An attempt to determine the concentration of active sites in supported Ziegler–Natta catalysts

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By use of kinetic data of the polymerization of hexene-(1) and octene-(1) an attempt is made to determine the concentration of active sites. The complex kinetics of the supported Ziegler–Natta catalyst investigated, however, does not allow an explicit calculation of the concentration of active sites. With certain conditions met, the yield factor of active sites was determined. For the polymerization of hexene-(1) and octene-(1) the yield factors gave very low values. This is attributed to the fact that in the case of hexene-(1) and octene-(1) no disintegration of the catalyst particles was observed as is the case for ethylene polymerization.

INTRODUCTION

The concentration of active sites of Ziegler–Natta catalysts can be determined by two different methods[1,2]:

(1) For chemical determination, radioactive species like ^{14}CO, $^{14}CO_2$, CH_3O^3H, $^{131}J_2$ are added that are able to react with the active sites[3,4]. The concentration of active sites as a function of time during polymerization are to be determined by analyses. These methods have large errors and they are not uniquely accepted[5,6].

(2) Under certain circumstances, the concentration of active sites can be obtained from the time-dependence of conversion and the number average degree of polymerization. The accuracy of this method will be discussed in this paper.

EXPERIMENTAL

Preparation of the magnesium–titanium-compound

Ground $Mg(OEt)_2$ was suspended in n-heptane and heated to 353 K under purified nitrogen as inert gas. $TiCl_4$ dissolved in n-heptane was added slowly and the suspension was stirred for 6 h at 353 K. The molar ratio was Mg:Ti = 1:2. The solid was washed with n-heptane until no titanium was found in the washing liquid. The titanium content of the solid was determined colorimetrically with hydrogen peroxide. It was approximately 12% by weight.

Polymerization and determination of molecular weight

The catalyst used for the experiments presented was prepared by reaction of the suspended magnesium–titanium solid with an organoaluminium compound.

In order to eliminate the influence of mass transfer processes in the polymer particle, monomers, forming soluble polymers, were polymerized. Since polyhexene and polyoctene are easily soluble in toluene or cyclohexane, respectively, hexene-(1) and octene-(1) were used as monomers. The polymerization was carried out batchwise and isothermally in purified toluene or cyclohexane in a 500 ml flask with purified nitrogen as inert gas. The time–conversion plots were set up by taking samples from the reacting volume at discrete intervals. The polymer was precipitated from the samples in hydrochloric methanol, dried and weighed. The reproducibility of the measurements was $\sim \pm 2\%$.

The number average of molecular weight of polyhexene and polyoctene was determined by membrane osmometry. The reproducibility of the measurements was $\sim \pm 5\%$ using the same membrane.

RESULTS

Table 1 shows the time-dependence of conversion and number average of molecular weight for the polymerization of octene-(1) with the catalyst $TiCl_4$-$Mg(OEt)_2$-$AlEt_3$ activated 1 h at room temperature. The initial concentration of monomer and the temperature of polymerization were varied.

Within experimental error, the *MW* of the product remains constant with conversion increasing. This leads to the assumption that at least one kind of chain transfer reaction takes place or that active sites are formed during the polymerization. In order to receive information about the velocity of formation of the active sites, hexene-(1) was polymerized with a $TiCl_4$-$Mg(OEt)_2$-$Al(i\text{-}Bu)_3$ catalyst activated for 0.5 and 27 h at 273 K. The temperature of polymerization was also 273 K. Conversions and molecular weights are given in *Table 2*.

At equal times of polymerization, the catalyst with the 27-h-activation yields a higher conversion and higher *MW* of the polymer formed than that with one of 0.5 h.

In another polymerization with hexene-(1) the $TiCl_4$-$Mg(OEt)_2$-$AlEt_3$ catalyst was pretreated at 333 K. The reaction temperature was also 333 K. The initial monomer conversion for different times of pretreatment and for different aluminum–titanium ratios are given in *Table 3*.

