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# Modification of polyethylene by sequential homo- and copolymerization of ethylene and α-olefins over homogeneous zirconocene catalysts[**)]

**Summary** — Ethylene was sequentially homopolymerized (35°C, 15—90 min) and copolymerized (35°C, 25—30 min) with 1-hexene or 1-octene over a $Cp_2ZrCl_2/MAO$ or a $C_2H_4(Ind)_2ZrCl_2/MAO$ catalyst in toluene as solvent; α-olefin conversions were 55—60 mol %. The preliminary homopolymerization of ethylene was found to affect only slightly the composition and the MW and MWD property data of the resulting ethylene-hexene (CEH) and ethylene-octene (CEO) copolymers. HDPE/CEH and HDPE/CEO reactor mixtures (RM) were synthesized, containing various proportions of the copolymers (Table 2). The RM components were found to cocrystallize during the polymerization process. Mechanical property data were determined for pure and for modified HDPE (Table 3). With the copolymer endowed with desired properties and introduced into HDPE in an appropriate amount, high-strength and simultaneously high-MFR materials can be prepared.
**Key words**: zirconocenes, methylaluminoxane, homogeneous catalysts, α-olefins, polymerization, polyethylene, copolymers, cocrystallization, mechanical properties.

Incorporation of long-chain branches into a high density polyethylene (HDPE) is a well-known method to modify HDPE. While acquiring improved properties thereby, such materials are produced by copolymerization of ethylene with long-chain α-olefins ($C_4$—$C_{18}$) over Ziegler—Natta catalysts [1—6] as well as by mechanical blending of previously synthesized HDPE with ethylene/α-olefin copolymers (CP) or of HDPE with branched low-density polyethylene (LDPE) [7, 8]. Now, a new "reactor" method of synthesis of HDPE modified with ethylene/α-olefin CP has been developed intensively. This method consists in a multi-step sequential homo- and copolymerization of ethylene with α-olefins in the presence of titanium magnesium catalysts (TMC) [9]. The combination of TMC and homogeneous zirconocene catalysts has also been applied to modify isotactic polypropylene [10].

Unlike the TMC, homogeneous single-site zirconocene catalysts allow to synthesize the ethylene/α-olefin CPs endowed with a high comonomer content, narrow molecular-weight distribution (*MWD*), and a more uniform distribution of branches in the macromolecule [1,

3, 4]. The microstructure of CP in HDPE/LLDPE mechanical blends is known to affect crystallization processes and morphology [8, 11] and thus also the physical properties of the material. Hence, the introduction of CP of desired properties into HDPE by the reactor method is of particular scientific and practical interest.

This work is aimed at synthesizing modified HDPE and at studying the two-step sequential process involving homopolymerization of ethylene followed by copolymerization of ethylene/1-hexene or ethylene/1-octene over homogeneous $Cp_2ZrCl_2/MAO$ or $C_2H_2(Ind)_2ZrCl_2/MAO$ catalysts. The composition and molecular weight characteristics were studied in HDPE/CP reactor mixtures (RM) and in their components. Density, thermal behavior and mechanical property data were compared in pure and modified HDPE.

## EXPERIMENTAL

### Materials

Zirconium compounds $Cp_2ZrCl_2$ and $C_2H_2(Ind)_2ZrCl_2$ and cocatalyst MAO (10 wt. % MAO in toluene) were purchased from Aldrich and used without further puri-

fication. Aldrich's toluene was stored over molecular sieves and distilled from sodium in argon. Ethylene was of polymerization grade purity. Comonomers 1-hexene and 1-octene were dried over molecular sieves and distilled from sodium in argon (comonomers b. ps. were 64 and 121°C, resp.).

