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Synthesis of Hydroxyl Group Containing Polyolefins with Metallocene/Methylaluminoxane Catalysts

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ABSTRACT: Ethylene and propylene were copolymerized with 10-undecen-1-ol, using stereorigid $Et[Ind]_2ZrCl_2$, $Me_2Si[Ind]_2ZrCl_2$, $Me_2Si[2\text{-}MeInd]_2ZrCl_2$, and $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$ catalysts activated with methylaluminoxane (MAO). As a reference, ethylene copolymerization was also carried out with the nonstereospecific catalyst $[Ind]_2ZrCl_2$/MAO. Characterization of the copolymers by ^{13}C and ^{1}H NMR spectroscopy revealed that the polymerization product was a true copolymer and that the conversion of the polar comonomer was strongly favored by the chiral geometry of the catalyst. The pretreatment of 10-undecen-1-ol with MAO before initiating the copolymerization increased the ethylene polymerization rate markedly and slightly improved the reactivity of the polar comonomer. A major improvement in the polymerization rate of 10-undecen-1-ol was obtained when the polymerization temperature and Al/Zr mole ratio were increased.

Introduction

The manufacturing of functionalized polyolefins has long been an area of scientific interest, since the lack of reactive groups in polyolefins significantly limits many of their end uses, especially where adhesion, paintability, printability, or compatibility is required. In general, there are two ways to functionalize polyolefins: direct copolymerization with a functional monomer[1] and chemical modification of preformed polymers.[2] Direct copolymerizations suffer, however, from a loss of catalyst activity, due to the tendency of functional groups of the monomers to form complexes with the Lewis acid components of the catalyst.[3] The modification reactions of polyolefins, in turn, are accompanied by undesirable side reactions such as cross-linking and degradation.[4] A new approach involves the copolymerization of olefins with borane-containing monomers.[5] The resulting copolymers are then converted to various functional polymers in postpolymerization processes.

Recently, we found that the catalyst system $[n\text{-}BuCp]_2ZrCl_2$/MAO promotes the copolymerization of 10-undecen-1-ol with ethylene.[6] However, a rapid deactivation of the catalyst occurs upon addition of the functional monomer. In the work presented here, 10-undecen-1-ol was copolymerized with ethylene and propylene in the presence of several other metallocene catalysts combined with methylaluminoxane. The aim was to determine whether the polymerization activity of the polar monomer can be improved through change in the catalyst geometry and optimization of the polymerization conditions.

Experimental Section

Chemicals. $Me_2Si[Ind]_2ZrCl_2$, $Me_2Si[2\text{-}MeInd]_2ZrCl_2$, and $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$ were synthesized according to Spaleck et al.[7] $[Ind]_2ZrCl_2$, $Et[Ind]_2ZrCl_2$, and methylaluminoxane (10 wt % solution in toluene) were obtained from Witco GmbH. 10-Undecen-1-ol was purchased from Fluka. Toluene was distilled over $NaAl(C_2H_4)_4$ and stored under argon.

Method of Polymerization. The copolymerizations were performed in a 0.25 dm^3 glass autoclave at 25 °C and 2.0 bar monomer gas overpressure. A propeller-like stirrer was used at 1200 rpm to stir the reaction mixture. The reactor was filled with toluene, comonomer, and methylaluminoxane, thermostated, and saturated with ethylene or propylene gas. The preactivated metallocene solution was then blown into the reactor with argon overpressure from a funnel. The total volume of the liquid phase was 160 mL. The pressure of the gaseous monomer was kept constant by continuously monitoring the consumption of the gaseous monomer with a mass flow meter and replacing it as it was consumed. Polymerization was stopped through the addition of CH_3OH. The reaction mixture was stirred in a mixture of CH_3OH and HCl overnight, after which the polymer was filtered, washed with CH_3OH, and dried in vacuum.

Polymer Characterization. The ^{13}C and ^{1}H NMR spectra of the copolymers were recorded with a JEOL NMR spectrometer. The molar masses of the copolymers were determined with a Waters high-temperature gel permeation chromatograph, and the melting endotherms with a Perkin-Elmer differential scanning calorimeter.

