Ethylene polymerization process with a highly active Ziegler-Natta catalyst: 1. Kinetics*

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The suspension polymerization of ethylene using a highly active Ziegler–Natta catalyst has been investigated. It has been shown that, under appropriate experimental conditons, the monomer transport is hindered neither by pore diffusion inside the suspended particle, nor by film diffusion at the surface of the suspended particle. It was found that there exists an extraordinarily high number of active sites, which at 85°C is in the range of about 70% of all titanium atoms. On the other hand, the overall propagation rate constant has the same order of magnitude as that published for some other Ziegler–Natta catalysts.

INTRODUCTION

In 1953 Ziegler and coworkers[1] found that catalysts for ethylene polymerization at normal pressure and moderate temperatures are formed by reaction of transition metal compounds like $TiCl_4$ with organoaluminium compounds. On the basis of this discovery, technical processes were developed within a few years. If the polymerization is carried out at temperatures lower than the solubility temperature of the polymer[2], the polymer precipitates as a semicrystalline phase. This process is called suspension polymerization, and it has been intensively investigated for classical Ziegler–Natta catalysts[3–7]. From these investigations it is clearly seen that this process is complicated, and that there are a number of physical and chemical processes occurring sucessively and/or simultaneously. The main processes are the transfer of the different components from the gaseous phase through the suspension medium and the polymer to the active sites at the surface of the catalyst; the chemical reactions at these active sites have been discussed in detail in a previous paper[8], as has the formation of the semicrystalline polymer phase[9]. The formation of a semicrystalline phase in the pores of the heterogeneous catalyst must lead to a disintegration of the catalyst particles, or to a deactivation of active sites by filling these pores with polymer, and thus hindering the monomer to reach the active sites. If the growing polymer particle becomes greater there may be a diffusional hindering of the different components, and a temperature gradient within the particle, which implies that its average temperature is higher than the temperature of the surrounding medium, as pointed out be Wicke[10]. As these phenomena can interact in different ways depending on the nature of the catalyst and other parameters, it is very important to analyse the different processes separately. This prompts us to find experimental conditions under which only one or a few processes are taking place. It is the author's opinion that this aim has not been approached in many previous investigations. The first point is to characterize the catalyst and to investigate its reaction with the cocatalyst. The second point is to elucidate the stationary or steady state conditions for the polymerization process. Under these conditions, the kinetic behaviour, the molecular weight regulation and the molecular weight distribution can then be investigated to obtain significant results.

The present investigations were performed using a highly active catalyst[11] which is at least 20 times as active as classical Ziegler–Natta catalysts.

EXPERIMENTAL

Investigation of the catalyst morphology

The bulk density and density was measured using standard methods[12,13]. To obtain the density, the catalyst was suspended in n-hexane. The particle size distribution was determined using the Zeiss TGZ 3 instrument[14]. In this case the particles were approximated by equivalent spheres. The specific surface and the porosity were measured as described elsewhere[15]. The specific surface was determined, using an apparatus developed by Schlosser[16]. The porosity was measured with a mercury porosimeter of Carlo Erba, Milan. The X-ray diffraction pattern was obtained using a computer controlled single crystal diffractometer (Siemens). The catalyst was sealed in a small tube. This tube was fixed on the diffractometer and rotated about the y-axis. The scanning electron micrographs were made using a stereoscan from Cambridge Instruments. The preparation of the samples was performed as described elsewhere[17].

Polymerization

All polymerization runs were performed in diesel oil. Diesel oil is a completely hydrogenated mixture of aliphatic hydrocarbons, which contains only traces of aromatic compounds (<100 ppm). The boiling points were in the range of 135° to 170°C. The distilled diesel oil had been purified with molecular sieves (10 Å) under N_2 or Ar (highly purified gases from Messer Griesheim). This diesel oil was stored under N_2 or Ar.

The monomer was polymerization grade ethylene with a maximum of 40 vol ppm impurities. The impurities were C_2H_2, CO, CO_2, CH_3OH, acetone, O_2 and H_2O. These compounds may react with the cocatalyst[18] which, for this

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reason, was usually used in excess. The cocatalyst was triethylaluminium from Schering AG, Bergkamen. This compound was used without further purification.

The polymerization runs were performed in pressure vessels of different size (1, 2 and 200 dm^3). The vessels were made of glass or stainless steel. They were equipped with a stirrer and flow disturbers. The number of revolutions of the stirrer could be chosen to be infinitely variable. All vessels were equipped with a temperature control. The temperature could be monitored continuously. The scattering of the temperature lay within ± 1K as a maximum. All vessels could be purged with N_2 or Ar.

The monomer consumption was measured using calibrated rotameters (Fischer and Porter, Göttingen) or flow meters (Elster Co. AG, Mainz). To trace the conversion with time, samples were withdrawn from the reactor to find the amount of the polymer. There was a loss in the range of less than 2% of low molecular weight material which was soluble in diesel oil at room temperature. The conversion curves measured using both methods coincide within experimental error.

The hydrogen concentrations in the gaseous phase were measured using a thermal conductivity cell (Siemens, Karlsruhe) or an i.r. instrument (H. Maihak AG, Hamburg). These instruments were calibrated with mixtures of gases, which had been established with calibrated pumps (H. Wösthoff oHG, Bochum). All experiments were performed at constant pressure.

To obtain reproducible results it is very important not to exceed 35 vol % of polymer in diesel oil. This means that 1 dm^3 diesel oil may contain at most 150 g polymer with a bulk density of about 0.4 g/cm^3.

The polymer formed was investigated by viscometry. These measurements are made at 135°C with decalin as solvent[19,20]. The measurements are extrapolated to obtain the viscosity number using the Martin equation[21]. M_v was calculated with the equation $[\eta] = 5.13 \times 10^{-4} M_v^{0.71}$. This equation was averaged using the equations given by several authors[22–25]. It is similar to an equation which was established for trichlorobenzene[26].

