Donor Atom-Stabilized Aluminum Alkyls as Cocatalysts for the Ziegler–Natta Polymerization of Propene

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Abstract: A number of organoaluminum compounds, stabilized with intramolecular nitrogen- or oxygen-donor functions, have been used as cocatalysts for the $MgCl_2/TiCl_4$-catalyzed homopolymerization of propene as well as for the copolymerization of ethene with propene. The polymerization behavior of these aluminum alkyls was examined at different Al/Ti ratios within the range of 2 to 50 and compared with the reference of triethylaluminum (TEA). Especially the alkyls [2-(*N,N*-dimethylaminomethyl)phenyl]dimethylaluminum (**1**) and [2-(*N,N*-dimethylaminomethyl)phenyl]diethylaluminum (**2**) show the highest activities at very low Al/Ti ratios in the homopolymerization of propene, whereas TEA is almost inactive. The species [8-(*N,N*-dimethylamino)naphthyl]dimethylaluminum (**4**) reaches the highest activity of all examined alkyls and is very close to the highest value obtained with TEA. Bulky *iso*-butyl groups at the aluminum center are responsible for the very poor performance of the nitrogen stabilized cocatalysts [8-(*N,N*-dimethylamino)naphthyl]diisobutylaluminum (**5**) and [2-(*N,N*-dimethylaminomethyl)phenyl]diisobutylaluminum (**3**). The properties of the polypropenes synthesized with the stabilized organoaluminum species are similar to those produced with TEA but with a distinctly higher molar mass. In the case of **1**, it was possible to increase the molar mass by a factor of three. For the copolymerizations, the compounds [2-(*N,N*-diethylaminomethyl)phenyl]diethylaluminum (**7**) and (2-methoxybenzyl)diisobutylaluminum (**8**) were found to be most suitable, producing polymers with significantly higher activities than TEA. For all copolymers two fractions were obtained, one crystalline fraction with a low and an amorphous part with a high amount of comonomer. In both fractions, **7** and **8** provide a higher comonomer incorporation than TEA.

Keywords: donor atom-stabilized aluminum alkyls; ethene-propene copolymerization; propene polymerization; Ziegler–Natta catalysis

Introduction

For several decades, the Ziegler–Natta olefin polymerization has been the topic of various academic and industrial studies. Their main focus was the development of catalysts which has made enormous progress since the discovery of the activity for α-olefin polymerization of $TiCl_4$ in combination with aluminum alkyls by Ziegler[1] and Natta.[2] In 1976 Sinn and Kaminsky found that soluble metallocene catalysts in combination with methylalumoxan (MAO) achieve extremely high activities for the polymerization of ethene and α-olefins.[3] The synthesis of chiral *ansa*-metallocenes by Brintzinger in 1982[4] then initiated the production of stereoregular polymers like isotactic[5] or syndiotactic[6] polypropene. These types of catalysts reach more and more industrial relevance,[7] but a significant part of the worldwide production of polyethene and polypropene still uses the classic heterogeneous Ziegler–Natta process.[8] Catalysts of the fourth and fifth generation, optimizing the titanium/$MgCl_2$ complex by donors, are able to produce very high yields of polyethene and isotactic polypropene.[9] There was less attention paid to the development of new cocatalysts. In these processes triethylaluminum is normally used as cocatalyst.

Copolymers of ethene and propene are important technical elastomers. They are mainly produced by vanadium-based catalysts like VCl_4 and $VOCl_3$ in combination with diethylaluminum chloride as cocatalyst.[10] As aluminum compounds like triethylaluminum

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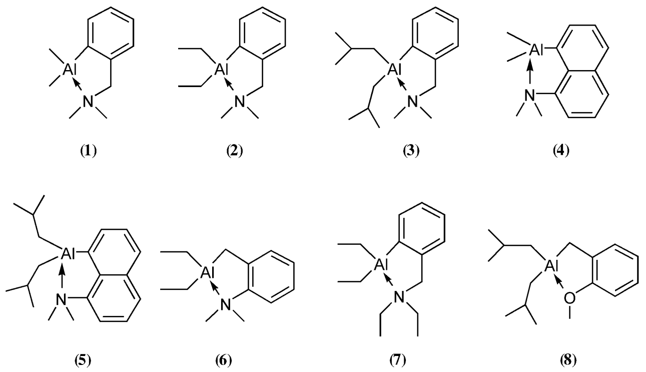