## Polymerization procedures

Two-step polymerization was carried out at 35°C in a 400 mL glass reactor equipped with an electromagnetic stirrer. The reactor was evacuated at 35°C and filled with 70 mL toluene, MAO and a zirconocene compound previously dissolved in 10 wt % solution of MAO in toluene ([Al]/[Zr] = 100 (by moles)). Then ethylene was added. After ethylene had been allowed to polymerize for an appropriate period of time, the comonomer was introduced into the reaction zone and the copolymerization step was begun. Each step of the process was carried out at a constant ethylene concentration of $3.2 \cdot 10^{-2}$ mol/L, a zirconocene concentration of $5 \cdot 10^{-5}$ mol/L, and at [Al]/[Zr] = 2000. The concentration of the α-olefin in copolymerization was equal to $6.4 \cdot 10^{-2}$ or $16 \cdot 10^{-2}$ mol/L. The time of the ethylene polymerization step was varied from 15 to 90 min depending on the desired composition of RM. The time of the copolymerization step was 25—30 min, the conversion of α-olefins was 55—60 mol %. Polymerization was terminated by adding a 5 wt. % hydrochloric acid solution in ethanol. The polymer product obtained was filtered, washed with ethanol, and dried in vacuum at 40°C.

## Polymer characterization

Branch contents (α = $CH_3$/1000 C) in the pure copolymers and RM were determined by infrared analysis. IR spectra were recorded with a Beckman IR 4260 spectrophotometer. The spectral band at 1378 $cm^{-1}$ was used [12]. The contents of 1-hexene ($C_H$, mol %) and 1-octene ($C_O$, mol %) in the pure copolymers were respectively calculated as

$$Q_H = \frac{\alpha \cdot 100}{500 - 2\alpha} \qquad (1)$$

$$C_o = \frac{\alpha \cdot 100}{500 - 3\alpha} \qquad (2)$$

The copolymer quantities in RM were determined in the following way: (1) the quantity of 1-hexene ($Q_H$, mol) and 1-octene ($Q_O$, mol) in the RM was calculated as

$$Q_H = \frac{\alpha \cdot Q_E}{500 - 2\alpha} \qquad (3)$$

$$Q_o = \frac{\alpha \cdot Q_E}{500 - 3\alpha} \qquad (4)$$

where: $Q_E = Q_E{}^I + Q_E{}^{II}$ — ethylene consumption in the homopolymerization step ($Q_E{}^I$, mols) and in the copolymerization step ($Q_E{}^{II}$, mols);

(2) the contents of 1-hexene ($C_H{}^{CEH}$, mol %) and 1-octene ($C_O{}^{CEO}$, mol %) in the copolymer portions of the RM were determined as

$$C_H^{CEH} = \frac{Q_H \cdot 100}{Q_E^I} \qquad (5)$$

$$C_O^{CEO} = \frac{Q_O \cdot 100}{Q_E^{II}} \qquad (6)$$

The molecular weight and MWD of the polymers were measured with a GPC Waters 150 C chromatograph in o-dichlorobenzene at 140°C. Polymer density was determined gravimetrically. Melting curves were recorded with a Dupont Instruments 910 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The melt flow rates (MFR) of the polymer products were measured at 190°C under 2.16 and 21.6 kg dead-weight loads. Mechanical tests were performed by using a JJ Instruments T5k tensile machine at ambient temperature and deformation speed of 50 mm/min. The test specimens were taken from plates 0.5 mm thick, which were made by compression molding at 150°C and 10 MPa.

## RESULTS AND DISCUSSION

The catalytic systems $Cp_2ZrCl_2$/MAO and $C_2H_4(Ind)_2ZrCl_2$/MAO were used for the synthesis of reactor mixtures HDPE—ethylene/1-hexene copolymer (CEH) and HDPE—ethylene/1-octene copolymer (CEO), respectively. Figures 1a and 1b illustrate the behavior of these catalysts in the homopolymerization of ethylene (Figs. 1a, 1b, curve 1), in the copolymerization of ethylene with 1-hexene (Fig. 1a, curve 2) and 1-octene (Fig. 1b, curve 2), and in the two-step sequential ethylene homopolymerization followed by ethylene/hexene copolymerization (Fig. 1a, curve 3) or ethylene/octene copolymerization (Fig. 1b, curve 3). The rate of ethylene consumption in the copolymerization over either of the two catalysts is seen to be greater than that in ethylene homopolymerization. In the sequential polymerization, the catalysts at the second copolymerization step were also found to have been activated, provided the preliminary ethylene homopolymerization was continued for 10—15 minutes (Fig. 1a, 1b, curve 3). If the copolymerization step was started in 35 minutes of ethylene homopolymerization, the effect did not occur any longer. The enhancement of the rate of ethylene consumption upon addition of the comonomer in the copolymerization step [1, 3, 4] and also one following a preliminary ethylene homopolymerization [13, 14] is known to occur for both heterogeneous and homogeneous catalysts. The decrease of the monomer effect as the time of ethylene polymerization is protracted, has also been reported [13].