The molecular weight distributions were established by g.p.c. chromatography. A Waters 200 g.p.c. chromatograph, equipped with columns filled with styragel (10^5, 10^4, 10^3, 10^2 nm) was used. The measurements were performed at 135°C with 1,2,4-trichlorobenzene as solvent stabilized with 1 g Ionol®/dm^3 (Shell AG). The concentration was 1 g/dm^3 and the flow rate 1 cm^3/min. The apparatus was calibrated with polystyrene standards to obtain a universal calibration curve as pointed out by Benoit and coworkers[27]. To check the validity of this calibration, M_v was compared with the value calculated from viscometric data. Both values agree within experimental error. To establish the molecular weight distribution no corrections of the g.p.c. curve have been made.

Catalytic system

Ziegler and coworkers[1] showed that the combination of a transition metal compound with an organoaluminium compound leads to a catalytically active system. So the transition metal compound may be termed the catalyst and the organoaluminium compound the cocatalyst. This also holds in the case of highly active catalytic systems.

The catalyst used in the present investigations was the reaction product of $Mg(OC_2H_5)_2$ with $TiCl_4$. During this reaction $-OC_2H_5$ groups are replaced by $-Cl$. The reaction conditions, such as temperature, reaction time, and the relation of the amount of substance of both components determine the amount of Ti in the catalyst. The catalyst used contains 8.5% by wt of titanium. This catalyst is a fine powder with a bulk density of 0.226 g/cm^3. The density was found to be 1.335 g/cm^3, i.e. a little higher than the density of $Mg(OC_2H_5)_2$, which is 1.18 g/cm^3 (ref 28). The preparation of catalysts of this type is described in patent literature[11].

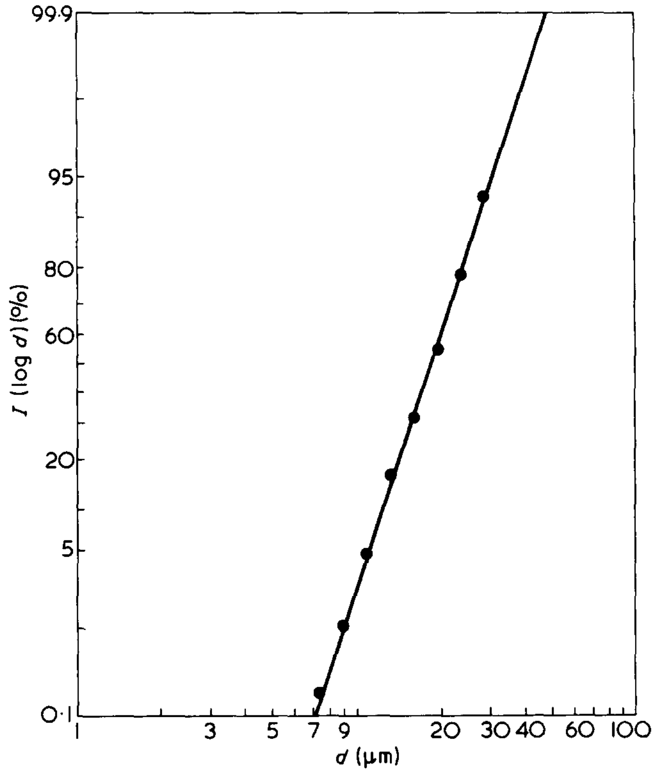

Figure 1 Particle size distribution of the catalyst; sum of wt % as a function of diameter

Within experimental error the particle size distribution can be described by a logarithmic normal distribution function[29–31]. This is shown in *Figure 1*.

The particle size distribution is characterized by two values, the median value, d_0, and the standard deviation, s. d_0 was found to be 18.5 µm and s equal to 0.315. This implies that the catalyst has a narrow particle size distribution.

Using d_0 and s, it is possible to calculate the specific surface O according to the following equation[31].

$$O = \frac{6 \exp(s^2/2)}{d_0 \rho} \phi \qquad (1)$$

ρ is the density and ϕ the form factor, which is 1 if the particles are spheres. If we make this assumption, the specific surface is 0.26 m^2/g. This value has to be compared with the experimentally determined value of 60 ± 5 m^2/g. The difference between these two values shows that the particles must have a large inner surface and thus a great porosity. This conclusion can be proved experimentally by measuring the porosity. The integral specific volume of the pores as a function of the pore radius is shown in *Figure 2*.

To obtain *Figure 2* it has been assumed that all the pores are cylinders and that the compressibility of the catalyst can be neglected. By doing this it is very difficult to estimate the error. On the other hand the results in *Figure 2* should

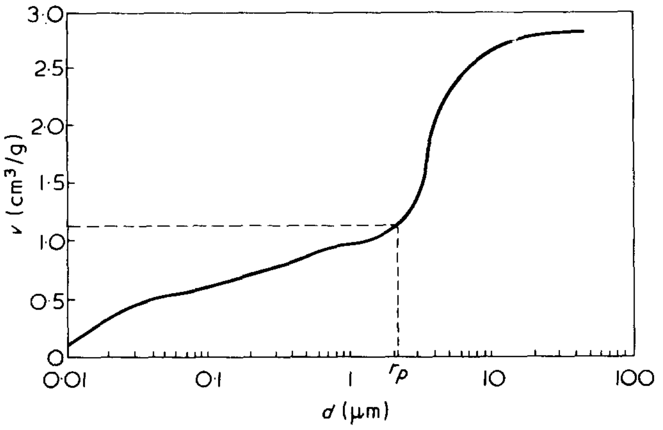

Figure 2 Porosity of the catalyst: integral specific pore volume as function of pore radius r_p (see equation 2)

give a realistic picture of the porosity of the catalyst.

If the porosity of powder is measured with a mercury porosimeter the volume of the pores within the particles as well as the volume between the particles is measured. The specific volume of the pores in the particles is the volume belonging to r_p, which can be calculated using the particles size distribution according to the following equation[32]:

$$r_p = d^*/13 \tag{2}$$

d^* corresponds to the 90% value on the ordinate in *Figure 1*. Thus $r_p = 2.1$ μm. As pointed out by the dotted lines in *Figure 2*, the specific volume of the pores can be determined. The total specific volume of the pores was found to be 1.16 cm^3/g, which means that 61% of a catalyst particle consists of cavities.