Figure 1. Donor atom-stabilized aluminum alkyls used as cocatalysts in this work.

and diethylaluminum chloride are extremely sensitive to traces of air and moisture, they are quite difficult to handle and imply various risks, especially for industrial processes. Schumann et al. synthesized a large variety of sulfur-, nitrogen- and oxygen-stabilized aluminum alkyls, thus providing a certain stability towards oxygen and moisture.[11,12] A number of these stabilized aluminum alkyls were tested by us regarding their potential as cocatalysts in combination with $MgCl_2/TiCl_4$ as catalyst for the polymerization of ethene. Some of the oxygen-stabilized compounds have been found to reach higher activities for the polymerization of ethene compared with TEA.[13,14,15,16,17,18] In this paper, we present first results for the homopolymerization of propene and for the copolymerization of ethene with propene under usage of a variety of these stabilized alkyls as cocatalysts.

Results and Discussion

All polymerizations were performed at 60 °C in *n*-hexane as solvent and $TiCl_4$ supported on $MgCl_2$ as catalyst. To enhance the reliability of the results, all experiments were reproduced. Figure 1 shows the used cocatalysts.

Propene Homopolymerizations

In the propene homopolymerizations, no internal or external donors were added to increase the stereoselectivity of the catalyst systems. The role of the aluminum alkyl for the isospecific working catalyst centers is still under investigation.[19] It is thus interesting to see whether the structure of the cocatalyst, especially the compounds with internal donor functions used in this work, has an influence on the isotacticity. The tacticity of the polymers was specified by the portion of the [*mmmm*]-pentade in the ^{13}C NMR spectra. The atactic part was separated by extraction in boiling *n*-heptane with a Soxhlet apparatus only for a few examples. In these cases, the percentage of the [*mmmm*]-pentade was, independent of the used aluminum alkyl, increased up to 85%. For all cocatalysts the Al/Ti ratio was varied within the range of 2 to 50 and the results were compared to the reference cocatalyst TEA.

In a series of experiments, it was found that aromatic aluminum alkyls are more suitable for the polymerization than aliphatic species. A number of parameters of the molecular structure were systematically modified to identify the relationship between structure and reactivity. The aluminum alkyls (**1**), (**2**) and (**3**) have either methyl-, ethyl- or *iso*-butyl groups bonded to the aluminum to determine the influence of the steric environment at the reactive center. The results are listed in Table 1.

Compound (**1**) shows a similar behavior to (**2**), the maximum activity of both species is about $350\ \mathrm{kg_{PP}\ mol_{Ti}^{-1}\ h^{-1}\ M_{propene}^{-1}}$, which is approximately 75% of the highest TEA activity. The stabilized compounds reach their highest value at very low Al/Ti ratios: 2 in case of (**1**) and 3 for (**2**). Using TEA as cocatalyst, nearly no activity is observed at an Al/Ti ratio of 2. The isotacticity of the product is not impaired by the use of a different cocatalyst. It merely depends on the Al/Ti ratio. Bimetallic catalyst species are generally supposed to produce highly isotactic polymer, it is therefore not surprising that the isotacticity increases with the growth of the amount of aluminum compound. However, the type of the aluminum alkyl is obviously not the decisive factor for the isotacticity a catalyst system works with. The melting point increases with the isotacticity and therefore shows the same behavior. As expected, due to the steric hindrance of the *iso*-butyl groups at the metal center, (**3**) provides very poor results. Beside the very low activity, the atactic polymer part is much larger than for all other aluminum alkyls. All three cocatalysts, especially (**1**), produce polypropene with a significantly higher molar mass than TEA.

In structure (**2**) the aluminum and in (**6**) the donor atom is directly adjacent to the aromatic ring. This changes the electron density at the metal and the donor atom. In (**4**) and (**5**), as opposed to structures (**1**) and (**3**), the phenyl ring is substituted by a naphthalene, which primarily alters the distance between metal center and donor function. Finally, (**8**) has an oxygen instead of a nitrogen donor. Complete results for the remaining cocatalysts are given in Table 2.

In the aluminum alkyl (**6**), the aluminum atom is not directly bonded to the aromatic ring. Compared to the corresponding structure (**2**), both cocatalysts give similar results, activities are also in the same range. The effect of direct adjacencies of the aluminum to the aromatic system is obviously not very pronounced. The polymer properties are also similar, with only slightly higher values for molar mass, isotacticity and melting temperature in the case of (**2**). With $405\ \mathrm{kg_{PP}\ mol_{Ti}^{-1}\ h^{-1}\ M_{propene}^{-1}}$, (**4**) reaches the highest activity of all

Table 1. Results of the polymerization of propene using aluminum alkyls with different alkyl chain lengths at the aluminum center.

