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Kinetic studies of two-step polymerization of propylene over a titanium-aluminum catalyst

Summary — The influence was studied of the modification of an unsupported titanium-aluminum catalytic system with an internal Lewis base incorporated, *via* prepolymerization, on the activity of this system in propylene polymerization. In order to clarify the reasons for the activating effect of prepolymerization, comparative studies were carried out on the kinetics of polymerization catalyzed by a titanium system and its prepolymerized counterpart. Based on the kinetic model suggested for the polymerization mechanism, the concentration of active sites and rate constants were determined for chain propagation, chain transfer and termination reactions. The following conclusions were deduced: *(i)* the initial rate of propylene polymerization is higher over a prepolymerized catalyst on account of the increased number of active sites formed, *(ii)* in the course of polymerization, the difference between the process rates offered by two catalytic systems becomes higher, on account of different rates of the chain termination reactions, the rate over the prepolymerized catalyst being slower owing to advantageous changes in its morphology, *(iii)* prepolymerization has no influence on the reactivity of active sites as the propagation rates in either case are similar, just like the molecular characteristics of the polymers obtained.

The rate-enhancement effect of α-olefins on ethylene polymerization over Ziegler—Natta catalysts has frequently been reported [1—7]. Removal of a higher co-monomer from the reaction medium at some later moment was found to have no lowering effect on the polymerization rate of the basic monomer [8]. In order to understand better this phenomenon, the catalyst activation stage was separated from the polymerization itself. This way of carrying out a process is known as the two-step polymerization. Hence, the ethylene or propylene polymerization catalysts are often activated in preliminary polymerization processes which usually employ small volumes of a higher olefin and are carried out under mild conditions. This step is called the „catalyst prepolymerization". The resulting catalyst is then employed in the basic polymerization process which is carried out under typical conditions. Increased polymerization rates are generally observed when catalyst prepolymerization is employed [8—14], yet the reasons underlying this effect have not been explained so far, except for the supposed formation of new active centers [8, 9] or reactivation [10, 14, 15]. Detailed studies on polymerization kinetics [9, 10] can elucidate this problem. Our earlier studies [16] showed prepolymerization modification of the titanium catalyst to make active sites more resistant to deactivation in the polymerization process.

This paper sets out to describe a kinetic study on propylene polymerization over a $TiCl_3$-based catalyst which was activated through a preliminary prepolymerization of the same monomer. Results are compared with those obtained by employing a non-prepolymerized catalyst and discussed in terms of the characteristics of the catalysts employed and properties of the polymerization products.

EXPERIMENTAL

Preparation and analysis of the catalysts and the polymerization process were carried out in a dry and oxygen-free argon.

Materials

Polymerization-grade propylene ("Petrochemia" SA, Płock, Poland) and pure argon ("Liquid Carbonic Polska", Warsaw, Poland) were purified by passing through a 4 Å molecular sieve column. Pure-grade hexane ("Petrochemia" SA, Płock, Poland) was refined with sulfuric acid, dried by refluxing in argon over sodium metal and stored

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*) University of Opole, Institute of Chemistry, Opole.

) Institute of Heavy Organic Synthesis, Kędzierzyn Koźle (now with Technical University of Rzeszów, Rzeszów) over 4 Å molecular sieves. The catalyst named the **cat, *viz.*, a second generation $TiCl_3$ catalyst modified with di-*n*-butyl ether, was prepared as described elsewhere [17]. The co-catalyst, diethyl aluminum chloride (Witco, Germany), was used without further purification.

Prepolymerization

Hexane, **cat** and Et_2AlCl were added in predetermined amounts to a 250 mL glass reactor equipped with a magnetic stirrer and propylene was bubbled through the solvent with continuous stirring. The prepolymerization conditions were: Al/Ti mole ratio, 5; temp., 25°C; atmospheric pressure; and propylene/Ti mole ratio, 10. Finally, the solvent was removed and the prepolymerized catalyst was preserved in the form of a dry powder under argon. It was named the **precat**.

