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Synthesis and characterization of ethylene-1-hexene copolymers prepared by using $\text{MgCl}_2(\text{THF})_2$ -supported Ziegler—Natta catalysts

RAPID COMMUNICATION

Summary — Ethylene was copolymerized with 1-hexene over vanadium (VOCl_3 and VCl_4) and titanium (TiCl_4) catalysts supported on $\text{MgCl}_2(\text{THF})_2$ and activated with Et_2AlCl . So far these catalyst systems have not been known as initiators of ethylene-1-hexene copolymerization. The vanadium catalysts were more active than the titanium catalyst and, at identical comonomer concentrations in the feed, gave rise to a greater incorporation of 1-hexene into the copolymer. Even at relatively low fractions of 1-hexene, the $\text{MgCl}_2(\text{THF})_2$ -supported catalysts affected much the copolymer properties like density, melting point and crystallinity.

Key words: copolymerization of ethylene with 1-hexene, VOCl_3 , VCl_4 and TiCl_4 catalysts supported on $\text{MgCl}_2(\text{THF})_2$ and activated with Et_2AlCl , density, melting point and crystallinity of copolymers.

The linear low density polyethylene (LLDPE) prepared by copolymerization of ethylene with α -olefins is an important product in the petrochemical industry. Monomers that decrease the melting point and crystallinity of polymers at low concentrations are of great interest. It is known that longer-chained comonomers such as 1-hexene are more effective at the same concentration than the shorter units such as propene. The different reactivities of the olefins are important for copolymerization. Moreover, they depend not only on the type of comonomer but also on the catalytic system used.

In our earlier studies we have prepared and characterized two vanadium-based catalysts supported on complex magnesium chloride: $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$ and $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$, showing a high activity and stability in ethylene polymerization [1, 2]. In view of the beneficial role of the vanadium systems in copolymerization processes, we have decided to study the catalytic properties of these two vanadium catalysts, and for comparison, their titanium counterpart based on TiCl_4 , in the synthesis of ethylene-1-hexene copolymers.

EXPERIMENTAL

Polymerization

All the operations were always performed under dry and oxygen-free argon. Polymerization-grade ethylene

and pure argon were used after having been passed through a column of sodium metal supported on Al_2O_3 . Pure-grade hexene was refined with sulfuric acid, dried by refluxing in argon over sodium metal, and stored over 4 Å molecular sieves. 1-Hexene (Aldrich) was stored over 4 Å molecular sieves and used without further purification. VOCl_3 , VCl_4 (Aldrich), TiCl_4 (Merck) and Et_2AlCl (Fluka) were used without further purification. $\text{MgCl}_2(\text{THF})_2$ was prepared at the Institute of Chemistry, University of Wrocław (Poland), and was used as received. The supported vanadium or titanium magnesium catalyst precursors were prepared by ball-milling $\text{MgCl}_2(\text{THF})_2$ with VOCl_3 , VCl_4 or TiCl_4 in a slurry (hexane) at room temperature for 24 h. The polymerizations were carried out in a 1-dm³ reactor equipped with a mechanical stirrer. The reactor was filled with hexane (0.7 dm³) and required amounts of Et_2AlCl and catalyst precursor ($\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3$, $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4$, $\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4$, respectively). Then 1-hexene was charged into the reactor and copolymerization was initiated by introducing ethylene. The monomer pressure was kept constant during the polymerization by continuous addition of ethylene. The reaction was stopped by addition of an acidic methanol solution, the polymer was subsequently filtered off, washed with methanol and dried. The copolymerization conditions were (values in parentheses refer to copolymerization over titanium catalyst): $[\text{VOCl}_3] = 1.5 \cdot 10^{-5} \text{ mol/dm}^3$, $[\text{VCl}_4] = 1 \cdot 10^{-3} \text{ mol/dm}^3$ ($[\text{TiCl}_4] = 4.5 \cdot 10^{-5} \text{ mol/dm}^3$); $[\text{Al}] =$

$25 \cdot 10^{-3} \text{ mol/dm}^3$ ($30 \cdot 10^{-3} \text{ mol/dm}^3$); $P_{Et} = 0.5 \text{ MPa}$, $T = 35^\circ\text{C}$ (50°C); $t = 60 \text{ min}$.