The pictures which can be monitored with a scanning electron microscope confirm these measurements insofar as they show a porous particle (*Figure 3*).

The X-ray diffraction pattern of the catalyst show that this catalyst is mostly amorphous. There are only some broad lines and a strong diffuse scattering. This means that the crystalline particles must be very small. The X-ray diffraction pattern is shown in *Figure 4*.

Table 1 summarizes physical data for this catalyst.

Activation reaction of the catalyst

The catalyst was activated with triethylaluminium. In a rapid reaction, the catalytically active system is formed, probably in the same way as described elsewhere[33]. It was found that the reaction was complete after 5 min. Thus the polymerization reaction started 5 min after the activation reaction had been initiated by combining catalyst and cocatalyst.

The activity of the catalytic system depends on the ratio between catalyst and cocatalyst. To demonstrate this, the velocity of the polymerization reaction at the beginning of the reaction[8] has been measured as a function of the trialkylaluminium cocatalyst/catalyst ratio. both expressed as the quantities of the trialkylaluminium and titanium compounds. The results are shown in *Figure 5*.

The results in *Figure 5* show that the activity approaches a maximum for a cocatalyst/catalyst ratio between 10 and 20. If the cocatalyst/catalyst ratio rises to very high values the activity drops but does not reach 0, even if this ratio is 1000. This only holds if the time of activation is 5 min, because at

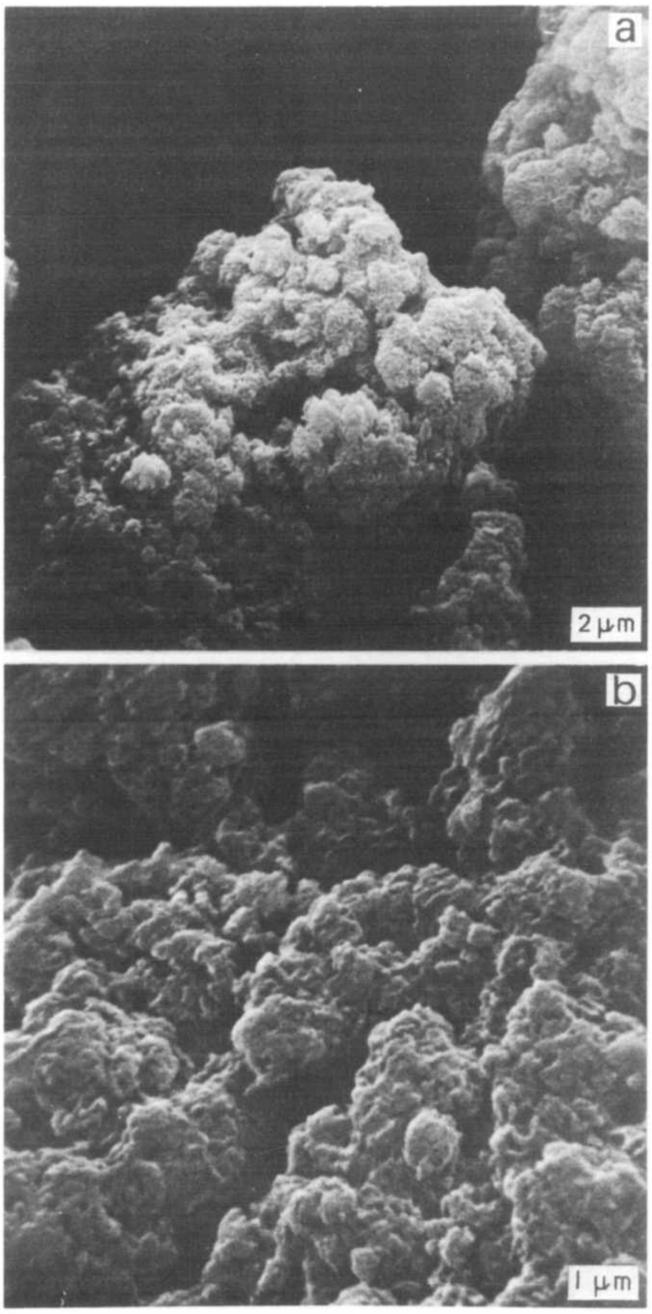

Figure 3 Scanning electron micrographs of the surface of catalyst; magnification (a) 6000, (b) 12 000

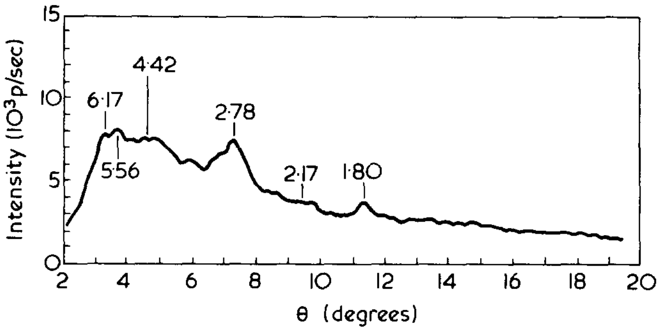

Figure 4 X-ray (MoK$_\alpha$) diffraction diagram of the catalyst; the numbers give distances of lattice planes

Table 1 Physical data of the catalyst

Bulk density (g/cm^3)	0.226
Density (g/cm^3)	1.335
Particle size distribution:	
d_0 (μm)	18.5
s	0.315
r_p (μm)	2.1
Specific surface:	
Equation (1) (m^2/g)	0.26
BET (m^2/g)	60
Integral specific pore volume (cm^3/g)	1.16

