Articles

Copolymerization of Ethylene and Propylene with the Sterically Hindered Monomer 3-Methyl-1-butene by Homogeneous Catalysis

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ABSTRACT: Homogeneous catalysts in addition with MAO were used to synthesize copolymers of 3-methyl-1-butene (3MB1) with ethylene and propylene. Three series of ethylene/3MB1 copolymerizations were catalyzed by the organometallic compounds $[Me_2Si(Me_4Cp)(N^tBu)]TiCl_2$ (**1**), $[Ph_2Si(OctHFlu)(Ind)]ZrCl_2$ (**2**), and *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**3**). For the copolymerization of 3MB1 with propylene, the metallocenes *rac*-$[Me_2C(Ind)_2]$-$ZrCl_2$ (**3**) and $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) were used. For each metallocene, the influence of the molar fraction of 3MB1 in the feed as well as the influence of the polymerization temperature on the copolymerization behavior was investigated. In this regard copolymerization parameters were calculated. All copolymers were characterized by ^{13}C NMR spectroscopy, differential scanning calorimetry, and gel permeation chromatography techniques. Very small amounts of incorporated 3MB1 have a remarkable effect on the melting temperatures of the obtained polymers. Already by incorporation of 1 mol % of 3MB1 in the polymer, the melting temperature of the obtained LLDPE is lowered to 120 °C, whereas twice as much 1-butene is necessary to achieve the same effect, which should facilitate the processing.

Introduction

The copolymerization of sterically hindered monomers with ethylene or propylene leads in general to remarkable losses in activity. Nevertheless, the copolymerization with some of them is an interesting chapter, for the properties of the polymers can be significantly influenced by incorporation of small amounts of the sterically hindered olefins. One example is the synthesis of COCs, which are treated elsewhere in the literature in detail.[1−4] Another group of sterically hindered monomers are branched α-olefins, like 4-methyl-1-pentene and 3MB1, which was used in this study, a class, which is considerably less investigated. There are several publications about 4-methyl-1-pentene as a comonomer,[5,6] but 3MB1 as a comonomer still is a little neglected. This sterically hindered monomer has been nearly exclusively polymerized via classical Ziegler−Natta catalysis with supported catalysts until present, while most series were made as homopolymerizations.[7,8] There are some publications dealing with the properties of the obtained poly(3-methyl-1-butenes).[9,10] Tincul's experiments[11] concerning the ethylene/3MB1 copolymerization by heterogeneous catalysis have shown that the branched monomer works more strongly reducing concerning the density than the corresponding linear α-olefin 1-pentene. Tincul has achieved an incorporation of 10 mol % of the branched olefin by Ziegler−Natta catalysis. With a low incorporation of 1 mol % 3MB1 in the copolymer a maximum concerning the impact strength is reached, while the impact strength decreases with further increasing monomer incorporation. In the case of linear α-olefins, the impact strength of the obtained polymers increases with increasing monomer incorporation, until a plateau (at an incorporation of 4 mol % for 1-pentene and 1-hexene) is approached.

The maximum in impact strength of the ethylene/ 3MB1 copolymers exceeds the maximum values of ethylene/1-hexene or 1-pentene copolymers about ∼15 kJ/m^2.

To the best of our knowledge, only one publication concerning ethylene/3MB1 copolymers produced by metallocene catalysis has been published, which comes from our workgroup some years ago. Beulich[12] used the metallocenes $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$ and $[Me_2Si(Ind)(Flu)]ZrCl_2$ in addition with MAO for the synthesis of these polymers. The new study aims at a broader variety of the applied catalysts and therewith on wider polymer properties. Besides, the successful synthesis of propylene/3MB1 copolymers was accomplished. There has not been any report about these copolymers in the literature yet.

Figure 1 shows the organometallic complexes which were used in the present study. For the copolymerization of ethylene with 3MB1, with the complexes **1**, **2**, and **3** three rather different catalyst precursors were used. For the copolymerizations of propylene with 3MB1, metallocenes **3** and **4** were used.

Compound **1**, $[Me_2Si(Me_4Cp)(N^tBu]TiCl_2$, was developed by Bercaw[13,14] and belongs to the group of the constrained geometry catalysts that were patented at the beginning of the 1990s by Dow Chemicals and Exxon.[15−19] Because of its relatively open structure, normally no steric control is given, and copolymers with a good incorporation rate also in the case of steric hindrance are accessible.

Catalyst precursor **2**, $[Ph_2Si(OctHFlu)(Ind)]ZrCl_2$, was first time synthesized in our workgroup.[20] It contains a highly substituted fluorenyl ligand. The substituent is the 1,1,4,4,7,7,-

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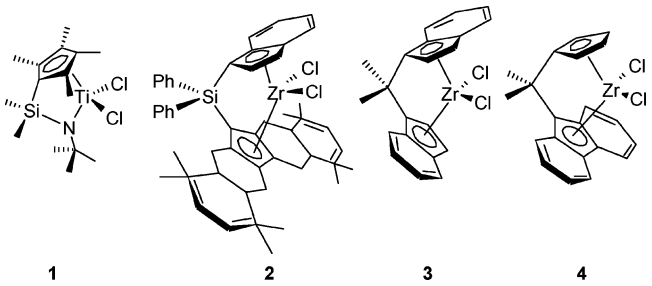

Figure 1. Catalyst precursors used in this work for the copolymerization of ethylene or propylene with 3-methyl-1-butene.

10,10-octamethyl-1,2,3,4,7,8,9,19-octahydrodibenzo rest, which has a positive influence on the syndiotacticity.[21] *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**3**) is a C_2-symmetric metallocene and thus produces isotactic polypropylene, whereas [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (**4**) as a C_s-symmetric metallocene produces syndiotactic polypropylene. Hence, for the propylene/3MB1 copolymerizations two metallocenes were used which transfer different stereoregularity.

For each metallocene, two series were made, analyzing the effect of the variation of the both most important parameters in a polymerization process: the polymerization temperature and the ratio between one monomer and the other one, expressed through the molar fraction.

Experimental Section

General Remarks. All manipulations were conducted under an argon atmosphere using standard Schlenck, syringe, and glovebox techniques. Argon was purchased from Linde and purified by passage through a Messer Oxisorb cartridge. Propylene and ethylene were also purchased from Linde and purified by passing through two columns from which the first one was filled with BASF R3-11 catalyst and the second one with 3 Å molecular sieve. Toluene, used as solvent for the polymerization process and the preparation of the metallocene solutions, was purified in a similar manner.