Results and Discussion

Activity of the Catalysts. Ethylene and propylene were homopolymerized and copolymerized with 10-undecen-1-ol in the presence of several stereorigid metallocene catalysts with methylaluminoxane (MAO) added as cocatalyst. As a reference, ethylene and 10-undecen-1-ol were also copolymerized with the nonstereospecific $[Ind]_2ZrCl_2$/MAO catalyst. The structures of the catalysts are presented in Figure 1. The experiments were carried out by keeping other polymerization conditions constant and increasing the amount of functional monomer in the feed. The addition of polar compound resulted in a decrease in the activity of the catalysts, detected as a decline in the consumption rate of the gaseous monomer. The polymerization rates of ethylene and propylene with the stereorigid catalyst system $Et[Ind]_2ZrCl_2$/MAO and analogous silylene-bridged catalyst $Me_2Si[Ind]_2ZrCl_2$/MAO are displayed

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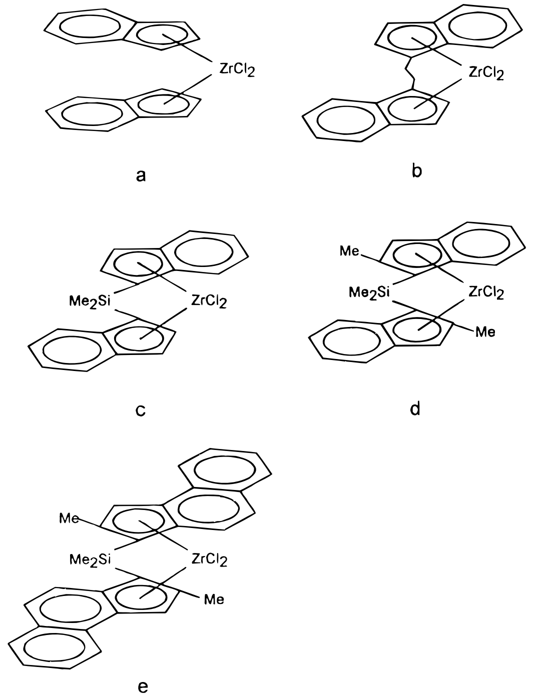

Figure 1. Structures of the catalysts: (a) $[Ind]_2ZrCl_2$, (b) $Et[Ind]_2ZrCl_2$, (c) $Me_2Si[Ind]_2ZrCl_2$, (d) $Me_2Si[2\text{-}MeInd]_2ZrCl_2$, and (e) $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$.

in Figures 2a and 2b as a function of the 10-undecen-1-ol concentration. The polymerization rate curves show the two catalysts to have almost the same activity in the homopolymerizations of ethylene, and with the addition of the functional monomer they exhibit similar, decay type, kinetics. As Figure 2b shows, the productivity of the silylene-bridged catalyst was slightly higher in the propylene homopolymerization, whereas the ethylene-bridged analogue seemed to tolerate the addition of the polar monomer better.

Figures 3a and 3b show the polymerization rate curves of ethylene and propylene plotted against the mole amount of 10-undecen-1-ol with the substituted catalysts $Me_2Si[2\text{-}MeInd]_2ZrCl_2$/MAO and $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO. As Figures 2 and 3 show, the methyl-substituted catalyst $Me_2Si[2\text{-}MeInd]_2ZrCl_2$/MAO was only about half as active as the corresponding nonsubstituted catalysts in homopolymerizations. The lower activity may be explained by the sterically more crowded coordination sphere of the catalyst caused by the methyl substituents, which hinder the coordination of the monomer to the active center. The bulky $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO catalyst showed extremely high activity in the ethylene homopolymerization comparable to the activity of the nonbridged catalyst system $[Ind]_2ZrCl_2$/MAO. According to Spaleck et al.,[7] the high activity may be due to the electron-donating substituents, which stabilize the active cationic species and thus increase the number of active sites or weaken the coordination of the counterion. In the copolymerizations, however, the activity of the catalyst declined steeply with the addition of the polar comonomer.

Characterization of the Copolymers. The chemical structures of ethylene and propylene copolymers with 10-undecen-1-ol were characterized by ^{13}C NMR spectroscopy. The formation of true copolymer was clearly evident from the carbon spectrum of the ethylene/10-undecen-1-ol copolymer, which is presented in Figure 4. The signal due to the branching carbon appeared at 38.2 ppm and the resonances of the α-, β-, and γ-carbons at 34.5, 27.3, and 30.5 ppm, respectively. The carbon spectrum also showed a signal at 62.8 ppm, which originated from the chain end carbon of the alcohol branch and indicated the presence of a hydroxyl group at the chain end (labeled number 6 in the scheme of Figure 4). Other signals arising from the alcohol branch were also detected and are labeled accordingly. The ^{13}C NMR spectrum of the propylene/10-undecen-1-ol copolymer showed resonances correspondingly.