Characterization of polymers

Copolymer compositions were determined by the IR method [3] by using a Philips PU 9800 FT-IR spectrophotometer. Samples were investigated in the form of powdered polymer — KBr pellets.

The heat of fusion (ΔH_f) and melting temperature (T_m) were measured for the samples which had been previously melted and recrystallized in a TA Instruments 2010 DSC calorimeter, heating rate 5 K/min. Polymer crystallinity (%) was calculated as $X_c = \Delta H_f (100/290)$ [4]. The density of the copolymers was measured according to Polish Standard PN-92/C-89035.

RESULTS AND DISCUSSION

Catalyst activity and reactivity

The copolymerization of ethylene with 1-hexene was conducted over the vanadium catalyst based on VOCl_3 or VCl_4 and, for comparison, on a TiCl_4 catalyst. Each catalyst was supported on magnesium chloride complexed with a Lewis base, $\text{MgCl}_2(\text{THF})_2$, and activated with Et_2AlCl . The results of the ethylene polymerization as well as its copolymerization are shown in Table 1. In-

Table 1. Results of homo- and copolymerization of ethylene over catalysts investigated

Homopolymerization		Copolymerization	
Catalytic activity, kg PE/(g-atomV,Ti)	M_H/M_E	1-hexene content, m_H , % mol	catalytic activity, kg PE/(g-atomV,Ti)
$\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$			
8496	0.0117	0.259	5655
$\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$			
12 369	0.0117	0.297	8016
$\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}$			
1286	0.0148	0.255	828

M_E and M_H — ethylene and 1-hexene contents in polymerization feed, respectively, m_H — 1-hexene content in copolymer.

roduction of 1-hexene into the polymerization feed is seen to have suppressed the catalyst activity of each catalytic system investigated. It should be stressed, however, that each of the vanadium catalysts was clearly more active than the titanium counterpart, as demonstrated earlier in the polymerization of ethylene [1].

To study the effect of the catalyst system on the reactivity of hexene, it is necessary to know the composition of the copolymerization products. The composition of

ethylene- α -olefins copolymers is usually determined by IR [5–7] or $^{13}\text{C-NMR}$ [8–10] method. Unfortunately, the low solubility of our copolymers in the solvent commonly used for polyethylene and the high temperature (up to 150°C), made our attempts to record $^{13}\text{C-NMR}$ spectra unsuccessful. The copolymerization products obtained on the catalysts supported on $\text{MgCl}_2(\text{THF})_2$ have high molecular weights, similar to those of ethylene homopolymers synthesized on identical systems [1, 2, 11]. For this reason the composition of the copolymers was measured by the IR method using the A_{1379}/A_{1368} absorbance ratios which were obtained by separation of analytical bands [3]. How the 1-hexene content in the copolymer changes with the concentration of the comonomer in the feed is shown in Table 2.

Table 2. 1-Hexene content in the copolymers obtained over catalysts investigated

Catalyst	$M_H \cdot 10^2$ mol/ dm^3	M_E mol/ dm^3	M_H/M_E	m_H , % mol
$\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$	0.57	0.4880	0.0117	0.259
	5.67		0.1162	0.388
	8.48		0.1737	0.465
	11.26		0.2308	0.595
$\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$	0.57	0.4880	0.0117	0.297
	1.14		0.0234	0.323
	2.85		0.0583	0.406
	5.67		0.1162	0.466
$\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}$	0.57	0.3865	0.0148	0.255
	11.26		0.2914	0.571
	22.21		0.5747	0.789

M_E and M_H — ethylene and 1-hexene contents in polymerization feed, respectively, m_H — 1-hexene content in copolymer.