3MB1 was purchased from Sigma Aldrich and was also provided by the OXENO Olefinchemie GmbH respectively. It was condensed in a flask and stirred with TIBA for 4 h. A good cooling of the flask with an ice bath was important, for the 3MB1 has a boiling-point of 20 °C. Afterward the monomer was condensed into a lecture bottle, which was cooled with liquid nitrogen.

Compound (**1**) [$Me_2Si(Me_4Cp)(N^tBu)$]$TiCl_2$ was provided by the CK Witco Corp. The metallocenes [$Ph_2Si(OctHFlu)(Ind)$]$ZrCl_2$ (**2**), *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**3**), and [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (**4**) were synthesized in our workgroup. For further information the appropriate literature is recommended.[22−24] The organometallic compounds were stored under an argon atmosphere in a glovebox.

Polymerization Procedure. The polymerizations were performed in a 1 L Büchi glass autoclave, in which can be worked under gastight conditions up to 6 bar monomer pressure. The pressure during a polymerization run was kept constant by using a pressure control. The gas flow was recorded with a Brooks 5850 TR mass flow meter and an Ahlborn Almemo 2390-5 data logger. Temperature was adjusted with a heat jacket which allowed to keep the temperature constant during the polymerization with an accuracy of ±0.5 °C. For a typical copolymerization procedure, the autoclave was heated in vacuo for 1 h and afterward cooled to the desired temperature. The reactor was charged with 400 mg of MAO, 200 mL of toluene, and 3MB1. After saturation with ethylene or propylene up to the desired feed composition, the polymerization was started by injecting the catalyst solution. The reaction was quenched with 5 mL of ethanol after an adequate reaction time (3MB1 conversion <5%).

The polymer solution was stirred overnight with a solution of diluted hydrochloric acid in ethanol (1 volume part of concentrated hydrochloric acid, 2 volume parts of ethanol, and 7 volume parts of distilled water). In the case of toluene soluble polymers, the organic phase was washed after phase separation with sodium hydrogen carbonate solution and three times with water. Subsequently, the solutions were concentrated to 50 mL in vacuo by means of a rotary evaporator. The polymer was felled by addition of ethanol. Toluene insoluble polymers were also washed. In both cases the polymers were dried in vacuo at 40 °C until the weight remained constant.

Polymerization Parameters. All polymerizations were conducted in 200 mL of purified toluene with 400 mg of MAO. Because of the very high differences in activity, the catalyst concentration had to be varied between the ethylene/3MB1 copolymerizations. All polymerizations were reproduced.

The ethylene/3MB1 copolymerization parameters for the series aiming at an investigation on the influence of the comonomer composition in the feed were—besides the ones mentioned above—as follows: polymerization temperature: 60 °C; polymerization time: in general, 45 min; molar fraction of 3MB1 in the feed (X_{3MB1}): 0.00, 0.20, 0.40, 0.60, 0.80, 0.90, 0.95, 0.98; ethylene pressure: 0.25−4 bar; catalyst concentration: 7.5×10^{-5}−3.75×10^{-4} mmol for **1**, 3.0×10^{-4}−1.5×10^{-3} mmol for **2**, and2.0×10^{-5}−3.75×10^{-4} mmol for **3**.

The polymerization conditions of the other copolymerization series are taken from the footnotes to Tables 2−4.

Polymer Analysis. The samples for ^{13}C NMR spectroscopy were prepared by dissolving 200 mg of the polymer in 2.5 mL of hexachloro-1,3-butadiene and 0.5 mL of 1,1,2,2-tetrachloroethane-d_2 and were measured at 100 °C with a Bruker 400 MHz spectrometer.

Differential scanning calorimetry curves for the determination of the thermal behavior were recorded on a Mettler Toledo DSC 821^e instrument, which had been calibrated with *n*-heptane (−90.6 °C), mercury (−38.8 °C), gallium (29.8 °C), indium (156.6 °C), and zinc (419.5 °C). The samples were heated with a heating rate of 20 °C min^{-1}. Only the second heating cycle was used for the interpretation of the obtained curves. In the case of glass transition temperatures the samples were heated again, this time with a lower heating rate (10 °C min^{-1}).

Size exclusion chromatography was carried out by means of the high-temperature instrument Alliance GPC 2000 from Waters, equipped with an attached viscosity detector unit combined with a refractive index detector, allowing the calculation of the appropriate Mark−Houwink constants for each polymer, and three Styragel type columns (HT6, HT5, HT3). The calibration of the system was made using polystyrene standards with a narrow molecular weight distribution. The measurements were performed in 1,2,4-trichlorobenzene at a temperature of 140 °C and 1.0 mL min^{-1} flow rate. 2,6-Di-*tert*-butylmethylphenol was used as thermostabilizer.

The Py-GC MS was conducted with a GC-17A/QP5000 device from Shimadzu, which was equipped with a Pyr-4A pyrolysis oven. It was calibrated with a PFTBA standard. The ionization was effected by electron bombardment at 70 eV. The carrier gas was helium, and the depolymerization took place at a temperature of 700 °C. Approximately 100 μg of the polymer was put in a platinum crucible and hung over the pyrolysis part. After a short inertization time, the crucible holding was simultaneously opened with the start of the mass spectrometer and of the temperature program of the gas chromatograph.

Results and Discussion

Copolymerizations of Ethylene with 3-Methyl-1-butene. Activities. An important fact was found during the copolymerization series: The ability to be polymerized of different charges of the purchased 3MB1 differs a lot. Also after stirring with TIBA, the activities of the polymerizations for unequal charges are not equal by approximation. There must be impurities in very small amounts like dienes or other sterically hindered monomers than 3MB1, which hinder the polymerization process so that the activities remarkably decrease. In the

Table 1. Signal Assignment of the Carbon Atoms of the Ethylene/3-Methyl-1-butene Copolymers in the ^{13}C NMR Spectrum

^{13}C δ^a [ppm] calculated[b]	^{13}C δ **[ppm]** experimental	assignment[c]	triads[d]	integration area
41.0	44.5	$T_{\delta\delta}$	EME (1)	A
39.1	42.0	$T_{\beta\delta}$	(MME+EMM) (2)	B
36.9	40−39[e]	$T_{\beta\beta}$	MMM (1)	C
34.8	34 − 33[e]	$S_{\gamma\alpha\alpha\gamma}$	MMM (1); (MME + EMM) (1)	D
34.2		$S_{\alpha\alpha\gamma}$		D
33.7	33.4	$S_{\alpha\alpha}$		D
32.3−31.8	32.5−31	$S_{\alpha\delta}$, $S_{\alpha\delta}$	EME (1); MEM (1); (MEE+EEM) (1); (MME + EMM) (1)	E
30.5−29.5	31−29	2iP3	EME (1); (MME + EMM) (2); MMM (1)	F
30.9−29.9	31−29	$S_{\delta\delta}$, $S_{\gamma\delta}$, $S_{\gamma\gamma}$	EEE (2); (MEE + EMM) (1)	F
28.0	28.3	$S_{\beta\delta}$	(EEM + MEE) (2)	G
26.1	26.5	$S_{\beta\beta}$	MEM (1)	H
19.9−19.7	19.8−19	1iP3	EME (2); (EMM + MME) (2); MMM (2)	I

