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Articles

Chain-Walking Olefin Polymerizations with Donor-Substituted Half-Sandwich Chromium Complexes: Ethylene/Propylene Copolymer Look-Alikes by Polymerization of Propylene

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ABSTRACT: Six half-sandwich chromium complexes, in which the carbocyle is substituted by a nitrogen containing heterocycle as additional ligand were investigated regarding their polymerization behavior toward propylene. For each catalyst precursor, polymerization series in which the influence of the monomer concentration and of the polymerization temperature were analyzed, were conducted, using methylaluminoxane (MAO) as cocatalyst. Besides, several polymerizations with 1-butene were made, which brought further aspects into the interpretation of the for the polymerization of propylene complex NMR spectra. Because of the chain-walking tendency of all investigated systems, by sole polymerization of propylene, polymers are obtained, which have a structure which resembles those of ethylene/propylene copolymers with regioinverted propylene units. The ethylene share of the polymers with a value up to 30 mol % is astonishingly high. The different tendencies toward 2,1-insertions with succeeding chain-straightening of the chromium complexes and of each single catalyst by variation of the polymerization conditions is expressed in a broad range of the glass transition temperatures of the synthesized polymers, which vary between −14 and −38 °C.

Introduction

Heterogeneous chromium catalysts, as the well-established Phillips catalyst, belong to the most important commercially available catalysts. While the Union Carbide catalyst, also a heterogeneous chromium catalyst, is highly active in the polymerization of ethylene, it fails in the polymerization of α-olefins.[1,2]

Although the avalanche-like research on the area of the metallocene catalysis already started in the end of the 1950s, it took some decades until also homogeneous chromium single-site catalysts really quickened interest. The impulse for the development of single-site chromium complexes lay in the will to clarify the activities happening on the active sites of the heterogeneous complexes, including their oxidation states.

Already in 1970, Karapinka synthesized a bis(cyclopentadienyl)chromium complex, the said Union Carbide catalyst, which he used on a support for the polymerization of ethylene, but it took nearly 30 years until polymerization experiments were conducted with homogeneous chromium complexes with increased effort.[3−6]

Since then, several articles have been published, in which new homogeneous chromium complexes, most of them donor-substituted, are presented.[7,8] The focus here lies on the complex synthesis and on discussions of the structure, frequently with DFT calculations.[9,10] For some complexes, as for example $(Me_2NC_2H_4C_5Me_4)CrCl_2$ or complexes with quinolyl- and *N,N*-dimethylanilinyl-functionalized cyclopentadienyl ligands, the coordination of the nitrogen donor atom to the chromium has been confirmed by X-ray crystallography.[11,12] The number of publications concerning this research since the year 2000 are countable. Most of them are originating from the Basell Polyolefins Corp. and are patents. A multitude of differently substituted monocyclopentadienyl, indenyl, fluorenyl, and heterocyclopentadienyl chromium complexes have been synthesized.[9−26] Although the structural variety and the literature about it are remarkable, the data really dealing with polymerization

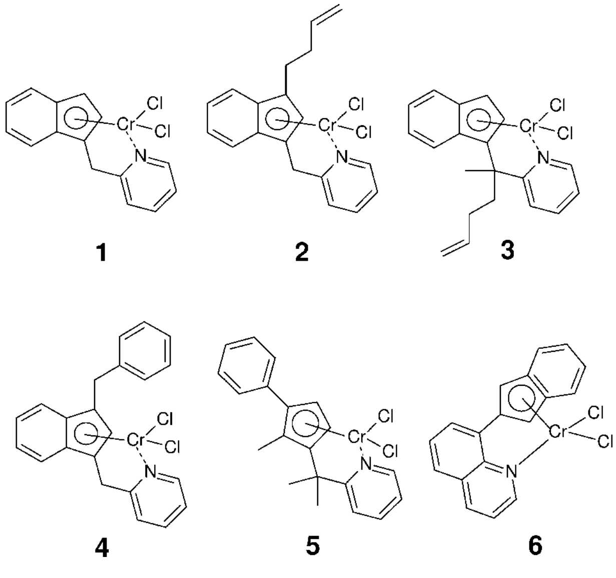

Figure 1. Donor-substituted half-sandwich chromium complexes **1**−**6** used for the α-olefin polymerizations. The catalysts were provided by Basell Polyolefins Corp.

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Table 1. Reaction Conditions for the Polymerizations of Propylene, Catalyzed by the Donor-Substituted Half-Sandwich Chromium Complexes 1−6/MAO

	run 1[a]	run 2[b]
polymerization temperature	30 °C	0/15/30/45/60 °C
propylene concentration	0.5/1.0/1.5/2.0/2.5 mol/L	1.0 mol/L
polymerization time	2 h	2 h
toluene	200 mL	200 mL
MAO	200 mg	200 mg
catalyst	1×10^{-2} mmol	1×10^{-2} mmol

[a] Investigation of the influence of the monomer concentration. [b] Investigation of the influence of the polymerization temperature.

results are scarce. Nearly exclusively, the polymerization of ethylene is described, which in general leads to high or very high molecular weights of the products at very high activities.

The present study, however, presents detailed polymerization results about the mechanistically seen much more interesting polymerization of propylene, catalyzed by the chromium complexes **1**−**6** in combination with MAO (Figure 1).

For each chromium complex, two series were made, analyzing the influence of the two most important parameters in a polymerization process: the monomer concentration and the polymerization temperature. All polymers obtained were characterized by means of DSC, GPC (or viscometry), and ^{13}C NMR spectroscopy.

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 was purchased from Messer 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 polymerizations and for the preparation of the solutions of the chromium complexes, was purified in a similar manner.

All polymerizations were reproduced.

The chromium complexes **1**−**6** were provided and synthesized by the Basell Polyolefins Corp. The cocatalyst methylaluminoxane was bought as a 10% trimethylaluminum-containing solution in toluene from Crompton. The solution was filtrated through a D4 frit, and the solvent as excessive TMA was removed at 40 °C in vacuo. The methylaluminoxane was dried in vacuo for 2 days. Afterward, it was kept in the glovebox. MAO was used as a pure white solid.

Polymerization Procedure. The polymerizations were performed in a glass autoclave from Büchi (volumetric capacity: 1 L), in which can be worked under gastight conditions up to a monomer pressure of 6 bar. The propylene pressure during a polymerization run was kept constant by using a pressure control. The flow of the monomer gas was recorded by 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 process with an accuracy of ±0.5 °C.

