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Studies on ethylene/1-hexene copolymerization over the zirconocene catalyst supported on MAO-modified $\text{MgCl}_2(\text{THF})_2$. The effect of copolymerization conditions on catalyst activity and copolymer properties

RAPID COMMUNICATION

Summary — The activity of a $\text{MgCl}_2(\text{THF})_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst was studied in copolymerization of ethylene with 1-hexene in relation to Al:Zr mole ratio (1500—7000 at 50°C), experimental temperature (20—70°C), and time (20—90 min at 50°C; 10—55 min at 65°C). As the temperature and the Al:Zr ratio were increased, the activity of the catalyst rose. At the same time, the degree of incorporation of 1-hexene into the polymer chain increased and the M , melting point and crystallinity of the copolymer decreased. The catalyst was stable throughout the copolymerization. The process rate and copolymer properties were not affected by copolymerization time.

Key words: copolymerization of ethylene with 1-hexene, supported zirconocene catalyst, catalyst activity, copolymerization conditions, copolymer properties.

Nowadays studies on olefin polymerization and copolymerization have been centered around metallocene catalysts. Metallocenes are attractive because they are very active and make it possible, by tailoring the coordination environment of the metal center, to control the molecular weight (M) and its distribution (MWD), comonomer incorporation and polymer stereochemistry [1]. The effect of metallocene structure on catalyst performance in ethylene polymerization and copolymerization and the catalyst copolymerization reactivity and copolymer properties have been extensively studied [2—19]. Other group of studies deal with the heterogenization of a soluble metallocene catalyst on a solid support and describe the character of supported catalysts in the polymerization and copolymerization of olefins [20—30]. Nevertheless, the literature data on the parameters of polymerization and copolymerization carried out over supported metallocene catalysts as well as on their influence on product properties are limited.

Previously we studied the influence of immobilization of a homogeneous $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst on the magnesium dichloride complex with tetrahydrofuran on the behavior of the resulting heterogeneous catalyst in the synthesis of ethylene/1-olefin copolymers. An-

choring the Cp_2ZrCl_2 compound on the magnesium support was found to yield an effective system for copolymerization of ethylene with 1-hexene. The effect of modification of the magnesium support by the organoaluminum compound (MAO, Me_3Al , and Et_2AlCl) on the activity and reactivity of the supported catalyst as well as the properties of the copolymers obtained were also investigated. The modification of the support by an organoaluminum compound as well as the kind of the compound used as a modifier were found to affect the activity of the catalyst system. The MAO-pretreated support allowed to increase the activity of this catalyst system. The modified support increased also the copolymer molecular weight and intermolecular heterogeneity distribution. However, incorporation of the comonomer into the polymer chain and some other properties of the copolymer like molecular weight, melting point, and crystallinity, were not affected by the type of the modifier.

Beside the catalytic system, copolymerization productivity and the microstructure and properties of copolymers are also dependent on copolymerization parameters [31]. Therefore, we tried to establish a correlation between the parameters of the process and the properties of the product obtained.

This paper gives a further insight into the behavior of the zirconocene catalyst supported on the $\text{MgCl}_2(\text{THF})_2$ carrier modified with methylaluminoxane in the copolymerization of ethylene with 1-hexene. We described the activity of this system and the properties of the copolymers obtained under various conditions of copolymerization. The copolymerization parameters evaluated included the Al:Zr mole ratio, time and temperature of the process.

EXPERIMENTAL

Materials

1-Hexene (Aldrich) and toluene (POCh) were purified by refluxing over sodium metal. Cp_2ZrCl_2 (Fluka) and MAO (Witco's 10% solution in toluene) were used without further purification. Further materials were used as described previously [32, 33].

Catalyst preparation and copolymerization

$\text{MgCl}_2(\text{THF})_2$ was stirred with MAO in toluene solution for 1 h at an Al/Mg 1:1 mole ratio to modify the support. The supported zirconocene catalyst precursors were prepared by ball-milling the modified $\text{MgCl}_2(\text{THF})_2$ with Cp_2ZrCl_2 (Mg/Zr = 10) in a slurry (toluene) at room temperature for 24 h. The supported catalyst had been activated with MAO (Al/Zr = 4000) before comonomer and ethylene were introduced as a reaction feed. The ethylene/1-hexene copolymerization procedures were as described previously [32, 33].

Characterization of copolymers

Copolymer compositions were determined by the IR method [34] by using a Philips PU 9800 FT-IR spectrophotometer. The melting temperatures and crystallinity of the polymers were measured with a TA Instruments 2010 DSC calorimeter. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a Waters model 150-C instrument; details of measuring the copolymer characteristics were published previously [32, 33].