[a] δ = chemical shift. [b] According to Lindeman and Adams. The assignment and the calculations of the chemical shift are given according to the work of Beulich.[25] [c] Carbon atoms of the triad in the corresponding integration area. iP3 = isopropyl side chain counted from the end. S = secondary carbon atom. T = tertiary carbon atom. [d] M = 3MB1. E = ethylene. [e] Poly(3-methyl-1-butene).

Table 2. Properties of the Ethylene/3-Methyl-1-butene Copolymers Synthesized at Different Polymerization Temperatures

catalyst precursor	t_p[a] [°C]	x_{3MB1}[b] [mol %]	T_m or T_g[c] [°C]	M_n[d] [g/mol]	M_w[e] [g/mol]	M_w/M_n
1	45	5.0	83.8	21 400	39 300	1.8
1	60	4.6	90.3	14 300	28 500	2.0
1	75	6.0	96.6	12 800	26 000	2.0
2	45	11.7	53.6	113 500	218 600	1.9
2	60	9.7	63.7	94 800	197 900	2.1
2	75	8.0	74.0	77 900	159 000	2.0
3	45	21.7	-48.4	26 800	43 500	1.6
3	60	19.4	-48.9	15 500	28 100	1.8
3	75	15.6	-50.0	19 300	33 200	1.7

[a] Polymerization temperature. Further polymerization conditions: 0.3 bar ethylene pressure; $X_{3MB1} = 0.90$; 200 mL of toluene; 400 mg of MAO; $n_{Cat} = 2.5 \times 10^{-4}$ mmol for **1**, 1.0×10^{-3} mmol for **2**, and 1.0×10^{-4} mmol for **3**; polymerization time: 45 min for **2** and **3**, 90 min for **1**. [b] Molar fraction of 3MB1 in the polymer. [c] T_m = melting temperature; T_g = glass transition temperature. Glass transition temperatures were detected in the case of metallocene **2**. Additional smaller melting peaks in the DSC curves are neglected in this table. For further information, the supporting tables, which are available as Supporting Information, are recommended. [d] Number-average molecular weight. [e] Weight-average molecular weight.

Table 3. Properties of the Propylene/3-Methyl-1-butene Copolymers Obtained with *rac*-[$Me_2C(Ind)_2$] $ZrCl_2$ (3) and [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (4) at 30 °C

catalyst precursor	X_{3MB1}	x_{3MB1} [mol %]	T_m or T_g [°C]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
3	0.00	0.0	133.9	5 000	9 300	1.9
3	0.20	(>)0.0	130.3	4 600	8 200	1.8
3	0.40	1.0	125.1	4 900	8 100	1.7
3	0.60	3.5	116.9/*−10.2*	4 000	7 600	1.9
3	0.80	8.9	88.5/*−12.5*	52 000	6800	1.3
3	1.00	100.0	295.2	n.d.[c]	n.d.[c]	n.d.[c]
4	0.00	0.0	122.2/133.3/*0.7*	38 300	66 100	1.7
4	0.20	<0.5	123.8/134.5/*1.4*	48 200	78 000	1.6
4	0.40	<0.5	120.5/132.0/*−0.7*	39 200	68 300	1.7
4	0.60	<1	119.9/131.2/*−2.0*	39 300	65 400	1.7
4	0.80	<1	102.0/1162./*−5.0*	30 600	51 200	1.7
4	1.00	100.0	n.d.[b]	n.d.[c]	n.d.[c]	n.d.[c]

[a] Further polymerization conditions: 0.7 bar propylene pressure (exception: $X_{3MB1} = 0.80$: 0.35 bar); 200 mL of toluene; 400 mg of MAO; $n_{Cat} = 2 \times 10^{-3}$ mmol except for the 3MB1 homopolymerization (1×10^{-2} mmol); polymerization time: 1 h. [b] Not detected. [c] Not detected because of insolubility.

case of the purchased 3MB1, the specification promises a purity of 95%, which is fulfilled, which was gas chromatographically proved.

Regarding the catalyst activity for the three catalysts, the following results were obtained, as can be seen in Figure 2 and Figure 3: A comonomer effect was found for all investigated metallocenes. This means that certain, not too high rates of the comonomer in the feed led to a higher activity in comparison to the ethylene homopolymerization. This effect is particularly developed for *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**3**), for which an increase in activity from about 230 000 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}$ for the homopolymerization of ethylene up to 290 000 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}$ for the polymerization of ethylene with a molar fraction of 3MB1 in the feed = 0.20 is given. Further augmentation of the share of the comonomer in the feed leads to a loss of activity. With increasing fraction of 3MB1 in the feed there is a significant decrease in activity. For [Ph_2Si-(OctHFlu)(Ind)]$ZrCl_2$ (**2**) the activities are in a range about a factor of 200.

Concerning the activity against the temperature, one would expect an increase with increasing polymerization temperature, for the activity exponentially depends on the temperature according to the Arrhenius law. Although this simple correlation usually is not given in reality, for termination reactions, which leave the catalyst deactivated behind, increasingly emerge, and for an incorporation of sterically hindered monomers aggravates the next insertion step, the main content of that sentence applies in general, at least to a certain polymerization temperature: As expected, also the investigated metallocenes show the augmentation of the activity with an increase in the polymerization

Table 4. Properties of the Propylene/3-Methyl-1-butene Copolymers Obtained with *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (3) and [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (4) at Different Polymerization Temperatures

catalyst precursor	t_p[a] [°C]	x_{3MB1} [mol %]	T_m or T_g [°C]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
3	15	8.5	88.5/*−13.2*	9 300	14 500	1.6
3	30	9.3	91.1/*−9.8*	4 600	8 200	1.8
3	45	10.0	89.4/*−10.2*	1 900	7 500	3.9
3	60	9.1	66.3/*−17.5*	5 600	8 700	1.6
4	15	<1	128.5/117.2/*−1.1*	41 100	68 000	1.7
4	30	<1	118.6/105.0/*−0.8*	33 500	59 600	1.8
4	45	<1	97.5/*−1.5*	24 300	39 700	1.6
4	60	<1	96.8/*−0.5*	15 600	23 000	1.5

[a] Further polymerization conditions: 0.3 bar propylene pressure; $X_{3MB1} = 0.80$; 200 mL of toluene; 400 mg of MAO; $n_{Cat} = 2 \times 10^{-3}$ mmol; polymerization time: 1 h. [b] Not detected. [c] Not detected because of insolubility.