Table 1 lists the compositions of CEH and CEO obtained with $Cp_2ZrCl_2$/MAO and $C_2H_4(Ind)_2ZrCl_2$/MAO at different time intervals of the preliminary ethylene homopolymerization. The content of branches in the to-
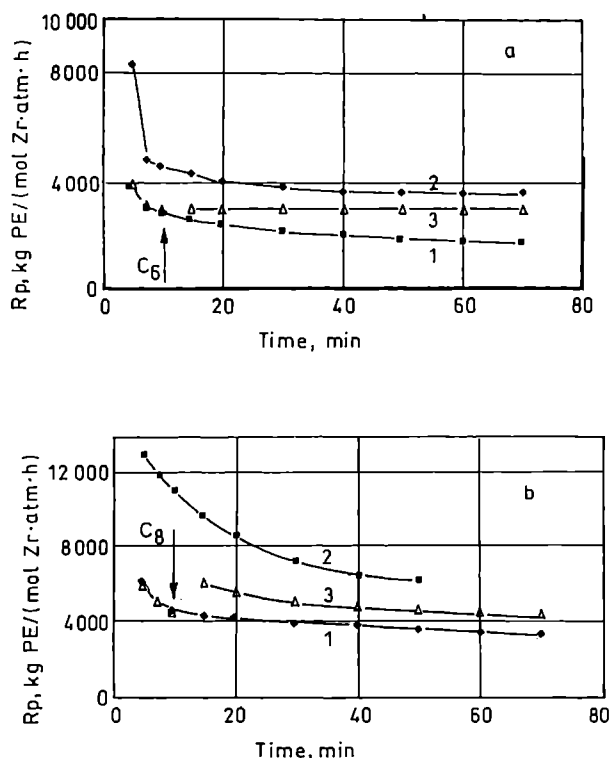
*Fig. 1. The two-step sequential and the one-step processes of homo- and copolymerization of ethylene with 1-hexene and 1-octene over catalysts: (a) Cp₂ZrCl₂/MAO and (b) C₂H₄(Ind)₂ZrCl₂/MAO at 35°C, in toluene as solvent, at [Zr] = 5 · 10⁻⁵ mol/L, [Al]/[Zr] = 2000, [C₂H₄] = 3.2 · 10⁻² mol/L; 1a: 1 — ethylene homopolymerization; 2 — ethylene/1-hexene copolymerization, [C₆H₁₂] = 6.4 · 10⁻² mol/L; 3 — sequential homo- and copolymerization of ethylene and 1-hexene, [C₆H₁₂] = 6.4 · 10⁻² mol/L, time of preliminary homopolymerization of ethylene, 15 min. 1b: 1 — ethylene homopolymerization; 2 — ethylene/1-octene copolymerization, [C₈H₁₆] = 6.4 · 10⁻² mol/L; 3 — sequential homo- and copolymerization of ethylene and 1-octene, [C₈H₁₆] = 6.4 · 10⁻² mol/L, time of preliminary homopolymerization of ethylene, 15 min*

tal polymer products was evaluated from IR spectral data and then the content of 1-hexene or 1-octene in the copolymer portions of the reactor mixtures HDPE/CEH and HDPE/CEO was calculated as described in the Experimental. The compositions of CEH and CEO obtained in one-step copolymerization and in the second step of the sequential polymerization are seen to be practically identical, provided the conditions of the two processes were identical, regardless of the length of time of the preliminary ethylene polymerization. This fact indicates that CP of desired composition can be introduced into PE by sequential polymerization.