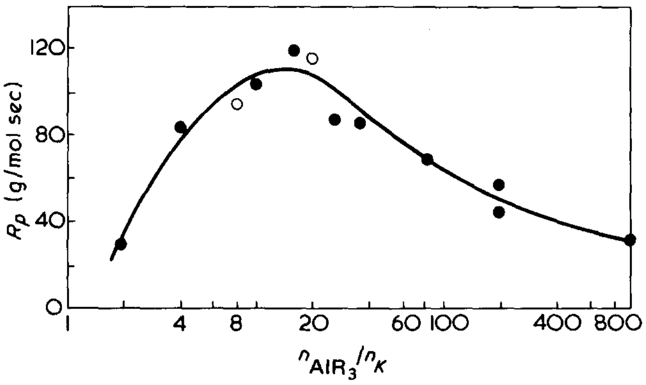

Figure 5 Velocity of the polymerization reaction extrapolated to the beginning of the reaction, R_p, as a function of the cocatalyst–catalyst ratio n_{AlR_3}/n_K; 1 dm^3 reaction vessel, 0.6 dm^3 diesel oil, 750 rpm, 85°C, n_K = 2.5 × 10^{-5} mol Ti compound, ethylene pressure 1 bar; ●, time of activation 5 min; ○, time of activation 4 h

high cocatalyst/catalyst ratio a deactivation process takes place as a function of activation time.

It is surprising that this catalyst works even if there is an extreme excess of cocatalyst. The decrease of activity can be attributed to an inhibition of the catalytically active centres by the cocatalyst as pointed out in a previous paper[8]. If the cocatalyst/catalyst ratio becomes smaller, the system does not reach its full activity. The interpretation is that in this region the activation reaction does not run completely. The following experiments are performed exclusively at cocatalyst/catalyst ratios greater than 20.

Determination of steady state conditions during polymerization

Since there are a number of different processes in heterogeneous Ziegler–Natta polymerization which can interfere in different ways, it is necessary to find the steady state conditions. It is possible that high concentration and temperature gradients exist in the system, depending on both the amount of catalyst and the conditions of stirring.

The first task is to eliminate stirring as a variable which influences the velocity of the polymerization reaction. To do this, the velocity of the polymerization at the beginning of the reaction R_p has been measured as a function of the revolution of the stirrer ω. The results are presented in *Figure 6*.

The results in *Figure 6* show that the velocity R_p becomes smaller at a rate of revolutions less than 500 rpm. Above 500 rpm R_p becomes constant and independent of the revolution. In this range the material flow from the gaseous phase through the suspension medium to the polymerizing particles does not influence the velocity of the polymerization process. As the velocity in this range, R_p, does not depend on the revolution of the stirrer this means that there is a stationary monomer concentration in the solvent. All further experiments were made at 750 rpm or under similar conditions.

We must now check whether the velocity of the polymer formation, dm_p/dt, at 750 rpm is influenced by the amount of the catalyst n_K. The experimental results are given in *Figure 7*.

These results show that the velocity of the polymer formation is proportional to the amount of catalyst expressed in moles of titanium compound within an experimental error of ± 10%. This means that the amount of catalyst can be changed up to 2.5 x 10^{-5} g atoms Ti without decreasing the monomer concentration in the liquid phase. The monomer

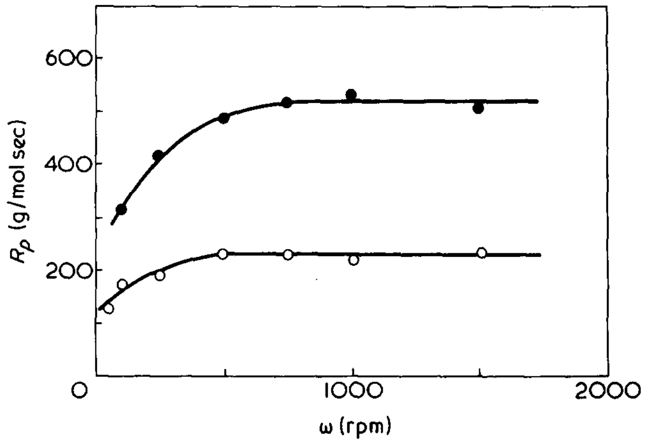

Figure 6 Velocity of the polymerization reaction extrapolated to the beginning of the reaction, R_p, as function of the revolution of the stirrer in rpm, ω; 1 dm^3 reaction vessel, 0.6 dm^3 diesel oil, 85°C, pressure 6 bar, n_K = 2.5 × 10^{-5} mol Ti compound, n_{AlR_3}/n_K = 200; ●, without hydrogen, ○, with hydrogen (28.6 vol %)

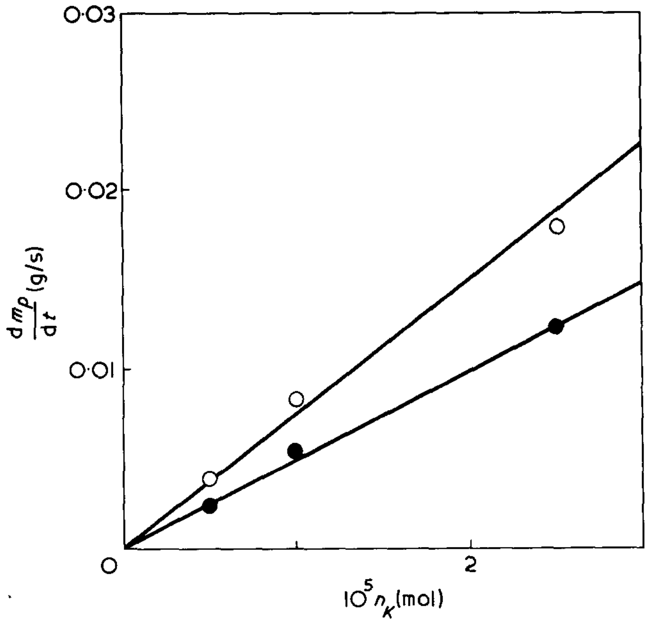

Figure 7 Velocity of polymer formation dm_p/dt as a function of the amount of catalyst n_K; 1 dm^3 reaction vessel, 0.6 dm^3 diesel oil, 750 rpm, 85°C, ethylene pressure 6 bar; ○, n_{AlR_3}/n_K = 200; ●, n_{AlR_3}/n_K = 80