Cocatalyst	Al/Ti ratio	Activity[a]	Isotacticity[b]	Molar mass [g/mol]	Melting point [°C]
TEA	2	20	n.d.	n.d.	n.d.
TEA	3	269	28	n.d.	152
TEA	5	380	39	165,000	153
TEA	10	440	47	191,000	152
TEA	20	456	54	218,000	154
TEA	50	343	62	214,000	157
(**1**)	2	348	31	n.d.	154
(**1**)	3	319	39	477,000	156
(**1**)	5	279	45	528,000	156
(**1**)	10	203	50	465,000	156
(**1**)	20	113	55	710,000	157
(**2**)	2	295	34	n.d.	152
(**2**)	3	347	45	306,000	153
(**2**)	5	312	47	523,000	155
(**2**)	10	234	50	389,000	156
(**2**)	20	120	54	559,000	157
(**3**)	5	63	23	233,000	151
(**3**)	10	71	21	249,000	151
(**3**)	20	75	22	n.d.	152
(**3**)	50	83	26	326,000	152

[a] $kg_{PP}\,mol_{Ti}^{-1}\,h^{-1}\,M_{propene}^{-1}$.
[b] Percent of the [*mmmm*]-pentade in ^{13}C NMR spectra.
n.d. = not determined.

Table 2. Results for the polymerization of propene with different aluminum alkyls.

Cocatalyst	Al/Ti ratio	Activity[a]	Isotacticity[b]	Molar mass [g/mol]	Melting point [°C]
(**6**)	2	218	32	n.d.	152
(**6**)	3	275	40	336,000	153
(**6**)	5	320	45	419,000	154
(**6**)	10	311	48	385,000	154
(**6**)	20	295	53	432,000	156
(**4**)	2	161	29	n.d.	154
(**4**)	3	297	37	340,000	154
(**4**)	5	405	41	414,000	155
(**4**)	10	339	45	428,000	156
(**4**)	20	313	48	n.d.	156
(**5**)	10	5	30	264,000	152
(**5**)	20	55	26	287,000	152
(**8**)	2	10	n.d.	n.d.	n.d.
(**8**)	3	28	31	220,000	152
(**8**)	5	64	35	228,000	152
(**8**)	10	342	42	258,000	153
(**8**)	20	349	50	317,000	155
(**8**)	50	308	58	369,000	155

[a] $kg_{PP}\,mol_{Ti}^{-1}\,h^{-1}\,M_{propene}^{-1}$.
[b] Percent of the [*mmmm*]-pentade in ^{13}C NMR spectra.
n.d. = not determined.

examined aluminum alkyls, its value is almost 90% of the highest activity achieved by TEA. Even though the maximum value is reached at an Al/Ti ratio of 5, which is clearly higher than for (**1**) and (**2**), it is still lower than for TEA. The analogous structure of (**4**) is (**1**) with a phenyl ring instead of a naphthalene. This species shows a lower activity, assuming that the longer Al–Ti bond in the case of (**4**) implicates a higher reactivity of the molecule. As

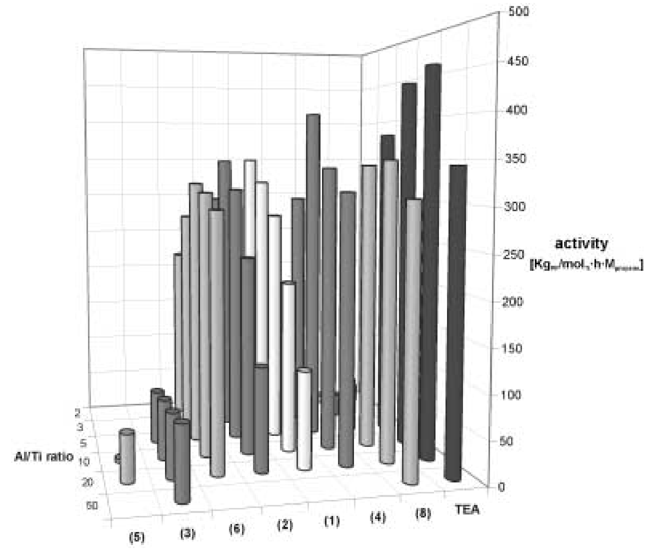

Figure 2. Activities of all examined aluminum alkyls for the homopolymerization of propene.

