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Copolymerization of ethylene with 1-hexene over vanadium catalysts immobilized on sol-gel silica

RAPID COMMUNICATION

Summary — Silica-type materials with different structure and morphology, synthesized using sol-gel process, were applied as a carriers of organometallic catalytic systems ($\text{VOCl}_3/\text{AlEt}_2\text{Cl}$) for ethylene-1-hexene copolymerization. Carrier materials, prior to immobilization of the vanadium compound, were pre-treated using two modes: one-step thermal modification and two-steps modification including additional reaction with AlEt_2Cl . It was found that the carrier's type and way of its modification significantly influence the catalysts activity in ethylene-1-hexene copolymerization as well as the incorporation of higher 1-olefin. The favourable effect of two-step modification mode on the catalysts activity and 1-hexene incorporation efficiency was proposed.

Key words: silica support, sol-gel technique, ethylene copolymerization, organometallic catalyst.

KOPOLIMERYZACJA ETYLENU Z 1-HEKSEMEM WOBEC KATALIZATORÓW WANADOWYCH IMMOBILIZOWANYCH NA KRZEMIONCE ZOL-ŻELOWEJ

Streszczenie — Proszki krzemionkowe o zróżnicowanej morfologii i charakterze chemicznym powierzchni, otrzymane techniką zol-żelową, stosowano jako nośniki metaloorganicznych katalizatorów wanadowych ($\text{VOCl}_3/\text{AlEt}_2\text{Cl}$) do niskociśnieniowej kopolimeryzacji etylenu z 1-heksenem. Nośniki, przed zakotwiczeniem związku metalu przejściowego, poddawano jedno lub dwustopniowej modyfikacji, polegającej na wygrzewaniu w temp. 200 °C wraz z ewentualnym dodatkowym działaniem AlEt_2Cl . Stwierdzono, że typ zastosowanego nośnika układu katalitycznego oraz sposób jego modyfikacji znacząco wpływają na aktywność zarówno w procesie homopolimeryzacji etylenu jak i jego kopolimeryzacji z 1-heksenem. Szczególnie aktywnym i efektywnym w odniesieniu do zdolności wbudowania 1-olefiny w łańcuch polietylenu okazał się układ zakotwiczony na nośniku posiadającym powierzchniowe grupy metylowe, poddanym dodatkowo modyfikacji związkiem glikoorganicznym. Zaproponowany mechanizm korzystnego działania dwustopniowej modyfikacji polega najprawdopodobniej na pełnieniu przez wprowadzony związek glikoorganiczny roli "łącznika" odseparowującego centra aktywne od powierzchni nośnika, a tym samym wpływającego na zwiększenie ich dostępności dla cząsteczek monomeru, co jest szczególnie istotne w przypadku wyższej olefiny.

Słowa kluczowe: nośnik krzemionkowy, metoda zol-żelowa, kopolimeryzacja etylenu, katalizator metaloorganiczny.

The anhydrous magnesium chloride [as well as a complex with electron donor *i.e.* tetrahydrofuran (THF)] is a preferred support for Ziegler-Natta catalysts, specially based on titanium chloride [1—3]. However MgCl_2 -supported systems exhibit two basic disadvantages: the product contamination with chlorine and sometimes worse polymer particles' morphology (low bulk density). These disadvantages may be omitted by

application of a silica support including silica type materials that are produced in a sol-gel process.

In earlier investigations [4, 5] we have found that the sol-gel method offered a high versatility and flexibility in production of potential carrier materials with a different structure and morphology. Besides immobilization of transition metal compound, such supported catalysts appeared to be active in low-pressure ethylene polymerization. It was found that their catalytic activity and their stability during ethylene polymerization course seemed to be dependent on the morphology of the car-

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rier and method of its modification. Two-step modification of the support, including reaction with organoaluminum compound, clearly increases the activity as well as stability of the catalytic system. It was proposed then that the reason of favourable properties of such a catalyst was most likely a separation of the active species from the surface of a support with a "spacer" that was formed by the organoaluminum compound introduced in the modification step [4].

To confirm this suggestion in the present work we have extended the study to the ethylene-1-hexene copolymerization process which in the case of more exposed active sites of the catalysts should be even more vulnerable for incorporation of higher 1-olefin into polyethylene chain.

EXPERIMENTAL

Materials

All operations were conducted under inert atmosphere (nitrogen) using standard Schlenk technique.

Ethylene (PKN Orlen, Poland) and nitrogen (Messer) were used after having been passed through a column of sodium metal supported on alumina.