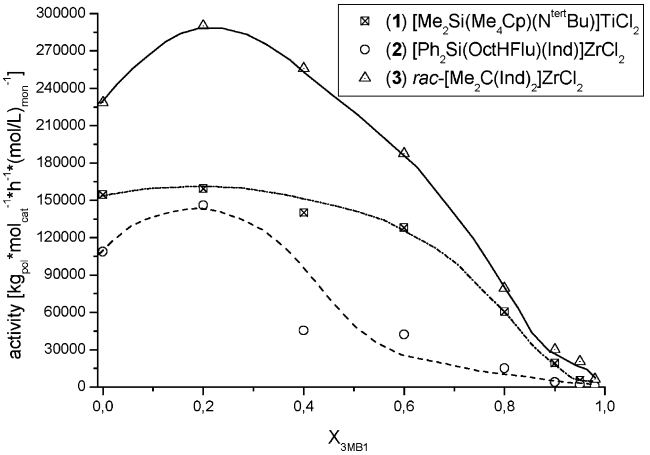

Figure 2. Influence of the molar fraction of 3-methyl-1-butene in the feed on the activity in the series of ethylene/3-methyl-1-butene copolymerizations at a polymerization temperature of 60 °C. For catalyst **1** a former charge of buyable 3-methyl-1-butene was used, which has shown to give higher activities in the polymerization process. X_{3MB1} = molar fraction of 3MB1 in the feed.

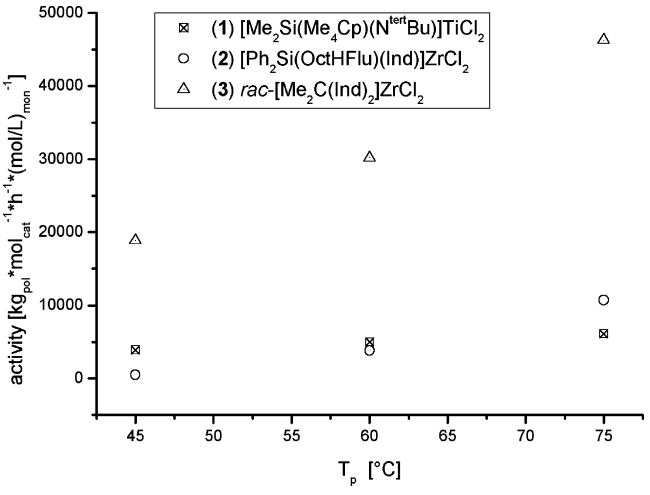

Figure 3. Influence of the polymerization temperature on the activity in the series of ethylene/3-methyl-1-butene copolymerizations at $X_{3MB1} = 0.90$. T_p = polymerization temperature. X_{3MB1} = molar fraction of 3MB1 in the feed.

temperature. This tendency is strongly developed for the metallocene [Ph_2Si(OctHFlu)(Ind)]$ZrCl_2$ (**2**), although compound **1** shows distinctly higher activities. As the monomer flow during the polymerizations was observed, it can be said that the catalysts showed an excellent stability during the polymerizations and that a remarkable deactivation of the catalyst systems **2** and **3** during the polymerization periods was only observed for the polymerizations at 75 °C but for metallocene **3** at 60 °C, probably because of isomerization processes.

Comparing the results for the constrained geometry catalyst **1**, there is a factor of 4 difference between the activities obtained within the two series which has its origin in the fact that two different charges of buyable 3MB1 were used for the ethylene/3MB1 copolymerizations.

Incorporation of 3-Methyl-1-butene. The incorporation of 3MB1 into the ethylene/3MB1 copolymers was quantified by means of ^{13}C NMR spectroscopy according to the interpretation of Beulich,[25] who has assigned the carbon atoms and calculated the triad distribution of obtained copolymers on the basis of calculated shifts by Lindeman and Adams[26] and by comparison with other ethylene/α-olefin copolymers. Besides, Busico et al.[27,28] and Asakura et al.[29] describe the assignment of resonances of poly(3-methyl-1-butenes) in the ^{13}C NMR spectrum. The assignment was confirmed by means of ^{13}C NMR DEPT spectroscopy experiments.

^{13}C NMR spectra of the obtained ethylene/3MB1 copolymers with the respective highest achieved comonomer incorporation x_{3MB1} of each metallocene are shown in Figure 4. Integration areas are additionally marked; the signal assignment is given in Table 1. For further calculation steps the literature is recommended. If integration area C is included into these calculations, a higher share of 3MB1 double blocks than triple blocks is obtained, which is a contradiction. Therefore, this integration area is not considered in the present study; it can probably be ascribed to end groups or misinsertions.

For catalyst precursor **1**, several additional signals can be detected, which can be assigned to end groups and misinsertions because of 2,1-insertions.[30,31] In the case of catalyst **2**, no additional signals are obtained and for the polymers synthesized with metallocene **3** there is just one additional signal in the ^{13}C NMR spectrum at a shift of about 20.4 ppm, which refers to isoheptyl or isopentyl end groups.

As can be seen in Figure 5, high incorporation rates of 3MB1 can only be achieved with very high shares of the comonomer in the feed. With [$Me_2Si(Me_4Cp)(N^tBu)$]$TiCl_2$ (**1**) at $X_{3MB1} = 0.98$, an incorporation rate of 18 mol % of 3MB1 in the copolymer was obtained ($r_E = 165.1$; $r_{3MB1} = 6.60 \times 10^{-8}$). Although the metallocene [Ph_2Si(OctHFlu)(Ind)]$ZrCl_2$ (**2**) leads to higher incorporation rates at lower molar fractions of 3MB1 in the feed, the maximum incorporation rate obtained is hardly higher (19 mol %). The copolymerization parameters for this metallocene, calculated according to Markov first order, are $r_E = 119.9$ and $r_{3MB1} = 1.63 \times 10^{-9}$. A remarkable high incorporation rate is achieved with the bis-indenyl system (**3**) with a maximum value of 37 mol % incorporated 3MB1 at $X_{3MB1} = 0.98$. The much lower copolymerization parameter $r_E = 27.7$ ($r_{3MB1} = 7.10 \times 10^{-8}$) shows the much better copolymerization behavior toward 3MB1.