With a catalyst formed '*in situ*', for all Al–Ti ratios

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Table 1 Polymerization of octene-(1) in toluene: $TiCl_4$–$Mg(OEt)_2$–$AlEt_3$; $c_{Ti} = 5.10^{-4}$ mol l^{-1}; Al/Ti = 10; activation conditions: $c_{Ti} = 10^{-3}$ mol l^{-1}; Al/Ti = 10; $T_{act} = 298$ K; $t_{act} = 1$ h

Polymerization time (h)	Concentration of octene-(1) (mol l^{-1})	Temperature (K)	Conversion	Number average of molecular weight (10^3 g mol^{-1})
1	1	353	0.17	24
2	1	353	0.19	25
3.5	1	353	0.21	26
1	2	353	0.21	35
2	2	353	0.25	34
3.5	2	353	0.27	34
1	3	353	0.23	40
2	3	353	0.28	40
3.5	3	353	0.32	39
0.25	2	333	0.11	49
1	2	333	0.31	48
2.5	2	333	0.45	48

Table 2 Polymerization of hexene-(1) in cyclohexane: $TiCl_4$–$Mg(OEt)_2$–$Al(i\text{–}Bu)_3$; $c_{M,o} = 2$ mol l^{-1}; $c_{Ti} = 1.10^{-3}$ mol l^{-1}; Al/Ti = 10; $T = 273$ K: activation conditions: $c_{Ti} = 2.10^{-2}$ mol l^{-1}; Al/Ti = 10; $T_{act} = 273$ K

	Conversion		Number average of molecular weight (10^3 g.mol^{-1})	
Polymerization time (h)	Activation time (h) 0.5	27	Activation time (h) 0.5	27
0.5	0.01	0.02	103	124
1	0.02	0.03	105	131
3	0.05	0.09	111	155
6	0.10	0.14	119	178
10	0.17		128	
27	0.39	0.42	138	222

Table 3 Polymerization of hexene-(1) in cyclohexane: $TiCl_4$–$Mg(OEt)_2$–$AlEt_3$; $c_{M,o} = 1$ mol l^{-1}; $c_{Ti} = 1.10^{-3}$ mol l^{-1}; Al/Ti = 30; $T = 333$ K: activation conditions: $c_{Ti} = 2.10^{-2}$ mol l^{-1}; Al/Ti = 2, 4, 8; $T = 333$ K

Activation time (min)	Conversion after 10 min of polymerization time Al/Ti ratio during the activation time 2	4	8
0	0.25	0.25	0.25
5	0.20	0.16	0.07
10	0.16	0.12	0.04
20	0.11	0.09	0.02

investigated, the highest conversions of monomer were found, i.e. the formation of active sites proceeds rapidly when $AlEt_3$ is used at activation temperatures of 333 K. The drop in monomer conversion at rising pretreatment times is attributed to a deactivation of active sites. The decline in the initial rate of polymerization increases with rising Al–Ti ratios which indicates a participation of triethylaluminium in the deactivation of the active sites.

The polymerization of hexene-(1) with different organoaluminium compounds are described in *Table 4*. Within experimental error, no induction period was observed. The catalyst was formed *in situ*, i.e. the presence of the monomer.

The rate of polymerization decreases in the order

$$AlEt_3 > AlOct_3 > Al(i\text{-}Bu)_3$$

DISCUSSION

Kinetic determination of the concentration of active sites

Under certain circumstances a time-dependent yield factor can be determined from the accessible data of conversion and molecular weight. It is defined as follows:

$$f_{Ti}(t) = \frac{\text{conc. of all sites active in polymerization formed up to the time } t}{\text{conc. of Ti}}$$