With each investigated catalyst, incorporation of 1-hexene increased as the 1-hexene concentration in the feed was increased. However, the 1-hexene content in the copolymer varied with the type of the catalytic system. Each vanadium catalyst was more effective and gave the higher concentration of the comonomer in the polymerization product than did the titanium catalyst.

Table 2 shows that, in each case, the copolymers were synthesized with a very low hexene content. Thus ethylene is seen to exhibit a much higher activity than that of 1-hexene, and $r_E \gg 1$ and $r_H \ll 1$. Therefore, the well-known copolymer composition equation can be replaced by the following simplified equation [5, 7].

$$\frac{m_H}{m_E} = \frac{1}{r_E} \cdot \frac{M_H}{M_E} \quad (1)$$

Comparison of the r_E -values for the three catalysts studied shows (Table 3) that there are no marked differences in comonomer reactivity with the two vanadium

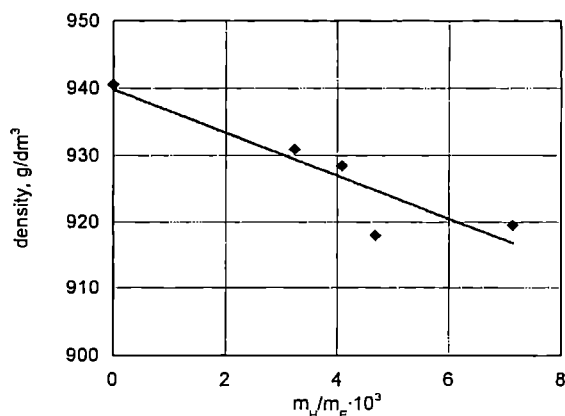
Table 3. The reactivity ratios r_E in ethylene-1-hexene copolymerization

Catalyst system	Reactivity ratio r_E
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$	66.7
$MgCl_2(THF)_2/VCl_4/Et_2AlCl$	54.2
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$	104.0

catalyst systems. On the other hand, it should be stressed that, in the copolymerization with ethylene, 1-hexene is clearly more reactive in the presence of each vanadium catalyst than titanium catalyst. The latter exhibited not only the smallest activity but also produced a copolymer with the lowest hexene content (higher r_E -value).

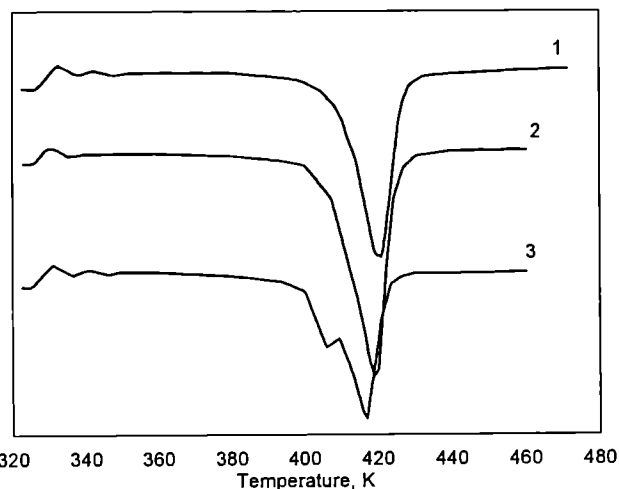
Properties of copolymers

In Fig. 1, the density of the copolymer is plotted against the feed ratio. In another study, the density of the copolymerization product clearly decreased as the comonomer content in the feed was increased. It should

**Fig. 1.** Copolymer density in relation to 1-hexene content in the polymer; catalyst: $MgCl_2(THF)_2/VCl_4/Et_2AlCl$

be stressed, however, that the present catalysts supported by being milled on $MgCl_2(THF)_2$ complex show a very attractive copolymerization behavior. Relatively low fractions of hexene are required to reach the desired densities. Figure 2 shows the thermal behavior of the copolymers obtained on the $VOCl_3$ -based catalyst. When the concentration of 1-hexene in the feed was increased, the melting point of the copolymer decreased and the peak was broader. In an earlier study on ethylene-1-hexene copolymers obtained over homogeneous metallocene catalysts, similar effects were observed [12].