Polymerization

The polymerization reaction was performed in a swinging design 400 mL steel reactor at 70°C at a constant pressure of the monomer. Hexane (250 mL), Et_2AlCl, and **cat** or **precat** (Al/Ti mole ratio, 7) were charged into the reactor. Polymerization was initiated by introducing propylene. The reaction was terminated by adding methanol containing 5 wt.% HCl. The resulting polymer was filtered off, washed with methanol, and dried.

Measurements

MW and MWDs of the polymers were measured with a Waters model 150-C instrument by using: (i) one Waters HMW 6E „linear" column (M range according to producer: $5 \cdot 10^3$—10^7); (ii) 1,2,4-trichlorobenzene (TCB) as solvent, flow rate, 0.6 mL/min; (iii) Santanox-R, 0.25 g/dm^3 TCB, as antioxidant; (iv) concentration of samples, 0.05% (wt./vol.); (v) injection volume: 200 *m*L; (vi) measurement temperature, 142°C. MWDs and averages were determined by using the universal calibration curve obtained with broad MWD polypropylene standards.

RESULTS

Results of propylene polymerizations catalyzed by **cat** and **precat** systems (Table 1) suggest the activating impact induced by the catalyst modified *via* prepolymerization to be just as observed elsewhere [8—14] and presumably caused by:

— increased number of the active sites formed (C_0^*) on the prepolymerized catalyst,

— active sites modified by the prepolymerization process changing the ligand environment of the transition metal raised in reactivity and yielding increased propagation rate (k_p),

— more-stabilized active sites and thus the lower rate of catalyst deactivation.

Table 1. EFFECT OF CATALYST PREPOLYMERIZATION ON CATALYST ACTIVITY IN PROPYLENE POLYMERIZATION

Catalyst	Polymerization rate mol/(molTi·min) in t, min		Activity kgPP/(molTi·h)
	$t = 0$	$t = 60$	
Cat	61.69	27.03	104.28
Precat	68.42	42.08	135.67

Propylene polymerization rates (Table 1, Fig. 1) show both the **cat** and the **precat** systems to undergo deactivation in the course of polymerization, with neither monomer nor organoaluminum co-catalyst involved, as found earlier [16].

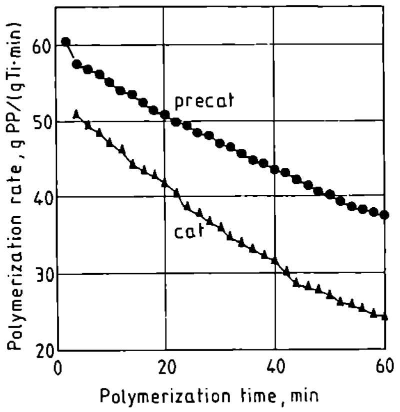


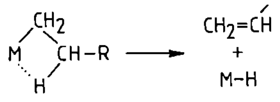
Fig. 1. Effect prepolymerization of catalyst on its stability during propylene polymerization

Deactivation of the catalytic active site is known to be accompanied by the termination reaction of the polymer chain. This process can also result from the chain transfer reaction which recovers another active site capable of initiating the growth of a new molecule. On the basis of the relation:

$$[N_t] = W_t/\overline{M}_{n,t} \tag{1}$$

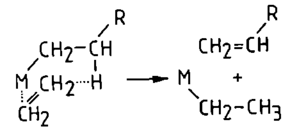
the experimental polymerization yield (W_t) and the number-average molecular weight of the polymer produced ($\overline{M}_{n,t}$) allow to find the number of the macromolecules formed over defined polymerization time intervals (N_t). The corresponding data, illustrated in Fig. 2, show the number of macromolecules to increase with the polymerization time thereby confirming the contribution of chain transfer reactions.