RESULTS AND DISCUSSION

Effect of Al:Zr mole ratio

In general, the mole ratio of the cocatalyst (MAO) to the catalyst has a significant impact on the catalytic properties of metallocene catalysts. It is known that a very large quantity of MAO is necessary to achieve a high polymerization activity of homogeneous metallocene catalysts [35]. Figure 1 shows the activity of immobilized catalyst as a function of the Al:Zr ratio. The catalyst

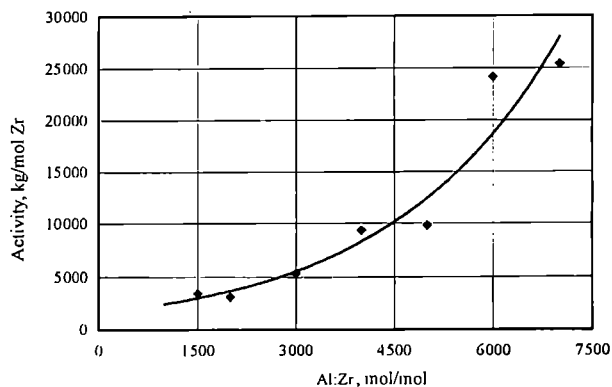


Fig. 1. The activity of $\text{MgCl}_2(\text{THF})_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst in ethylene/1-hexene copolymerization in relation to Al:Zr mole ratio in the catalytic system; copolymerization conditions: $c_{\text{Zr}} = 5 \cdot 10^{-6} \text{ mol/dm}^3$, $T = 50^\circ\text{C}$, $p_{\text{Et}} = 0.5 \text{ MPa}$, $c_{1\text{-hexene}} = 0.432 \text{ mol/dm}^3$, $t = 30 \text{ min}$

activity in the copolymerization process increased as the Al:Zr ratio was increased. A similar trend has been reported for the homopolymerization of ethylene over a MgCl_2 -supported catalyst [36]. In the case of a SiO_2 -supported metallocene catalyst [37], polymerization activity increased as the Al:Zr ratio was raised up to 2000. Ratios up to 5000 did not result in a significant increase in catalyst activity.

Modification of the support with MAO appears to have eliminated the organoaluminum cocatalyst. However, the present study shows the activity of the catalytic system with no cocatalyst to be insufficient and to be increased by using an activator such as MAO cocatalyst in excess. The MAO adsorbed on the support surface is likely to transform the zirconocene into a "cation-like" species but an organoaluminum activator is necessary to deactivate trace impurities from the solvent, comonomer, and mainly from ethylene which is introduced in a continuous way to the reaction feed.

Table 1 shows the effect of cocatalyst concentration on copolymer properties. Incorporation of the comonomer is seen to increase but slightly as the Al:Zr mole ratio was increased from 1500 to 5000. As the Al:Zr ratio was

Table 1. The effect of Al:Zr mole ratio on properties of copolymers. Catalyst: $\text{MgCl}_2(\text{THF})_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, copolymerization conditions: $c_{\text{Zr}} = 5 \cdot 10^{-6} \text{ mol/dm}^3$, $T = 50^\circ\text{C}$, $p_{\text{Et}} = 0.5 \text{ MPa}$, $c_{1\text{-hexene}} = 0.432 \text{ mol/dm}^3$, $t = 30 \text{ min}$

Al:Zr	Comonomer incorporation % mol	Melting point, $^\circ\text{C}$	Crystallinity, %	Bulk density, g/dm^3
1500	4.11	120.05	41.2	100
2000	3.83	120.08	47.2	—
3000	4.15	119.08	41.6	117
4000	4.36	118.04	44.3	133
5000	4.58	118.05	44.1	119
6000	6.04	113.01	47.5	295
7000	6.54	114.06	38.9	317

further increased still bigger changes occurred in the incorporation of the comonomer. At the same time, the melting point of the copolymer decreased.

Effect of copolymerization temperature

Temperature is known [38] to affect the olefin copolymerization processes run in the presence of homogeneous metallocene catalysts, *viz.*, catalyst activity, comonomer incorporation, polymerization kinetic profile, melting point, molecular weight, and polydispersity of polyolefins, *etc.* In propylene polymerization [22], changes in activity, molecular weight, isotacticity and polymer bulk density were found to be more moderate with a supported catalyst than those observed for a solution (homogeneous) catalyst.

In the presence of homogeneous zirconocene systems the rate of ethylene polymerization reaches a maximum value in the range of 45–50°C and decreases as the temperature is further increased [39]. On the other hand, Meshkova *et al.* [40] have shown the rate of ethylene polymerization in toluene over the Et[Ind]₂ZrCl₂ catalyst supported on the zeolite modified by TMA to increase over the temperature range 34–73°C. The activity of the MgCl₂-supported zirconocene catalyst also increases as temperature is increased from 50 to 70°C. However, beyond 70°C, the activity decreases [36]. The SiO₂-supported zirconocene catalyst has exhibited a maximum activity also at 60°C [37].