As regards the incorporation rate in dependence on the polymerization temperature (Table 2), the incorporation rate in the cases of metallocenes **2** and **3** decreases with increasing

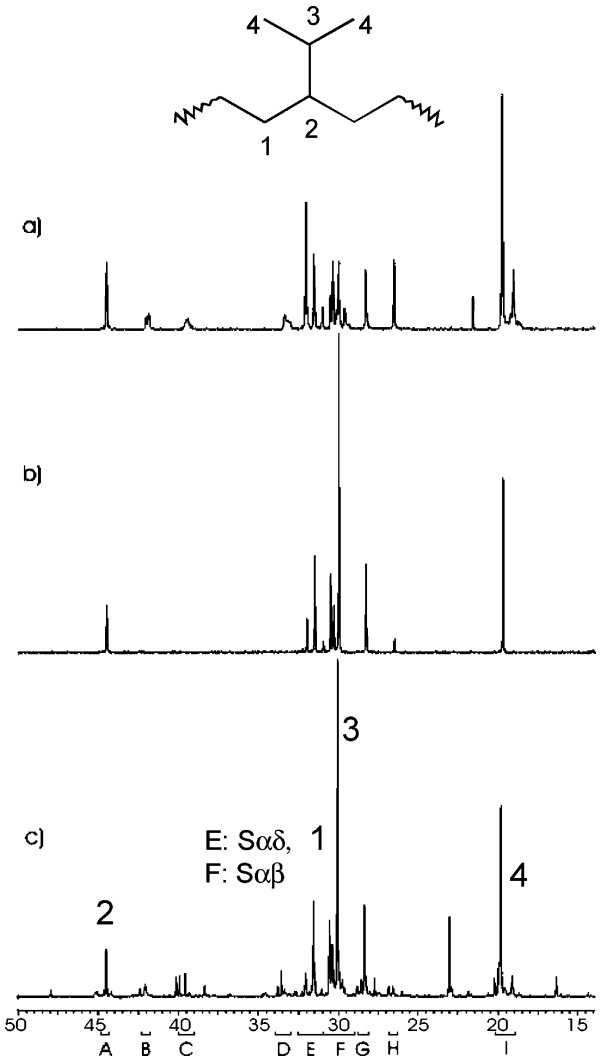

Figure 4. ^{13}C NMR spectra of the obtained ethylene/3-methyl-1-butene copolymers with the respective highest achieved comonomer incorporation produced with (a) *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**3**) (x_{3MB1} = 37 mol %), (b) [Ph_2Si(OctHFlu)(Ind)]$ZrCl_2$ (**2**) (x_{3MB1} = 19 mol %), and (c) [Me_2-$Si(Me_4Cp)(N^tBu)$]$TiCl_2$ (**1**) (x_{3MB1} = 18 mol %). The scale is given in ppm.

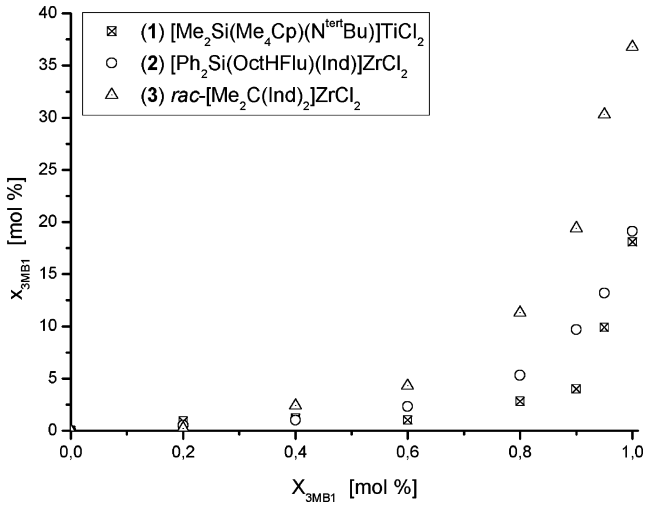

Figure 5. Incorporation of 3-methyl-1-butene into the ethylene/3-methyl-1-butene copolymers for different catalyst precursors at a polymerization temperature of 60 °C. X_{3MB1} = molar fraction of 3MB1 in the feed. x_{3MB1} = percentage of 3MB1 in the polymer.

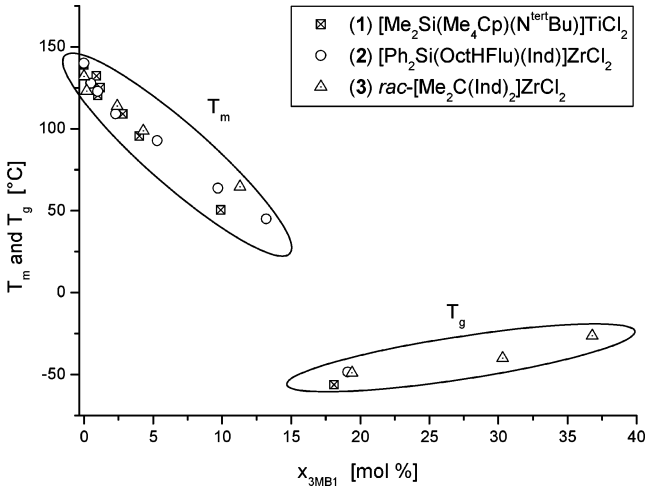

Figure 6. Thermal behavior of the ethylene/3-methyl-1-butene copolymers, produced at 60 °C with different catalysts. x_{3MB1} = molar fraction of 3MB1 in the polymer. T_g = glass transition temperature. T_m = melting temperature.

polymerization temperature as was to be expected. In general, the catalyst selectivity is higher at lower polymerization temperatures. For the constrained geometry catalyst **1**, on the other hand, the polymerization temperature seems to have no influence on the incorporation rate. This behavior is not astonishing since compound **1** has a very open structure by itself.

Thermal Behavior. The thermal behavior of the obtained ethylene/3MB1 copolymers is shown in Figure 6 and in Table 2.