In the processes involving organometallic catalysts it is usually assumed [18] that, when hydrogen is absent (hydrogen is a reactant frequently employed for the adjustment of the polymer molecular weight), the chain transfer reaction results from spontaneous β-elimination of hydrogen:



(2)

or a similar monomer-involving reaction:



(3)

If a monomer takes part in the chain transfer reaction (3), increasing the concentration of the monomer in the polymerization medium should increase the number of macromolecules formed. The data in Table 2 confirm the monomer involvement in the chain transfer reaction.

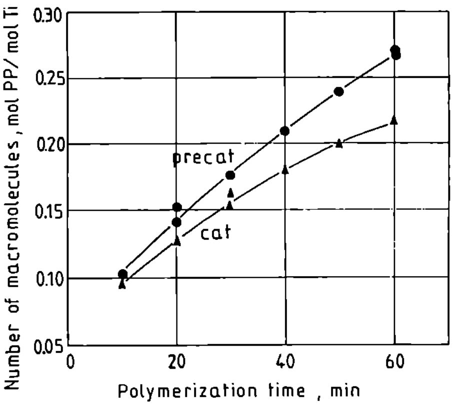


Fig. 2. Number of macromolecules formed as a function of polymerization time

Table 2. NUMBER OF MACROMOLECULES FORMED AS A FUNCTION OF MONOMER CONCENTRATION IN POLYMERIZATION MEDIUM

Catalyst	Monomer pressure, MPa	Activity kg/(molTi·h)	$10^{-3}\cdot\overline{M}_{n,h}$	$\overline{N}_h$, mol/molTi
Cat	0.2	34.56	300	0.115
	0.4	67.20	520	0.129
	0.6	104.28	622	0.168
Precat	0.2	45.12	320	0.141
	0.4	86.22	550	0.157
	0.6	135,67	625	0.217

On the other hand, it was found that the hydrogen β-elimination reaction (2), yielding a metal hydride, becomes important only at sufficiently high temperatures and at low monomer concentrations [19], hence it is negligible under normal polymerization conditions [20, 21]. In propylene polymerizations over the present catalysts the propagation reaction is accompanied by chain termination resulting either from spontaneous deactivation of an active site or from the monomer impact leading to chain transfer with simultaneous recovery of an active site. Similar relationships were also observed earlier in our study on ethylene polymerization over an oxide-supported titanium catalyst [22]. Thus, on the basis of the kinetic model suggested there, we tried to find concentrations of active sites in the catalytic systems discussed here together with the rates for elementary reactions occurring in the propylene polymerization process investigated. For this purpose, relations were found between the number of macromolecules (N_t, calculated from Eqn. 1) and $\exp(-k_t \cdot t)$ (k_t-values were found in [16]) from the equation derived earlier [22]:

$$[N_t] = [C_o^*] + (k_{tr}/k_t)\cdot[C_o^*]\cdot[M] - (k_{tr}/k_t)\cdot[C_o^*]\cdot[M]\cdot\exp(-k_t t) \tag{4}$$

where: $[C_o^*]$ — *concentration of active sites at time t = 0, [M] — monomer (propylene) concentration,* k_{tr} — *transfer rate constant,* k_t — *termination rate constant, t — time of polymerization.*

Linear plots (Fig. 3) were obtained in accordance with the equation:

$$[N_t] = W_t/\overline{M}_{n,t} = A - B\exp(-k_t t) \tag{5}$$

where: $A = [C_o^*] + B$, $B = (k_{tr}/k_t)\cdot[C_o^*]\cdot[M]$

and with regression coefficients r proving the linear equations to offer good fits to experimental data. This allows to use Eq. (5) to calculate the concentration of active sites $[C_o^*]$ and the transfer rate constant k_{tr}. In turn, the known equation for polymerization rate:

$$R_{p,o} = k_p\cdot[M]\cdot[C_o^*] \tag{6}$$

allows to calculate values of the propagation constant k_p.