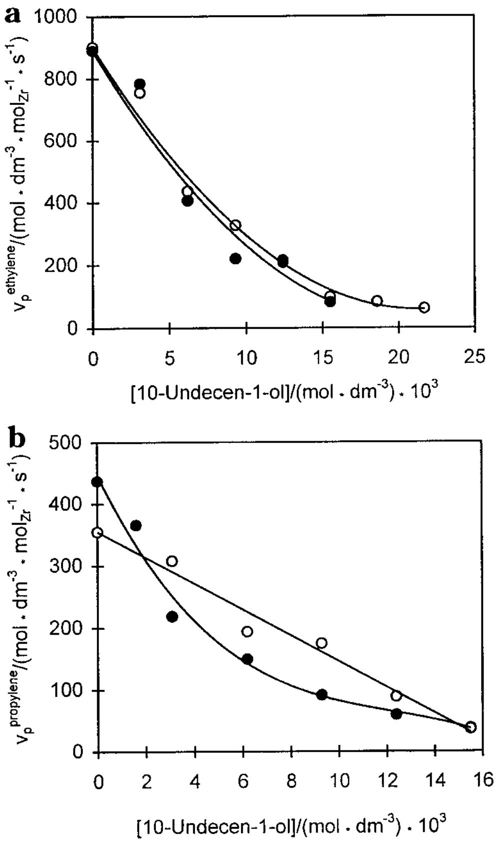

Figure 2. (a) Ethylene polymerization rate ($v^{p}_{ethylene}$) as a function of the molar amount of 10-undecen-1-ol in the polymerization medium with catalysts (○) $Et[Ind]_2ZrCl_2$ and (●) $Me_2Si[Ind]_2ZrCl_2$. Polymerization conditions: $[Zr] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Al]/[Zr] = 4300$, $p_{ethylene} = 2.0$ bar, polymerization temperature = 25 °C. (b) Propylene polymerization rate ($v^{p}_{propylene}$) as a function of the molar amount of 10-undecen-1-ol in the polymerization medium with catalysts (○) $Et[Ind]_2ZrCl_2$, $[Al]/[Zr] = 4300$, and (●) $Me_2Si[Ind]_2ZrCl_2$, $[Al]/[Zr] = 3900$. Polymerization conditions: $[Zr] = 1.6 \times 10^{-5}$ mol dm^{-3}, $p_{propylene} = 2.0$ bar, polymerization temperature = 25 °C.

^{1}H NMR spectroscopy was used to determine the comonomer content of the copolymers. The ^{1}H NMR spectrum of the ethylene/10-undecen-1-ol copolymer is shown in Figure 5 and the characterization data are summarized in Table 1. As can be seen, the capabilities of the catalysts to polymerize polar comonomer were different and strongly dependent on the catalyst structure. The best performance was shown by the silylene-bridged catalysts, which converted over 10% of the comonomer to polymer. The highest comonomer content, 13.4 wt %, was detected in the copolymer prepared with the $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO catalyst system; the ethylene-bridged catalyst appeared to perform somewhat more poorly. Attempts to copolymerize ethylene and 10-undecen-1-ol with the nonstereospecific catalyst $[Ind]_2ZrCl_2$/MAO failed: only 0.8 wt % of polar groups were detected in the copolymer and the conversion of the comonomer did not rise above 0.3%.

