Kinetics of Ethylene Polymerization at High Temperature with Ziegler–Natta Catalysts

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Synopsis

A kinetic technique is developed for the study of ethylene polymerization reaction at high temperature with Ziegler–Natta catalysts. The technique is based on the calculation of polymerization rate parameters from the data on ethylene consumption vs. time. It takes into account increase of reaction temperature at the beginning of the reaction. Kinetic data in coordinates "polymerization rate–time" are presented for several pseudohomogeneous catalysts ($TiCl_4$–$AlEt_2Cl$, $Ti(OiC_3H_7)_4$–$AlEt_2Cl$), heterogeneous catalysts (δ-$TiCl_3$–$AlEt_3$, δ-$TiCl_3$–$AlEt_2Cl$, $TiCl_4/MgCl_2$–$AlEt_3$, $TiCl_4/MgCl_2$–$AlEt_2Cl$), and solubilized catalysts (δ-$TiCl_3$–poly-1-hexene–$AlEt_2Cl$) at 180°C and reaction pressure 14.6 atm for first 10 min of the reaction. These data are useful for the selection of Ziegler–Natta catalysts for testing in ethylene polymerization reaction in continuous high pressure reactors at short residence times.

INTRODUCTION

Ethylene polymerization in solution at high temperatures (160–200°C) has significant advantages compared with the traditional commercial technology of ethylene polymerization in suspension at 50–90°C.

The first of the advantages is the ready separation of the main part of the solvent used in the polymerization reaction (usually hydrocarbons C_5–C_8) from polyethylene through fast solvent evaporation after pressure decrease. The second advantage is the possibility to produce polyethylene granules immediately after the polymer melt leaves a reactor. The third advantage is the efficient method for utilization of reaction heat—it is used to sustain high reaction temperature rather then being removed by a cooling system. The fourth advantage is the possibility of utilizing reactors traditionally used for the synthesis of high pressure polyethylene for the catalytic process. In such case, only the first ethylene compression stage needs to be used (600–700 atm), which will result in a significant economical gain due to the avoidance of the second compression stage used for the radical polymerization reaction.

There are several obvious requirements for catalysts used for ethylene polymerization in solution:

1. Such catalysts should be active at high temperatures. If one takes into account the significant reducing power of organoaluminum compounds usually used as cocatalysts in Ziegler–Natta systems, it is evident that not all catalysts used at lower temperatures qualify automatically as high temperature catalysts.

2. The catalysts should exhibit polymerization activity high enough to exclude the need for catalyst removal from polymer after the polymerization reaction

by polymer washing. Such catalyst removal, expensive under any circumstances, becomes prohibitive for polymer melt or granules.

3. If the polymerization reaction is carried out in high pressure autoclaves used for ethylene radical polymerization, an additional requirement should be met. Residence time in such autoclaves is of the order 2–5 min and cannot be increased substantially for economic reasons. Therefore, catalysts chosen for application in such reactors should exhibit the highest activity immediately after the beginning of the polymerization reaction. No significant induction period or acceleration stage can be tolerated. On the other hand, catalysts exhibiting polymerization activity for long periods of time (0.5–1 h) have no advantage over short-lived catalysts. Moreover, such stable activity can be detrimental because it will leave active polymerization centers (compounds containing transition metals in a reduced state) accessible for oxidation by air—a reaction which can be accompanied by polymer degradation.

Publications dealing with ethylene polymerization at high temperature are scarce.[1-3] Machon et al.[2] have presented important data on the effect of temperature and concentration of organometallic compounds on activity and stability of catalytic systems utilizing δ-$TiCl_3 \cdot 0.33AlCl_3$ as the solid component. Baulin and Kopylov[3] have studied kinetics of ethylene polymerization with four different catalytic systems ($TiCl_4$–$AlEt_2Cl$, $TiCl_3 \cdot 0.33AlCl_3$–$AlEt_3$, and two supported $TiCl_4$-based catalysts), but their kinetic data cover a large time span (60 min) and demonstrate very complex kinetic behavior.

The objective of our work was the development of a procedure for the investigation of kinetics of ethylene polymerization at high temperature and the study of kinetics of ethylene polymerization with several Ziegler–Natta catalysts as the first step in their evaluation as candidates for large-scale testings.

POLYMERIZATION PROCEDURE

Kinetics of ethylene polymerization at high temperature were studied in an Autoclave Engineers 0.5-L autoclave equipped with zipper sealing and a Magnedrive stirrer. The autoclave was heated through an external jacket by an oil bath. It had several inlets for vacuum pumping, solvent supply, monomer supply, etc.