Pure hexane (POCh Gliwice, Poland) was refined with sulfuric acid, dried with sodium hydroxide, rectified and then dried by refluxing over the sodium metal. Tetraethylorthosilicate (TEOS, Fluka), triethoxymethylsilane (TEMS, Fluka), vanadiumoxytrichloride (VOCl_3 , Aldrich), solution of aluminumdiethyl chloride (AlEt_2Cl) in hexane (Aldrich) and 1-hexene (Aldrich) were used without further purification.

A commercial silica DAVISIL (DAV, Grade 645, Aldrich) was ground in a ball-mill to obtain particle sizes ranging from 5 to 20 μm prior to application.

Catalyst preparation

The preparation of silica sol-gel powdery materials were described elsewhere [5, 6]. Sol-gel powders were synthesised using TEOS, water, ethanol (solvent) and ammonia (catalyst) according to the literature procedure [7, 8]. In several runs the procedure was modified by the partial replacement of TEOS with TEMS to introduce some methyl groups to resulting silica powder surface. Molar fractions of components used to produce carrier materials are listed in Table 1. The obtained materials, prior to immobilization of the transition metal compound, were annealed at 200 °C and some samples were additionally modified with AlEt_2Cl (*i.e.* catalyst sample B-Me/Al) as it was done during earlier investigations [4–6]. Supported catalyst for slurry polymerization were prepared by the impregnation of thermally pre-treated carrier with VOCl_3 in a hexane slurry at room temperature. In case of additional modification with AlEt_2Cl the reaction with this compound was made in hexane slurry,

just after thermal treatment, prior to immobilization of VOCl_3 (sample B-Me/Al). Excess of AlEt_2Cl and of VOCl_3 was removed by subsequent washing with hexane (5×20 mL). Received solid catalyst was dispersed in hexane prior to polymerization process.

Table 1. Molar fractions of reagents in synthesis reactions of the silica materials

Symbol of carrier sample	Reagents			
	TEOS	TEMS	NH_3	H_2O
A [8]	1	0	0.07	4.5
B-Me	0.2	0.8	10.2	29.6

Ethylene/1-hexene copolymerization

The copolymerization reactions were carried out in a Büchi glass reactor (equipped with a stirrer and heating jacket) in a hexane slurry (0.7 L), at constant temperature 50 °C and ethylene pressure 0.5 MPa. AlEt_2Cl activator, 1-hexene and catalyst slurry were charged into the reactor and the polymerization was initiated by introducing of ethylene. Commonly the polymerization and copolymerization conditions were as follows: polymerization time 30 min, catalysts' amount 0.06 g/0.7 L, activator AlEt_2Cl concentration in the feed 28 mmol/L. The process was quenched by addition of methanol containing 5 wt. % of HCl. Polymer was filtered off, washed with methanol and dried.

Methods of testing

Degree of 1-hexene incorporation to copolymer was determined by FT-IR method using Philips PU 9800 FTIR spectrometer according to method described in [9].

The melting temperatures (T_m) of polymer products were measured by differential scanning calorimetry method using a TA Instruments 2010 DSC calorimeter at the heating rate 10 deg/min.

RESULTS AND DISCUSSION

The study of ethylene-1-hexene copolymerization process was carried out using VOCl_3 supported on different sol-gel silica materials and on commercial silica DAVISIL as a reference. The sol-gel silica powders showed a typical silica structure (sample A, Table 1) as well as improved hydrophobicity due to some methyl groups which were introduced during the sol-gel process (sample B-Me, Table 1) [4, 5]. Obtained results of the copolymerization process were compared in Figure 1 with former study of ethylene homopolymerization over similar catalytic systems. This comparison shows that introduction of 1-hexene, at the concentration in the feed about 0.432 mol/L, causes almost double activity drop. Similar behavior was reported earlier for the catalysts supported on $\text{MgCl}(\text{THF})_2$ [10–13].

Comparison of the efficiency of the catalysts supported on different materials in the copolymerization process shows noticeable variation according to type of the carrier and methods of its modification. The activity of systems immobilized on commercial silica DAV is relatively low and does not exceeds 200 kg PE/mol V. Similar level of activity demonstrates catalytic system supported on sol-gel material A calcined at 200 °C.