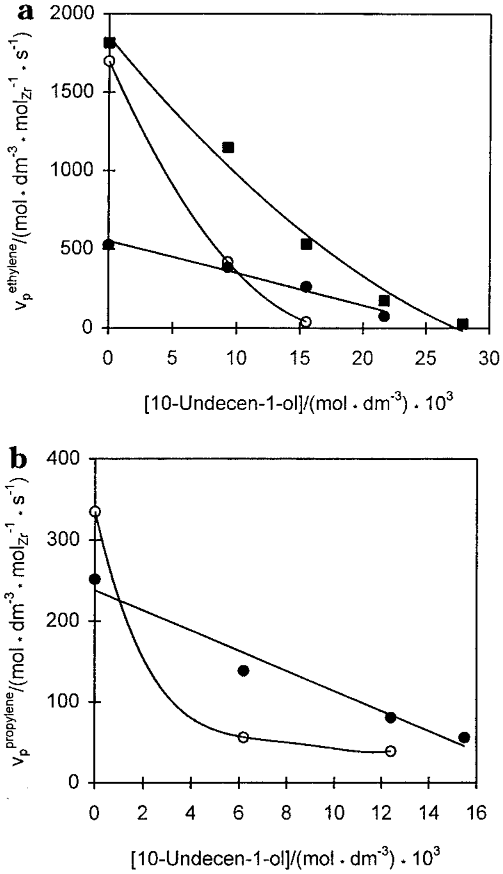

Figure 3. (a) Ethylene polymerization rate ($v^{p}{}_{\text{ethylene}}$) as a function of the molar amount of 10-undecen-1-ol in the polymerization medium with catalysts (■) $[Ind]_2ZrCl_2$, (●) $Me_2Si[2\text{-}MeInd]_2ZrCl_2$, and (○) $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$. Polymerization conditions: $[Zr] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Al]/[Zr] = 4300$, $p_{\text{ethylene}} = 2.0$ bar, polymerization temperature = 25 °C. (b) Propylene polymerization rate ($v^{p}{}_{\text{propylene}}$) as a function of the molar amount of 10-undecen-1-ol in the polymerization medium with catalysts (●) $Me_2Si[2\text{-}MeInd]_2ZrCl_2$ and (○) $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$. Polymerization conditions: $[Zr] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Al]/[Zr] = 4300$, $p_{\text{propylene}} = 2.0$ bar, polymerization temperature = 25 °C.

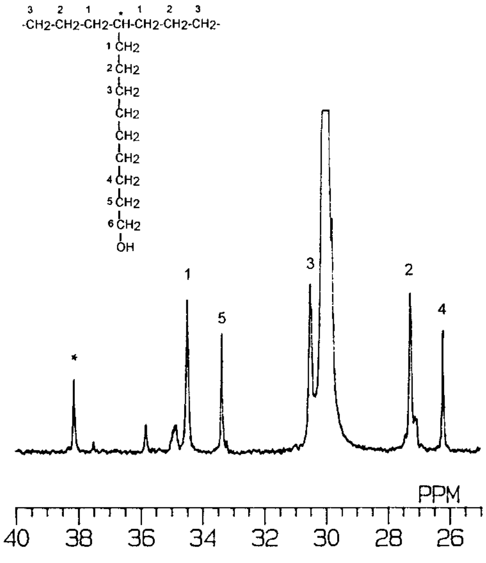

Figure 4. ^{13}C NMR spectrum of ethylene/10-undecen-1-ol copolymer.

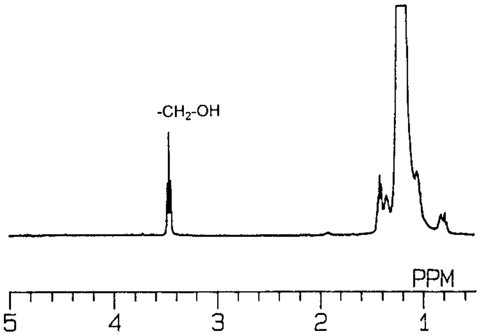

Figure 5. ^{1}H NMR spectrum of ethylene/10-undecen-1-ol copolymer.

The ^{1}H NMR spectroscopy data for the propylene/10-undecen-1-ol copolymers, which are summarized in Table 2, are consistent with the findings reported above for ethylene copolymerizations. Accordingly, the highest conversion of the polar monomer was obtained with the silylene-bridged catalysts $Me_2Si[2\text{-}MeInd]_2ZrCl_2$/MAO and $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO. The slightly lower productivity of the $Me_2Si[Ind]_2ZrCl_2$/MAO catalyst may have been due to the lower Al/Zr mole ratio used in the experiments. As in the ethylene copolymerizations, the ethylene-bridged catalyst was slightly less active in polymerizing the polar comonomer than were its substituted silylene-bridged counterparts.

The molar mass of the synthesized polyethylene was high with each of the metallocene compounds but decreased significantly with the addition of the functional monomer. The molar mass distributions, in turn, were narrow and were not affected by the addition of comonomer when stereorigid catalysts were used, as shown in Table 1. Figure 6 shows the typical GPC curves of the ethylene/10-undecen-1-ol copolymers with different amounts of comonomer in the polymerization medium. The same pattern of behavior was observed in the melting temperatures and crystallinities of the copolymers, which systematically decreased with increasing amount of comonomer in the feed. The DSC curves of the ethylene/10-undecen-1-ol copolymers are presented in Figure 7.

In our earlier investigations with the achiral catalyst $[n\text{-}BuCp]_2ZrCl_2$/MAO, the molar mass distributions of the ethylene/10-undecen-1-ol copolymers were strongly broadened upon addition of the polar comonomer to the reactor.[6] Similar behavior was observed in the present study when polymerizations were carried out in the presence of the nonstereospecific catalyst $[Ind]_2ZrCl_2$/MAO. The characterizing data of the polymerization, which are summarized in Table 3, show the molar mass distribution of the homopolymer to have been narrow ($M_w/M_n = 2.4$), but with the addition of the polar comonomer, the molar mass distribution broadened markedly ($M_w/M_n = 5.0$). The broadening took place in the high molar mass end of the copolymer, resulting in an increase in the weight-average molar mass. The broadening in the molar mass distribution indicated that the catalyst contained multiple active species which most likely were formed by reactions between functional comonomer and catalyst components.