Purified ethylene (after initial gas drying by molecular sieves, oxygen removal with a reduced copper catalyst at 100°C, and final gas drying by molecular sieves) was fed into a stainless steel high pressure cylinder (volume 2.02 L) used as an ethylene reservoir in polymerization experiments. Ethylene pressure decrease in the cylinder was measured by a gauge.

Before every experiment, the reactor was cleaned and kept under vacuum at 90°C for 1–1.5 h. After cooling it was filled with 170 mL of purified n-heptane (dried over molecular sieves and distilled under Ar over metallic sodium) containing a cocatalyst—an organoaluminum compound. The solvent was heated in the autoclave at an ethylene pressure 2 atm lower than the reaction pressure to the desired reaction temperature, and after that a suspension or solution of catalyst in 30 mL of heptane was added to the reactor with an ethylene flow, raising reactor pressure to the polymerization pressure which was maintained constant by a pressure regulator (Anin Valve) equipped with a pressure transmitter (Foxboro). The polymerization reaction was followed by measuring

pressure drop in the ethylene reservoir. After polymerization for some period of time (usually 1–2 h) the polymerization process was stopped by a rapid ethylene discharge from the reactor and by system cooling.

CATALYTIC SYSTEMS

Catalytic systems used in this study were several typical Ziegler–Natta catalysts. They included pseudohomogeneous systems (original components of which are soluble in hydrocarbons) $TiCl_4$ and $Ti(OiC_3H_7)_4$ in combination with $AlEt_3$, $AlEt_2Cl$, and $AlEtCl_2$, heterogeneous systems based on $TiCl_3$ and $TiCl_4/MgCl_2$, and "solubilized" heterogeneous systems obtained by a method similar to that described in Ref. 1.

$TiCl_3$ used in this study was the δ-form of $TiCl_3 \cdot 0.33AlCl_3$ produced by Stauffer Co. [type $(AA)TiCl_3$]. Supported $TiCl_4/MgCl_2$ catalyst was obtained by $TiCl_4$ deposition from its concentration solution in heptane at 100°C for 3 h on a special type of highly dispersed $MgCl_2$ (Ti content in it is 12.52 wt %).

"Solubilized" $TiCl_3$-based catalysts were obtained by the following procedure: 1 g of $(AA)TiCl_3$ was reacted with an equimolar amount of an organoaluminum compound (20–25 wt % solution in heptane) at 20°C for 1–2 min and then with 4 molar equivalents of 1-hexene (purified by drying over molecular sieves and metallic sodium) and additional 1.5 molar equivalents of the same organoaluminum compound, and then was diluted by n-heptane up to a total volume of 100 mL. The resulting mixtures have significant viscosity due to the formation of a small amount of poly-1-hexene grafted to the surface of the catalyst. These catalysts remained suspended in heptane for long periods of time and were fed to the reactor as 10-mL aliquots. In the case of $AlEt_3$, $TiCl_3$ changed color to black, whereas in the case of $AlEt_2Cl$ it retained its violet color.

KINETIC STUDY—MEASUREMENTS AND CALCULATIONS

Kinetics of ethylene consumption in the polymerization reaction were studied by measuring ethylene pressure decrease from the ethylene reservoir. Taken into account was substantial deviation of the ethylene pressure–density dependence from the ideal behavior. This dependence in the ethylene pressure range 0–55 atm at 20°C can be satisfactorily approximated by the equation

$$d \text{ (g/L)} = 5.374 \times 10^{-3} \cdot P + \exp(3.469 \times 10^{-4} \cdot P) \tag{1}$$

where P = ethylene pressure in the reservoir (atm).

Preliminary experiments on ethylene polymerization at high temperature showed that the reaction rate R decreases in time to some level after which it can be regarded as constant to a first approximation. There exists a most common formal method for the kinetic description of such $R(t)$–t dependencies.

According to the method, all polymerization centers C^* on the catalyst surface are divided into two groups—kinetically stable centers (amount C_1^*, they provide a stable rate of ethylene polymerization, obvious at the final stage of the polymerization reaction) and the kinetically unstable centers (amount C_2^*). These unstable centers decay in the first order reaction with the decay rate constant K_d.

$$C_2^* \xrightarrow{K_d} \text{inactive products} \tag{2}$$

In such a case, the total amount of polymerization centers in a catalyst at time t is

$$C^* = C_1^* + C_2^* e^{-K_d t} \tag{3}$$

If one assumes that the value of the propagation rate constant K_P for ethylene polymerization is the same for both types of polymerization centers, the expression for the rate of polymerization is

$$R(t) = K_p C_m C^* = K_p C_m (C_1^* + C_2^* e^{-K_d t}) \tag{4}$$

where C_m = monomer concentration in solution.