The concentration of all sites active in polymerization formed up to the time t, i.e. the concentration of the active sites having initiated chain-growth without being deactivated, is given by the rate of the first insertion step. This gives the yield factor:

$$f_{Ti}(t) = \frac{\int_0^t r_i \mathrm{d}t}{c_{Ti}} \qquad (1)$$

The number average degree of polymerization as a function of time is given by

$$\bar{P}_n(t) = \frac{\text{conc. of monomer polymerized until the time } t}{\text{conc. of chains at the time } t}$$

The concentration of the monomer, polymerized until the time t is derived from the rate of chain-growth. This gives for the number average degree of polymerization:

$$\bar{P}_n(t) = \frac{\int_0^t r_p \mathrm{d}t}{c_C(t)} \qquad (2)$$

Furthermore the catalyst yield at the time t can be defined as:

$$Y(t) = \frac{\text{conc. of monomer polymerized until the time } t}{\text{conc. of Ti}}$$

Table 4 Polymerization of hexene-(1) in cyclohexane $TiCl_4$–$Mg(OEt)_2$–AlR_3; $c_{M,o}$ = 1 mol l^{-1}; c_{Ti} = 1.10^{-3} mol l^{-1}; Al/Ti = 10; T = 333 K; t_{act} = 0

Polymerization time (h)	Conversion			Number average of molecular weight (10^3 g mol^{-1})		
	$AlEt_3$	$AlOct_3$	$Al(i\text{-}Bu)_3$	$AlEt_3$	$AlOct_3$	$Al(i\text{-}Bu)_3$
0.5	0.37	0.24	0.15	30	79	106
1	0.56	0.41	0.30	28	77	103
3	0.80	0.75	0.59	26	72	99
8	0.93	0.90	0.82	25	68	91
24	0.98	0.96	0.95	24	63	79

Table 5 Time dependence of the efficiency of the titanium for different transfer reactions

	Rate law of transfer reaction	Kinetic relation	Constant	Boundary conditions
Polymerization of hexene-(1) and octene-(1) $r_p = k_p \cdot c_{P^*} \cdot c_M$	$r_{tr} = k_{tr} \cdot c_{P^*} \cdot c_M$	$e_{Ti}(t \geq t_i) = f_{Ti} + K \cdot Y(t \geq t_i)$	$K = \frac{k_{tr}}{k_p}$	
	$r_{tr} = k_{tr} \cdot c_{P^*} \cdot c_{Al}$	$e_{Ti}(t \geq t_i) = f_{Ti} + K \cdot \ln \frac{c_{M,o}}{c_M(t \geq t_i)}$	$K = \frac{k_{tr}}{c_{Ti} \cdot k_p}$	$c_{Al} \simeq$ constant, $r_p \simeq \frac{dc_M}{dt}$
	$r_{tr} = k_{tr} \cdot c_{P^*}$		$K = \frac{c_{Al} \cdot k_{tr}}{c_{Ti} \cdot k_p}$	$r_p \simeq \frac{dc_M}{dt}$
Polymerization of ethylene $r_p = k'_p \cdot c_{P^*}$ $k' = k_p \cdot c_M$	$r_{tr} = k'_{tr} \cdot c_{P^*}$ $k'_{tr} = k_{tr} \cdot c_M$		$K = \frac{k_{tr}}{k_p}$	c_M = constant
	$r_{tr} = k_{tr} \cdot c_{P^*} \cdot c_{Al}$	$e_{Ti}(t \geq t_i) = f_{Ti} + K \cdot Y(t \geq t_i)$	$K = \frac{c_{Al} \cdot k_{tr}}{c_M \cdot k_p}$	c_M = constant, $c_{Al} \simeq$ constant
	$r_{tr} = k_{tr} \cdot c_{P^*}$		$K = \frac{k_{tr}}{c_M \cdot k_p}$	c_M = constant

$$Y(t) = \frac{\int_0^t r_p dt}{c_{Ti}} \tag{3}$$

The efficiency of the titanium as a function of time is

$$e_{Ti}(t) = \frac{\text{conc. of chains at the time } t}{\text{conc. of Ti}}$$

$$e_{Ti}(t) = \frac{c_C(t)}{c_{Ti}} \tag{4}$$

From the equations (2), (3), and (4) derives

$$e_{Ti}(t) = \frac{Y(t)}{\bar{P}_n(t)} \tag{5}$$

So the efficiency of the titanium and hence the concentration of chains at the time t can be determined from the catalyst yield and the number average degree of polymerization.