The copolymers prepared with the achiral $[Ind]_2ZrCl_2$/MAO catalyst showed melting behavior that was in agreement with the GPC data described above. The melting endotherm of the pure polyethylene sample appeared at 136 °C, which, however, with the addition of 10-undecen-1-ol decreased below 130 °C. Further increase in the comonomer feed finally provided a copolymer that contained 0.8 wt % of alcohol and melted at 135 °C. In accordance with the melting behavior, the crystallinities, calculated from the heat of fusion, first

Table 1. Data Characterizing Ethylene/10-Undecen-1-ol Copolymers[a]

cat.	alcohol in feed (mol dm^{-3}) × 10^2	activity (g mol_{Zr}^{-1} h^{-1}) × 10^{-5}	alcohol in polymer (wt %)	conv (%)	M_w (g × mol^{-1}) × 10^{-3}	M_w/M_n
$[Ind]_2ZrCl_2$	2.8	1.2	0.8	0.3	452	5.0
$Et[Ind]_2ZrCl_2$	2.2	3.5	5.5	5.6	123	2.3
$Me_2Si[Ind]_2ZrCl_2$	1.6	6.7	7.1	10.1	155	2.4
$Me_2Si[2\text{-}MeInd]_2ZrCl_2$	1.9	5.2	8.0	11.0	203	2.2
$Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$	1.2	1.2	13.4	11.9	177	2.3

[a] Polymerization conditions: [Zr] = 1.6 × 10^{-5} mol dm^{-3}, [Al]/[Zr] = 4300, p_{ethylene} = 2.0 bar, polymerization temperature = 25 °C.

Table 2. Data Characterizing Propylene/10-Undecen-1-ol Copolymers[a]

cat.	alcohol in feed (mol dm^{-3}) × 10^2	activity (g mol_{Zr}^{-1} h^{-1}) × 10^{-5}	alcohol in polymer (wt %)	conv (%)	M_w (g × mol^{-1}) × 10^{-3}	M_w/M_n
$Et[Ind]_2ZrCl_2$	1.6	2.7	3.8	6.3	21	2.1
$Me_2Si[Ind]_2ZrCl_2$[b]	1.6	2.6	3.7	6.1	48	2.0
$Me_2Si[2\text{-}MeInd]_2ZrCl_2$	1.6	5.6	2.8	9.9	208	2.1
$Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$	1.2	4.3	2.7	8.8	260	2.1

[a] Polymerization conditions: [Zr] = 1.6 × 10^{-5} mol dm^{-3}, [Al]/[Zr] = 4300, p_{ethylene} = 2.0 bar, polymerization temperature = 25 °C. [b] [Al]/[Zr] = 3900.

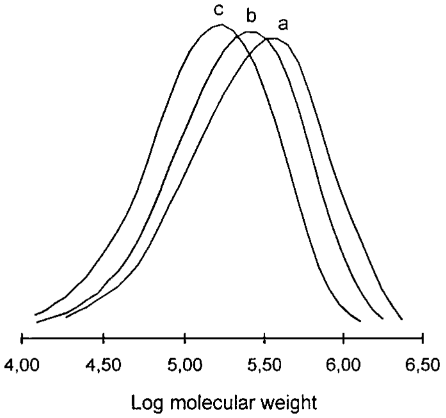

Figure 6. GPC curves of ethylene/10-undecen-1-ol copolymers prepared with the catalyst $Me_2Si[2\text{-}MeInd]_2ZrCl_2$: (a) 6.2 × 10^{-3}, (b) 1.2 × 10^{-2}, and (c) 1.9 × 10^{-2} mol dm^{-3} of 10-undecen-1-ol in the polymerization medium.

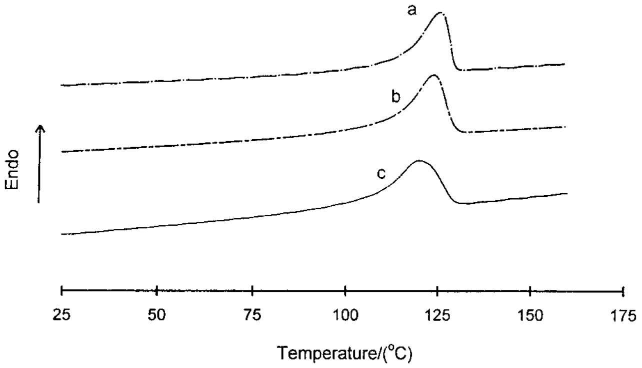

Figure 7. DSC curves of ethylene/10-undecen-1-ol copolymers prepared with the catalyst $Me_2Si[2\text{-}MeInd]_2ZrCl_2$: (a) 6.2 × 10^{-3}, (b) 1.2 × 10^{-2}, and (c) 1.9 × 10^{-2} mol dm^{-3} of 10-undecen-1-ol in the polymerization medium.