The expression for polymer yield $Q(t)$ for polymerization duration t can be obtained by integration of eq. (4):

$$Q(t) = \int_0^t R(t) \, dt = K_p C_m [C_1^* t + (C_2^*/K_d)(1 - e^{-K_d t})] \tag{5}$$

This expression describes reasonably well experimental $Q(t)$–t dependencies for ethylene polymerization at high temperature in several cases (see further). It was noticed, however, that in many cases, eq (5) is not adequate, especially if solid catalysts are used for olefin polymerization, because it does not account for the early stages of the polymerization reaction when ethylene consumption is slower than expected from eq. (5). It was suggested that this effect is due to an acceleration stage of the polymerization reaction—the period of time (however short) when the polymerization rate increases in time and reaches a maximum before deceleration phenomena dominate the kinetics.

The acceleration stage can be represented, for example, by the stage of chain initiation

$$C^i + M \xrightarrow{K_i} C^* \tag{6}$$

where C^* = polymerization centers (both C_1^* and C_2^*) and C^i = initiation centers.

For the stable centers, the differential equation describing the change of C_1^* in the initiation reaction in eq. (6) is

$$dC_1^*/dt = K_i C_m C_1^i \tag{7}$$

where $C_1^* + C_1^i = C_1^0$ = the initial amount of the stable centers.

The solution of eq. (7) is

$$C_1^* = C_1^0 (1 - e^{-K_i C_m t}) \tag{8}$$

For the unstable centers, the differential equation similar to eq. (7) should include two chemical reactions, eqs. (2) and (6):

$$dC_2^*/dt = K_i C_m C_2^i - K_d C_2^* \tag{9}$$

where $C_2^* + C_2^i = C_2^0$ = the initial amount of unstable centers.

Integration of eq. (9) gives

$$C_2^* = C_2^0 [K_i C_m/(K_d - K_i C_m)] \cdot [e^{-K_i C_m t} - e^{-K_d t}] \tag{10}$$

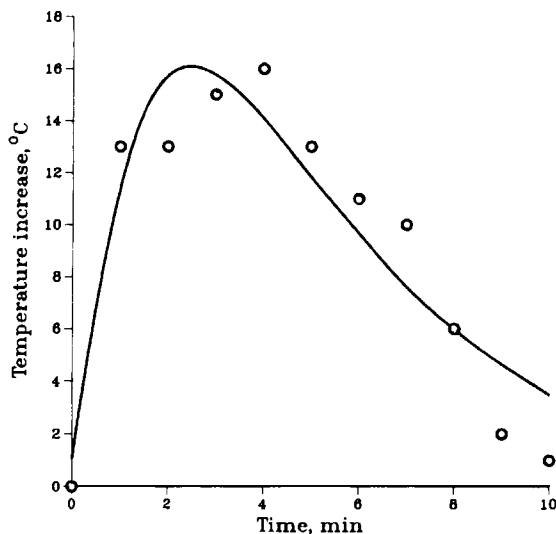Substituting eqs. (8) and (10) into

$$R(t) = K_p C_m (C_1^* + C_2^*) \tag{11}$$

Fig. 1. Approximation of temperature profiles for ethylene polymerization at high temperature with eq. (15). Experimental data are for the $TiCl_4/MgCl_2$–$AlEt_3$ system. The curve was calculated with eq. (15) for $m = 0.28$ and $g = 64°C$.

gives the following expression for polymerization rate as the function of time:

$$R(t) = K_p C_m \{C_1^0 (1 - e^{-K_i C_m t})$$
$$+ C_2^* [K_i C_m / (K_d - K_i C_m)][e^{-K_i C_m t} - e^{-K_d t}]\} \quad (12)$$

Integration of this equation gives the expression for polymer yield as a function of time for a polymerization reaction with slow initiation

$$Q(t) = \int_0^t R(t) \, dt$$
$$= K_p C_m \{C_1^0 t - [C_1^0 - C_2^0 K_i C_m / (K_i C_m - K_d)] \cdot (1/K_i C_m) \cdot (1 - e^{-K_i C_m t})$$
$$+ [C_2^0 K_i C_m / (K_i C_m - K_d)] \cdot (1/K_d) \cdot (1 - e^{-K_d t})\} \quad (13)$$

TEMPERATURE EFFECTS IN ETHYLENE POLYMERIZATION AT HIGH TEMPERATURES

It was found that, in the overwhelming majority of runs, ethylene polymerization with Ziegler–Natta catalysts at high temperatures is quite vigorous at the beginning of the polymerization reaction and is accompanied by a significant increase of reactor temperature—up to 15–20°C. This temperature increase usually lasts for 10–15 min and is difficult to control. One of this effect is shown schematically in Figure 1.

