Reaction model for Ziegler-Natta polymerization processes*

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A reaction model for Ziegler–Natta polymerization processes which is in accordance with the results of previous studies and which is able to explain the phenomena known in this process, at least qualitatively, has been formulated. It was assumed that complexation, as pointed out by Cossee and Henrici-Olivé and Olivé, is the fundamental process followed by a series of reactions at the active site. On this basis it was possible to develop a kinetic scheme applicable to homogeneous and heterogeneous catalysts. By making certain assumptions, simple equations which could be checked experimentally were derived.

INTRODUCTION

It is generally accepted that Ziegler–Natta polymerization is a catalytic process[1–5]. As pointed out by Michaelis and Menten[6] for enzyme reactions, there must be an interaction between the substrate molecules and the active site before a reaction at the catalytic active centre can occur. For Ziegler–Natta polymerization this concept holds irrespective of whether the catalytic system is soluble or insoluble in hydrocarbon solvents. In the case of a soluble catalytic system, interaction implies formation of an α-olefin–catalyst complex. In the case of a heterogeneous catalyst, interaction means adsorption of the α-olefin at the surface of the catalyst. However, complexation and adsorption can be considered identical, since both processes may occur as pointed out by Cossee[7], and later by Henrici-Olivé and Olivé[8]. Therefore the same reaction model can be developed for homogeneous and heterogeneous systems.

A reaction model must be able to explain, at least qualitatively, all phenomena which are concerned with chemical reactions observed in Ziegler–Natta polymerization processes. To these phenomena belong the kinetic behaviour, the molecular weight control by different transfer processes, as well as the explanation of structural peculiarities of the polymer chain formed in this process. The reaction model must also be able to explain the inhibition of the polymerization process by the cocatalyst and by hydrogen, which is used as a transfer agent. It should also be shown that molecular weight control, as well as inhibition, depends on the nature of the cocatalyst.

A number of attempts have been made in recent years to derive reaction models which are generally applicable to Ziegler–Natta polymerization processes. Natta[9] presented a reaction scheme for propylene polymerization in which all important reactions were formulated. A similar scheme was given by Grievenson[10] for ethylene polymerization. The different elementary reactions so far published[9,10] must be included in a reaction scheme for Ziegler–Natta polymerization processes. It is reasonable to assume that such a scheme holds for heterogeneous polymerization processes as well as homogeneous ones.

For heterogeneous catalysts it is very likely that adsorption is an important process, as pointed out by Eirich and Mark[11]. On this basis Saltman[12], and Reich and Stivala[13] developed reaction schemes for heterogeneous polymerization processes. Tait and coworkers[14] presented a general kinetic scheme for Ziegler–Natta catalysis. First they assumed that there were equilibria due to the adsorption process of monomer and cocatalyst. Consequently, the rate constants of adsorption and desorption for monomer must be very high in comparison to the propagation rate constant. Second they postulated an initiation process which described the insertion of a monomer molecule into an active centre–carbon bond for the case of a small alkyl group fixed at the active centre. However, such an initiation process cannot exist since Fink and coworkers[15,16] have shown that the insertion of an ethylene molecule is more rapid in the case of a small alkyl group fixed at the transition metal, and that the reaction rate drops if the alkyl group becomes longer. Therefore the assumptions of adsorption and desorption equilibria and of an initiation process are not considered relevant in this paper.

Recently, Zakharov and coworkers[17] presented a reaction scheme to explain their experimental results with a classical Ziegler–Natta catalyst. This reaction scheme is based on the assumption of a monometallic catalytic process. In contrast to Tait and coworkers[14] these authors do not assume an equilibrium due to monomer adsorption, and the existence of an initiation process. These assumptions agree well with conclusions made in this paper. On the other hand, Zakharov and coworkers[17] assume equilibrium for complex formation with the cocatalyst which can be considered as a restriction. Furthermore, in their reaction scheme they do not include molecular weight regulation with hydrogen, which is the most important process to influence the molecular mass of the polymer.

The reaction model proposed in this paper includes all reactions which are considered relevant in Ziegler–Natta catalysis. So this reaction model is able to explain, at least qualitatively, the phenomena observed in Ziegler–Natta polymerization, even in details like structural peculiarities along the polymer chain. It is demonstrated that this reaction