The concentration of chains at the time t is made up:

(a) according to Natta–Pasqon[7]: of the concentration of active chains and that of terminated chains,

$$c_C(t) = c_P{}^*(t) + \int_0^t \Sigma r_t dt + \int_0^t \Sigma r_{tr} dt \tag{6}$$

(b) according to Kagiya[8,9]: of the concentration of chains formed by chain insertion (first step) and by chain transfer,

$$c_C(t) = \int_0^t r_i dt + \int_0^t \Sigma r_{tr} dt \tag{7}$$

The efficiency of the titanium is, derived from equations (4), (6), and (7),

$$e_{Ti}(t) = \frac{c_{P^*}(t)}{c_{Ti}} + \frac{1}{c_{Ti}} \cdot \int_0^t \Sigma r_t dt + \frac{1}{c_{Ti}} \cdot \int_0^t \Sigma r_{tr} dt$$

$$= \frac{1}{c_{Ti}} \cdot \int_0^t r_i dt + \frac{1}{c_{Ti}} \cdot \int_0^t \Sigma r_{tr} dt \tag{8}$$

It should be noted here that equation (8) is of general validity since no assumption or limitations are made.

If the kinetics of termination and transfer or initiation reactions are known, it would be easy to calculate the concentration of the active sites explicitly.

Kinetic data of these steps are seldom known in coordinative polymerization, so equation (8) only gives an approach to the yield factor in case the formation of active sites can be assumed terminated at the time t_i.

Equation (1) derives for $t \geq t_i$

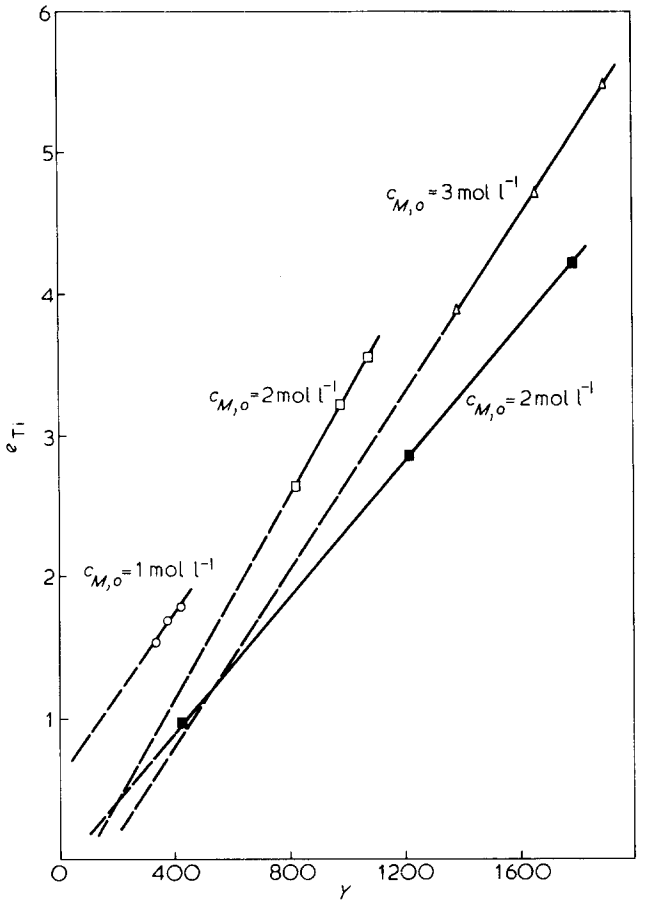

Figure 1 Efficiency of titanium as a function of the catalyst yield of the polymerization of octene-(1) in toluene: $TiCl_4$–$Mg(OEt)_2$–$AlEt_3$; c_{Ti} = 5.10^{-4} mol l^{-1}; Al/Ti = 10; t_{act} = 1 h at 298 K. ○, □, △: T = 353 K; ■: T = 333 K

$$f_{Ti}(t \geqslant t_i) = \frac{\int_0^{t \geqslant t_i} r_i \mathrm{d}t}{c_{Ti}} = \text{const.} = f_{Ti} \qquad (9)$$