Temperature rise in a polymerization reaction should result in the increase of all reaction rate constants, and, first of all, in the increase of the propagation rate constant, thus affecting the rate of ethylene consumption and complicating the $Q(t)$–time dependence predicted by eqs. (5) and (13). This temperature rise was accounted for empirically using the following assumptions:

1. Only the temperature effect on the propagation rate constant K_p was considered.

2. Experimental curves similar to that shown in Figure 1 were approximated as a product of two exponential dependencies, one increasing in time, $1 - \exp(-m_1 t)$, and the second decreasing in time, $\exp(-m_2 t)$, where m_1 and m_2 are parameters of the temperature change:

$$\Delta T = g(1 - e^{-m_1 t}) \cdot e^{-m_2 t} = g(e^{-m_2 t} - e^{-(m_1 + m_2)t}) \qquad (14)$$

where ΔT = temperature increase above a reaction temperature; g is a parameter.

It was found by trial and error that eq. (14) can be simplified assuming $m_1 = m_2 = m$:

$$\Delta T = g(e^{-mt} - e^{-2mt}) \qquad (15)$$

Parameters m and g in this equation are estimated for a particular polymerization experiment in the following way: the m value is calculated from the position of the maximum (t_{max}) on the temperature curve in Figure 1

$$d\Delta T/dt = g(2m \cdot e^{-2mt_{max}}) - m \cdot e^{-mt_{max}}) = 0 \qquad (16)$$

and

$$m = \ln 2/t_{max} \qquad (17)$$

The g value is estimated with eq. (15) from ΔT_{max} and t_{max}.

The ΔT–t curve calculated with eqs. (15) and (17) is shown in Figure 1 also. Usually the difference between real ΔT values and the ΔT value calculated with eq. (15) does not exceed 2–3°C.

The temperature effect on the propagation rate constant is usually described by the Arrhenius equation

$$K_p = A \cdot e^{-E/(RT)} \qquad (18)$$

TABLE I
Ethylene Polymerization at High Temperature[a]

Catalytic system	Transition metal compound (g)	Al compound (mmol)	Catalyst activity (g/g cat)
TiCl$_4$–AlEt$_3$	0.086	4.68	57
	0.086	4.68	69
TiCl$_4$–AlEt$_2$Cl	0.086	4.65	353
	0.086	4.65	184
TiCl$_4$–AlEt$_2$	0.086	4.20	92
Ti(OiC$_3$H$_7$)$_4$–AlEt$_2$Cl	0.096	4.65	348
	0.096	7.75	472
Ti(OiC$_3$H$_7$)–AlEtCl$_2$	0.096	4.20	0
(AA)TiCl$_3$–AlEt$_3$	0.050	3.12	375
(AA)TiCl$_3$–AlEt$_2$Cl	0.048	3.10	1190
(AA)TiCl$_3$–AlEt$_3$–poly-1-hexene	0.10	—	2
(AA)TiCl$_3$–AlEt$_2$Cl–poly-1-hexene	0.10	—	134
	0.10	—	194
TiCl$_4$/MgCl$_2$–AlEt$_3$	0.052	3.12	869
	0.023	3.12	753
TiCl$_4$/MgCl$_2$–AlEt$_2$Cl	0.027	3.10	1159

[a] Polymerization Conditions: heptane 200 mL, reaction pressure 14.6 atm, temperature 180°C.

where the activation energy E for olefin polymerization reaction is of the order 10 kcal/mol. However, in the narrow temperature range 180–200°C, this exponential dependence can be well approximated by a linear dependence (for E = 10 kcal/mol)

$$K_p(T) = K_p(180°C) \cdot (1 + 0.028\Delta T) \tag{19}$$

Thus, to obtain $Q(t)$–t dependencies for ethylene polymerization in the case when this reaction is accompanied by a temperature increase, one should substitute eqs. (15) and (19) into eqs. (4) and (12) and repeat integration.

