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Halogen-Free Soluble Ziegler Catalysts with Methylalumoxan as Catalyst

Jens Herwig and Walter Kaminsky

Institut für Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, Federal Republic of Germany

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SUMMARY

A soluble, halogen-free Ziegler-catalyst can be obtained when using bis(cyclopentadienyl)dimethyltitanium together with methylalumoxane. It is possible to polymerize both ethylene as well as propene with high activities. The so formed polypropylene is 100 % atactic. Polymerization activities in dependence upon Al- and Ti-concentrations and polymerization rates of ethylene and propylene are shown.

INTRODUCTION

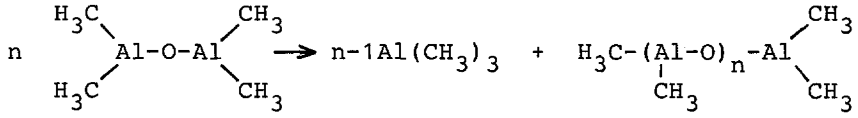
Halogen-free soluble Ziegler catalysts based on bis(cyclopentadienyl)titanium IV-compounds and trialkylaluminium are usually considered to be catalytically inactive, for halogen is postulated to have a bridge-function within the active species (1,2). When, nevertheless, water is added to these systems in equimolar quantities alkylaluminium catalysts with an exceptionally high polymerization activity can be obtained, as we have reported earlier (3). The UV-spectrum of such polymerization experiments shows the formation of an olefin complex with a band maximum at 390 nm.

Although water was considered to be a catalyst poisoner for many Ziegler-type systems, Reichert and Meyer (4) and Breslow and Long (5) obtained increases in activity by adding water to Ziegler catalysts based on bis(cyclopentadienyl)titaniumdichloride. Recently Mejzlick et al. (6) reported about similar observations when treating other Ziegler catalysts containing chloride, with water.

RESULTS AND DISCUSSION

Some time ago we already postulated that alumoxanes formed from trimethylaluminium and water with the elementary formula $(CH_3)_2Al-O-Al(CH_3)_2$ cause the increase in activity. Alumoxanes have long been known to act as catalysts for propeneoxide and acetaldehyde polymerization (7,8,9).

There are several methods (7,10,15) for the preparation of alumoxanes, which must be carried out slowly and with a controlled reaction rate, because of their high enthalpies. The careful hydrolysis of trimethylaluminium by crystal water of $CuSO_4 \cdot 5\ H_2O$ was proved to be the most effective method of obtaining uniform products of solid methylalumoxane with a high yield. In contrast to alumoxanes which are formed from greater alkyls, the methyl-type does not stop at the first step of the elementary unit $R_2Al-OAlR_2$, but it continues to condense in sovents during the separation of trimethylaluminium and forms longer units, which precipitate from the solvent, when they have reached a certain size.



$$n\ (H_3C)_2Al-O-Al(CH_3)_2 \longrightarrow n-1\,Al(CH_3)_3 + H_3C-(\underset{CH_3}{Al}-O)_n-Al(CH_3)_2$$

Similar reactions were observed during the formation of

$$CH_3(Al(CH_3)-CH_2)_n-Al(CH_3)_2 \quad (16,17)$$

Because of this dismutation there is no change to isolate the monomeric elementary unit of the methylalumoxane. Nevertheless a solid, colourless and glassy methylalumoxane with an average of 12 Al-atoms was obtained under experimentically constant conditions of preparation (18).

From one alumoxane preparation a product was succesfully isolated by fractional precipitation, which under mass spectroscopy showed a ring structure containing 5 aluminium units.