Table 3. Copolymerization of Ethylene/10-Undecen-1-ol with $[Ind]_2ZrCl_2$ Catalyst[a]

alcohol in feed (mol dm^{-3}) × 10^2	activity (g mol_{Zr}^{-1} h^{-1}) × 10^{-6}	M_w (g × mol^{-1}) × 10^{-3}	M_w/M_n	T_m (°C)	X_c (%)
0	15.1	673	2.4	136.1	49
0.9	13.2	573	2.2	129.6	40
2.2	1.4	386	2.9	132.3	44
2.8	0.1	452	5.0	134.9	49

[a] Polymerization conditions: [Zr] as $[Ind]_2ZrCl_2$ = 1.6 × 10^{-5} mol dm^{-3}, [Al]/[Zr] = 4300, p_{ethylene} = 2.0 bar, polymerization temperature = 25 °C.

Table 4. Comparison of Metallocenes in Propylene Polymerization[a]

cat.	activity (g mol_{Zr}^{-1} h^{-1}) × 10^{-6}	M_w (g mol^{-1}) × 10^{-3}	M_w/M_n	T_m (°C)
$Et[Ind]_2ZrCl_2$	4.5	42	1.8	138.0
$Me_2Si[Ind]_2ZrCl_2$[b]	5.1	78	2.0	146.8
$Me_2Si[2\text{-}MeInd]_2ZrCl_2$	2.7	272	2.0	149.0
$Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$	3.7	413	2.0	153.1

[a] Polymerization conditions: [Zr] = 1.6 × 10^{-5} mol dm^{-3}, [Al]/[Zr] = 4300, p_{ethylene} = 2.0 bar, polymerization temperature = 25 °C. [b] [Al]/[Zr] = 3900.

decreased from 49% of the pure polyethylene to 40% of the copolymer. Further addition of the comonomer led to an increase in the degree of crystallinity as shown in Table 3.

The major limitation of many stereospecific catalysts in propylene polymerization is the low molar mass of the obtained polymer. Certain substitution patterns, however, tend to improve the performance of the catalyst. Table 4 summarizes the GPC and DSC data of polypropylenes prepared with the four stereospecific catalysts of this study. The addition of a methyl substituent in the α-position of each C_5 ring resulted in a dramatic increase in the molar masses of the polymers. This can be attributed to the steric influence of the substituents, which favors conformations of the polymer chain that hinder β-hydrogen interaction with the zirconium atom. Chain termination is thus made more difficult. In addition, the electron-releasing substituents may lower the Lewis acidity of the active zirconium atom and reduce its tendency toward hydrogen abstraction.[8] The molar masses and melting temperatures of the propylene/10-undecen-1-ol copolymers decreased relative to those of the homopolymers. The molar mass distributions of the copolymers remained narrow, indicating that the catalysts contained only one type of active site (Table 2).

Effect of Pretreatment of 10-Undecen-1-ol with MAO. The effect of pretreating 10-undecen-1-ol with MAO was investigated by reacting the alcohol with an excess of MAO in toluene before initiating the polymerization. The aim was to improve the tolerance of the catalyst to the addition of the polar comonomer. The reactions were carried out at room temperature with the catalyst system $Et[Ind]_2ZrCl_2$/MAO with times ranging from a few minutes to several hours. After the

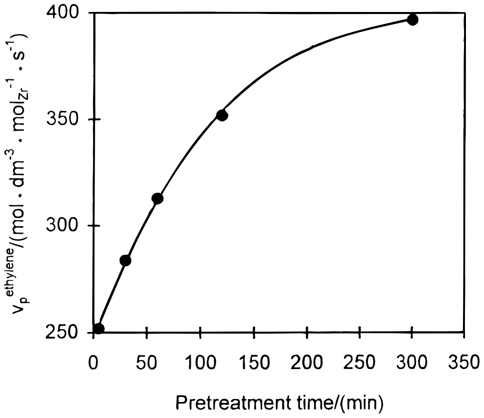

Figure 8. Ethylene polymerization rate ($v^p_{ethylene}$) as a function of the MAO/10-undecen-1-ol pretreatment time. Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [Al]/[Zr] = 4200, [10-undecen-1-ol] = 1.2×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0, polymerization temperature = 25 °C.