In the case of the polymerization reaction without an acceleration stage [eq. (4) is used]

$$R(t) = K_p[1 + 0.028g(e^{-mt} - e^{-2mt})]C_m[C_1^0 + C_2^0 e^{-K_d t}] \tag{20}$$

Integration of this equation gives

$$Q(t) = \int_0^t R(t)\,dt$$

$$= K_p C_m C_1^0 t + \frac{K_p C_m C_2^0}{K_d}(1 - e^{-K_d t}) + \frac{K_p C_m C_1^0 0.014g}{m}(1 - 2e^{-mt} + e^{-2mt})$$

$$+ K_p C_m C_2^0 0.028g \left[\frac{m}{(m + K_d)(2m + K_d)} - \frac{1}{m + K_d}e^{-(m+K_d)t} \right.$$

$$\left. + \frac{1}{2m + K_d}e^{-(2m+K_d)t} \right] \tag{21}$$

Substitution of eqs. (15) and (19) in eq. (12) and subsequent integration of eqn. (12) gives the following expression for consumption of ethylene in the polymerization reaction with an acceleration stage:

$$Q(t) = \int_0^t R(t)\,dt$$

$$= K_p C_m C_1^0 t - \left(K_p C_m C_1^0 + \frac{K_i K_p C_m^2 C_2^0}{K_i C_m - K_d} \right) \frac{1}{K_i C_m}(1 - e^{-K_i C_m t})$$

$$+ K_p C_m C_2^0 \frac{K_i C_m}{K_i C_m - K_d} \frac{1}{K_d}(1 - e^{-K_d t})$$

$$+ 0.028g K_p C_m C_1^0 \left\{ \frac{1}{m}(1 - e^{-mt}) - \frac{1}{m + K_i C_m}[1 - e^{-(m+K_i C_m)t}] \right\}$$

$$- 0.028g K_p C_m C_2^0 \left[\frac{K_i C_m}{K_i C_m - K_d} \frac{1}{m + K_i C_m}(1 - e^{-(m+K_i C_m)t}] \right.$$

$$\left. - \frac{1}{m + K_d}[1 - e^{-(m+K_d)t}] \right]$$

$$- 0.028g K_p C_m C_1^0 \left\{ \frac{1}{m}(1 - e^{-2mt}) - \frac{1}{2m + K_i C_m}[1 - e^{-(2m+K_i C_m)t}] \right\}$$

$$+ 0.028g K_p C_m C_2^0 \frac{K_i C_m}{K_i C_m - K_d} \left\{ \frac{1}{2m + K_i C_m}[1 - e^{-(2m+K_i C_m)t}] \right.$$
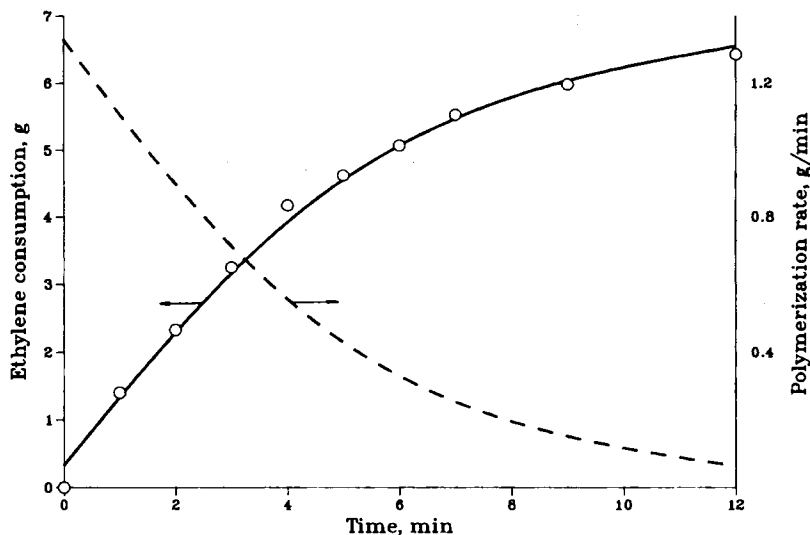
$$\left. - \frac{1}{2m + K_d}[1 - e^{-(2m+K_d)t}] \right\} \tag{22}$$

Fig. 2. Kinetics of ethylene polymerization with the TlCl$_4$–AlEt$_2$Cl system at 180°C. Consumption vs. time: (O) experimental data; (——) calculations with eq. (21). Rate vs. time calculated with eq. (4). Calculation parameters are given in Table II.

Equations (21) and (22) were used for the comparison of experimental curves in coordinates $Q(t)-t$ and kinetic models. This comparison allowed one to estimate kinetic parameters of the models by adjustment of Eqs. (21) and (22) to experimental data. In the case of Eq. 21, three parameters were adjusted, $K_p C_m C_1^0$, $K_p C_m C_2^0$, and K_d, and, in the case of eq. (22), four parameters, $K_p C_m C_1^0$, $K_p C_m C_2^0$, $K_i C_m$, and K_d. In all cases, m and g values were estimated from temperature profiles of kinetic experiments as described above. The adjustment was carried out with the help of SAS nonlinear regression program NLIN.