Up to an incorporation of 3MB1 of ~15 mol % in the polymer melting temperatures can be detected. Glass transition temperatures were detected for higher incorporation rates of the comonomer. The melting temperatures decrease with an increase in the incorporation of 3MB1 into the polymer chain, because an increasing incorporation of 3MB1 intercepts the EEE block structure to an increasing degree, resulting in a decreased crystallinity. Besides, melting temperatures decrease with increasing molar masses in general. There were no significant differences between the catalysts to detect. The glass transition temperatures show their lowest value at −57 °C at an incorporation of 3MB1 of 18 mol %. With a further increase in incorporated 3MB1, glass transition temperatures increase. It might be tentatively estimated that this behavior can be ascribed to an increasing crystallinity, for the relatively high shares of 3MB1 in the polymer chain might form crystallizable regions by themselves. This coherence exceeds the influence of the decreasing molar masses, which lead to decreased glass transition temperatures in general. An explanation may be the increasing existence of 3MB1 double blocks, which disturb the alternating structure. With metallocene [Ph_2Si(OctHFlu)(Ind)]-$ZrCl_2$ (**2**) beginning with an incorporation of 3MB1 of 10 mol % and with *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**3**) starting at 4 mol % incorporated 3MB1, there are additional melting peaks to detect in the DSC curves, which are not shown in Figure 6. Their share on the whole copolymers, assessable from the peak area in the thermogram, is low. These additional melting temperatures decrease with increasing incorporation of 3MB1 and are ≥120 °C. They are probably to ascribe to EEE block structures. Because of GPC experiments, a bimodality of the copolymers could be excluded.

As for the investigations of the thermal behavior in dependence on the polymerization temperature, one would expect that with increasing incorporation of 3MB1 into the polymer chain, thus with lower polymerization temperature, there should be a

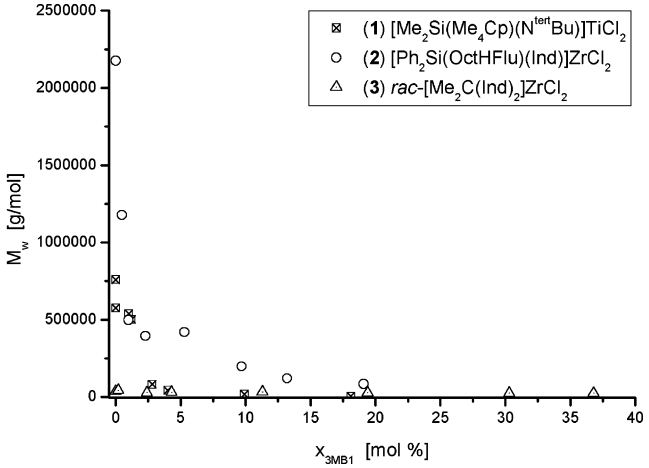

Figure 7. Molecular weight in dependence on the incorporation of 3-methyl-1-butene in the polymer. This graph is based on the investigations on the influence of different molar fractions of 3-methyl-1-butene in the feed on the polymerization results. x_{3MB1} = percentage of 3MB1 in the polymer. M_w = weight-average of the molecular weight.

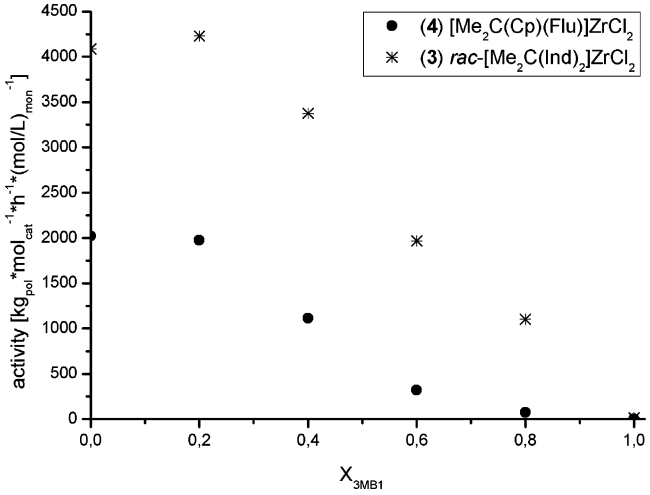

Figure 8. Influence of the molar fraction of 3-methyl-1-butene in the feed on the activity in the series of propylene/3-methyl-1-butene copolymerizations at $T_p = 30$ °C. X_{3MB1} = molar fraction of 3MB1 in the feed. T_p = polymerization temperature.

decrease in the melting temperatures, for the sterically hindered comonomer complicates the arrangement of the polymer chains. This expectance is accomplished for catalyst **2**. For the constrained geometry catalyst **1**, however, the melting temperatures increase the higher the polymerization temperature, although there is no tendency in the incorporation rate with a variation of the polymerization temperature. For the copolymers produced with *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**3**), glass transition temperatures are obtained because of quite high incorporation rates. These glass transition temperatures decrease with lower shares of 3MB1 in the copolymer, hence with rising polymerization temperature.

Molecular Weight. The molecular weight in dependence on the molar fraction of the comonomer 3MB1 in the feed can be seen in Figure 7.

The comparison of the obtained molar masses shows the for many metallocenes typical half U-shaped trend which is particularly distinctive for the fluorenyl-substituted metallocene (**2**). By using this metallocene, the highest molecular weights are achievable, whereat the molecular weight (M_w) at an incorporation rate of 19 mol % still constitutes 84 000 g/mol. A reason for this might be that the termination reaction is intensely hindered because of the sterically demanding ligands of the catalyst. With the constrained geometry catalyst **1** lower molecular masses were obtained, which are already for copolymers with a low incorporation rate of 4 mol % with a value under 20 000 g/mol in the range of oligomers. The copolymers synthesized with *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**3**) all have molecular weights in the range of 30 000 g/mol as an approximation. There is just a low decrease in the molecular weights with increasing incorporation of 3MB1 into the polymer.

As concerning the dependence of the molecular weight on the polymerization temperature, the molecular weight decreases with increasing polymerization temperature (Table 2). This behavior is also observed in the case of the constrained geometry complex **1**, for which incorporation rates seem to be nearly independent of the polymerization temperature. The main reason for the decline of the molecular weight should be given by an increase in termination reactions.