The catalyst supported on sol-gel silica B-Me (with methyl groups embedded into surface) shows remarkably higher activity in comparison to the others and such a positive effect of the carrier's surface structure (improved hydrophobicity) was already observed for the ethylene homopolymerization process [5]. Comparing all studied catalysts, the order of their activity in copolymerization as well as homopolymerization processes is:



To evaluate the influence of the concentration of the 1-hexene in the polymerization feed on the catalytic activity, several copolymerization runs were carried out for different catalysts and various concentrations of 1-hexene.

Independently on the type of the catalyst applied, their activities clearly decrease when the 1-hexene concentration in the feed increases, however a trend for all the systems is kept (Fig. 1). Similar results were observed in earlier studies for 1-hexene, 1-octene and 1-decene which were copolymerized with ethylene over vanadium catalyst supported on magnesium chloride [10]. It should be stressed that the most active systems (B-Me and B-Me/Al) show the best efficiency in the whole range of initial 1-hexene concentration, even when compared with the homopolymerization in the presence of the other catalytic systems (A and DAV).

The ability to incorporate a comonomer molecule effectively is another important feature of a copolymeriza-

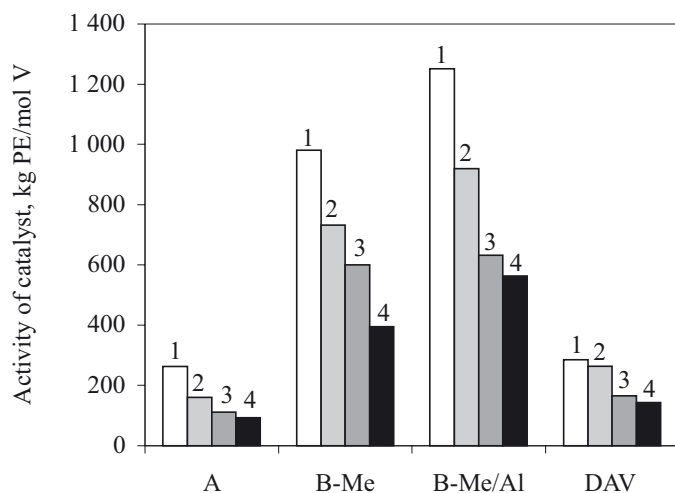


Fig. 1. Effects of 1-hexene initial concentration in the polymerization feed and type of catalyst on the catalysts' activity; initial concentration of 1-hexene: 1 — 0, 2 — 0,113 mol/L, 3 — 0,432 mol/L, 4 — 0,82 mol/L

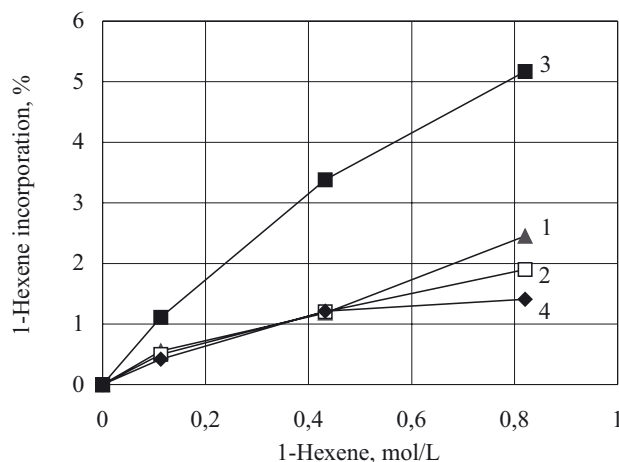


Fig. 2. Effects of 1-hexene initial concentration in the feed on 1-hexene incorporation in the copolymers for different catalyst type: 1 — A, 2 — B-Me, 3 — B-Me/Al, 4 — DAV

tion catalyst. Suggested effect of the "spacer" that enhances the accessibility of active species should be more significant for the incorporation of the higher 1-olefin into the polyethylene chain than for the activity of the catalyst. Hence, to check the influence of the comonomer initial concentration on its incorporation into the main chain for different catalysts, the copolymer samples were analyzed to estimate the 1-hexene share in the final product [13]. For all of studied catalytic systems the comonomer incorporation increases with 1-hexene concentration increase nevertheless the incorporation clearly depends on the type of the catalyst applied (Fig. 2).