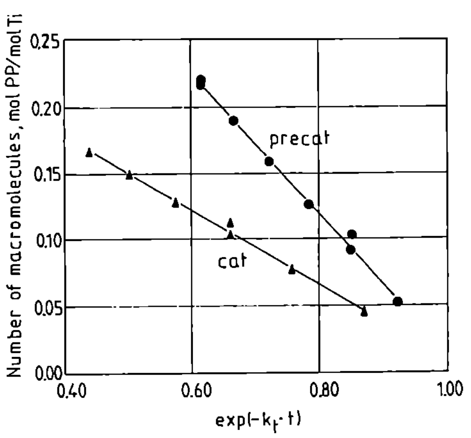


Fig. 3. Number of macromolecules formed as a function of $\exp(-k_t\cdot t)$ *calculated according to Eq. (5);* ***cat:*** $N_t = W_t/\overline{M}_{n,t} = 0.2955 - 0.2808\exp(-k_t\cdot t)$; $r = 0.997$; ***precat:*** $N_t = W_t/\overline{M}_{n,t} = 0.5431 - 0.5268\exp(-k_t\cdot t)$; $r = 0.994$

The results presented in Table 3 suggest that the increased productivity of the prepolymerized catalyst results from the increased number of active sites which additionally are more resistant to deactivation. As we found earlier [23], this latter phenomenon is more eminent for catalysts with microporous structure. Hence, one can expect that the **precat's** higher resistance to

Table 3. KINETIC PARAMETERS OF PROPYLENE POLYMERIZATION DEPENDING ON PREPOLYMERIZATION OF CATALYST

Catalyst	**Cat**	**Precat**
$[C_0^*]\cdot 10^2$, mol/molTi	1.47	1.63
k_p,dm^3/(mol·s)	35.56	35.61
$k_{tr}\cdot 10^3$, dm^3/(mol·s)	2.22	2.21
$k_t\cdot 10^4$, s^{-1}	2.29	1.34
$R_{p,0}/R_{p,60}$	2.28	1.62

deactivation as compared with the **cat**, results from fragmentation of the initial agglomerates of catalyst crystallites. This produces macropores and makes it easier for the monomer to diffuse to active sites [8, 16]. In fact, increased porosity was observed in a catalyst which was subjected to prepolymerization with an ethylene/1-butene mixture [8] or growing macromolecules in the case of copolymerization of ethylene and 1-hexene [2].

Because a reliable determination of porous structure of the catalyst grains covered with a polymer layer, **precat**, *via* physical absorption of nitrogen was problematic, changes in the catalyst morphology were evaluated on the basis of observation of polymer samples. The shape and the distribution of polymer particles produced over heterogeneous Ziegler—Natta catalysts have been reported to be closely related to those of solid catalyst particles [24, 25]. We found the polymer clusters produced on catalyst grains to be practically replicas of those grains, with due allowance for the particle size growth (Table 4). Hence, observations of polymer samples may help deduce changes in catalyst morphology.

Table 4. PARTICLE-SIZE DISTRIBUTION OF CATALYST AND POLYMER OBTAINED OVER THIS CATALYST

Cat		Polymer	
particle size, μm	%	particle size, μm	%
4.5—10	7.0	45—100	4.6
10—26	22.0	100—200	24.3
26—40	63.3	200—400	60.3
>40	7.7	>400	10.8

We took advantage of this method for polypropylene produced over **cat** and **precat**. Scanning electron microscoppy (SEM) was resorted to: Figures 4 and 5 show differences in the polymer granule size and in morphology of the granules; improved porosity can be observed for the prepolymerized catalyst as compared with its unmodified counterpart. This is probably the reason for the monomer to diffuse more easily to active sites; at the same time, deactivation of active sites by blocking with the polymer formed, is retarded under the polymerization conditions.

The initially higher polymerization rate observed over the prepolymerized catalyst (Fig. 1, Table 1) seems to show activation to result from the higher number of active sites available for the monomer, originating by fragmentation of the initial catalyst agglomerates during the prepolymerization process. The data in Table 3 confirm the higher participation of the titanium introduced to the system in creating active sites C_0^* in the prepolymerized catalyst.