The properties of the polymers produced by the three catalytic systems investigated as well as the concentration of hexene incorporated in the polymer chains are

**Fig. 2.** DSC thermograms of polyethylene (1) and ethylene/1-hexene copolymers (2 and 3) (1-hexene in the feed: 2 — $0.57 \cdot 10^{-2} \text{ mol/dm}^3$, 3 — $11.26 \cdot 10^{-2} \text{ mol/dm}^3$) prepared over $MgCl_2(THF)_2/VOCl_3/Et_2AlCl$ catalyst**Table 4.** Properties of ethylene/1-hexene copolymers

M_H/M_E	1-Hexene in copolymer, m_H , % mol	Melting temperature, °C	Degree of crystallinity, %
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$			
0.0177	0.259	140.0	64.0
0.1162	0.388	138.7	49.3
0.1737	0.465	138.3	47.8
$MgCl_2(THF)_2/VCl_4/Et_2AlCl$			
0.0117	0.297	138.0	52.0
0.0583	0.406	137.9	47.7
0.1162	0.466	137.7	43.0
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$			
0.0148	0.255	139.9	—
0.2914	0.571	137.6	—

shown in Table 4. As expected with each investigated system the melting point and the crystallinity decreased as the of 1-hexene content was increased.

CONCLUSION

Titanium and vanadium catalysts supported by milling on $MgCl_2(THF)_2$ have produced ethylene-1-hexene copolymers efficiently. Similarly as in the ethylene polymerization, vanadium catalysts are much more active in the copolymerization than is the titanium counterpart.

The reactivity of 1-hexene in the copolymerization with ethylene is clearly higher in the presence of each vanadium catalyst examined than that of the titanium catalyst.

The catalysts investigated, supported on a

MgCl₂-THF complex, can efficiently change the properties of the copolymer even at relatively low fractions of 1-hexene.

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Na rynku wydawniczym ukazała się książka autorstwa Włodzimierza Szlezyngiera pt. **Tworzywa sztuczne tom III**, która stanowi bardzo cenną kontynuację dwóch wydanych już tomów, pod tym samym tytułem.

Tom III składa się z siedmiu rozdziałów, zawierających: nowe i zmodyfikowane rodzaje tworzyw sztucznych, jakie ukazały się na rynku w ostatnich kilku latach; nowe (perspektywiczne) polimery, które mają szansę praktycznego ich zastosowania; polimerowe tworzywa elektroprzewodzące; polimery biodegradowalne i perspektywy ich rozwoju; tworzywa sztuczne stosowane w medycynie i farmacji; ogólne prognozy i kierunki rozwoju tworzyw sztucznych po 2000 roku; omówiono również nowsze rodzaje środków pomocniczych do tworzyw sztucznych.

W aneksie podano m.in. zestaw tabel i rysunków, dotyczący ilościowego rozwoju i dziedzin zastosowania poszczególnych tworzyw sztucznych na świecie, w tym również prognozy po 2000 roku.

Książka zawiera bardzo bogaty wykaz najnowszej literatury (za lata 1996—1999), dotyczący głównie chemii i technologii polimerów, w tym również wiele opracowań monograficznych.

Książka, tom III wraz z tomami I i II, obejmuje całokształt wiedzy o tworzywach sztucznych, w tym również o środkach pomocniczych stosowanych do ich otrzymywania i przetwarzania. Jest ona przeznaczona dla studentów wyższych uczelni na kursach magisterskich, inżynierskich, podyplomowych i doktoranckich, a także nauczycieli szkół wyższych i średnich, pracowników instytutów branżowych, inżynierów przemysłu chemicznego oraz pokrewnych itp.

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