For a typical polymerization run, the autoclave was heated in vacuo for ∼1 h and afterward tempered to the desired polymerization temperature. 200 mg of MAO was filled in in argon counter flow, and afterward the reactor was charged with 200 mL of toluene. After saturation with propylene up to the desired monomer pressure, the polymerization was started by injection of the chromium complex solutions, which exhibit a poor solubility in toluene at room temperature, so that indeed the actual condition of the "complex solutions" rather was between a suspension and a solution.

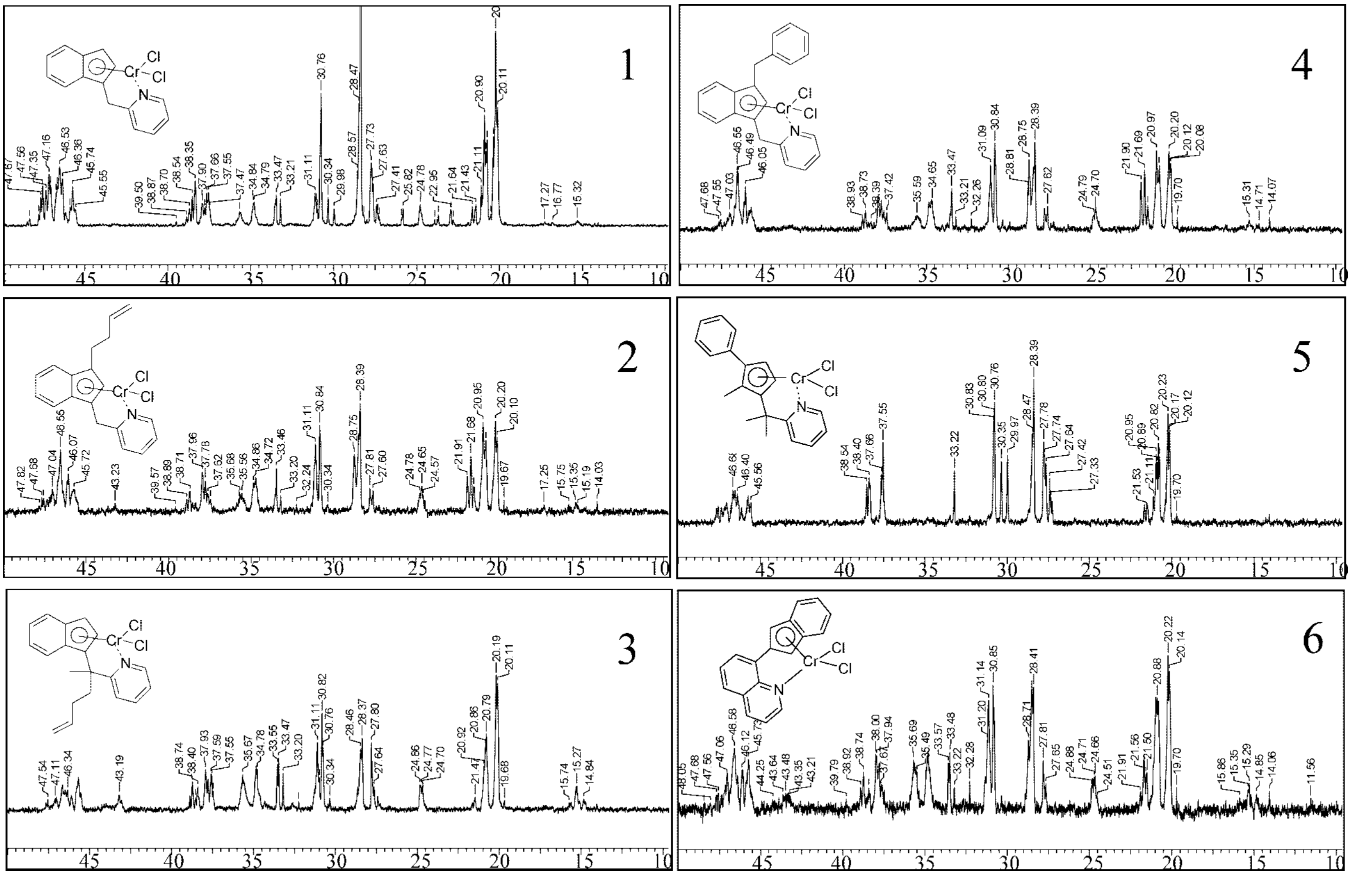

Figure 2. ^{13}C NMR spectra of the polymerization products of propylene, synthesized at 30 °C and a monomer concentration of 1 mol/L with the six chromium complexes **1**−**6**/MAO. The scale is given in ppm.

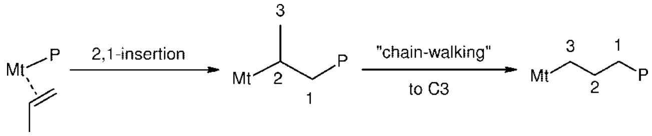

Figure 3. Chain walking after a 2,1-insertion of propylene.

The polymerization was stopped by addition of 5 mL of ethanol after disruption of the monomer feeding.

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 softened water). As the polymers were soluble, after phase separation, the organic phase was washed with sodium hydrogen carbonate solution and three times with water. Subsequently, the solvent was removed by means of a rotary evaporator. The polymers were dried in vacuo at 40 °C until the weight remained constant.

For the polymerizations of 1-butene, the desired amount of 1-butene was condensed into the reactor at low pressure in the autoclave via weight control after charging with MAO and toluene.

Polymerization Conditions. All polymerizations were conducted in 200 mL of toluene and with 200 mg of MAO as cocatalyst. The polymerization conditions for the polymerizations of propylene are listed in Table 1. The chromium complexes were also used for polymerizations of 1-butene, for which analogue polymerization conditions were chosen, i.e. the same polymerization time, catalyst precursor, and cocatalyst amount and volume of toluene.

For an investigation of the influence of the polymerization temperature, 1-butene polymerizations catalyzed by the chromium complexes **4**, **5**, and **6** were conducted at 30 and at 60 °C and a monomer concentration of 1 mol/L. Additionally, a polymerization at a monomer concentration of 0.75 mol/L 1-butene in feed and a polymerization temperature of 30 °C using chromium complex **6**/MAO as catalyst system were also conducted.

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 as reference (74.24 ppm) and were measured at 100 °C with a Bruker Avance Ultrashield-400 spectrometer at 100 MHz.

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 where heated with a heating rate of 20 °C min^{-1}. Only the second heating cycle was used for the interpretation of the obtained curves.

The 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*-butyl-4-methylphenol was used as thermostabilizer.

In case of chromium complex **6**, the molar masses of the synthesized polymers were determined using viscometry because of a defect of the GPC device. For this purpose, an Ubbelohde viscometer was used. The runtime was detected by means of a Viscoboy 2 from Lauda. For the calculation of the molar masses, the constants for polypropylene were used ($K = 0.234$ mL/g, $a = 0.725$).