Table 2 Viscosity-average molecular weight M_v as a function of polymerization temperature. Reaction conditions: 1 dm^3 reaction vessel; 0.55 dm^3 diesel oil; ethylene pressure 6 bar; reaction time 2 h; $n_K = 2.5 \times 10^{-5}$ mol; $n_{AlR_3}/n_K = 200$; 750 rpm

T(°C)	M_v
85	1.2×10^6
65	2.7×10^6
50	4.3×10^6
35	$\sim 7.0 \times 10^6$

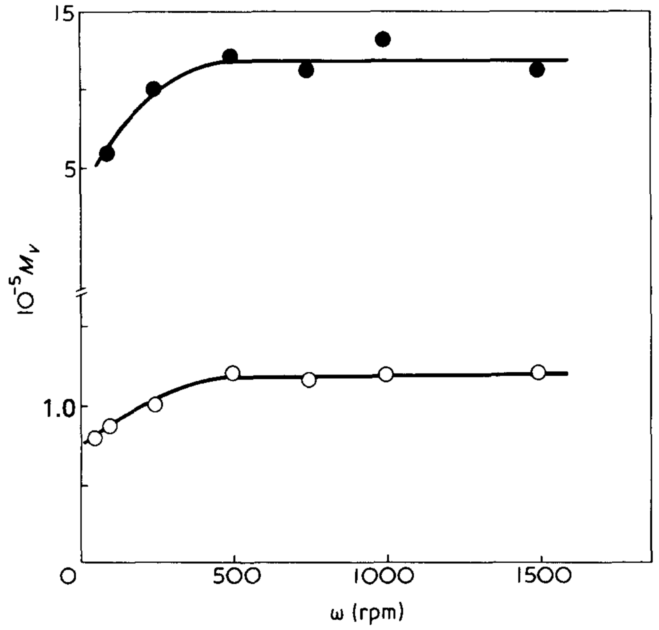

Figure 8 Viscosity-average molecular weight M_v as a function of the rate of revolution of stirrer, ω. Reaction conditions as in *Figure 6*

concentration is given by the partial pressure of the monomer according to Henry's law.

A further important point is to obtain information about the temperature at the surface of the catalyst where the polymerization takes place. As the polymerization is a strong exothermic reaction ($\Delta H \sim 100$ kJ/mol in diesel oil[34]) it is possible that temperature gradients exist inside the polymerizing system. A suspended particle may have a higher temperature than the bulk and there may also be a temperature gradient inside the growing particle[10].

Whether the average temperature of a polymerizing particle is higher than the bulk measured temperature has to be determined experimentally. The viscosity-average molecular weight strongly depends on the temperature at which the polymerization process is performed as shown in *Table 2*.

Thus the viscosity-average of molecular weight indicates a change of the temperature at the polymerization sites as a function of polymerization conditions. The corresponding results are presented in *Figure 8*.

The experimental results show that above 500 rpm M_v becomes constant. In the range of small revolutions M_v drops, which may signify that the temperature rises within a particle. But this is not convincing because in this range the velocity of the polymerization drops as well (*Figure 6*)

These results, as presented in *Figures 6* and *8*, confirm that at revolutions of the stirrer higher than 500 rpm, and catalyst amounts equal to or less than 2.5×10^{-5} moles of titanium compound in 0.6 dm^3 diesel oil there are steady state conditions with respect to material and heat flow. This means that within a suspended polymerizing particle there are constant values or at least constant gradients of concentration and temperature. Thus all further investigations were performed at 750 rpm or using a 200 dm^3 reactor under comparable conditions and catalyst amounts in the range up to 5×10^{-5} moles in 1 dm^3 diesel oil.

Investigation of the polymerization process

To investigate the kinetic behaviour of this polymerization process the catalyst yield KA, as defined elsewhere[8], was measured as a function of time at different ethylene concentrations. The monomer concentration in the solvent can be calculated for this system according to the following equation: $[M] = \lambda_M p$, where p is the partial pressure of ethylene in bar. The Henry constant λ_M is given by $\log \lambda_M = -2.209 + 410/T$ and $[\lambda_M] = \text{mol/dm}^3$ bar. The monomer concentration was constant during polymerization. The experimental results are presented in *Figure 9*.

The curves in *Figure 9* show that there is no initiation process for the polymerization. The catalytic system reaches full activity immediately. On the other hand, full activity is maintained over a long period of at least 1 h, although the catalyst yield increases rapidly. In this range the polymer particles which include the catalyst extend by a factor of approximately 5–10. This shows that in this range there cannot be a diffusional hindering of the monomer transport inside the pores of the growing particle. At longer reaction times the activity becomes smaller, probably because the polymer includes catalyst particles so that the amount of catalyst drops, or because there is a pore diffusion of monomer as the diameter of pores becomes smaller as a function of catalyst yield. It is also possible that the active sites are slowly deactivated. The velocity of polymerization R_p can be determined exactly as the slope of