Table 5. Effect of Pretreatment Time of 10-Undecen-1-ol with MAO on Ethylene/10-Undecen-1-ol Copolymerization[a]

pretreatment time (min)	activity (g mol$_{Zr}^{-1}$ h^{-1}) × 10^{-6}	alcohol in polymer (wt %)	conv (%)
5	2.3	4.0	11.8
60	2.7	3.8	13.5
300	3.4	3.4	15.0

[a] Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [Al]/[Zr] = 4200, [10-undecen-1-ol] = 1.2×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0 bar, polymerization temperature = 25 °C, polymerization time = 10 min.

pretreatment, the polymerization was initiated and the rate of the ethylene consumption recorded. The rate curve for the ethylene polymerizations after different pretreatment times is presented in Figure 8. As can be seen, the productivity of the catalyst was dependent on the precontacting time of 10-undecen-1-ol and MAO, the ethylene polymerization rate increasing with the length of the pretreatment.

The copolymers prepared after different precontacting times were analyzed by ^{1}H NMR spectroscopy and the amounts of comonomer determined. The spectral data, which are summarized in Table 5, show the comonomer contents of the copolymers to depend on the pretreatment time only slightly. The highest comonomer content, 4.0 wt %, was obtained when the polymerization was initiated after a few minutes of contacting 10-undecen-1-ol and MAO. However, when the polymerization was initiated after 5 h of precontacting time, the comonomer content was 3.4 wt %. At that point, the ethylene polymerization rate was increased by almost 60%. The comonomer conversions calculated from the polymer yield varied from 12 to 15%, depending on the pretreatment time. The increase in the polymerization rate may indicate, that during the precontacting, reactions take place between 10-undecen-1-ol and MAO and the products that are formed at short pretreatment times are more detrimental to the catalyst than those formed during several hours. The reactivity of the comonomer is not, however, markedly affected by precontacting it with MAO.

Effect of Al/Zr Mole Ratio. Generally, with metallocene catalysts, the polymerization activity increases with the Al/Zr mole ratio, reaching a maximum value at a certain mole ratio. If the molar quantity of aluminum alkyl is increased beyond this point, the activity usually remains constant, or decreases slightly.

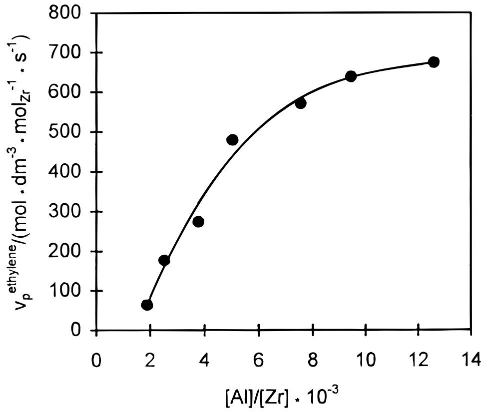

Figure 9. Ethylene polymerization rate ($v^p_{ethylene}$) as a function of the Al/Zr mole ratio. Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [10-undecen-1-ol] = 1.2×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0 bar, polymerization temperature = 25 °C, pretreatment time of 10-undecen-1-ol with MAO = 60 min.

Table 6. Effect of Al/Zr Mole Ratio on Ethylene/10-Undecen-1-ol Copolymerization[a]

Al/Zr (mol/mol)	activity (g mol$_{Zr}^{-1}$ h^{-1}) × 10^{-6}	alcohol in polymer (wt %)	conv (%)
1890[b]	0.5	4.5	5.5
3780	2.2	3.9	11.3
12600	6.7	3.1	26.7

[a] Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [10-undecen-1-ol] = 1.2×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0 bar, polymerization temperature = 25 °C, polymerization time = 10 min, pretreatment time of 10-undecen-1-ol with MAO = 60 min. [b] Polymerization time = 20 min.

The effect of the Al/Zr mole ratio on the ethylene polymerization rate was studied by keeping the amount of comonomer constant and increasing the molar quantity of MAO. The catalyst system was Et[Ind]$_2$ZrCl$_2$/MAO. As Figure 9 clearly shows, the ethylene polymerization rate was low when the Al/Zr mole ratio was below 2000 (Al/10-undecen-1-ol = 2.5). When the concentration of MAO was increased, the activity rose rapidly until a Al/Zr mole ratio of 9450 (Al/10-undecen-1-ol = 12.5) had been reached. With higher molar quantities of MAO, only a slight increase occurred in the ethylene polymerization rate.