Results and Discussion

Microstructure of the Obtained Polymers. Awaiting the ^{13}C NMR spectrum of a polypropylene, one is quite astonished, examining the spectrum of one of the obtained polymerization products of propylene (Figure 2). It is evident that this is not about the spectrum of a polypropylene; too many signals in relation originating from secondary carbon atoms are detectable.

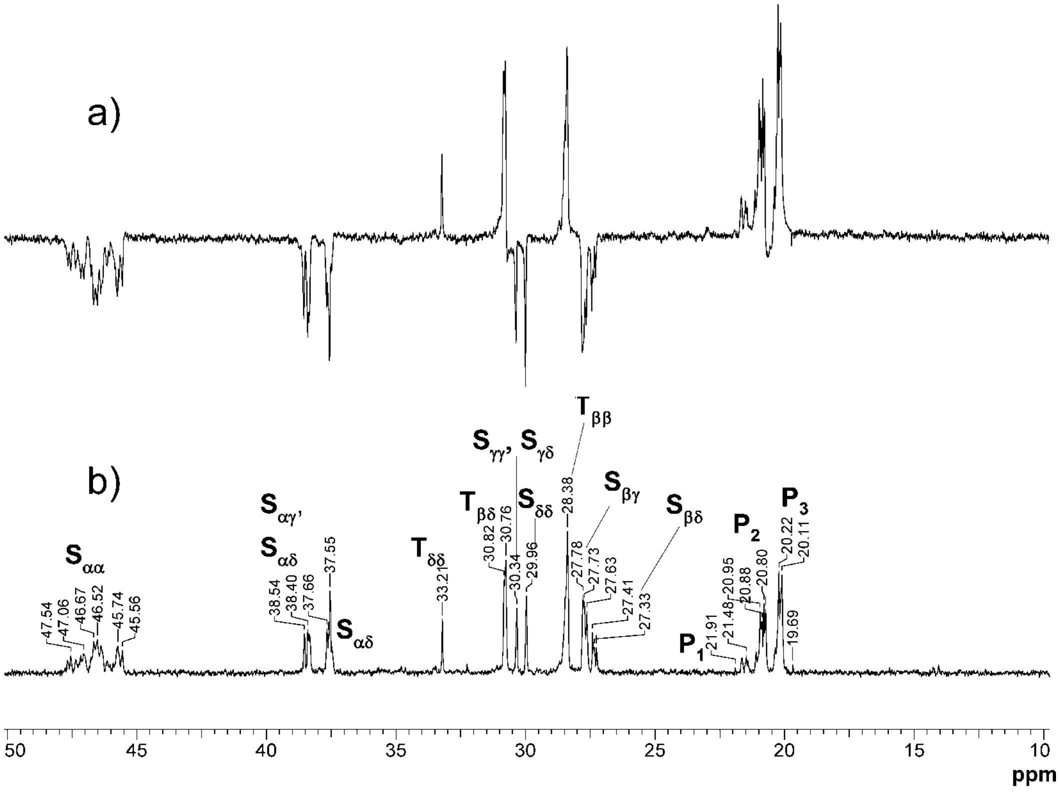

Figure 4. ^{13}C NMR spectra (a) DEPT and (b) ^{1}H broadband-decoupled of the polymer, which was obtained with chromium complex **5**/MAO at a propylene concentration of 1 mol/L and a polymerization temperature of 30 °C.

Table 2. "Ethylene Share" (in mol %) of the Polymerization Products of Propylene, Which were Obtained with the Chromium Compounds 1−6/MAO at Different Propylene Concentrations and a Polymerization Temperature of 30 °C

	"ethylene share" [mol %]					
	1	**2**	**3**	**4**	**5**	**6**
$c_{\text{propylene}}{}^{a} = 1.0$ mol/L	16	9	14	10	27	8
$c_{\text{propylene}} = 2.5$ mol/L	12	7	10	8	27	7

[a] Propylene concentration in feed.

Table 3. "Ethylene Share" (in mol %) of the Polymerization Products of Propylene, Which were Obtained with the Chromium Compounds 1−6/MAO at Different Polymerization Temperatures and a Propylene Concentration of 1 mol/L

	"ethylene share" [mol %]					
	1	**2**	**3**	**4**	**5**	**6**
$T_{\text{poly}}{}^{a} = 15$ °C	12	6	9	9	24	6
$T_{\text{poly}} = 60$ °C	21	18	23	22	30	15

[a] Polymerization temperature.

The signals could be ascribed to a microstructure,[27] which is similar to those of ethylene/propylene copolymers with regio-inverted propylene units, so that the share of ethylene-alike units can be calculated.[28,29]

Concerning the polymerization mechanism, a parallel to Brookhart's (α-diimine)nickel(II) complexes is given. These complexes show a distinct chain isomerization behavior, usually described as "chain walking".[30,31] In the polymerization of propylene, the chain walking becomes important after 2,1-insertions, as it leads to a 3,1-incorporation of propylene. This means that no methyl branch is obtained in this case, while however a "chain straightening" results (Figure 3).

The signal assignment is pictured examplary for a polymer, which was obtained with the chromium complex **5**, in Figure 4. In the nomenclature used, "P" stands for primary carbon atoms, "S" stands for secondary carbon atoms, and "T" stands for tertiary carbon atoms, i.e. carbon atoms, from which the methyl branches originate. The Greek letters "α", "β", "γ", and "δ", used as indices, indicate the distance between the considered carbon atom and the next branch carbon atom. Hereat, "δ" means a carbon atom, which is at least four carbon atoms far from the next branch point. This nomenclature was originally suggested by Carman and Wilkes.[33] The signal assignment was confirmed by the ^{13}C DEPT NMR spectrum.

The signal group for the methyl carbon atoms can be separated into "P_1", "P_2", and "P_3", which stand for the primary carbon atoms in methyl groups. "P_1" means the triad PPP (*mm*), i.e. $P_{\beta\beta}$ (*mm*), "P_2" stands for the triads PPP (*mr*), PPE (*m*), i.e. $P_{\beta\gamma}$ (*mr*), $P_{\beta\beta}$ (*mr*), $P_{\beta\delta}$ (*m*), and "P_3" encloses PPP (*rr*), PPE (*r*) and EPE, i.e. $P_{\beta\delta}$ (*r*), $P_{\gamma\gamma}$, $P_{\beta\gamma}$ (r), $P_{\beta\beta}$ (*rr*). Within this nomenclature of triads, "*m*" and "*r*" give the configurations of the methyl groups of the propylene share, which means "meso" or "rac". "P" and "E" of a triad xxx stand for propylene (P) and ethylene (E).