The molecular weight characteristics of polymer products show (Table 2) the introduction of copolymer into PE by the reactor method to result in a decreased average molecular weight and in an increased polydispersity index of the total polymer products. There are two peaks in the MWD curves of the RM containing res-

**Table 1.** The composition of CEH and CEO obtained on one-step copolymerization and in the second step of sequential polymerization over Cp₂ZrCl₂/MAO and C₂H₄(Ind)₂ZrCl₂/MAO

| Run | Copoly-mer | [α-ole-fin]/[C₂] ratio in re-action zone | Time of ethylene polymeri-zation, min | Branch content in reactor mixture, CH₃/1000 C | Comono-mer con-tent in co-polymer, mol % |
|---|---|---|---|---|---|
| | | | Cp₂ZrCl₂/MAO | | |
| 1 | CEH | 2.0 | 0 | 19.9 | 4.4 |
| 2 | CEH | 2.1 | 82 | 3.9 | 4.9 |
| 3 | CEH | 2.3 | 30 | 3.3 | 4.8 |
| 4 | CEH | 4.0 | 0 | 24.8 | 5.7 |
| 5 | CEH | 5.0 | 81 | 19.1 | 7.2 |
| 6 | CEH | 5.2 | 19 | 25.3 | 6.6 |
| | | | C₂H₄[Ind]₂ZrCl₂/MAO | | |
| 7 | CEO | 2.1 | 0 | 30 | 7.7 |
| 8 | CEO | 2.2 | 10 | 29.9 | 8.0 |

35°C, toluene, [Zr] = 5 · 10⁻⁵ mol/L, [Al]/[Zr] = 2000, [C₂H₄] = 3.2 · 10⁻² mol/L

**Table 2.** Property data for HDPE, CEH, CEO and for reactor mixtures HDPE/CEH and HDPE/CEO

| Run | CP[*] | Co-poly-mer in RM wt. % | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | d g/cm³ | Melting point, °C[**] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | nascent ma-terial | | second heating | |
| | | | | | | $t_1$ | $t_2$ | $t_1$ | $t_2$ |
| | | | | Cp₂ZrCl₂/MAO | | | | | |
| 1 | HDPE | 0 | 320000 | 3.2 | 0.946 | 133 | — | 131 | — |
| 2 | CEH | 15 | 262000 | 3.2 | 0.934 | 131 | 116 | 128 | 116 |
| 3 | CEH | 30 | 117000 | 8.7 | 0.933 | 129 | — | 126 | — |
| 4 | CEH | 50 | 131000 | 7.0 | 0.931 | 127 | 104 | 123 | 103 |
| 5 | CEH | 90 | 91000 | 4.0 | 0.921 | 128 | 109 | 126 | 108 |
| 6 | CEH | 100 | 47000 | 2.0 | 0.912 | — | 112 | — | 111 |
| | | | | C₂H₄[Ind]₂ZrCl₂/MAO | | | | | |
| 7 | HDPE | 0 | 320000 | 7.3 | n.d.[***] | 131 | — | 130 | — |
| 8 | CEO | 90 | 190000 | 8.7 | n.d. | 127 | 104/92[****] | 124 | 95.5 |
| 9 | CEO | 100 | 185000 | 4.1 | n.d. | — | 111.5 | — | 109 |

*[*] 1-Hexene in CEH, 5 mol %; 1-octene in CEO, 8 mol %; [**] $t_1$ — melting point of PE portion in RM; $t_2$ — melting point of copolymer portion in RM; [***] n.d. — not determined; [****] Melting peak in DSC curves was relatively broad.*

pectively 30 and 50 wt. % of CEH, viz., one in the high and one in the low molecular weight region (Fig. 2, curves 3, 4). In this case, the position of each peak coincides with the position of the peak for pure PE (Fig. 2, curve 1) and for pure CEH (Fig. 2, curve 6). The character of the MWD curves, especially in the region of low molecular weights, allows to suggest that the preliminary ethylene homopolymerization does not affect essentially the molecular-weight characteristics of the copolymers.