Copolymerizations of Propylene with 3-Methyl-1-butene. Activities. The activities for the copolymerizations of 3MB1 with propylene (Figure 8) are much lower than those with ethylene. With an increase in the share of 3MB1 in the feed there is an extreme decrease in activity, for example in the case of $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) as a catalyst precursor from ~2000 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$ for the propylene homopolymerization about factor 27 to 73 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$ at $X_{3MB1} = 0.80$. The activities for the homopolymerization of 3MB1 are hardly measurable with a low activity of 2 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$. For the metallocene **3**, *rac*-$[Me_2C(Ind)_2]ZrCl_2$, the qualitative development of the activities is alike, although the activities altogether are higher. Particularly ostentatious is the relatively high activity at $X_{3MB1} = 0.80$ with a value of 1100 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$, which corresponds to ~15 times the value of the activity achieved with the C_s-symmetric metallocene **4**. The homopolymerization of 3MB1 is realizable with this metallocene with an activity of 15 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$. On investigating the dependence of the polymerization temperature on the activity at $X_{3MB1} = 0.80$, one detects a maximum in activity for $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) between a polymerization temperature of 30−45 °C whereas activities continuously increase with increasing polymerization temperature within the considered temperature region using the bis-indenyl system **3**. From a polymerization temperature of 15 °C with an activity of 500 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$ there is a nearly 5 times higher activity for the polymerization at 60 °C, which shows an activity of 2300 $kg_{pol}\cdot mol_{cat}^{-1}\cdot h\cdot(mol/L)_{mon}^{-1}$ (Figure 9).

Incorporation of 3-Methyl-1-butene. There is no report in the literature about propylene/3MB1 copolymers; therefore, it was necessary, first, to assign the signals from the ^{13}C NMR spectrum with consideration of the DEPT experiment. In the case of the copolymers produced with the C_2-symmetric metallocene **3**, the incorporation of the comonomer in the polymer was determined via the signal for the chain branching of the isopropyl group (39.1 ppm) in relation to the signal of the tertiary carbon atom of the propylene share (28.0−29.1 ppm). A proposal for the assignment of the carbon atoms in the ^{13}C NMR spectrum is given in Figure 10.

The indices P and C stand for propylene and comonomer. $(CH)_P$ means a carbon atom belonging to a methine carbon atom originating from a propylene under neglect of the methyl groups originating from "chain runs".

Under comparison of the ethylene/3MB1 and the propylene/3MB1 copolymers there is no significant difference in incorporation ratios originating from the steric difference because

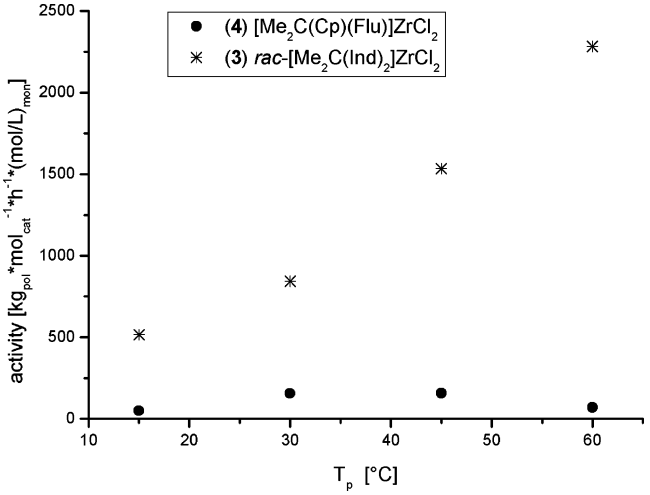

Figure 9. Influence of the polymerization temperature on the activity in the series of propylene/3-methyl-1-butene copolymerizations at $X_{3MB1} = 0.80$. T_p = polymerization temperature. X_{3MB1}= molar fraction of 3MB1 in the feed.

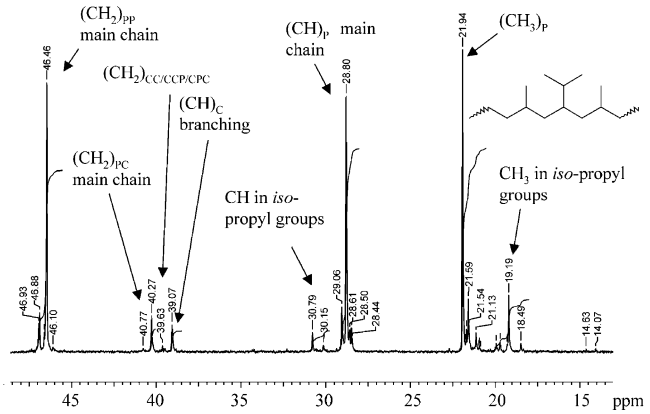

Figure 10. Suggested assignment of the carbon atoms in the ^{13}C NMR spectrum of a propylene/3-methyl-1-butene copolymer. The copolymer was obtained by using *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**3**)/MAO as catalyst system at $X_{3MB1} = 0.80$ and $t_p = 30$ °C.

of the methylene group of the propylene group to detect. The steric hindrance of 3MB1 is that high in comparison to both other monomers that this is the determining factor for incorporation rates. With the highest investigated 3MB1 molar fraction in the feed, $X_{3MB1} = 0.80$, an incorporation of 8.9 mol % 3MB1 in the polymer was achieved (Table 3).

Copolymerization parameters are not listed in this case, for no reactions with higher molar fractions of 3MB1 in the feed and therefore higher incorporation rates were made, which have a significant influence on the amount of the copolymerization parameters. With $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) instead there was hardly any 3MB1 in the polymer to detect.

It was not possible to draw a conclusion about the molar share of 3MB1 in the polymer by means of ^{13}C NMR spectroscopy for this catalyst. An evidence for the incorporation of 3MB1 was given by Py-GC-MS. Via a characteristic peak for each of both homopolymers and from the ratio of these two peaks in the copolymer chromatograms it was possible to draw conclusions about the incorporation rates for the copolymers on the basis of the peak ratios and by means of ^{13}C NMR spectroscopy determined incorporation ratios for the C_2-symmetric metallocene **3**. The conclusion which can be drawn from this investigations is that the incorporation rates are very low with values far below 1 mol %.

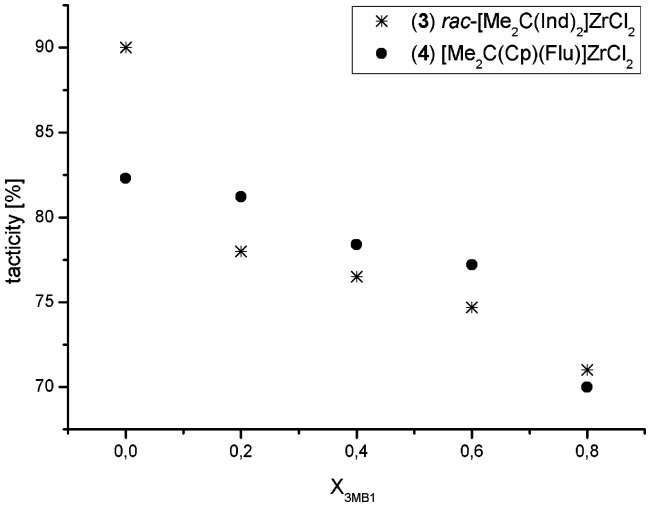

Figure 11. Influence of the molar fraction of 3-methyl-1-butene in the feed on the tacticity on the obtained copolymer. X_{3MB1}= molar fraction of 3MB1 in the feed.