A comparison of the NMR spectra of the polymers, synthesized by catalysis with different chromium complexes, shows some differences. A good agreement is between the spectra of the indenyl−chromium complexes **1**, **2**, **3**, and **4**, which show additional signals at $\delta = 24.7$ ($S_{\beta\beta}$), 34.8 ($S_{\alpha\beta}$), 35.7 (also $S_{\alpha\beta}$), and 43.2 ppm (CH_2, also $S_{\alpha\alpha}$) in comparison to the cyclopentadienyl−chromium complex **5**.

The spectra of the polymers, which were produced with complex **5**, however, show clear signals at $\delta = 30.4$ and 30.0 ppm ($S_{\gamma\delta}$ and $S_{\delta\delta}$), which are missing or much less developed in most of the spectra of the polymers obtained with the other catalysts at 30 °C. Only in the case of chromium complex **1** are there also these two signals to detect in a mentionable amount. $S_{\gamma\delta}$ in the ^{13}C NMR spectra of the synthesized polymers can also be found in the case of the other chromium complexes, but the intensities are very low.

The signal for $T_{\beta\gamma}$ (31.1 ppm) is very distinctive in the case of nearly all catalysts except for chromium complex **5**, showing only a weak signal at this place; the same is to ascertain for the signal for $S_{\alpha\beta}$ (34.6−35.7 ppm). This indicates that all chromium complexes, except compound **5**, tend to a high share of 1,2-insertions followed by 2,1-misinsertions without a succeeding chain walking. The signals $S_{\gamma\delta}$ and $S_{\delta\delta}$, important for the polymers obtained with the chromium compounds **1** and particularly **5**, indicate a high chain-straightening tendency, i.e. a high tendency toward chain-walking after two or more succeeding 2,1-insertions. Nevertheless, the signals between $\delta = 37$ and 39 ppm ($S_{\alpha\gamma}$, $S_{\alpha\delta}$), detectable in all cases, point to at least isolated 2,1-insertions with chain-walking resulting in a chain-straightening.

In dependence on the polymerization temperature, a significantly increased tendency toward 2,1-insertions with chain-walking can be detected for the investigated chromium complexes because the signals for $S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\beta\gamma}$, and $S_{\beta\delta}$ indicating longer CH_2 sequences gain importance. Only for complex **5**, the decrease of the branching level, meaning longer CH_2 sequences, is very small. Also the signals for $S_{\gamma\delta}$ and $S_{\delta\delta}$ become more important, which shows the with increasing temperature growing tendency toward two or more succeeding 2,1-insertions with chain-walking to C3 of the inserted propylene unit.

On the basis of an article of Cheng, Eisenhardt has proposed a calculation for the determination of the propylene share of ethylene/propylene copolymers (x_P* in mol %) with regioinverted propylene units.[28,29]

For the calculation, secondary and tertiary carbon atoms are considered:

$$x_P{}^* = [p/(p + e)] \times 100 \text{ mol } \%$$

with

$$p = 0.5[S_{\alpha\alpha} + 0.5(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta}) + T_{\gamma\gamma} + T_{\gamma\delta} + T_{\delta\delta} + T_{\beta\beta} + T_{\beta\gamma} + T_{\beta\delta}]$$

and

$$e = 0.5[S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 0.5(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})]$$

The share of "ethylene units" for selected polymers, what should make dependences on the monomer concentration and the polymerization temperature clear, is given in Tables 2 and 3. This allows the confirmation of tendencies, which were registrated at examining the signals in the ^{13}C NMR spectra just by view: (1) With increasing polymerization temperature, there is an augmented occurrence of chain-walking to C3 after 2,1-insertions, as the "ethylene share" is higher. (2) With increasing monomer concentration, there is less chain-straightening, as the "propylene share" within the polymer chain is higher. With increasing monomer concentration, there are more monomer units pressing after the active center, which lowers the probability of a chain-walking after an insertion; instead, an insertion directly followed by another one becomes more likely.

In regard to the fact that only propylene was used as a monomer, the ethylene-alike units ratio is enormous. For the monocyclopentadienyl−chromium complex **5**, an "ethylene share" of 30 mol % at a monomer concentration of 1 mol/L and a polymerization temperature of 60 °C could be determined.

But also with the quinolyl-substituted system **6**, which shows the least chain-straightening tendency, a polymer was produced

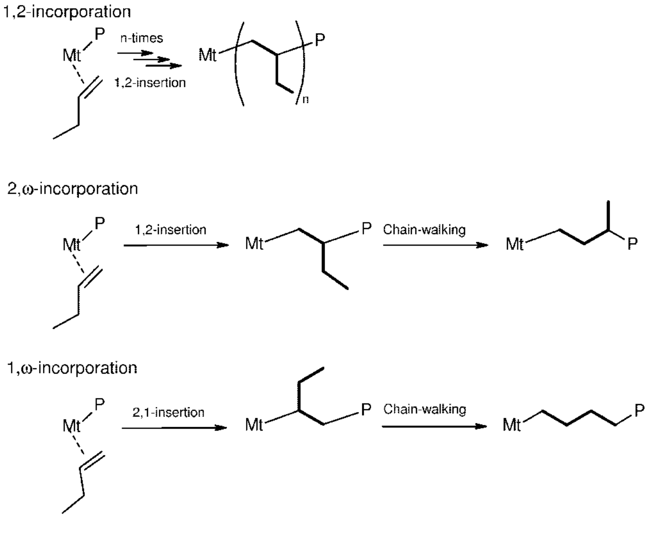

Figure 5. Possible insertions of a 1-butene monomer unit into the metal−carbon atom bond.

at these polymerization conditions, which anyhow has 15 mol % of ethylene-alike units.

Additionally, Tables 2 and 3 permit to make a ranking for the chromium complexes with a from right to left increasing tendency toward chain-straightening: **5** > **1** > **3** > **4** > **2** > **6**.

In the case of chromium complex **1**, there are additional signals to detect in the ^{13}C NMR spectrum in the range between $\delta = 22$ and 25 ppm (Figure 2), what might be due to the particularly low molar masses.

Except for the polymers obtained with chromium complex **5**, there is also a weak signal to detect at ~15 ppm. This signal might be assigned to the methyl carbon atom of a C3 branch[32] or to a 1,2-dimethyl branch.[27]

The chain-walking tendency of the chromium complexes has been also approved by the results of the polymerizations with 1-butene. In Figure 5, possibilities for the insertion of 1-butene into the metal/carbon atom bond are pictured. Besides the regular 1,2-insertion and the irregular 2,1-insertion of 1-butene, both resulting in the formation of ethyl branches, a chain-walking can appear. Methyl branches occur after 1,2-insertions with succeeding chain-walking, but also after 2,1-insertions with chain-walking to C_3. A chain-straightening, the 1,ω-incorporation, emerges from 2,1-insertions with chain-walking of the metal center to C_4 of the 1-butene unit. This behavior is known from nickel complexes.[34,35]

As chain isomerization with its diverse possibilities in combination with the different possible configurations of the branches leads to very complex microstructures of the polymers in the present case, resulting in complex, not completely solvable ^{13}C NMR spectra, it is forbeared to show a semifinished signal assignment, instead of selected signals, which can be unambiguously assigned, are discussed.