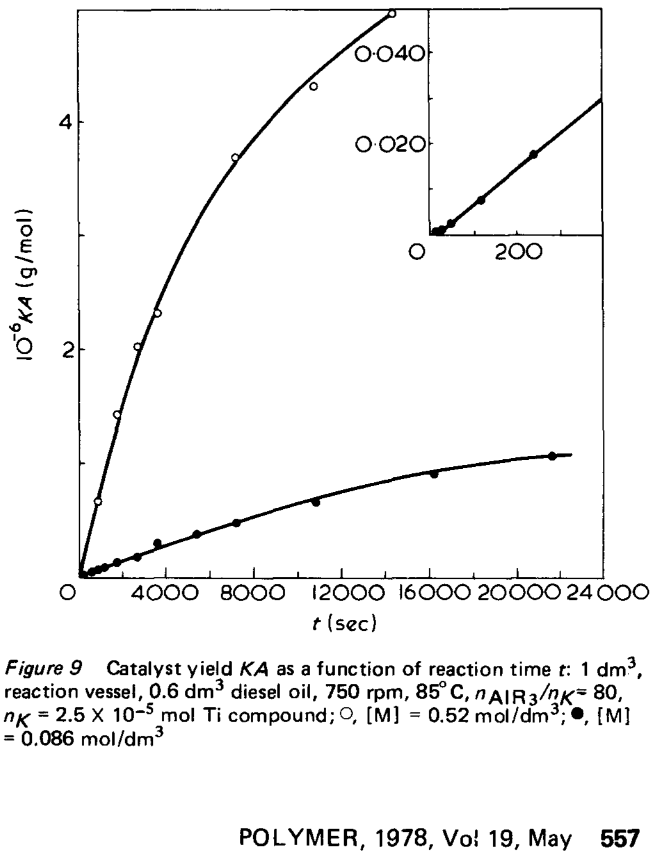

Figure 9 Catalyst yield KA as a function of reaction time t: 1 dm^3, reaction vessel, 0.6 dm^3 diesel oil, 750 rpm, 85°C, $n_{AlR_3}/n_K = 80$, $n_K = 2.5 \times 10^{-5}$ mol Ti compound; ○, [M] = 0.52 mol/dm^3; ●, [M] = 0.086 mol/dm^3

Table 3 Velocity of the polymerization at small reaction times, R_p, as a function of bulk monomer concentration [M] : $n_{\mathrm{AlR_3}}/n_K$ cocatalyst–catalyst ratio in mol $\mathrm{Al(C_2H_5)_3}$/mol Ti compound

$n_{\mathrm{AlR_3}}/n_K$	[M] (mol/dm^3)	R_p (g/mol sec)
1000	0.086	30
200	0.086	45
200	0.086	55
200	0.172	150
200	0.344	360
200	0.516	510
80	0.086	75
80	0.172	175
80	0.258	320
80	0.344	480
80	0.516	760
35	0.086	85
25	0.086	90
20	0.086	115
16	0.086	120

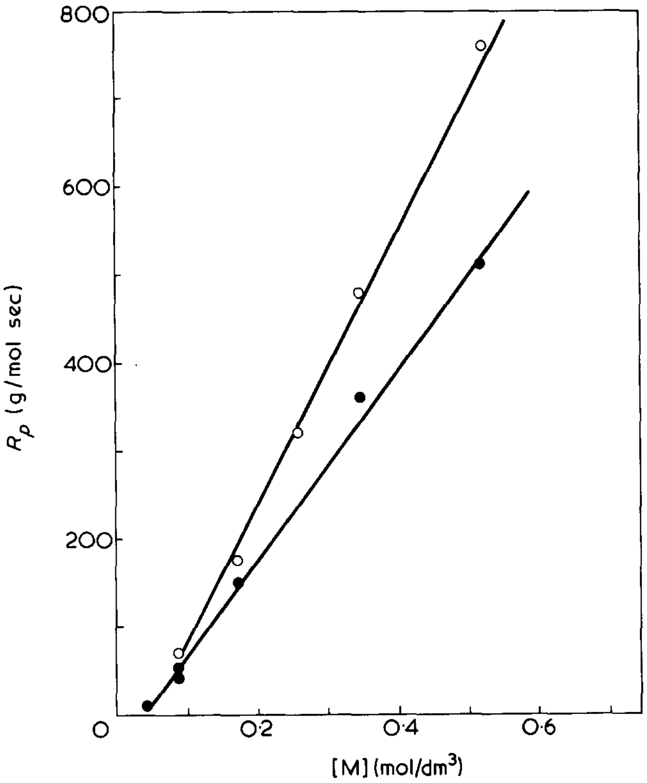

Figure 10 Velocity of the polymerization reaction extrapolated to the beginning of the reaction, R_p as function of bulk monomer concentration. Reaction conditions as in *Figure 9*; ●, $n_{\mathrm{AlR_3}}/n_K = 200$; ○, $n_{\mathrm{AlR_3}}/n_K = 80$

the curve in *Figure 9*. These values are summarized for different monomer concentrations in *Table 3* for two series of experiments with changing cocatalyst/catalyst ratio, $n_{\mathrm{AlR_3}}/n_{\mathrm{K}}$. These values are plotted in *Figure 10*.

The curves in *Figure 10* show that there is a linear relation between R_p and [M] over a wide concentration range. Only at small bulk monomer concentrations the catalytic system does not reach its full activity; the reason is not clearly understood.

The linear relationship of R_p and [M] is in accordance with the following equation which has been derived elsewhere[8]:

$$R_p = M_m \frac{k_p \cdot k_a[\mathrm{M}]_0}{k_p + k_d + k_a[\mathrm{M}]_0} \times \frac{1}{1 + \frac{b}{a} + \frac{c}{a}} \times \frac{n^*}{n_K} \tag{3}$$

if $k_p + k_d \gg k_a[\mathrm{M}]_0$; $[\mathrm{M}]_0 \sim [\mathrm{M}]$; and a, b, c and n^*/n_K are constant, or if b and c are 0.

As $a = k_p + k_d + k_a[\mathrm{M}]_0$[8] this means that $a \approx k_p + k_d$, and thus constant. b, c and n^*/n_{K} are constants within experimental error or are small[35]. c strongly depends on the concentration of the cocatalyst. Thus the question is how to explain the experimental finding that $k_p + k_d$ is greater than $k_a[\mathrm{M}]_0$. There may be two reasons: (1) $[\mathrm{M}]_0$ is smaller than the bulk concentration [M], but proportional to it, or (2) the elementary rate constants k_p and/or k_d must be greater than k_a.

As there is no indication of film diffusion at the surface of the particle (*Figure 6*) and of pore diffusion within the particle (*Figure 9*), $[\mathrm{M}]_0$ can only be smaller than [M] if there is a diffusion layer directly at the surface of the catalyst. In this case $[\mathrm{M}]_0$ is given by the following equation[36]:

$$[\mathrm{M}]_0 \approx \frac{\frac{D_e O}{x}}{\bar{k} + \frac{D_e O}{x}} [\mathrm{M}] \tag{4}$$

$$\bar{k} \approx \frac{k_p k_a}{k_p + k_d} \frac{1}{1 + \frac{b}{a} + \frac{c}{a}} \frac{n^*}{n_K} = \bar{k}_p \frac{n^*}{n_K} \tag{4a}$$

where D_e is the effective diffusion constant; O is the surface of the catalyst, related to 1 mole titanium compound; x is the thickness of the diffusion layer.