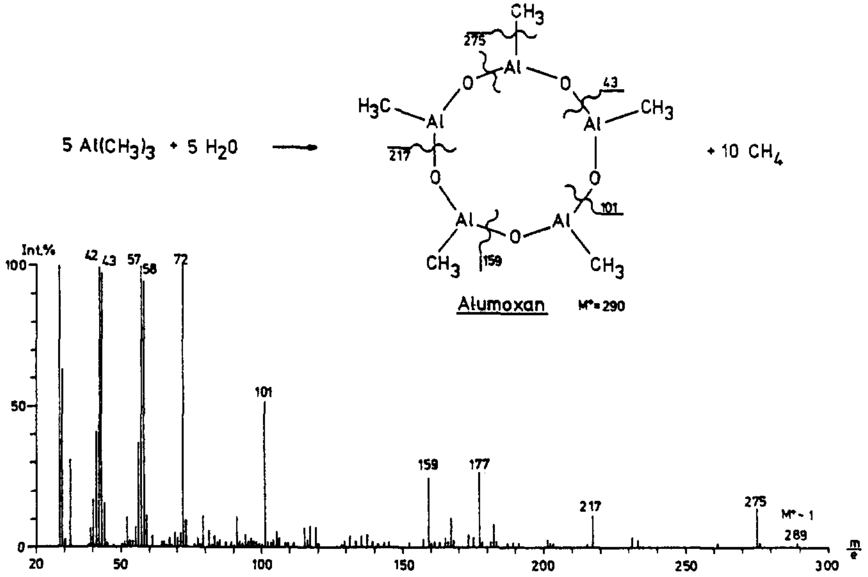


Fig. 1. Mass spectrum of a ring-alumoxane

Solid methylalumoxane with about 12 Al-units was used as cocatalyst together with bis(cyclopentadienyl)dimethyltitanium in polymerization of olefins and yielded catalyst productivities up to 10^6 g PE/g Ti and activities of more than 300 mol ethylene/mol Ti·sec.

The table shows that the relative molecular masses of PE increase with smaller titanium concentrations when the activity is optimized. On the other hand, the molecular masses are decreasing with higher Ti-concentrations leading to lower productivities. The highest polymerization activities are comparable with those of heterogenous Ziegler-contacts.

The catalyst can also be used in gasphase polymerization, especially if the contact is prepared in the presence of small amounts of ethylene.

TABLE Olefin polymerization with methylalumoxane as catalyst by 20 °C

Activity (gP/gTi·2h	$Cp_2Ti(CH_3)_2$ (mol)	Al-units (mol·10^3)	M_η	Remarks (Solvent)
250 PE	$1.34\cdot10^{-4}$	2.51	170.000	200 ml toluene
1.000 PE	$8.07\cdot10^{-5}$	2.29	470.000	200 ml toluene
80.000 PE	$3.07\cdot10^{-6}$	2.11	520.000	200 ml toluene
400.000 PE	$9.20\cdot10^{-7}$	2.2	530.000	200 ml toluene
3.500 PE	$1.25\cdot10^{-5}$	5.2	9.000	polymerization by 90 °C liquid α-olefin
70.000 PE	$1.2\cdot10^{-5}$	2.1	980.000	gas-phase
1.500 PP	$2.4\cdot10^{-5}$	1.9	88.000	50 ml toluene
10.000 PE/PP	$1.2\cdot10^{-5}$	1.8	$(\eta)=1.19$	50 ml toluene

Surprisingly this catalyst combination is able to polymerize propene in solution and as a concentration too, yielding atactic polypropylene. As the amorphous polypropylene remains in solution, the total systems is homogeneous even after the beginning of polymerization, contrary to precipitation polymerization of ethylene. So there is a possibility to make kinetic investigations, which prove the durabilityof the catalyst.

Particularly interesting products were obtained by the copolymerization of ethylene and propene in toluene and in a liquid mixture of monomers. These mixed polymers are composed of evenly distributed ethylene and propene units, whose ratio can be varied through the choice of polymerization parameters. The properties of these polymers can be modified by decreasing the contents of propene, changing from plastic to elastic, to treacly solid products.

Whereas ethylene quickly polymerizes already a few seconds after starting the experiment, the polyreaction of propene needs an induction period of several hours to develop maximum activity, as Figures 2 and 3 show.

The relative molecular mass of the polyethylene drops with increasing temperature and can easily be controlled by varying the polymerization temperature. At 90 °C oligomers can be produced, containing 75 % of α-olefins with an even C-number.