In Figure 6, the ^{13}C NMR spectra of the polymerization products of 1-butene, obtained by using the chromium complexes **4** and **5** in combination with MAO as catalyst systems at a polymerization temperature of 30 °C, are pictured.

As can be seen, there is not only a signal for the methyl carbon atoms of ethyl branches ($1B_2$), but also a strong signal for the methyl carbon atoms of methyl branches ($1B_1$). Besides, the signals for $S_{\gamma\gamma}$, $S_{\gamma\delta}$, and $S_{\delta\delta}$ show a high intensity. Accordingly, a significant amount of insertions are 2,1-insertions followed by chain-straightening and also probably 1,2-insertions also with succeeding chain-walking. A sole 1,2-insertion of 1-butene, with or without chain-walking, should lead to a branch density of 250 branches per 1000 carbon atoms. As all signals could be separated into methyl or methine carbon atoms and methylene carbon atoms under consideration of the respective ^{13}C DEPT NMR spectra, and as the methyl region is clearly to distinguish from the methine region, the branch density can be easily calculated from the share of signals of the carbon atoms of the methyl groups. A calculation from the methine carbon atoms is less exact, as the relevant signals partly overlap with those of the methylene carbon atoms. Potentially existing hyperbranches, which means branches with more than one methyl group, are neglected.

The branch densities in dependence on the polymerization temperature and on the chromium complex are listed in Table 4. These values demonstrate the in case of chromium compound **5** particularly high tendency toward chain-straightening, which is nearly independent of the polymerization temperature. A branch density from only about 180−185 branches instead of 250 per 1000 carbon atoms is remarkable. It means that this complex already gives at lower temperatures high shares of $(CH_2)_n$ segments and therefore undergoes high shares of 2,1-insertions followed by succeeding chain-walking to C_4.

Also for the other chromium complexes, a 1,ω-incorporation can be observed, although the values—clearly above 200 branches per 1000 carbon atoms—for the branches at a polymerization temperature of 30 °C are quite high. With an increased polymerization temperature of 60 °C, the branch density of the polymer produced with chromium complex **4** significantly decreases to a value which is comparable to that one obtained with catalyst compound **5**. With complex **6**, however, the branch density still constitutes 206.

Besides the branch density, which means the presence of methyl and ethyl groups, also the share of the methyl branches is important for the decision, whether a complex tends more or less than the others to chain-walking, as a not so large tendency toward chain-straightening just means a lower tendency toward 2,1-insertions with chain-walking to C_4, but still a large amount of 1,2-insertions with succeeding chain-walking or 2,1-insertions with chain-walking to C_3 might appear. The ratio methyl branches to ethyl branches ($1B_1$:$1B_2$) was calculated for the polymers.

In case of chromium compound **6**, this ratio amounts 4:1 at a polymerization temperature of 30 °C and 11:9 at a polymerization temperature of 60 °C. That might mean, also under consideration of the branch densities, at $T_{\text{poly}} = 30$ °C there are less 2,1-insertions with or without chain-straightening than at a polymerization temperature of 60 °C, and the many methyl branches probably are a result of 1,2-insertions followed by chain-walking. They could also be caused by 2,1-insertions followed by chain-walking to C_3, but because of the lower tendency toward chain-straightening, it seems less probable.

Nevertheless, at an increased polymerization temperature, the share of 2,1-insertions with chain-straightening significantly seems to increase, and the increase in ethyl branches in comparison to methyl branches is therefore more likely due to an increase in the share of 2,1-insertions. This is consistent with the fact that in general energetically unfavorable misinsertions become more likely with increasing polymerization temperature.

It should be pointed out that there is a further explanation for the obtained results. Raising the polymerization temperature facilitates the 2,1-insertion in comparison to the 1,2-insertion of the monomer unit into the metal-growing polymer chain bond. As there is a competition between a monomer insertion step and a chain-walking, the share of methyl groups, formed via 1,2-insertion and chain-walking, becomes less important.

Compared to the palladium-catalyzed polymerization of 1-butene,[27] the polymers obtained with the investigated chromium complexes show a comparatively high branching level.

In the palladium-catalyzed polymerization process, the structural units formed by 2,1-insertions are selectively converted