As CEH is introduced into HDPE (d = 0.946 g/cm³) by the sequential homo- and copolymerization of ethylene with 1-hexene, the density of the material decreases
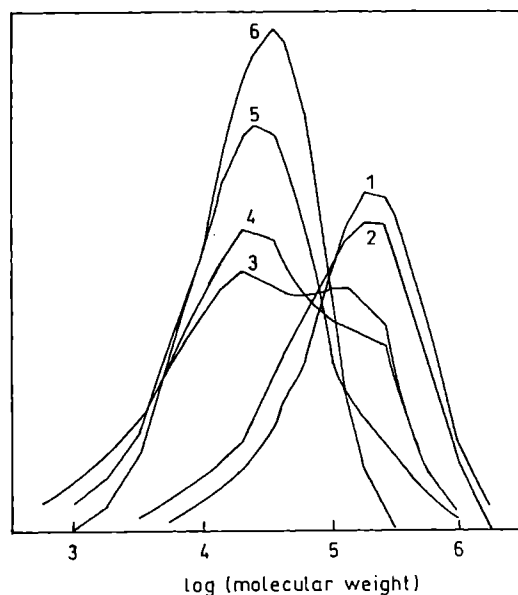
*Fig. 2. MWD curves for reactor mixtures HDPE/CEH:
1 — HDPE, 6 — CEH; reactor mixtures HDPE/CEH
with CEH content: 2 — 15, 3 — 30, 4 — 50 (4), and 5 —
90 wt. %*

T a b l e 3. **Mechanical property data for HDPE, CEH and reactor mixtures HDPE/CEH**

| Run | CEH content wt. % | $\sigma_y$, MPa | $\sigma_t$, MPa | $\varepsilon_t$, % | $E$, GPa | MFR, g/10 min at load | |
|---|---|---|---|---|---|---|---|
| | | | | | | 2.16 kg | 21.6 kg |
| 1 | HDPE | 24 | 46 | 650 | 0.7 | no flow | 0.08 |
| 2 | 15 | 21 | 35 | 640 | 0.6 | no flow | 0.08 |
| 3 | 30 | 18 | 23 | 890 | 0.5 | 0.01 | 5.5 |
| 4 | 50 | 16 | 19 | 860 | 0.4 | 0.1 | 16.4 |
| 5 | 90 | 12 | 15 | 560 | 0.3 | 7.6 | n.d. |
| 6 | 100 | 13 | 18 | 610 | 0.3 | 13.4 | n.d. |

(Table 2). Depending on the copolymer content, the RM densities are equal to 0.934—0.920 g/cm³.

The DSC m. ps. of the nascent polymer products are also presented in Table 2. The pure HDPE and CEH show single peaks at 133 and 112°C, respectively. At the same time, the RM containing 15, 50 and 90 wt. % of CEH exhibit two melting peaks which are associated with the melting of PE and copolymer portions of the reactor mixtures. Moreover, as the CEH content in the HDPE was increased, the PE portion melting point (m.p.) decreased from 133 to 127°C. The introduction of CEO into HDPE reduced the PE m.p. from 131°C to 127°C (Table 2, runs 7 and 8). Such phenomena are known to occur in mechanical blends HDPE/LLDPE and HDPE/LDPE and are explained by partial cocrystallization of PE and inter-branch segments of copolymer or LDPE [7, 8]. The present experimental data obtained for the nascent materials indicate that the components of RM are able to partially cocrystallize directly during the polymerization process. The most interesting result was found for the reactor mixture HDPE/CEH with 30 wt. % of CP. The DSC curve of this nascent product shows (Table 2, run 3), a single melting peak at 129°C which indicates that the components of the RM are well compatible and that, in this nascent system, there is a uniform crystalline phase.

The mechanical property data for the reactor mixtures HDPE/CEH (Table 3) show the increase in the CEH content in RM from 15 to 90 wt. % to be accompanied by the increase in the melting flow rate (MFR) and by the reduction of the yield value ($\sigma_y$), tensile strength ($\sigma_t$) and modulus ($E$) of the RM. Thus, the introduction of 30 and 50 wt. % of the copolymer into HDPE which itself does not flow at 190°C under a load of 2.16 kg, in-

creases the MFR of the material by up to 0.01 and 0.1 g/10 min, respectively. For pure HDPE, $\sigma_t$ was equal to 46 MPa and, for RM with 30 wt. % of CEH, $\sigma_t$ was equal to 23 MPa. At the same time, the ability of the material to undergo a plastic deformation passed through a maximum. For pure HDPE, elongation ($\varepsilon_t$) was equal to 650% and, for RM with 30 and 50% of copolymer, $\varepsilon_t$ were equal to 890 and 860%, respectively.

