

KRYSTYNA CZAJA, MARZENA BIAŁEK,  
WIOLETTA OCHĘDZAN

University of Opole, Institute of Chemistry  
Oleska 48, 45-052 Opole

## Organometallic $\text{VCl}_4$ -based catalyst supported on $\text{MgCl}_2(\text{THF})_2$ for ethylene polymerization

### RAPID COMMUNICATION

**Summary** — A Ziegler—Natta catalyst was obtained by milling  $\text{VCl}_4$  with the magnesium support in the form of the  $\text{MgCl}_2(\text{THF})_2$  complex, followed by activation with an organoaluminum compound. This catalyst was employed in low-pressure polymerization of ethylene. The system was found to offer a very high activity and to polymerize ethylene at a rate of a few hundred kg PE/(g V h) with the resulting molecular weight of the product very high. The kinetic investigation of the polymerization process revealed over 80% of the transition metal atoms to be involved in the forming catalytic active sites, undergoing virtually no deactivation over the period of time studied.

**Key words:** polymerization of ethylene, Ziegler—Natta type catalyst, activity, deactivation

High-performance titanium-magnesium catalysts are of great importance for commercial low-pressure polymerization of olefins; they are utilized predominantly in the production of HDPE, LLDPE, and isotactic polypropylene. These catalytic systems have also been studied in the synthesis of the ethylene-propylene copolymers [1–3] which so far were produced over catalysts based on vanadium compounds [ $\text{VCl}_4$ ,  $\text{VOCl}_3$ ,  $\text{V}(\text{Acac})_3$ ]. Vanadium-based catalysts were not employed in the synthesis of polyethylene because of their low productivity. Recently, however, these systems were found successfully applicable to the ethylene polymerization process [4]. This became possible first of all on account of the promoter, in most cases a halogen component [5, 6], which slowed down the deactivation of vanadium-based catalytic systems.

In our earlier study [7, 8] pinning down of the unstable and low-activity  $\text{VOCl}_3/\text{Et}_2\text{AlCl}$  catalytic system on the  $\text{MgCl}_2(\text{THF})_2$  support was found to improve considerably its efficiency and stability in the polymerization process. These positive results encouraged us to extend our study to include other vanadium-based systems.

### EXPERIMENTAL

All operations were carried out in dry and oxygen-free argon.

### Materials

Ethylene (Petrochemia SA, Płock) and pure argon (Polgaz) were used after having been passed through a column of sodium metal supported on  $\text{Al}_2\text{O}_3$ . Pure-grade hexane (Petrochemia SA, Płock) was refined with sulfuric acid, dried by refluxing in argon from sodium metal, and stored over 4 Å molecular sieves.  $\text{VCl}_4$  (Aldrich) and  $\text{Et}_2\text{AlCl}$  (Fluka) were used without further purification.  $\text{MgCl}_2(\text{THF})_2$  was prepared at the Institute of Chemistry, University of Wrocław.

The vanadium-magnesium catalyst precursor was prepared by ball-milling  $\text{MgCl}_2(\text{THF})_2$  with  $\text{VCl}_4$  in hexane at room temperature for 24 h.

### Polymerization

The polymerization reaction was carried out in a 1-dm<sup>3</sup> reactor equipped with a stirrer, in hexane, at a constant pressure of ethylene. Hexane, 0.7 dm<sup>3</sup>,  $\text{Et}_2\text{AlCl}$ , and catalyst precursor were charged into the reactor and then ethylene was introduced. The reaction was terminated by adding 5% methanolic HCl, the polymer was filtered off, washed with methanol, and dried.

### Analysis

Molecular weights of the resulting polymers were determined by the viscosity method in decalin at 135°C [9].

The melting points and degree of crystallinity of polymers were measured by differential scanning calorimetry (Unipan 605 calorimeter) at a heating rate of 5 K/min.