Thus equation (8) becomes

$$e_{Ti}(t \geqslant t_i) = f_{Ti} + \frac{1}{c_{Ti}} \cdot \int_0^{t \geqslant t_i} \Sigma r_{tr} \mathrm{d}t \qquad (10)$$

This shows that when the formation of active sites has finished, the titanium efficiency is only raised by chain transfer reaction.

If the dependence of titanium efficiency on the rate of all transfer reactions can be given as a linear function over the whole time range, the yield factor can be determined by linear extrapolation of the experimental values of $t \geqslant t_i$ towards zero.

In *Table 5*, three different kinds of transfer reactions were taken into account for the polymerization of hexene-(1), octene-(1), and ethylene.

In *Figures 1–4* the titanium efficiency is plotted against the catalyst yield and ln ($c_{M,0}/c_M$), for the polymerizations of hexene-(1) and octene-(1), according to their kinetic relationships from *Table 5*.

As seen in *Figures 1–4*, the kinetics of the transfer reactions cannot be described completely by means of the transfer reactions postulated.

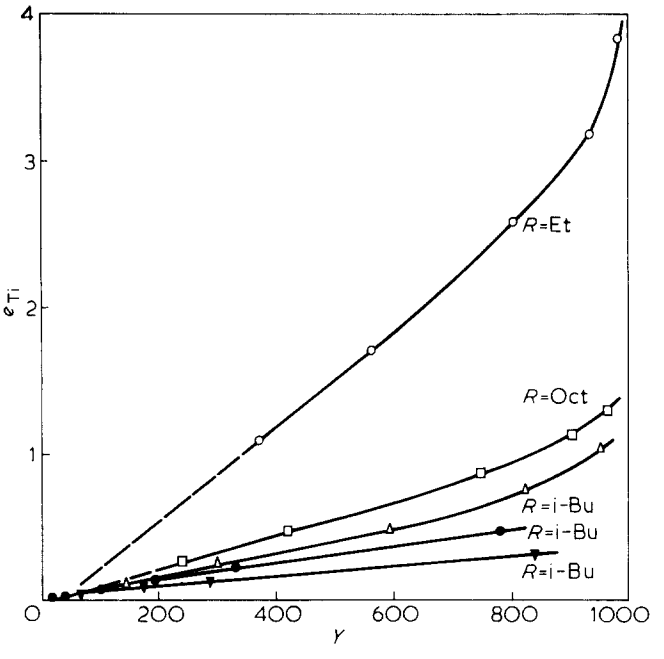

Figure 2 Efficiency of titanium as a function of the catalyst yield of the polymerization of hexene-(1) in cyclohexane: $TiCl_4$–$Mg(OEt)_2$–AlR_3; c_{Ti} = 1.10^{-3} mol l^{-1}; Al/Ti = 10; ○, □, △: t_{act} = 0; T = 333 K; $c_{M,o}$ = 1 mol l^{-1}; ●: t_{act} = 0.5 h; ▼: t_{act} = 27 h at 273 K and T = 273 K; $c_{M,o}$ = 2 mol l^{-1}