## CONCLUSIONS

The present experimental data allow to conclude that, in the synthesis of modified HDPE by sequential homo- and copolymerization of ethylene and α-olefins over zirconocene catalysts, the preliminary ethylene homopolymerization does not influence essentially the composition and molecular-weight characteristics of the copolymers. This fact allows to control the copolymer properties by modifying the conditions of the copolymerization step of the process. The components of RM are able to cocrystallize directly during the polymerization process. Introduction of an appropriate amount of ethylene/α-olefin copolymer of desired properties into the HDPE by the reactor method allows to produce the material combining a sufficiently high strength and plastic properties with high melt flow rates.

## REFERENCES

1. Uozumi T., Soga K.: *Makromol. Chem.* 1992, **193**, 823.
2. Stevens J. C. in: Proc. 11th International Congress on Catalysis — 40th Anniversary Studies in Surface Science and Catalysis 1996, **101**, 11.
3. Peeters M., Goderic B., Vonc C et al.: *J. Polym. Science. Part B Polymer Physics* 1997, **35**, 2689.
4. Lehmus P., Harkki O., Leino R. et al.:*Macromol. Chem. Phys.* 1998, **199**, 1965.
5. Quijada R., Rojas R., Guevatra J. L., Narvaez A., Delfin D., de Galland G. B.: *Polimery* 2000, **45**, 353.

6. Czaja K., Białek M.: *Polimery* 2000, **45**, 353.
7. Puig C. C.: *Polymer Bull.* 1997, **38**, 715.
8. Zhao Y., Liu S., Yang D.: *Macromol. Chem. Phys.* 1007, **198**, 1427.
9. Gally P.: *Plastics, Rubber and Composites Processing and Application* 1995, **23**, 1.
10. Gally P., Collina G., Sgazzi P. *et al.: J. Appl. Polym. Sci.* 1997, **66**, 1831.

11. Pracella M., Benedetti E., Galeschi F.: *Thermochim. Acta* 1990, **162**, 163.
12. Gol'denberg A. L.: *Zh. Prikl. Spektroskopii* 1973, **19**, 510.
13. Koivumaki J., Seppala J. V.: *Macromolecules* 1993, **26**, 5335.
14. Gul'tseva N. M., Ushakova T. M., Aladyshev A. M., Ruspopov L. N.: *Polymer Bull.* 1992, **29**, 639.

# KALENDARZ IMPREZ

**27—29 września 2001 r.** Kamienica (Chemnitz), Niemcy. **17. Konferencja naukowa nt. przetwórstwa i zastosowań polimerów „TECHNOMER 2001".**

Organizatorzy: Instytut Ogólnej Budowy Maszyn i Techniki Tworzyw Sztucznych Politechniki w Kamienicy (Institut für Allgemeinen Maschinenbau und Kunststofftechnik der Technischen Universität Chemnitz) + Centrum Tworzyw Sztucznych w Lipsku (Kunststoff-Zeutrum in Leipzing).

Tematyka: Wymiana doświadczeń w dziedzinach nauki i praktyki w zakresie przetwórstwa, zastosowań i recyklingu tworzyw wielkocząsteczkowych i gumy, konstrukcji wyrobów oraz techniki maszyn i narzędzi, jakości wyrobów i metod badań. W uzupełnieniu konferencji przewidziana jest prezentacja firm.

Terminy zgłoszeń: referatów (20-min) — 15 kwietnia 2001 r.; prezentacja firm — 15 lipca 2001 r.

Miejsce konferencji: Aula Politechniki w Kamienicy.

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**3—7 czerwca 2002 r.** Paryż, Francja. **„EUROPLAST 2002 — 12. Międzynarodowa wystawa materiałów z tworzyw sztucznych, gumy i kompozytów".**

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Organizator: European Membrane Society.

Termin zgłoszenia udziału: 15 września 2001 r.

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**30 września—4 października 2002 r.** Birmingham, Wlk. Brytania. **„INTERPLAS 2002".**

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