## RESULTS AND DISCUSSION

In keeping with the literature, the productivity of the  $\text{VCl}_4/\text{Et}_2\text{AlCl}$  catalytic system in the low-pressure polymerization of ethylene was found to be low, ranging from as little as a few hundred grams to a few kilograms of polyethylene per 1.0 gram vanadium per hour, depending on process operating conditions. However, pinning down  $\text{VCl}_4$  on a support in the form of a complex of  $\text{MgCl}_2$  with tetrahydrofuran improved the catalyst activity by a few orders of magnitude. Table 1 provides

Table 1. CONDITIONS AND RESULTS OF POLYMERIZATION OF ETHYLENE. Precatalyst:  $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4$ , polymerization conditions:  $\text{Mg}/\text{V} = 10$  (mole ratio),  $t = 30$  min

Cocatalyst	$C_V$ mmol/ $\text{dm}^3$	Mole ratio Al/V	Tempe- rature $^\circ\text{C}$	Pressure MPa	Activity kg PE/ (g V h)
$\text{AlEt}_3$	0.015	1666	25	0.5	46.2
$\text{Al}(i\text{-Bu})_3$	0.015	1666	25	0.5	94.8
$\text{AlEt}_2\text{Cl}$	0.015	1666	25	0.5	96.1
$\text{AlEt}_2\text{Cl}$	0.02	1250	25	0.5	80.9
$\text{AlEt}_2\text{Cl}$	0.01	2500	25	0.5	160.7
$\text{AlEt}_2\text{Cl}$	0.005	5000	25	0.5	271.5
$\text{AlEt}_2\text{Cl}$	0.0025	10000	25	0.5	317.4
$\text{AlEt}_2\text{Cl}$	0.01	2500	35	0.5	121.4
$\text{AlEt}_2\text{Cl}$	0.01	2500	50	0.5	106.5
$\text{AlEt}_2\text{Cl}$	0.01	2500	25	0.5	140.7
$\text{AlEt}_2\text{Cl}$	0.01	2500	25	0.4	104.5
$\text{AlEt}_2\text{Cl}$	0.01	2500	25	0.3	87.4

the data for ethylene polymerization versus the composition of the catalytic system and polymerization conditions. Diethylchloroaluminum proved to make the best activator for the supported vanadium precatalyst. It led to no deactivation of the system even when used in a

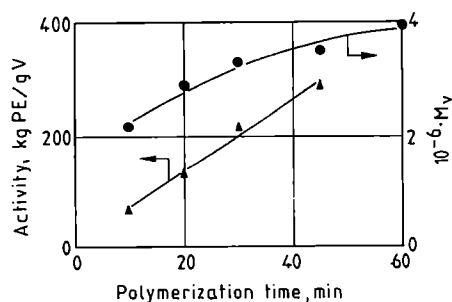


Fig. 1. Catalyst activity in polymerization of ethylene and viscosity-average molecular weight of polyethylene  $M_V$  as function of polymerization time over the  $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$  catalytic system; polymerization conditions:  $C_V = 0.005$  mmol/ $\text{dm}^3$ ,  $C_{Al} = 25$  mmol/ $\text{dm}^3$ ,  $p = 0.5$  MPa,  $T = 25^\circ\text{C}$

huge excess. This suggests that, if pinned down on the support used, the vanadium in the form of  $\text{VCl}_4$  was fairly resistant to reduction by the organoaluminum cocatalyst to the lower oxidation states that are inactive in the polymerization process. The catalytic system studied revealed a high activity, higher even than that of the analogous system containing  $\text{VOCl}_3$  [7, 8] and particularly  $\text{TiCl}_4$  [10]. And it was stable in the course of the polymerization reaction, just like the other systems mentioned (Fig. 1).

A kinetic analysis was performed for the polymerization process which involved the catalytic system studied. The analysis, based on experimental polyethylene yields and molecular weights (Fig. 1), gave a relationship between the number of macromolecules created and the time of polymerization (Fig. 2). The kinetic model presented elsewhere [7] was utilized to calculate the concentration of active sites and rate constants for elementary reaction (Table 2).