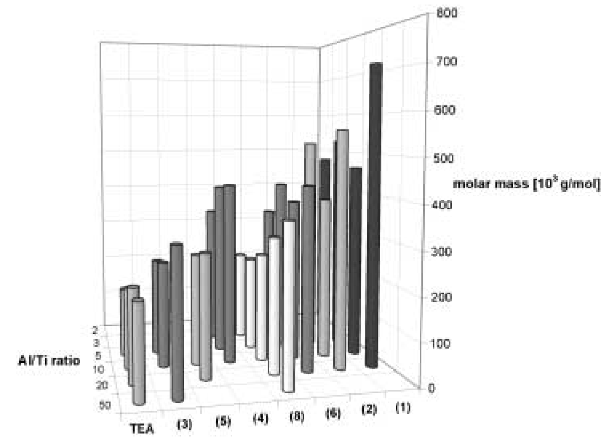

Figure 3. Molar masses of polypropene synthesized with different aluminum alkyls.

expected, using (**5**) produces the same effect as (**3**). The very low performance of both alkyls is due to their bulky *iso*-butyl groups. The only cocatalyst with an oxygen donor function in this comparison is (**8**). This species has already been tested for ethene polymerization and was found to be more active then TEA.[13] In the case of propene, (**8**) has a sufficient performance and is very close to the behavior of TEA, e.g., a comparatively high Al/Ti ratio needed to reach the maximum activity. A complete comparison of the activities of all used cocatalysts is shown in Figure 2.

As far as the polymer properties are concerned, only the molar masses show significant differences, isotacticity and therefore melting temperatures are only dependent on the Al/Ti ratio. As mentioned above, the type of aluminum alkyl seems to have no influence on the nature of isospecifically working catalyst centers. The molar masses of the polymers produced with the different cocatalysts are summarized in Figure 3.

It is conspicuous that all stabilized aluminum alkyls yield polymers with a higher molar mass than TEA. Even the values produced with (**5**) and (**3**), the alkyls with a very poor performance, are higher in comparison to TEA. The highest molar mass is obtained using (**1**). With over 700,000 g/mol it is 3 times higher than for the comparable polymer produced with TEA.

Ethene-Propene Copolymerizations

A number of donor atom-stabilized aluminum alkyls have also been tested as cocatalysts in the copolymerization of ethene with propene. The majority of these alkyls show no satisfying performance, but with the species (**7**) and (**8**), excellent results were obtained in comparison to TEA. The copolymerizations were performed at 60 °C, with an Al/Ti ratio of 20 and 60 mol % propene in the feed. The reactions yielded two fractions of polymers, an insoluble part of crystalline polymer with a low incorporation of propene as well as a soluble part of an amorphous polymer with a high amount of comonomer. The results are given in Table 3.

The results show that both aluminum alkyls (**7**) and (**8**) provide much higher activities than TEA. In case of TEA and (**8**) the major percentage of the obtained polymer is the insoluble, crystalline part with a very low amount of propene, 3% for TEA and 4% for (**8**), respectively. Both crystalline polymers have similar properties: Molar mass and melting temperature are in the same range. The soluble parts contain higher amounts of propene and have a significantly lower molar mass. In the case of the polymer produced with TEA, the propene content is low enough to achieve a crystalline polymer with a melting instead of a glass transition temperature. As seen for the homopolymerization of propene, (**8**) reaches more similar results to TEA than the nitrogen-stabilized aluminum compounds. Compound (**7**) differs extremely from TEA, for the activity, which is six times higher, as well as for polymer properties. By using this cocatalyst, half of the resulting polymer is crystalline and half is amorphous. Both parts achieve a much higher comonomer content and, accordingly, a lower molar mass.

Conclusion

For the propene polymerization, the tested aluminum alkyls give very satisfying results. Except for the nitrogen-stabilized species containing *iso*-butyl groups at the aluminum center, all cocatalysts reach activities in the range of TEA. Especially (**1**), (**2**) and (**4**) have their maximum activity at very low Al/Ti ratios between 2 and 5, permitting a low extent of a cocatalyst. Oxygen-

Table 3. Results for the copolymerization of ethene and propene with the aluminum alkyls (**7**) and (**8**).