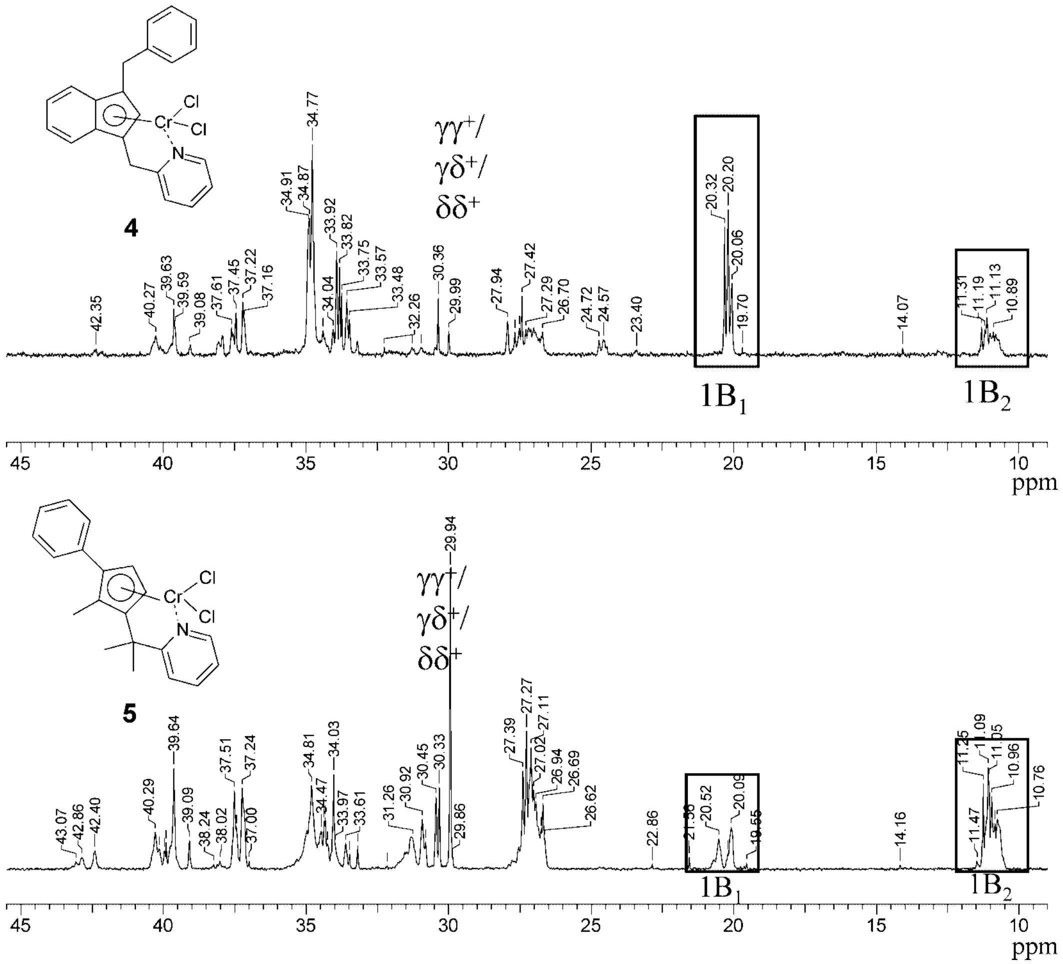

Figure 6. ^{13}C NMR spectra of the polymers obtained by a homopolymerization of 1-butene, using the complexes **4** and **5** in combination with MAO as catalyst systems at a propylene concentration of 1 mol/L and a polymerization temperature of 30 °C.

Table 4. Branch Density for the Polymers, Obtained at a Polymerization Temperature of 30 or 60 °C and a 1-Butene Concentration of 1 mol/L, Using the Catalysts 4, 5, and 6[a]

	branches per 1000 carbon atoms		
	4	**5**	**6**
T_{poly}[b] = 30 °C	217	185	232
T_{poly} = 60 °C	180	182	206

[a] The branch density was calculated via the signals of the methyl carbon atoms of the ^{13}C NMR spectrum. [b] Polymerization temperature.

to nonbranched units by chain-walking because of a sterically unfavored insertion of the 1-butene into the palladium-secondary carbon atom bond.

In the future, some experiments using ^{13}C-enriched 1-butene might deliver further insight into the polymerization mechanism of the higher α-olefin polymerization using chromium catalysts. It is important to know whether insertion of a 1-butene unit into a chromium secondary carbon atom bond really occurs. Therefore, the given interpretations at presence have to be handled with care and should just be taken as an encouragement for further experiments.

The chromium complex **4** shows a similar, but a little different, behavior concerning the ratio of $1B_1$ to $1B_2$, which is 3:2 at a polymerization temperature of 30 °C and 1:3 at a polymerization temperature of 60 °C. Consequently, the branches at a polymerization temperature of 60 °C are predominantly formed by 1,2- and 2,1-insertions without chain-walking, while at 30 °C, the branches mainly are formed by 1,2-insertions and a presumably comparatively low share of 2,1-insertions with succeeding chain-walking to C_3 of the 1-butene unit. Herefrom though, no higher tendency toward chain-walking at lower polymerization temperatures can be deduced, as the calculation of the branch density has given higher values at 30 °C. If only a 1,2-insertion would occur, independent of the extent of chain-walking, the branch density still would be 250 branches per 1000 carbon atoms. The lower branch density at a polymerization temperature of 60 °C is just explicable by 2,1-insertions followed by chain-walking. A quite different mechanistic behavior in the polymerization of 1-butene shows the cyclopentadienyl chromium complex **5**. At a polymerization tem-

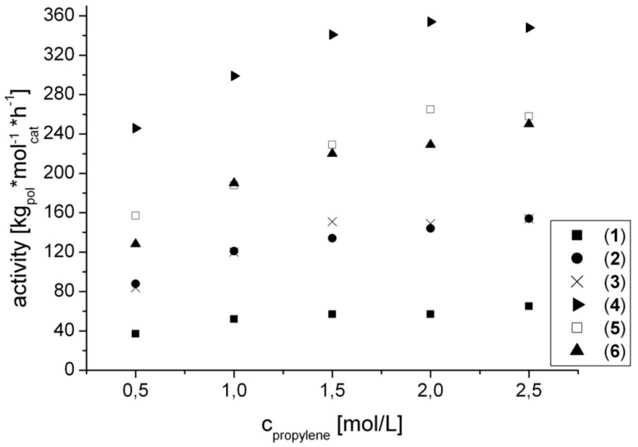

Figure 7. Influence of the propylene concentration on the polymerization activity for the chromium complexes **1**–**6**/MAO at T_{poly} = 30 °C. $c_{propylene}$ = propylene concentration in feed.

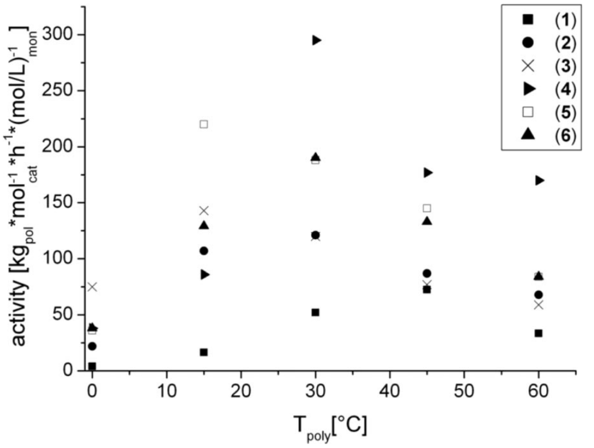

Figure 8. Influence of the polymerization temperature on the activity of the propylene copolymerizations catalyzed by the chromium compounds **1**−**6** in combination with MAO, conducted at a monomer concentration of 1 mol/L. T_{poly} = polymerization temperature.

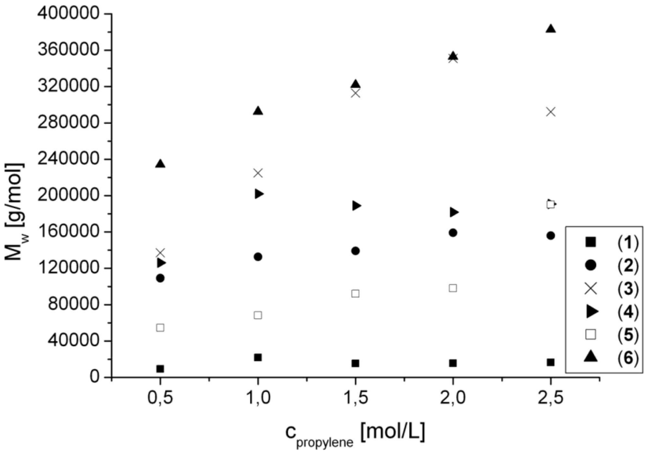

Figure 9. Influence of the propylene concentration on the molar masses of the obtained polymers. The chromium complexes **1**−**6** were used in combination with MAO as catalyst systems at a polymerization temperature of 30 °C. In case of compound **6**, M_η was determined instead of M_w because of a defect of the GPC device. $c_{propylene}$ = propylene concentration in feed. M_η = viscosimetric average molecular weight. M_w = weight-average molecular weight.