The comonomer contents of the ethylene/10-undecen-1-ol copolymers at different Al/Zr mole ratios are summarized in Table 6. With reference to the calculated comonomer conversions, it was readily apparent that the increase in the Al mole amount also resulted in a marked increase in the polymerization rate of the polar comonomer. At the Al/Zr mole ratio of 1890, only 5% of the comonomer had reacted in the copolymerizations. However, when the Al/Zr mole ratio was increased to 12 600, the increase in the comonomer conversion was fivefold. In view of the marked increase in the comonomer conversion, a short polymerization time (10 min) was applied in order to keep the polymerization conditions as constant as possible.

Effect of Polymerization Temperature. The effect of polymerization temperature was investigated using the Et[Ind]$_2$ZrCl$_2$/MAO catalyst system in ethylene/10-undecen-1-ol copolymerization. The activity of the catalyst was heavily dependent on the polymerization temperature, as illustrated in Figure 10. Polymerization activity was low at temperatures below 40 °C, but increased rapidly with an increase in the temperature. The activation energy of ethylene in the

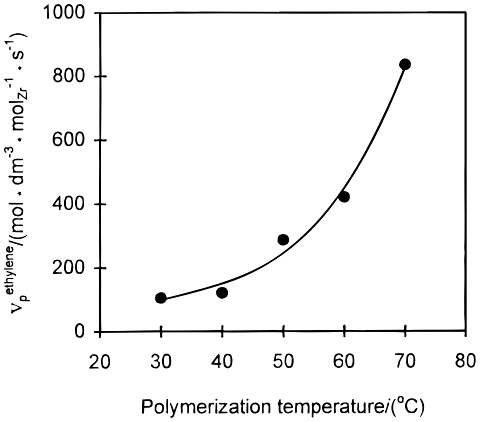

Figure 10. Ethylene polymerization rate ($v^p_{ethylene}$) as a function of the polymerization temperature. Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [Al]/[Zr] = 4200, [10-undecen-1-ol] = 2.5×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0 bar, pretreatment time of 10-undecen-1-ol with MAO = 60 min.

Table 7. Effect of Polymerization Temperature on Ethylene/10-undecen-1-ol Copolymerization[a]

temp (°C)	activity (g mol$_{Zr}^{-1}$ h^{-1}) $\times 10^{-6}$	alcohol in polymer (wt %)	conv (%)
30	1.0	6.7	4.4
50	1.9	9.0	11.0
70	6.9	6.3	28.2

[a] Polymerization conditions: [Zr] as Et[Ind]$_2$ZrCl$_2$ = 1.6×10^{-5} mol dm^{-3}, [Al]/[Zr] = 4200, [10-undecen-1-ol] = 2.5×10^{-2} mol dm^{-3}, $p_{ethylene}$ = 2.0 bar, polymerization time = 10 min, pretreatment time of 10-undecen-1-ol with MAO = 60 min.

copolymerizations, obtained as the slope of the Arrhenius plot, was 54 kJ/mol.

The influence of the polymerization temperature on the composition of the copolymer was investigated by ^{1}H NMR spectroscopy. From the data presented in Table 7, it is evident that the polymerization rate of the functional comonomer is strongly temperature dependent. The highest comonomer content of the copolymer was obtained when the polymerization was carried out at 50 °C; at both higher and lower polymerization temperatures, the concentration of the comonomer in the polymer was less. The strong temperature dependence became even more apparent when the conversions of the comonomer were calculated at different polymerization temperatures. When the polymerization was carried out at 30 °C, the conversion of 10-undecen-1-ol remained below 5%, whereas at the polymerization temperature of 70 °C, the conversion increased to 28% during 10 min of polymerization time.

Conclusions

Our investigations show quite clearly that, relative to conventional Ziegler–Natta catalysts, metallocenes offer a superior way to polymerize monomers containing functional groups. Several obstacles remain to be overcome nevertheless, the most serious being the decay of the catalyst with the addition of polar comonomer.

The copolymerizations of ethylene and propylene with bulky 10-undecen-1-ol revealed that the structure of the catalyst plays an important role in incorporating polar groups into polyolefins. In particular, a chiral structure of the catalyst with a silylene bridge connecting two indenyl ligands seemed to favor the polymerization of functional monomers; the nonbridged counterpart polymerized the polar comonomer to a much lesser degree.

Increase in the polymerization temperature and the Al/Zr mole ratio markedly enhanced the activity of the catalyst, as detected in the ethylene polymerization rate and also in the growing comonomer conversion. The tolerance of the catalyst to the addition of the polar monomer was slightly improved when the polar compound was pretreated with MAO before initiation of the copolymerization.

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