The influence of the ethylene/1-hexene copolymerization temperature in the range from 20 to 70°C on the activity of the MgCl₂(THF)₂/MAO/Cp₂ZrCl₂/MAO catalyst is presented in Fig. 2. The catalyst activity is seen to increase as the temperature is raised. The support surface seems to stabilize the active species and, as a consequence, supported metallocene catalysts achieve higher polymerization activities at higher temperatures than do homogeneous catalysts. The present results allowed to evaluate the activation energy of ethylene/1-hexene copolymerization as 45.25 kJ/mol.

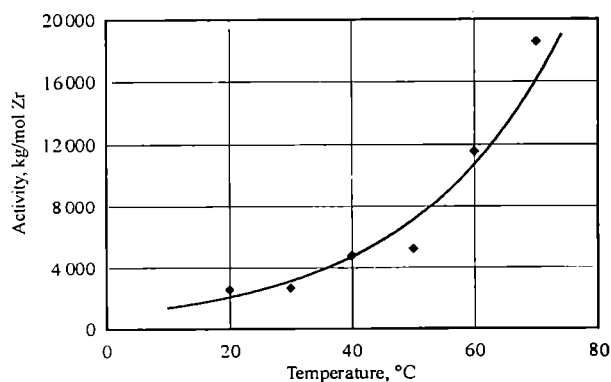


Fig. 2. The activity of MgCl₂(THF)₂/MAO/Cp₂ZrCl₂/MAO catalyst in ethylene/1-hexene copolymerization in relation to copolymerization temperature; copolymerization conditions: $c_{Zr} = 5 \cdot 10^{-6}$ mol/dm³, Al:Zr = 4000, $t = 60$ min, $p_{Et} = 0.5$ MPa, $c_{1-hexene} = 0.432$ mol/dm³

The properties of the copolymers prepared over the supported catalyst are presented in Table 2 as a function

Table 2. The effect of polymerization temperature on properties of copolymers. Catalyst: MgCl₂(THF)₂/MAO/Cp₂ZrCl₂/MAO, copolymerization conditions: $c_{Zr} = 5 \cdot 10^{-6}$ mol/dm³, Al:Zr = 4000, $t = 60$ min, $p_{Et} = 0.5$ MPa, $c_{1-hexene} = 0.432$ mol/dm³

Temperature °C	Comonomer incorporation % mol	Melting point °C	Crystallinity, %	M_w	M_w/M_n	Bulk density g/dm ³
20	2.641	122.22	36.1	65 600	4.27	—
30	3.081	120.89	40.0	55 400	4.85	—
40	2.765	121.48	44.7	47 700	4.68	—
50	3.322	122.09	52.9	31 100	—	98
60	3.907	121.12	55.8	21 000	5.44	124
70	4.780	119.53	51.1	14 900	4.33	269

of copolymerization temperature. Comonomer incorporation is seen to increase as the temperature is raised, presumably on account of the ethylene concentration varying with temperature. The molecular weight of copolymers also strongly depends upon the polymerization temperatures, decreasing drastically as the temperature was increased. A similar tendency occurs for the melting point. However, the present data show crystallinity to be inversely related to polymerization temperature.

Effect of copolymerization time

Some homogeneous metallocene catalysts are known to significantly lose their activity in the course of polymerization reaction [35]. To characterize the stability of the present zirconocene catalyst, the copolymer productivity was studied in relation to copolymerization time (Fig. 3). Within the time range tested, the catalyst was

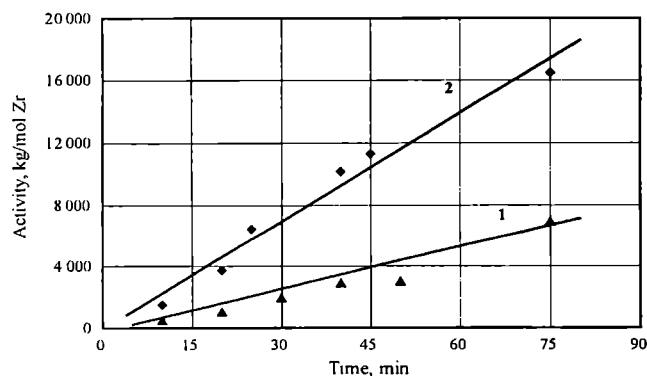


Fig. 3. The activity of MgCl₂(THF)₂/MAO/Cp₂ZrCl₂/MAO catalyst in ethylene/1-hexene copolymerization in relation to copolymerization time: 1 — copolymerization temperature 50°C, 2 — 65°C; copolymerization conditions: $c_{Zr} = 5 \cdot 10^{-6}$ mol/dm³, Al:Zr = 4000, $p_{Et} = 0.5$ MPa, $c_{1-hexene} = 0.432$ mol/dm³

stable independently from the temperature applied. This tendency seems to be common to supported zirconocene catalysts, especially magnesium-supported. In ethylene polymerization the MgCl_2 -supported zirconocene catalyst [36] has shown a high activity and a long life not only at 70°C but also at temperatures as high as 100°C in xylene as solvent.