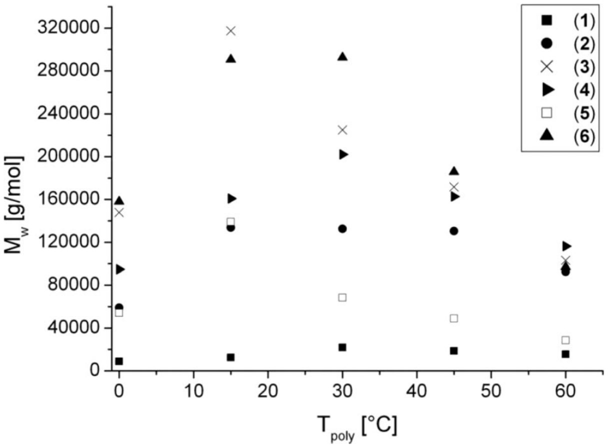

Figure 10. Influence of the polymerization temperature on the molar masses of the obtained polymers. The chromium complexes **1**−**6** were used in combination with MAO as catalyst systems at a monomer concentration of 1 mol/L. In case of chromium complex **6**, M_η was determined instead of M_w due to a defect of the GPC device. M_η = viscosimetric average molecular weight. M_w = weight-average molecular weight. T_{poly} = polymerization temperature.

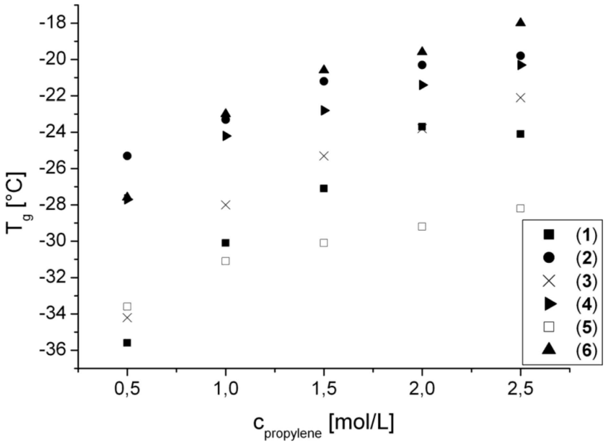

Figure 11. Influence of the propylene concentration on the glass transition temperatures of the obtained polymers, synthesized at a polymerization temperature of 60 °C. The chromium complexes **1**−**6** in combination with MAO were used as catalyst systems. $c_{propylene}$ = propylene concentration. T_g = glass transition temperature.

perature of 30 °C, the ratio of the signals $1B_1$ to $1B_2$ amounts 1:3 and at 60 °C 2:1. The relatively high share of ethyl branches in comparison to methyl branches of the obtained products at T_{poly} = 30 °C can be ascribed to 1,2- and 2,1-insertions without chain-walking. Because of the clear share of 2,1-insertions with succeeding chain-walking on the chain growth, as the comparatively low branch density shows, a clear share of the 2,1-insertions in the formation of ethyl branches can be assumed. But it has to be pointed out that Brookhart has already postulated that after 2,1-insertions with comparable (α-diimin)nickel complexes usually a chain-straightening follows and that 2,1-insertions appear rather isolated.

In combination with the low branch density, the predominance of methyl branches at 60 °C is most likely due to an increase in the share of 2,1-insertions with chain-walking to C_3 of the 1-butene unit.

Beside an influence of the polymerization temperature, the effect of two different monomer concentrations on the products of the polymerizations with 1-butene was investigated with chromium complex **6**, namely at 0.75 and 1.0 mol/L. The effect on the microstructure is very low, but a decrease of the share of the methyl branches from 80 to 77% in favor of the ethyl branches (20−23%) at higher monomer concentration could be recorded. This seems insofar as probable, as at higher monomer concentrations, new monomer units should reach the active center faster, and therefore there should be less time for chain-walking. This result is in accord with the conclusions of the propylene polymerizations.

Activities. For all chromium complexes, the activities increase with increasing monomer concentration and diverge toward different values, when the activity is expressed in the units $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}$, as can be seen in Figure 7. But when the monomer concentration is included into the calculation of the activity values ($[kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol/L)_{mon}^{-1}]$, a decrease in activity with increasing monomer concentration can be determined. As far as we know, this behavior has not been oberserved for metallocenes. Only for (α-diimine)nickel complexes are these coherences described for the polymerization of 1-butene and 1-hexene.[34,36] This behavior in its whole is not easily explicable. It suggests that the decrease in activity up to a monomer concentration of 1.5 or 2.0 mol/L is caused by a lack of monomer units staying ready near the active center for insertion at low monomer pressures. A raise of the monomer concentration therefore leads to an increase in activity, which is

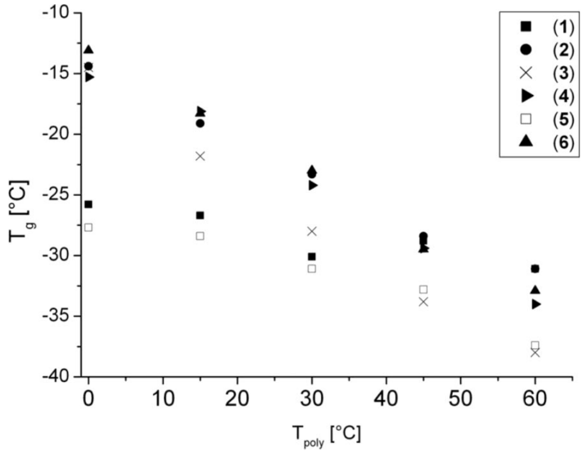

Figure 12. Influence of the polymerization temperature on the glass transition temperatures of the polymers, obtained at a propylene concentration of 1 mol/L. The chromium complexes **1**−**6** in combination with MAO were used as catalyst systems. T_g = glass transition temperature. T_{poly} = polymerization temperature.

nevertheless comparatively low. When at certain monomer concentrations the presence of ready-for-insertion monomer units at the active center is secured, the activities stagnate.