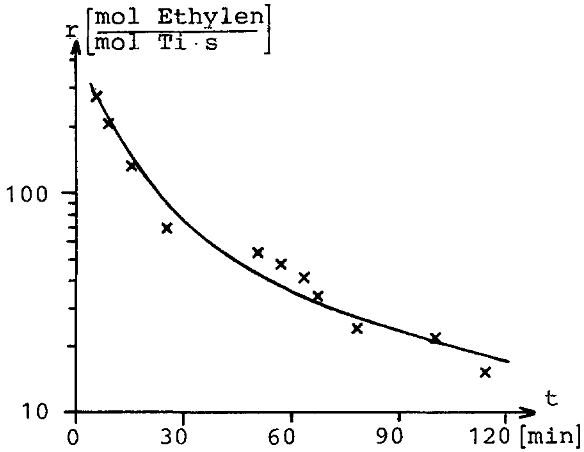


Fig. 2.
Polymerization rate of ethylene

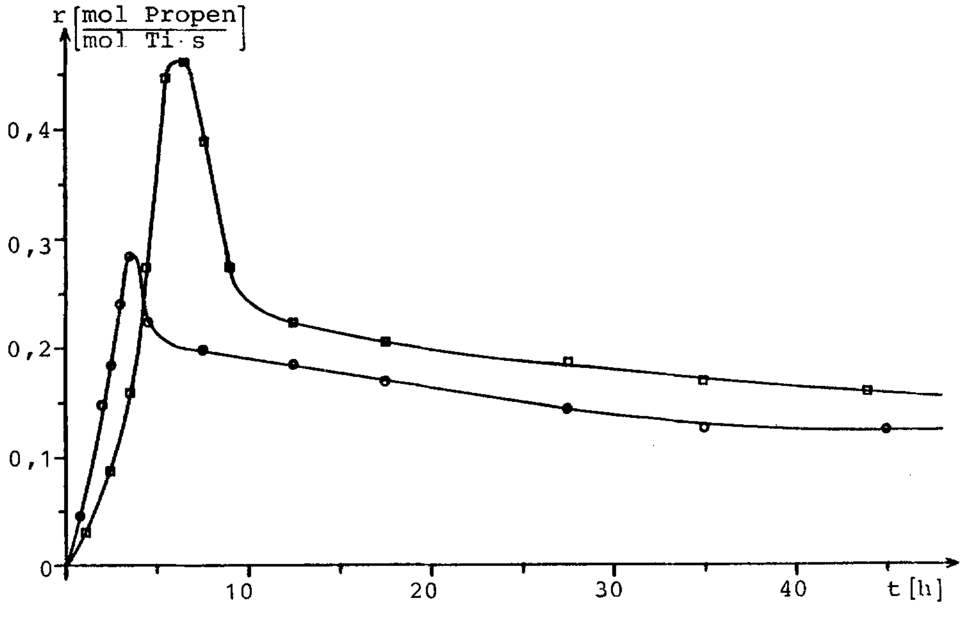


Fig. 3. Polymerization rate of propene

The activity of polymerization is decisively influenced by the concentrations of bis(cyclopentadienyl)dimethyltitanium and methylalumoxane. There is a linear dependence between the activity and the titanium concentration in a great range.

The polymerization activity as a function of aluminium concentration ata constant titanium concentration of 10^{-4} mol/l is shown in Fig.4.

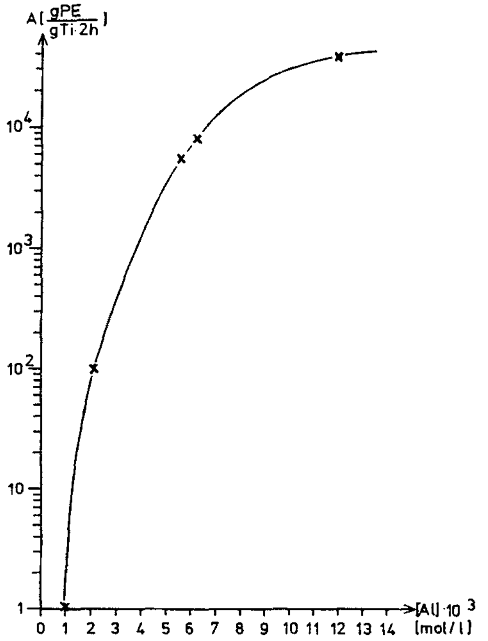


Fig. 4.

Polymerization activity as a function of Al-concentration

The increase of the Al-concentration always causes a rise in activity, which approaches a limit with large amounts of alumoxane. On the other hand, activity is decreased by low concentrations of aluminium. Below an aluminium value of about 10^{-3} mol/l nearly no polymerization activity is observed.

If the oligomeric methylalumoxane is exchanged for oligomeric isoprenylaluminium, little polymerization activity will be noticed. As soon as water is added, the activity increases tenfold.

When the Cp-ligand of the $Cp_2Ti(CH_3)_2$ is exchanged for the larger CH_3-Cp-ligand, activity decreases, retaining the same tacticity of the produced polypropylene. Other transition metal compounds like $VOCl_3$, $V(acac)_3$, $VO(acac)_2$, $Cr(acac)_3$, $Co(acac)_3$, $Ni(acac)_2$ and $Fe(acac)_3$ are also able to form catalysts for polymerization together with methylalumoxane.

The vanadium compounds represent the group of highest activity, the more so, since the alumoxane stabilizes the active oxidation number of the vanadium as well as functioning as an alkylcompound and partly as a substitute for the well known reactivators.

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