Clearly lower differences were found in the propagation rate (k_p) and in the transfer rate (k_{tr}) (Table 3) suggesting that polymerization induces no significant changes in the chemical nature of active sites. Some

Fig. 4. SEM micrographs of the polypropylene obtained over ***cat***

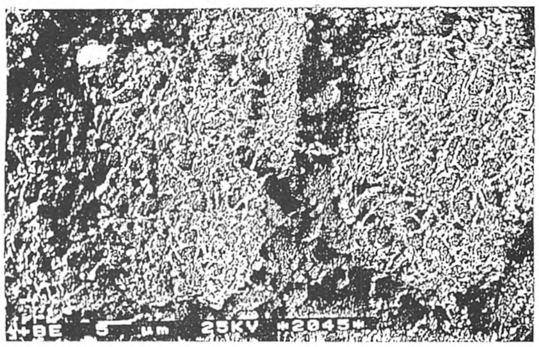


Fig. 5. SEM micrographs of the polypropylene obtained over ***precat***

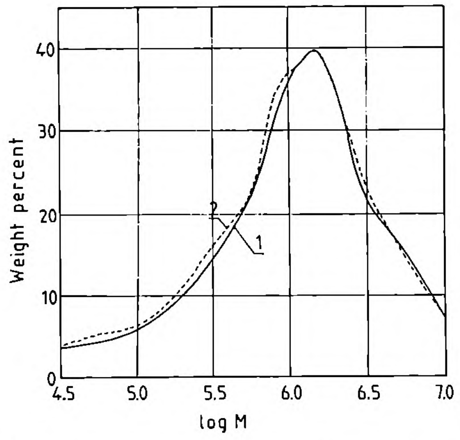


Fig. 6. GPC distribution plots for the polypropylenes obtained over (1) ***cat*** *and (2)* ***precat***

authors [26] have referred the difference in the propagation rate constants, which are related to the non-uniformity of active sites in Ziegler—Natta catalysts, to the difference in the molecular weight distributions of the polymers formed. Both molecular weight and its distribution (Table 1, Fig. 6) were found similar for the polymers obtained over **cat** and **precat**. Thus, the molecular characteristics of the polymer remained practically unaffected by the activation (prepolymerization) of the titanium catalyst, thereby suggesting the active sites in either system to be endowed with similar reactivities.

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W kolejnym zeszycie ukażą się następujące artykuły:

- Gospodarcze i ekologiczne aspekty przerobu odpadów z tworzyw sztucznych
- Zastosowanie polimerów jako katalizatorów w reakcjach katalizy międzyfazowej. Cz. I. Budowa katalizatorów i czynniki mające wpływ na ich aktywność katalityczną
- Fizykochemia i termodynamika układów semikoloidalnych polimer-bitum. Cz. I. Polimery jako modyfikatory asfaltu naftowego
- Struktura fraktalna cząstek polimerowych
- Kopolimeryzacja etylenu z tlenkiem węgla na katalizatorach metaloorganicznych typu kompleksów Zieglera—Natty *(wersja angielska)*
- Zeszklenie poli(tereftalanu etylenu) jako proces relaksacyjny — badania metodą kalorymetrii różnicowej
- Synteza α,ω-dikarboksylowych oligomerów amidowych
- Małocząsteczkowe dianowe żywice epoksydowe
- Higieniczne materiały skóropodobne z usieciowanego poli(chlorku winylu)
- Otrzymywanie wysokoaktywnych silikonowych środków przeciw pienieniu
- Model matematyczny procesu wytłaczania jednoślimakowego. Cz. VII. Elementy intensywnego ścinania i mieszania
- Zastosowanie teorii podobieństwa w projektowaniu wysoce intensywnych mieszalników do suchych nieplastyfikowanych mieszanek PVC (*wersja angielska*)