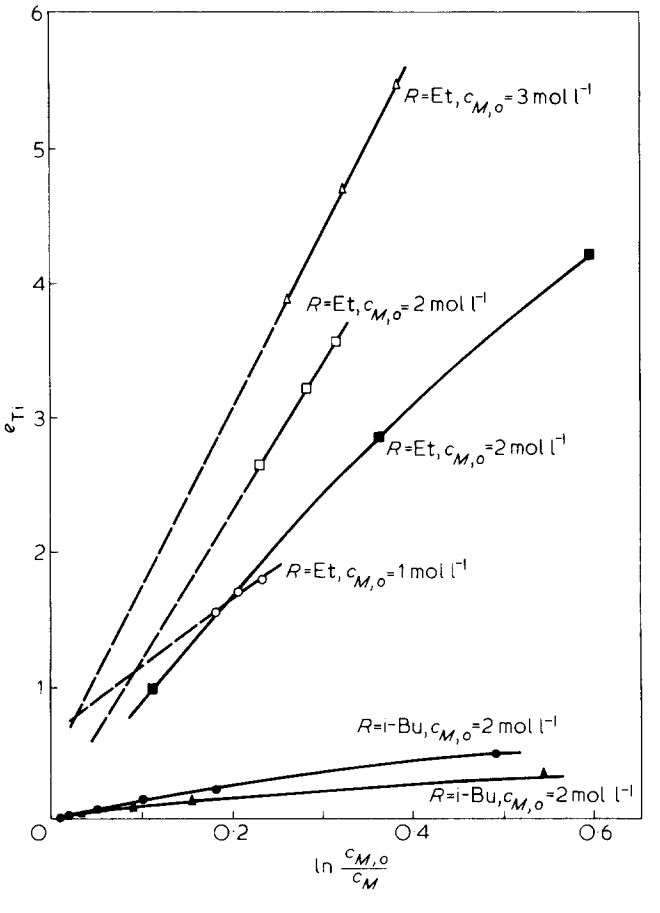

Figure 3 Efficiency of titanium as a function of ln($c_{M,o}/c_M$): $TiCl_4$–$Mg(OEt)_2$–AlR_3; Al/Ti = 10; ○, □, △: T = 353 K; ■: T = 333 K and t_{act} = 1 h at 298 K; c_{Ti} = 5.10^{-4} mol l^{-1}; octene-(1) in toluene; ●: t_{act} = 0.5 h at 273 K; ▲: t_{act} = 27 h at 273 K and T = 273 K; c_{Ti} = 1.10^{-3} mol l^{-1}; hexene-(1) in cyclohexane

Table 6 Kinetic data of the polymerization of ethylene with supported Ziegler–Natta catalysts

Catalyst	Efficiency (mol P*/mol Ti)	Rate constant (k_p) (l mol^{-1} s^{-1})	Molecular weight (g mol^{-1})	Method of determination of active sites	ref
$TiCl_4$–MgBuBr–$AlEt_3$	0.6 (323 K)	580	$2 \cdot 10^6$ ($\bar{M}_n$)	kin.	Haward[10]
$TiCl_4$–$Mg(OEt)_2$–$Al(i\text{-}Bu)_3$	0.016 (303 K)	2000	10^7 ($\bar{M}_w$)	kin.	Reichert[11]
	0.023 (333 K)	12000			
$TiCl_4$–$Mg(OEt)_2$–$AlEt_3$	0.7 ± 0.3 (358 K)	80 ± 30	$1.2 \cdot 10^6$ ($\bar{M}_w$)	kin.	Böhm[12,13]
	0.02 (358 K)	2900			
$Ti(C_6H_5)_4$–$Mg(OH)Cl$–$AlEt_2Cl$	0.001 (323 K)	540		chem.	Chien[14]
$TiCl_4$–R_xMgCl_y–$AlEt_3$	0.36	13000		chem.	Zakharov[15]