EXPERIMENTAL DATA ON HIGH TEMPERATURE ETHYLENE POLYMERIZATION

Table I contains data on ethylene polymerization with several Ziegler–Natta catalysts at 180°C and total reactor pressure 14.6 atm (heptane vapor pressure at this temperature is 6.6 atm).

Several conclusions are obvious from this table:

1. AlEt$_2$Cl, nearly in all cases, was a more active cocatalyst than AlEt$_3$, probably due to catalyst overreduction by AlEt$_3$ at high temperatures.

2. AlEtCl$_2$ made poor catalysts.

3. Catalysts exhibiting reasonable activity at high temperature were TiCl$_4$, Ti(OiC$_3$H$_7$)$_4$, TiCl$_3$, TiCl$_3$–poly-1-hexene, and supported catalyst TiCl$_4$/MgCl$_2$ in combination with AlEt$_2$Cl as well as (AA)TiCl$_3$ and TiCl$_4$/MgCl$_2$ in combination with AlEt$_3$. Kinetic behavior of these catalysts was studied in detail.

It was found that, in the case of all pseudohomogeneous catalysts [containing TiCl$_4$ and Ti(OiC$_3$H$_7$)$_4$)] and the TiCl$_3$–AlEt$_3$ system, kinetics of ethylene polymerization can be described precisely by the scheme assuming a very fast initiation step (eq. (21); see Fig. 2). This means that, at high temperatures, all catalyst formation and initiation reactions are complete in less than 1 min. For
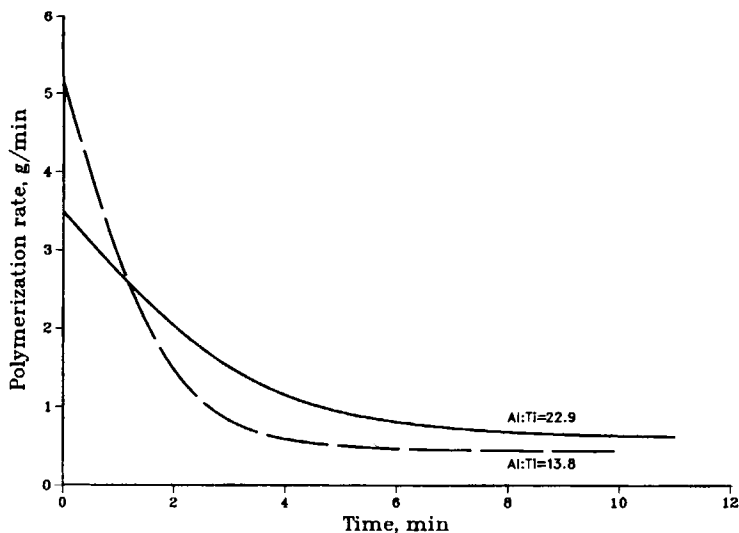
Fig. 3. Kinetics of ethylene polymerization with the $Tl(OiC_3H_7)_4$–$AlEt_2Cl$ system at 180°C: polymerization rate vs. time for two Al:Ti ratios. Calculated with eq. (4), calculation parameters are given in Table II.

such catalytic systems, reaction rate is maximal at the beginning of the poly-merization reaction (Figs. 2 and 3). On the other hand, kinetics of ethylene consumption with all other heterogeneous catalysts is much better described by the kinetic scheme involving the initiation step [eq. (22); see Fig. 4]. In such cases, reaction rate at the beginning of the polymerization reaction is lower than after the initiation step is completed (according to the scheme it is equal to 0 at
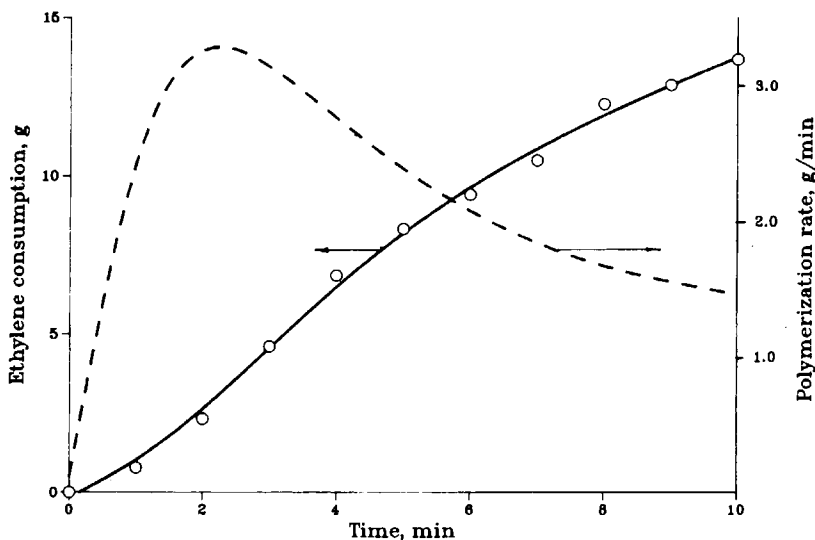