Table 3 shows the comonomer incorporation and selected properties of the copolymers in relation to copolymerization time. All are seen to be only slightly affected.

Table 3. The effect of polymerization time on properties of copolymers. Catalyst: $\text{MgCl}_2(\text{THF})_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, copolymerization conditions: $c_{\text{Zr}} = 5 \cdot 10^{-6} \text{ mol/dm}^3$, $\text{Al}:\text{Zr} = 4000$, $p_{\text{Et}} = 0.5 \text{ MPa}$, $c_{1\text{-hexene}} = 0.432 \text{ mol/dm}^3$

Temperature, °C	Comonomer incorporation, % mol	Polymerization time, min	Melting point, °C	Crystallinity, %	M_w	M_w/M_n
50	5.15	20	122.8	42.4	15 700	3.55
	4.49	30	121.07	49.9	16 700	4.99
	4.29	40	121.23	50.7	16 600	3.88
	4.59	50	120.59	51.9	15 300	5.43
	4.39	65	121.04	54.7	14 600	4.74
	4.11	90	121.58	55.4	19 300	5.49
65	7.24	10	119.36	41.9	—	—
	5.89	20	117.68	46.6	—	—
	—	35	117.55	47.4	—	—
	—	40	116.14	41.7	—	—
	5.53	50	118.65	46.2	—	—
	—	55	118.77	49.3	—	—

CONCLUSIONS

Both the catalyst activity and copolymer properties were found to depend considerably on copolymerization conditions. The activity of the catalyst increased as the temperature and Al:Zr mole ratio were increased. At the same time, the 1-hexene incorporation into the polymer chain rose whereas the molecular weight, melting point and crystallinity of the copolymers decreased. The catalyst investigated is stable in the course of copolymerization time. The process rate and copolymer properties do not depend on the copolymerization time. The bulk density of copolymers beneficially increases as the comonomer incorporation is raised (Tables 1 and 2).

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KALENDARZ IMPREZ

22—25 marca 2002 r. Zurich, Szwajcaria. „**European Thermoforming Conference 2002**”.

Organizator: Society of Plastics Engineers (SPE), Thermoforming Division, Antwerpen, Belgium.

Informacje: SPE-European Member Bureau, Bistkapellei 44, BE-2180 Antwerpen, Belgium. Mrs. Yetty Pauwels, tel.: +32 3 541 77 55/fax: +32 3 541 84 25; e-mail:spe-europe@pi.be.

27—29 maja 2002 r. Lyon-Villeurbanne, Francja. Sympozjum europejskie „**7th European Symposium on Polymer Blends**”.

Organizator: Centre Nationale de la Recherche Scientifique, Laboratoire des Matériaux Macromoléculaires, Lyon.

Tematyka: termodynamika mieszania, zmiany morfologii podczas mieszania i przetwarzania, środki kompatybilizujące, mieszanie reaktywne, materiały, zależność struktura-właściwości, nowe kierunki rozwoju, strategię i zastosowania przemysłowe mieszanin.

Informacje: Secreatariat 7th European Symposium on Polymer Blends, Laboratoire des Matériaux Macromoléculaires, Bat. Jules Verne, INSA Lyon; 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France. Fax: 33(0) 4 72 43 85 27, e-mail: polymerblends@insa-lyon.fr; <http://www.insa-lyon.fr/polymerblends/index.htm>.

27—31 maja 2002 r. Dniepropietrowsk, Ukraina. „**The Second Ukrainian-Polish Conference — Polymers for Special Applications**”.

Organizatorzy: Department of Plastics Materials Processing and Photo-polygraphic Materials Technology of

Ukrainian State Chemical-Technology University, Dniepropetrovsk, Ukraina + Department of Polymer Chemistry of Radom Technical University, Radom, Polska.

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3—7 czerwca 2002 r. Paryż, Francja. „**EUROOLAST 2002 — 12 th International Exhibition of Plastics, Rubber and Composite Materials**”.

Organizator: Reed Exhibition Companies, Reed Exhibitions France, Paris przy współpracy promotorów: ACDI (Association of Manufacturers, Distributors and Importers of Equipment for the Plastic Materials Industry), AFIM (French Association of Mould, Model and Mock-up Makers), AFICEP (The French Association of Rubber Syndicate).

Prezentacje: surowce i układy rozdzielcze, maszyny przetwórcze, formy i narzędzia, urządzenia peryferyjne, jednostki centralne, aparatura i urządzenia do badań laboratoryjnych i inne.

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