Cocatalyst	Part of polymer (percentage)	Incorporation of propene [mol %]	Activity[a]	Molar mass [g/mol]	Melting/glass transition temp. [°C]
TEA	Crystalline (79%)	3	95	1,100,000	108 (T_m)
TEA	Crystalline [b] (21%)	23	95	54,000	65 (T_m)[b]
(**7**)	Crystalline (52%)	13	580	410,000	102 (T_m)
(**7**)	Amorphous (48%)	36	580	160,000	– 51 (T_g)
(**8**)	Crystalline (83%)	4	480	1,200,000	117 (T_m)
(**8**)	Amorphous (17%)	32	480	130,000	– 69 (T_g)

[a] $kg_{Polymer}\ mol_{Ti}^{-1}\ h^{-1}\ M_{monomer}^{-1}$, activity is given for both fractions together.

[b] In this case, the soluble part is also crystalline and shows a melting and no glass transition temperature.

stabilized species have already been found to produce polyethene with higher activities than TEA, in the case of propene, the tested cocatalyst (**8**) cannot achieve this, although the results are promising.

Copolymerizations are much more successful with the aluminum alkyls (**7**) and (**8**) than with TEA. The activities are clearly higher, the resulting polymers contain much more propene and molar masses as well as glass transition temperatures that are in the range of technical requirements. These properties cannot be achieved with TEA, consequently these aluminum alkyls are the first which produce convenient ethene-propene copolymers with toxicologically harmless titanium catalysts, an advantage towards vanadium species. Despite the higher costs for their synthesis, donor atom-stabilized organoaluminum compounds have a very high potential in the Ziegler–Natta olefin polymerization. They show a certain stability towards oxygen and moisture and abate the risk of serious accidents while handling them. In spite of this, these species are able to produce polyethene, polypropene and their copolymers without any disadvantages. They reach high activities and yield polymers with no adverse properties compared to TEA.

Experimental Section

General Remarks

All operations were performed under inert argon atmosphere using standard Schlenk and glovebox techniques. For polymerizations, catalyst suspensions and cocatalyst solutions, dried solvents were used.

Chemicals

Ethene and propene were purchased from Linde and Gerling, Holz & Co. and purified by passage through columns filled with molecular sieve (4 Å) and the BASF-catalyst R3 – 11. Argon was purchased from Linde with a purity higher than 99.996% and was passed through a Messer-Griesheim Oxisorb cartridge to remove traces of oxygen. Hexane and toluene were purchased from Merck and stored for several days over potassium hydroxide before they were degassed and purified by passing through columns filled with molecular sieve (4 Å) and the BASF-catalyst R3 – 11. Catalyst and donor atom-stabilized aluminum alkyls were synthesized according to the described literature procedures.[11,12,13]

Polymer Analysis

^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 NMR spectrometer at 100.62 MHz and 100 °C in 1,2,4-trichlorobenzene and 1,1,2,2-tetrachloroethane-d_2 as internal standard with the reference signal at 74.24 ppm. Melting and glass transition temperatures were determined by differential scanning calorimetry analysis, performed on a Mettler-Toledo DSC 821^e. The samples were measured with a heating rate of 20 K/min in a temperature range from – 100 to 200 °C. Data were collected from the second heating run. Molar masses were determined with an Ubbelohde viscosimeter (capillary 530 0a, $K = 0.005\ mm^2/s^2$) at 135 °C in decahydronaphthalene stabilized with 1 g/L 2,6-di-*tert*-butyl-4-methylphenol.

Polymerization Procedure

Polymerizations were performed in a 1-L Büchi glass autoclave equipped with magnetic stirrer, supplies for monomers, argon and vacuum and inlets for solvent, cocatalyst and catalyst mixtures. The reactor was dried at 95 °C under vacuum for a minimum of 1 hour and flushed several times with argon before the polymerizations were performed. The reactor was filled with *n*-hexane as solvent and a solution of cocatalyst in toluene and saturated with the monomers before the reaction was started by addition of the catalyst suspension *via* a gas-tight syringe. Polymerizations were terminated by addition of 10 mL ethanol and the reaction mixtures were stirred overnight with dilute hydrochloric acid to remove catalyst and cocatalyst residues from the polymer. The organic layer was neutralized with sodium hydrogen carbonate and washed several times with water before the solvent was removed under vacuum. The polymers were dried at 60 °C under reduced pressure overnight.

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