Concerning the microstructure, it was found that the tacticity of the propylene share is perturbed by the amount of incorporated 3MB1. The isotacticity of the polypropylene, which was obtained by catalysis with metallocene **3**, constitutes at the chosen polymerization conditions 90%, which declines to a value of 71% for the copolymer with an incorporation of 3MB1 of about 9 mol %. It must be pointed out that the tacticity was determined assuming that no signals originating from the comonomer can be found in the methyl region of the polypropylene in the ^{13}C NMR spectrum. It was determined also under the assumption that the shift of the methyl carbon of propylene is due to a decline of tacticity instead of a heterosequence produced by the insertion of 3MB1. The small influence of heterosequences was neglected. Consequently, the data have to be treated with caution, not in a qualitative but in a quantitative respect. A heterosequence should cause a shift either to higher or to lower field, independent of the stereoregularity of the polymer. Hence, if such an influence of a heterosequence was given, the tacticity in the case of the polymer produced either with the C_s-symmetric catalyst or with the C_2-symmetric catalyst should increase and for the other catalyst the other way round. But in both cases, for the polymer obtained with the C_s-symmetric and for the one obtained with the C_2-symmetric catalyst, the tacticity decreases with increasing incorporation of the comonomer 3-methyl-1-butene. Another decision for the assumption, made by the authors, is given by the following fact: The decrease in tacticity (12%) of the copolymers obtained with the C_s-symmetric catalyst is enormous, although the incorporation rates are extremely low (less than 1 mol % for all investigated feed compositions). So, heterosequences definitely play a role, but the main reason has to be another one. The same coherence as with metallocene **3**, a decrease in tacticity with increasing 3MB1 incoporation rates, was found in the case of the copolymers obtained with the C_s-symmetric metallocene **4**. The higher the amount of incorporated 3MB1, the lower the syndiotacticity of the obtained copolymer. Although the incorporation rates are very low, an enormous influence on the tacticity is observed. While the polypropylene shows a syndiotacticity of 82%, the tacticity of the propylene share goes down to a value of 70% (Figure 11).

Thermal Behavior. It is eye-catching that there is not just one melting peak in the thermograms of the DSC curves of the polymers obtained with $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) to detect, but often two, which merge. This phenomenon is known in the

literature for syndiotactic polypropylene, sometimes explained with different crystallization phases and sometimes with recrystallization processes.[32,33] Besides, weakly distinct glass transition temperatures were detected, which indicate the existence of amorphous regions. For different amounts of 3MB1 in the feed there is a slight decrease in the glass transition temperatures of the obtained polymers and a clear decrease in the melting temperatures, as can be seen in Table 3. The same coherences can be observed in the case of metallocene **3**, although the polymers show just one melting temperature, and glass transition temperatures were only detected for copolymers with a minimum incorporation of 3MB1 of 3.5 mol %.

In dependence on the polymerization temperature it can be detected for both metallocenes that the melting temperatures of the obtained copolymers decrease the higher the polymerization temperature (Table 4). Comparing all the copolymer properties, it seems to be difficult to draw a conclusion, to which extent the decrease in one property leads to the tendency for another one, for the coherences are apparently more complex.

Molecular Weight. With increasing amount of 3MB1 in the feed, a reduction of the weight-average of the molecular weight can be observed (Table 3). For the C_s-symmetric metallocene **4**, the region of the obtained molecular weights is narrow. With increasing share of 3MB1 in the feed, it decreases from 9300 g/mol for the polypropylene to 6800 g/mol for a molar fraction of 3MB1 in the feed of 0.80. With metallocene **3**, higher molecular weights are achieved, which decline from 66 100 g/mol for the polypropylene to 51 200 g/mol for $X_{3MB1} = 0.80$, where a maximum is run through. The molecular weight distributions are narrow ($M_w/M_n < 2$).

In the case of $[Me_2C(Cp)(Flu)]ZrCl_2$ (**4**) the molecular weight decreases with increasing polymerization temperature. It falls from 68 000 g/mol for the polypropylene to about one-third, 23 000 g/mol, at $X_{3MB1} = 0.80$. As the incorporation rates were not analyzable low, these properties unfortunately cannot be linked to each other. But the most probable reason for the decrease in the molecular weight can be seen in a gain of termination reactions because of β-hydrid elimination with higher polymerization temperatures (Table 4). For metallocene **3**, the same tendency is observable, although only the molecular weight obtained at a polymerization temperature of 15 °C with a value of 14 500 g/mol is remarkably higher than the other ones, which differ between 7500 and 8700 g/mol (Table 4).

Conclusions

The present study shows the possibility to produce ethylene and propylene copolymers of 3MB1 with a wide range of different properties by means of homogeneous catalysis with MAO as cocatalyst. Ethylene/3MB1 copolymers with an incorporation rate between 0.5 and 19 mol % of 3MB1 have been produced. The molecular weight ranges between 4600 and 580 000 g/mol. It is noteworthy that only 1 mol % of incorporated 3MB1 reduces the melting temperature about nearly 20 °C, which should ease the processability significantly. As regards the propylene/3MB1 copolymers, copolymers up to an incorporation rate of 9 mol % have been synthesized. Until present, there is no other publication which provides information about propylene/3MB1 copolymers. Concerning the properties of the obtained copolymers, the molecular weights are lower than 10 000 g/mol for the C_2-symmetric metallocene **3** and somewhat higher for the C_s-symmetric metallocene **3**. In this case, they differ between 78 000 and 23 000 g/mol. By use of two catalysts, which transfer stereoinformation, it was possible to investigate the influence of the sterically hindered monomer 3MB1 on the stereoregularity. Under the assumption that no signals originating from the comonomer can be found in the methyl region of the polypropylene in the ^{13}C NMR spectrum, it was found that the tacticity decreases with increasing incorporation of 3MB1.

In the area of the NMR spectra interpretation probably some space is left for deeper investigations, although a good basis should be given with the present study.

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Supporting Information Available: Clearly arranged tables for all copolymerization series. This material is available free of charge via the Internet at http://pubs.acs.org.

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