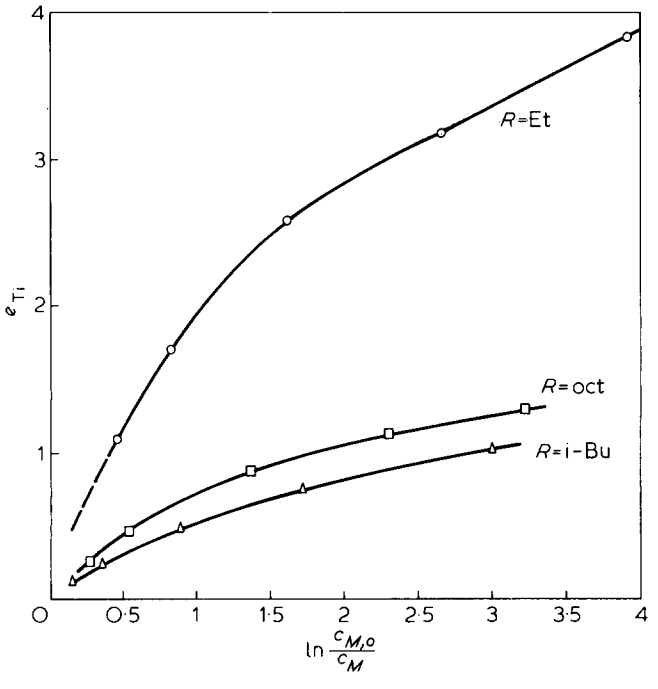

Figure 4 Efficiency of titanium as a function of $\ln(c_{M,o}/c_M)$ $TiCl_4$–$Mg(OEt)_2$–AlR_3; $c_{Ti} = 1.10^{-3}$ mol l^{-1}; Al/Ti = 10 $t_{act} = 0$; $T = 333$ K; $c_{M,o} = 1$ mol l^{-1}; hexene-(1) in cyclohexane

This means that in the polymerization of hexene-(1) and octene-(1) either several transfer reactions occur parallel to each other or the transfer mechanism is more complex.

Approximated extrapolations from the linear parts of the curves in *Figures 1–4* hint at yield factors close to zero. This does not contradict the higher values found for the polymerization of ethylene by other authors (*Table 6*). In contrast to the polymerization of ethylene, during the polymerization of hexene-(1) and octene-(1) no disintegration of the catalyst was observed. The value of the yield factor depends strongly on the activation conditions of the catalyst. With high pretreatment temperature and high concentration of triethylaluminium the maximum yield factor cannot be reached since during pretreatment a considerable deactivation of the catalyst can be observed (*Table 3*).

In conclusion, for the polymerization of hexene-(1) and octene-(1) the yield factor cannot be determined exactly since the relations assumed for the transfer reactions are approximations.

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NOMENCLATURE

c_{Al}	concentration of organoaluminum, mol l^{-1}
c_C	concentration of polymer chains, mol l^{-1}
c_M	concentration of monomer, mol l^{-1}
$c_{M,o}$	initial concentration of monomer, mol l^{-1}
c_p^*	concentration of the active sites, mol l^{-1}
c_{Ti}	concentration of titanium, mol l^{-1}
e_{Ti}	efficiency of titanium
f_{Ti}	yield factor
k_p, k_{tr}	rate constants, 1 mol^{-1} h^{-1}
$\bar{M}_n$	number average of molecular weight, g mol^{-1}
$\bar{M}_w$	weight average of molecular weight, g mol^{-1}
$\bar{P}_n$	number average degree of polymerization
r_i	rate of first insertion step, mol l^{-1} h^{-1}
r_p	rate of chain growth, mol l^{-1} h^{-1}
r_{tr}	rate of chain transfer, mol l^{-1} h^{-1}
r_t	rate of chain termination, mol l^{-1} h^{-1}
t_i	time where the formation of active sites can be assumed terminated
t_{act}	activation time for the catalyst, h
T_{act}	activation temperature, K
T	polymerization temperature, K
Y	catalyst yield
Al/Ti	molar ratio of organoaluminum/titanium compound
Et	ethyl
Oct	octyl
Bu	butyl
i-Bu	isobutyl