In equation (4) it is assumed that the total specific surface of the catalyst can take part in the polymerization reaction. This assumption is supported by the fact that at 85°C about 70% of the titanium atoms form active centres (see *Figure 11*).

The overall propagation rate constant can be evaluated using equations (3) and (4):

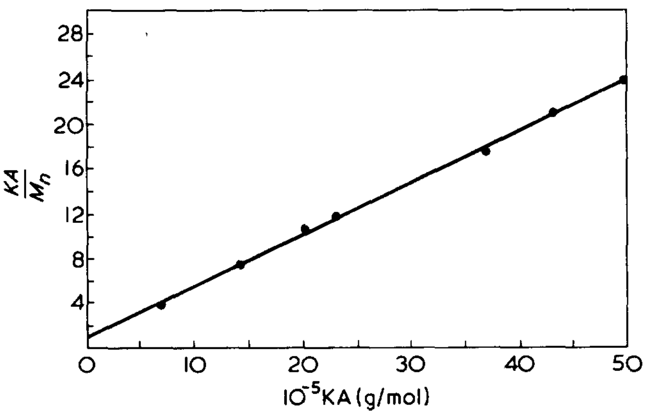

Figure 11 KA/M_n as function of catalyst yield *KA*. 1 dm^3 reaction vessel, 0.6 dm^3 diesel oil, 750 rpm, 85°C, $n_{\mathrm{AlR_3}}/n_K = 80$, $n_K = 2.5 \times 10^{-5}$ mol Ti compound; [M] = 0.52 mol/dm^3

Table 4 Results of kinetic investigations

T(°C)	n_{AlR_3}/n_K	n^*/n_K	$\bar{k}_p$ (dm^3/mol sec)
85	80	0.7 ± 0.3	80 ± 30
85	200	0.7 ± 0.3	55 ± 20

$$\frac{R_p}{M_m[M]} = \bar{k}\,\frac{\dfrac{D_eO}{x}}{\bar{k} + \dfrac{D_eO}{x}} \tag{5}$$

If the polymerization is diffusion controlled, and thus $\bar{k} \gg D_eO/x$ the following relation holds:

$$\frac{R_p}{M_m[M]} \approx \frac{D_eO}{x} \tag{6}$$

In equation (6) all values except x can be measured or can be estimated. From the data of Michaels and Bixler[37] a minimal value for D_e of ~4 x 10^{-7} cm^2/sec at 85°C can be calculated, if there is a thick layer of crystalline polyethylene covering the surface of the catalyst. $R_p/M_m[M]$ was measured to be 53 dm^3/mol sec, and O ~ 3.4 x 10^8 cm^2/mol. Using these values x was found to be 26 μm which means that the diffusion layer has the same order of magnitude as the catalyst particle itself (see *Table 1*). This is impossible. Thus the assumption $\bar{k} \gg D_eO/x$ cannot hold.

This means that $k_p + k_d$ must be greater than k_a. If k_p were greater than k_d, R_p could be approximated by (see equation 3):

$$R_p \approx M_m k_a [M] \frac{1}{1 + \dfrac{b}{a} + \dfrac{c}{a}} \times \frac{n^*}{n_K} \tag{7}$$

In this case R_p depends predominantly on k_a. The rate determining step is the formation of the α-olefin–active site complex.

If k_d is greater than k_p, equation (3) can be written as given by equation (8):

$$R_p = M_m k_p \frac{k_a}{k_d}[M] \frac{1}{1 + \dfrac{b}{a} + \dfrac{c}{a}} \frac{n^*}{n_K} \tag{8}$$

In this case R_p depends on the product $k_p K_a$ (where K_a is the association constant).

To obtain further information about this process it is important to evaluate n^*/n_K, which gives the number of active sites in relation to the total quantity of catalyst expressed in moles of titanium compound. To find this value by extrapolation the following equation was derived in a previous paper[8]:

$$\frac{KA}{M_n} = \frac{n^*}{n_K} + \frac{KA}{M_{n,\infty}} \tag{9}$$

According to equation (9) the catalyst yield KA divided by the number-average molecular weight M_n has been plotted as a function of KA; M_n has been calculated from g.p.c. measurements[35]. The experimental results are shown in *Figure 11*.

This Figure shows that the extrapolated value for n^*/n_K has a relatively high error. To find a significant value, $M_{n,\infty}$ should be high so that the slope becomes small. This is the case if the monomer concentration is high. It was found, for 85°C, that n^*/n_K lay in the range 0.4–1.0, which means that as an average 70% of all titanium atoms form active sites. This is a high value in comparison with other Ziegler–Natta catalysts[7] which usually have values in the range of 1% or even smaller. Only Boucher, Parsons, and Haward[38] reported a similar value for a highly active catalyst. *Table 4* summarizes the values n^*/n_K and the overall rate constants, $\bar{k}_p$, for the polymerization process (see equation 4a). $\bar{k}_p$ is an average value which gives no information about the range of k_p values if there are different active sites[35].

DISCUSSION

Table 4 shows that the reason for the high activity of this catalytic system can be attributed to an extraordinarily high amount of active sites which is higher by at least one order of magnitude than with other Ziegler–Natta catalysts[5–7]. This is in accordance with a value reported by Boucher, Parsons and Haward[38] for a similar system. On the other hand this means that the overall rate constants $\bar{k}_p$ are comparable to values so far published[5–7,39]. However, the high activity of this system is obtained only because the monomer is not hindered to reach the surface of the catalyst, although the average particle size increases rapidly. This is shown in *Figure 12*.