The catalysts immobilized on the carriers modified in one-step process show quite similar degree of 1-hexene incorporation, independently on the type of the carrier (A, B-Me or DAV). The catalytic systems supported on two-step modified carrier demonstrate more that double incorporation ability in comparison to the other systems. Considering all studied systems, the ability of comonomer incorporation follows the sequence:



If we compare the incorporation of 1-hexene for the catalysts immobilized on the same support (B-Me) but treated using two different methods it is clear that additional reaction with alkylaluminum improves not only the activity (Fig. 1), but mostly 1-hexene incorporation (Fig. 2). Hence, the effect of the "spacer" which separates the active species from the carrier surface and enhances its accessibility seems to be particularly important in case of higher 1-olefin since bulky comonomer molecule due to steric hindrance requires exposed and more accessible active sites. The spacer may be form only in case of two-step modification, thus the catalyst supported on B-Me/Al seems to be better "tailored" for the copolymerization process.

It is commonly known that the properties of ethylene-1-olefin copolymers are influenced by their composition — the type and share of comonomer in the main

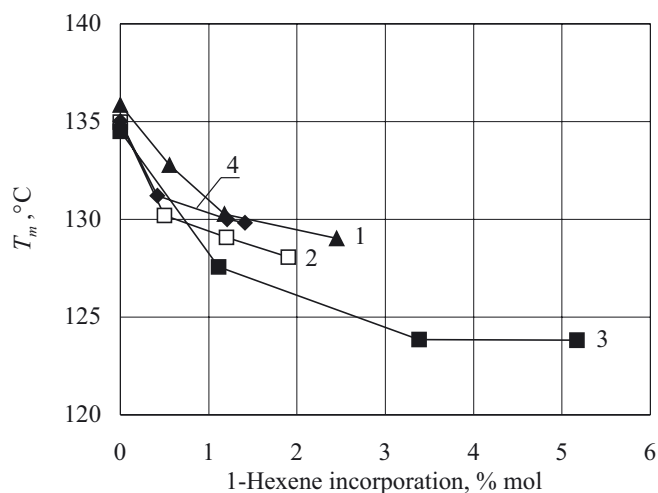


Fig. 3. Effects of the catalyst type and copolymer composition on its melting temperature (T_m); denotations as in Fig. 2

chain. Copolymers with higher 1-olefin contribution show lower density as well as lower crystallinity and T_m [13–16]. Figure 3 presents the effect of 1-hexene incorporation on T_m of copolymers obtained.

In any case T_m of copolymer decreases with increase of the share of incorporated 1-hexene however the strongest effect was observed for polymer produced over the catalytic system most active and most effective in the incorporation of higher 1-olefin.

CONCLUSIONS

The type of the carrier and mode of its preparation and modification were found to have important influence on the catalysts activity in the ethylene-1-hexene copolymerization process and on the comonomer incorporation. The most active and most effective is the cata-

lyst supported on sol-gel material with surface methyl groups, particularly when two-step modification of the carrier is applied prior to vanadium compound immobilization. It confirms that organoaluminum compound may act as a “spacer” that isolates the active sites from the carrier surface and makes them exposed for bulky 1-hexene molecules.

REFERENCES

1. Czaja K., Białek M.: *Macromol. Rapid. Commun.* 1996, **16**, 253.
2. Nowakowska M., Bosowska K.: *Makromol. Chem.* 1992, **193**, 889.
3. Bosowska K., Nowakowska M.: *J. Appl. Polym. Sci.* 1998, **69**, 1005.
4. Korach Ł., Czaja K., Mrowiec-Białoń J., Jarzębski A.: *Eur. Polym. J.* 2006, **42**, 3085.
5. Korach Ł., Czaja K., Kovaleva N. Yu.: *Eur. Polym. J.* submitted to press.
6. Korach Ł., Czaja K., Kovaleva N. Yu.: *Polimery* 2004, **49**, 641.
7. Stöber W., Fink A., Bohn E.: *J. Colloid Interface Sci.* 1968, **26**, 62.
8. Toki M., Takeuchi T., Miyasita S., Kanbe S.: *J. Mat. Sci.* 1992, **27**, 2857.
9. Sudol M., Czaja K., Białek M.: *Polimery* 2000, **45**, 405.
10. Białek M., Czaja K.: *Polymer* 2000, **41**, 7899.
11. Białek M., Krasoń T.: *Polimery* submitted to press.
12. Czaja K., Białek M.: *Polymer* 2001, **42**, 2289.
13. Białek M., Czaja K.: *Polimery* 2000, **45**, 293.
14. Białek M., Utrata A., Czaja K.: *Polimery* 2002, **47**, 59.
15. Białek M., Czaja K., Reszka. A.: *J. Polym. Sci., Part A: Polym. Chem.* 2005, **43**, 5562.
16. Białek M., Czaja K.: *Macromol. Chem. Phys.* 2006, **207**, 1651.

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