Fig. 4. Kinetics of ethylene polymerization with the $TlCl_4/MgCl_2$–$AlEt_2Cl$ system at 180°C. Ethylene consumption vs. time: (O) experimental data; (——) calculations with eq. (22). Rate vs. time calculated with eq. (12). See Table II for calculation parameters.
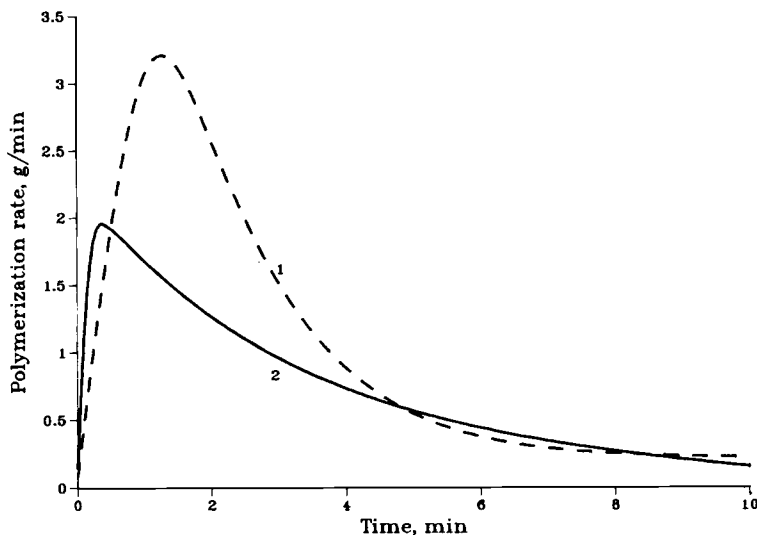
Fig. 5. Kinetics of ethylene polymerization at 180°C: (1) δ-TiCl$_3$–AlEt$_2$Cl system; (2) δ-TiCl$_3$–poly-1-hexene–AlEt$_2$Cl system. Calculated with eq. (12), calculation parameters are given in Table II.

$t = 0$, but rapidly increases in time) and reaches a maximum after some time, usually 0.5–2 min (see Figs. 4 and 5). The finding of the acceleration stage for some heterogeneous catalysts is very important if the polymerization reaction is carried out in a continuous mode at short residence times. In such cases, preliminary mixing of catalyst components (before they enter a reactor) will increase system productivity.

Table II contains information on kinetic parameters of these catalytic systems. Included in the table are temperature effect parameters, m and g [see eq. (5)], maximum effective polymerization rates (g PE/g cat·min and g PE/mole Ti·min) and parameters of eq. 21 (polymerization with the initiation step absent) and eq. 22 (polymerization with a slow initiation step). In all cases, values of $K_pC_mC_1^0$ and $K_pC_mC_2^0$ are related to the molar amount of catalyst. All kinetic parameters correspond to the situation when reaction temperature is constant and is equal to 180°C.

Figures 2–5 and Table II provide information on relative activity of various Ziegler–Natta catalysts during the few first minutes of polymerization reaction. Typically, the maximum polymerization rate in our conditions (ethylene pressure ∼8 atm) which is reached immediately after the beginning of the reaction or after a short acceleration stage is of the order 10–70 g/g cat·min. Of course, if the rates are compared on the basis of moles of Ti in the catalysts, the productivity of supported catalysts is higher than for the rest of the catalysts—a phenomenon typical for Ziegler–Natta catalysts in general and readily explainable by the fact that, in supported catalysts, transition metal atoms are positioned on the catalyst surface only whereas in the case of solid catalysts (both introduced into a reactor originally, as TiCl$_3$, or formed *in situ* in the case of pseudohomogeneous systems) only the part of transition metal atoms situated mostly on the catalyst surface form active centers whereas the metal atoms inside catalyst particles are inactive.