The particle size distributions are identical but the median values are shifted to higher values with increasing catalyst yield. The simplest interpretation of these results is that every catalyst particle forms a polymer particle. Therefore the effect, that there is no film or pore diffusion, cannot be attributed to a disintegration of the growing particles during the polymerization process. On the other hand, there is a complete disintegration of the catalyst particle during polymerization. Although the polymer contains the total amount of catalyst which can be proved by analysis of the titanium content, it has not been possible to detect catalyst residues in the polymer by electron microscopy. This means that the catalyst residues must be at least smaller than 50 Å.

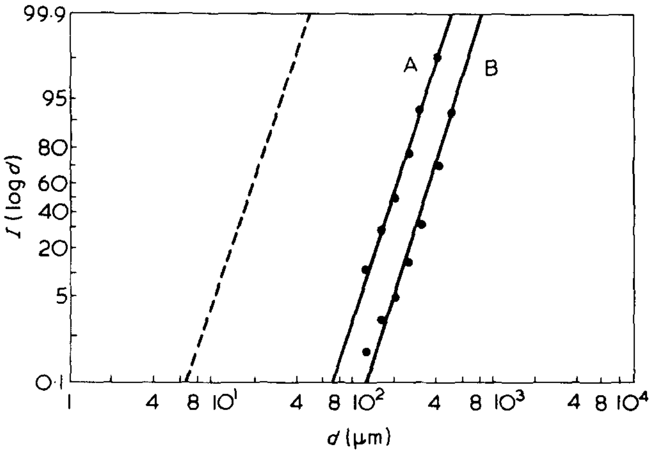

Figure 12 Particle size distribution of the catalyst (see Figure 1) and polymer; A, KA = 1.06 X 10^6 g/mol Ti compound; B, 11.4 X 10^6 g/mol Ti compound

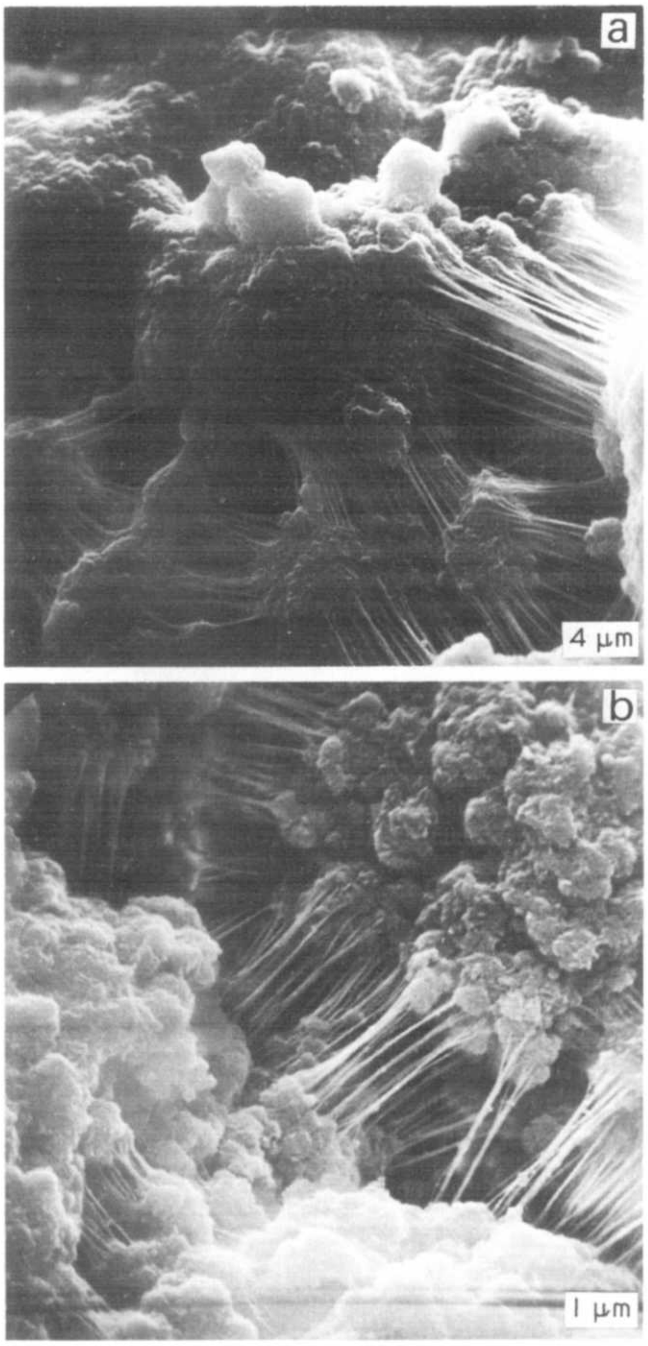

Figure 13 **Scanning electron micrographs of the surface of the polymer particle. Magnification: (a) 2400; (b) 6000**

The disintegration of the catalyst particle during polymer formation and polymer precipitation as a semicrystalline phase leads to a porous morphology of the polymer particle. This can be shown by investigating the particles with a scanning electron microscope. *Figure 13* shows two examples.

This morphology was described first by Graff, Kortleve, and Vonk[40]. They also gave an interpretation of the formation of this 'cobweb' structure.

On the basis of these results the high activity of this catalytic system can be interpreted by an extremely high number of active sites in connection with the formation of porous polymer particles so that the monomer transport is not hindered over a relatively long period of the polymerization process. This result only holds at monomer concentrations higher than 0.05 mol/dm^3. If [M] becomes smaller, the catalyst activity drops.

It was found that the velocity of the polymerization reaction, R_p, is proportional to the monomer concentration in the bulk [M]. On the basis of a reaction model proposed elsewhere[8] this implies that the formation of the α-olefin–active site complex is the fundamental and rate determining process although it is not possible to decide whether this process is kinetically or thermodynamically controlled. But this fact can be used to explain the experimental findings that higher α-olefins like propylene polymerize slowly in comparison to ethylene[5,7]. This is probably due to steric effects during complex formation.

It has been shown that the kinetics of the polymerization process can be described by equations derived elsewhere[8].

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