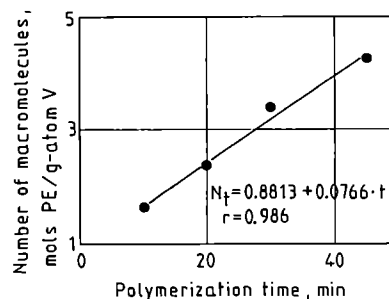


Fig. 2. Concentration of macromolecules  $N_t$  of polyethylene in the polymerization medium as a function of polymerization time

Table 2. KINETIC PARAMETERS OF ETHYLENE POLYMERIZATION OVER THE  $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$  CATALYTIC SYSTEM

$C_V$ mmol/ $\text{dm}^3$	$R_p$ kg/(g V min)	$[C']$ mol/g-atom V	$k_p$ $\text{dm}^3/(\text{mol s})$	$k_{tr} \cdot 10^4$ $\text{dm}^3/(\text{mol s})$
0.005	6.5	0.88	455	29.7

The high activity developed by the catalyst containing  $\text{VCl}_4$  and supported on  $\text{MgCl}_2(\text{THF})_2$ , results chiefly from the very high involvement ( $\sim 80\%$ ) of vanadium atoms in the forming active sites. Additionally, the high rate constant for the propagation reaction,  $k_p$ , is advantageous (Table 2).

Table 3. PROPERTY DATA FOR POLYETHYLENE PRODUCED OVER THE  $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$  CATALYTIC SYSTEM

$M_{V,h} \cdot 10^{-3}$	Melting point $^\circ\text{C}$	Degree of crystallinity (DSC) %	Yield point MPa	Tensile strength MPa	Elongation, %	Density g/ $\text{cm}^3$	Bulk density g/ $\text{dm}^3$
3950	140	54	20.7	36.8	250	0.949	72.5

A very high difference between the chain propagation and the chain termination rates ( $k_p$  is by a few orders higher than  $k_{tr}$ ) leads to polyethylene having a very high molecular weight. This material offers very good mechanical properties (Table 3), but its low bulk density is a disadvantage.

#### REFERENCES

1. Kim H. J., de Santa Maria L. C.: *Polymer* 1994, **35**, 1335.
2. Chu K.-J., Chang H.-S., Ihm S.-K.: *Eur. Polym. J.* 1994, **30**, 1467.
3. Koivumaki J., Seppala J. V.: *Eur. Polym. J.* 1994, **30**, 1111.
4. Karol F. J., Kao S.-Ch., Cann K. J.: *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 2541.
5. Adisson E., Deffieux A., Fontanille M., Bujadoux K.: *J. Polym. Sci., Part A, Polym. Chem.* 1994, **32**, 1033.
6. Deffieux A., Amarin C., Fontanille M., Adisson E., Bujadoux K.: *Polimery* 1994, **39**, 585.
7. Czaja K., Białek M.: *Macromol. Chem., Rapid Commun.* 1996, **17**, 253.
8. Czaja K., Białek M.: *Polimery* 1996, **41**, 412.
9. Sholte T. G., Nezerink N. L. J., Schoffeleers H. M., Browds A. K. G.: *J. Appl. Polym. Sci.* 1984, **29**, 3763.
10. Nowakowska M., Bosowska K.: *Makromol. Chem.* 1992, **193**, 889.

#### W kolejnym zeszycie ukaza się następujące artykuły:

- Instalacje do rozdziału odpadowych tworzyw sztucznych z opakowań
- Zastosowanie polimerów jako katalizatorów w reakcjach katalizy międzyfazowej. Cz. II. Katalizatory polimerowe — sole oniove, związki makrocykliczne oraz rozpuszczalniki aprotyczne na matrycy polimerowej
- Fizykochemia i termodynamika układów semikoloidalnych polimer-bitum. Cz. II. Polimery jako modyfikatory paku węglowego
- Wpływ nośników zawierających węgiel na proces stereospecyficznej polimeryzacji propylenu (*wersja angielska*)
- Sieciowanie w wyniku cyklotrimeryzacji nowych żywic z wiązaniami acetylenowymi
- Modyfikowanie polipropylenu jarzącymi wyładowaniami małej częstotliwości w powietrzu (*wersja angielska*)
- Wpływ zmiany stopnia polimeryzacji kondensacyjnej bloku oligo(tereftalanu tetrametyleny) na właściwości blokowego terpolimeru etero-estro-amidowego
- Model matematyczny procesu wytłaczania jednoślismakowego. Cz. VIII. Głowice wytłaczarskie