6.67 (dd, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 3.2$ Hz, 1H), 7.11 (dd, $J = 7.6$ Hz, 1H), 7.14 (s, 1H), 7.25 (d, $J = 8.6$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.54−7.61 (m, 6H), 7.84 (s, 1H), 7.93 (s, 1H), 8.17 (m, 2H), 8.34 (m, 2H). Elemental analysis: C: 71.23% (exp 71.22%), H: 6.31% (exp 6.22%).

[Dimethylsilyl-(2-methyl-1-η^5-indenyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)]zirconium dichloride (**7**). ^{1}H NMR: 1.13 (s, 3H), 1.24 (s, 3H), 1.28 (s, 3H), 1.30 (s, 6H), 1.34 (s, 3H), 1.38 (s, 3H), 1.39 (s, 3H), 1.48 (s, 3H), 1.49 (s, 3H), 1.62 (m, 4H), 1.72 (m, 4H), 2.27 (s, 3H), 6.61 (s, 1H), 6.75 (dd, $J = 7.6$ Hz, 1H), 7.06 (dd, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.49 (s, 1H), 7.60 (s, 1H), 7.67 (d, $J = 8.6$ Hz, 1H), 7.78 (s, 1H), 7.88 (s, 1H). Elemental analysis: C: 67.22% (exp 67.18%), H: 6.94% (exp 6.88%).

[Diphenylsilyl-(2-methyl-1-η^5-indenyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-9-η^5-fluorenyl)]zirconium dichloride (**8**). ^{1}H NMR: 0.77 (s, 3H), 0.84 (s, 3H), 1.02 (s, 3H), 1.03 (s, 3H), 1.33 (s, 6H), 1.40 (s, 3H), 1.47 (s, 3H), 1.54−1.70 (m, 8H), 2.07 (s, 3H), 6.54 (dd, $J = 7.8$ Hz, 1H), 6.70 (s, 1H), 7.05 (dd, $J = 7.8$ Hz, 1H), 7.17 (s, 1H), 7.20 (d, $J = 8.7$ Hz, 1H), 7.23 (s, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.83 (s, 1H), 7.94 (s, 1H), 7.49−7.55 (m, 6H), 8.21 (m, 2H), 8.29 (m, 2H). Elemental analysis: C: 71.42% (exp 71.46%), H: 6.39% (exp 6.35%).

Supporting Information Available: Complete copolymerization results at 30 °C and triad distribution of all copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233−247.
(2) Andresen, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem.* **1976**, *88*, 688−689.
(3) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252.
(4) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *107*, 1255−1283.
(5) Spaleck, W.; Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Winter, A. *New J. Chem.* **1990**, *14*, 499.
(6) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443−533.
(7) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.
(8) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982−3998.
(9) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapleton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 7930−7941.
(10) Razawi, A.; Bellina, V.; De Brauwer, Y.; Hortmann, K.; Peters, L.; Ssirole, S.; Van Belle, S.; Thewalt, S. *Macromol. Chem. Phys.* **2004**, *205*, 347−356.
(11) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934−945.
(12) Arndt, M.; Kaminsky, W.; Schauwienold, A.-M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135−1152.
(13) Fan, W.; Leclerc, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 9555−9563.
(14) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1999**, *18*, 1439−1443.
(15) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1−9.
(16) Jin, J.; Uozumi, T.; Sano, T.; Teranishi, T.; Soga, K.; Shiono, T. *Macromol. Rapid Commun.* **1998**, *19*, 337−339.
(17) Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 8619−8625.
(18) Fan, W.; Waymouth, R. M. *Macromolecules* **2003**, *36*, 3010−3014.
(19) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *522*, 39−54.
(20) Miller, S. A.; Bercaw, J. E. *Organometallics* **2004**, *23*, 1777−1789.
(21) Randall, J. C. *J. Macromol. Sci.* **1989**, *C29*, 201−317.
(22) Allegra, G.; Caccianotti, L.; Fusco, R. *Macromolecules* **1998**, *31*, 5487−5494.
(23) Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1996**, *29*, 4834−4845.
(24) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelae, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355.
(25) Rieger, B. *Organometallics* **2000**, *19*, 3767−3775.
(26) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954−963.
(27) Zetta, L.; Gatti, G.; Audioso, G. *Macromolecules* **1978**, *11*, 763−766.
(28) Rieger, B.; Jany, G.; Fawzi, R.; Steinmann, M. *Organometallics* **1994**, *13*, 647−653.
(29) Kajihaeshi, S.; Kadowaki, T.; Nishida, A.; Fujisaki, S.; Noguchi, M. *Synthesis* **1984**, 335−337.
(30) Kagechika, H.; Kawachi, E.; Hashimoto, Y.; Himi, T.; Shudo, K. *J. Med. Chem.* **1988**, *31*, 2182−2192.
(31) Bercaw, J. E.; Miller, S. A. US6469188, 2002; *Chem. Abstr.* **2002**, *137*, 311374.
(32) Alt, H. G.; Jung, M. *J. Organomet. Chem.* **1998**, *562*, 229−253.

MA048009Z