Regardless of this explanation, it remains arguable why exactly such results are obtained for the chromium complexes, but not for metallocenes, where also activities can be that low, if for example a sterically hindered monomer is used. A simple diffusion problem seems to be insofar improbable, as the activities in comparison to other olefin polymerizations, accompanied by low yields, are quite low.

A closer look at the activities shows that the besides unsubstituted pyridyl-substituted indenyl chromium complex **1** affords the lowest activities in the polymerization of propylene, with a maximum value of 65 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}$ in the investigated range. The maxium value for the most active compound, chromium complex **4**, on the other hand, amounts approximately nearly 5.5 times this value, with 354 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol/L)_{mon}^{-1}$. It is remarkable that even with chromium complex **6**, where the pyridyl donor ligand of compound **1** just is substituted by a quinolyl ligand, leads to nearly 4 times higher activities. It is assumed that this might be due to an optimization of the distance donor atom/metal atom, that the presence of the nitrogen atom in the coordination sphere of the chromium atom is somehow optimized. A reason might also be seen in a decreased tendency toward 2,1-insertions by this substitution. Also, an increased expulsion of the donor ligand from the chromium with higher monomer concentration could be discussed.

The activities in dependence on the polymerization temperature for each catalyst system are pictured in Figure 8. Maxima are observable, which have their origin in the following facts: According to the Arrhenius law, there is an exponential correlation between the reaction temperature and activity. But the activities in polymerization processes with metallocenes and half-sandwich complexes not unlimitedly increase with a rising polymerization temperature is due to an increase in catalyst deactivation at higher temperatures. This was determined by the monomer flow curves, registrated during the polymerization runs, which showed a faster decline of the monomer consumption after reaching the maximum flow, the higher the polymerization temperature was. Also, an increase of 2,1-insertions with higher polymerization temperature should have an influence on the activities.

Molar Masses. Concerning the polymer characterization, molar masses and glass transition temperatures have been determined. Like the metallocenes, the used chromium complexes/MAO are single-site catalysts, for which polydispersities of ~2 are characteristic. The analysis of the obtained polymers with GPC has shown that the polydispersities in these cases with values of majoritarily 1.6−1.8 or partly less, especially at the lowest polymerization temperature, are even lower, pointing at the direction of living polymerization (see Supporting Information).

The developing of the molar masses in dependence on the propylene concentration in feed resembles those of the respective activities (Figure 9). Except for the chromium complexes **5** and **6**, for which the molar masses of the obtained polymers continuously increase with ascendant monomer concentration, there is just an increase up to a propylene concentration of 1 or 1.5 mol/L, then the values stagnate. With the chromium complexes used, within these series, a broad range of molar masses between approximately M_w = 10 000 g/mol with complex **1** and M_η = 380 000 g/mol for complex **6** was obtained. It is eye-catching that the polymers synthesized with the two complexes **1** and **5** with the highest chain-straightening tendency have the lowest molar masses, while that one with the lowest tendency toward chain-straightening affords the polymers with the highest molar masses. Any substitution on chromium compound **1** leads to a significant increase in the molar masses of the obtained polymers.

Also in dependence on the polymerization temperature, the parallel developing of the molar masses and the activities is obvious. Maxima are detectable at a polymerization temperature about 15 or 30 °C, depending on the chromium complex used (Figure 10). The main reason for the decrease of the molar masses at higher polymerization temperatures has to be seen in an increased occurrence of termination reactions.

Glass Transition Temperatures. With higher propylene concentrations, there is a clear increase in the glass transition temperatures, as can be seen in Figure 11. This coherence is explicable with a lower share of ethylene-alike units of the synthesized polymer at higher monomer concentration. The reason therefore is that with increasing monomer concentration, the pressure of further monomer units, pressing after the active center, rises, so that a direct insertion after another one becomes more likely and a chain-walking is hindered. The polymers obtained with the chromium complexes **2**, **4**, and **6**/MAO, which already showed a good accordance concerning their ^{13}C NMR spectra, afford polymers at the respective monomer concentrations, which show a difference in their glass transition temperatures of only about 2 °C. The achievable difference concerning the glass transition temperatures between the polymers, produced with those chromium complexes and particularly chromium complex **5**/MAO, is remarkable with a range of up to 10 °C. By choosing a special monomer concentration and one of these chromium complexes **1**−**6** as catalyst component, glass transition temperatures of the obtained products in a range between −18 and −36 °C are adjustable.

As the tendency toward chain-straightening increases with increasing polymerization temperature, glass transition temperatures decrease with the higher shares of ethylene-alike units (Figure 12). The difference in achievable glass transition temperatures of the obtained polymers within the series of one catalyst is even wider than that by varying the monomer concentration: −14.5 at T_{poly} = 0 to −38 °C at T_{poly} = 60 °C in case of chromium complex **3**. For the catalyst system **2**, **3**, **4**, and **6**/MAO, the glass transition temperatures exhibit a particularly strong dependency on the polymerization temperatures, as the tendency toward 2,1-insertions with chain-walking to C_3 of the propylene unit, which means a chain-straightening, is even more dependent on the polymerization temperature than for the chromium complexes **1** and **5**.

Conclusions

Within the present study, the polymerization behavior of donor-substituted half-sandwich chromium complexes toward propylene has been intensely investigated. For a deeper consideration of mechanistic aspects, also polymerizations with 1-butene were conducted. Mechanistically interesting aspects are discussed, and datailed information is given about the influence of a variation of two very important polymerization parameters, which are the polymerization temperature and the monomer concentration.

The polymers which were obtained by polymerization of propylene are atactic and amorphous and exhibit a remarkably wide range of glass transition temperatures, what is directly associated with the microstructure of the polymers, which is similar to that one of an ethylene/propylene copolymer with regioinverted propylene units. All investigated chromium complexes show a chain-walking tendency. The complexes **1** and **5** exhibit the highest tendency toward two or more succeeding 2,1-insertions with consecutive chain-walking by far. For the chromium complexes **2**, **3**, **4**, and **6**, on the other hand, only small shares of maximal two succeeding insertions of that kind could be detected, and only system **4**, and this in a nearly neglectable extent, showed more than two of these insertions in a row. Nevertheless, the content of ethylene-alike units in the polymer chain is in any case surprising.

In this context, a ranking for the tendency of the complexes toward chain-straightening can be given: **6** < **2** < **4** < **3** < **1** < **5**. Additionally, with increasing polymerization temperature, a remarkably strong increase in the tendency toward 2,1-insertions with "chain straightening" could be detected. The glass transition temperatures reflect the calculated shares of ethylene-alike monomer units in the polymer chain and therefore approve the interpretation of the ^{13}C NMR spectra: The higher the content of ethylene-alike units is, the lower are the glass transition temperatures.

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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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