TABLE II
Kinetic Parameters of Ethylene Polymerization at 180°C

Catalytic system	Temp effect		R_{max}		Fast initiation			Slow initiation			
	m (min^{-1})	g (°C)	g PE/ g cat·min	g PE/ mm Ti·min	$K_p C_m C_1^0$/cat (10^3/min)	$K_p C_m C_2^0$/cat (10^3/min)	K_d, (min^{-1})	$K_p C_m C_1^0$/cat (10^3/min)	$K_p C_m C_2^0$/cat (10^3/min)	$K_i C_m$ (min^{-1})	K_d (min^{-1})
TiCl$_4$– AlEt$_2$Cl	—	0	8.0	1.5	0.51	0.99	0.059	—	—	—	—
Ti(OiC$_3$H$_7$)$_4$– AlEt$_2$Cl	0.099	40	16.3	3.1	0.003	3.09	0.244	—	—	—	—
	0.173	56	55.7	15.8	1.28	14.54	0.806	—	—	—	—
δ-TiCl$_3$– AlEt$_3$	0.06	52	39.3	11.2	1.80	9.36	0.46	—	—	—	—
	0.231	52	47.6	9.5	0.15	9.33	0.35	—	—	—	—
δ-TiCl$_3$– AlEt$_2$Cl	0.172	72	66.7	13.3	—	—	—	0.91	27.2	1.30	0.76
δ-TiCl$_3$– PH[a]–AlEt$_2$Cl	0.346	92	19.0	3.8	—	—	—	0.055	4.2	8.45	0.28
TiCl$_4$/MgCl$_2$– AlEt$_3$[b]	0.231	64	49.0	117.5	—	—	—	4.5	25.5	1.40	0.36
TiCl$_4$/MgCl$_2$– AlEt$_2$Cl[b]	0.346	24	50.0	119.8	—	—	—	4.9	36.6	0.72	0.53
	0.173	76	52.2	125.2	—	—	—	7.8	29.0	0.72	0.41

[a] PH = grafted poly-1-hexene.
[b] Calculations of all g PE/mmol Ti values are for 12.52 wt % of Ti in this catalyst.

All catalysts tested are very unstable at high temperature as follows from the fact that the $K_p C_m C_1^0$ values are always much lower than the $K_p C_m C_2^0$ values. Instability of the catalysts is determined by the K_d value as well as the C_2^0/C_1^0 ratio. It is different for various catalysts, the most stable being the $TiCl_4$–$AlEt_2Cl$ system and the least stable $Ti(OiC_3H_7)_4$–$AlEt_2Cl$ and $TiCl_3$–$AlEt_2Cl$ systems. It should be noted that the precision of the estimation of all kinetic parameters for such short runs is not high and can be evaluated approximately as ±50%; hence only the principal features of the kinetic behavior can be claimed with certainty.

The rate of the initiation reaction is determined by the $K_i C_m$ value (see Table II). It is approximately the same for all systems studied except for the system $TiCl_3$–$AlEt_2Cl$–poly-1-hexene. In this system, catalyst components were mixed before they were introduced into the reactor, and all catalyst formation reactions (apparently constituting some stages of the overall acceleration reaction, but not accounted for by the kinetic scheme we used) and the initiation reaction (with 1-hexene) were complete before contact of the catalyst with the monomer.

The following conclusions can be made about merits of different catalysts when used for high temperature ethylene polymerization.

It two pseudohomogeneous systems are compared [$TiCl_4$- and $Ti(OiC_3H_7)_4$-based], the second system has some advantages—it produces the catalyst which is highly active initially (compare Figs. 2 and 3) but rapidly deactivating, whereas the $TiCl_4$–$AlEt_2Cl$ system is much more stable—hardly a virtue when short residence time reactors are considered. The $Ti(OiC_3H_7)_4$–$AlEt_2Cl$ system can be regarded as a convenient experimental system for the preliminary evaluation of reactor performance at high temperatures and high pressures—the system can be easily introduced into a reactor, it is cheap and easily available, $Ti(OiC_3H_7)_4$ is much less air- and water-sensitive than $TiCl_4$, and polymers produced with the system will contain less acidic chlorine than in the case of the $TiCl_4$-based system.

Suspended $TiCl_3$-based systems with grafted higher polyolefins are used in some commercial processes of high temperature ethylene polymerization reactions (1). Our data confirm positive features of such systems—they are sufficiently active and can be easily introduced into a reactor.

The supported $TiCl_4/MgCl_2$ catalyst was proved to be an effective catalyst for high temperature ethylene polymerization. Its only drawback—acceleration of the polymerization reaction for the first few minutes can be overcome if it is treated with an organoaluminum compound prior to its introduction into a reactor. It probably can be transformed into a suspended form also by the same process as was used for the $TiCl_3$ suspension. In such a case, a decrease of the acceleration stage duration can be expected as happened with the $TiCl_3$–$AlEt_2Cl$ system (see $K_i C_m$ values in Table II).

References

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