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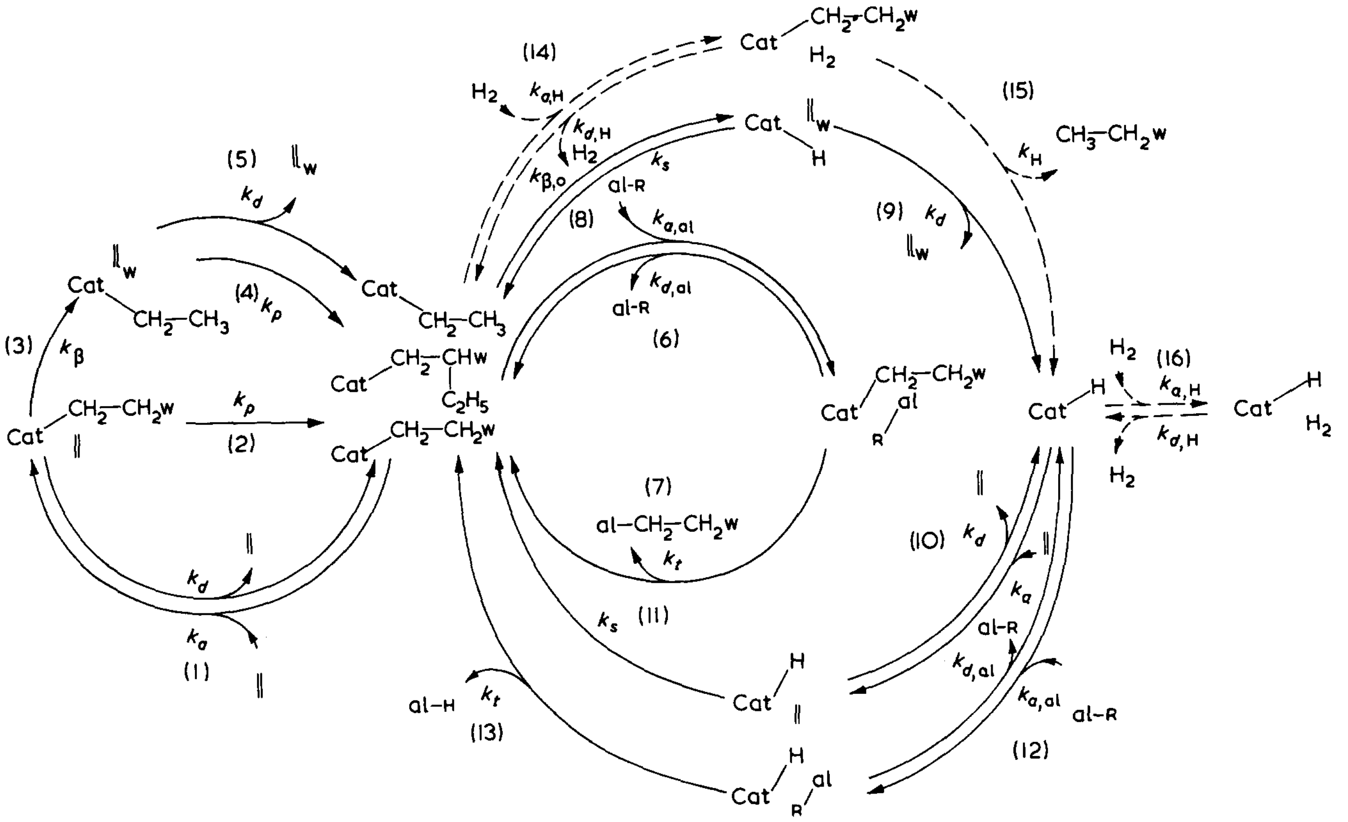


Figure 1 Reaction scheme of a Ziegler–Natta polymerization process; Cat, catalytic active centre; ‖ ethylene molecule; w, polymer chain; ‖w, polymer chain with a vinyl group. al, 1/3 Al; R, alkyl group (for example, C_2H_5); H, H_2, hydrogen atom or hydrogen molecule

model describes homogeneous and heterogeneous Ziegler–Natta processes as well. Equations can be formulated using variables, which are considered relevant for homogeneous or heterogeneous catalytic processes.

For heterogeneous catalytic processes this reaction model is a particular case of the Rideal mechanism[18]. Rideal states that a catalytic reaction at the surface of a heterogeneous catalyst takes place in the following way: the reaction between a covalently bound radical or atom at the active site and the substrate molecule occurs in such a manner that the covalent bond is re-established or another bond is formed. In both cases the substrate molecule is consumed. All reactions formulated in this reaction model coincide with this principle.

REACTION MODEL

First the different reactants (monomer, hydrogen, cocatalyst) which are involved in the catalytic process have to interact by complexation with a catalytic active centre. In further steps, these components react with the polymer, oligomer or hydrogen connected to the active centre by a covalent bond. This process can be described by a model for catalytic reactions as proposed by Rideal[18]. It is based on the following assumptions.

(a) The catalytic reaction takes place between a radical or atom fixed at the active centre by a covalent bond and an adsorbed molecule. The adsorbed molecule is assumed to be held in a deep van der Waals trough between the radicals or atoms at the active centres which form a chemisorbed layer. In this case, the van der Waals trough may consist of the free coordination site at the active centre as proposed by Cossee[7] and Henrici-Olivé and Olivé[8].

(b) The catalytic process takes place in such a way that the same covalent bond is re-established or a new one is formed.

The reaction model is shown in *Figure 1*. It is presented for ethylene as the monomer, but it also holds for other α-olefins. To form a catalytic active system a hydrocarbon radical (alkyl group) must be fixed at the transition metal compound. This alkyl group is transferred by an alkylation reaction from the cocatalyst, which is generally an organoaluminium compound[1–5], to the transition metal. The reaction model consists of two cycles. The first cycle which includes the reactions (1)–(5) describes the conversion of an ethylene molecule by insertion into the polymer chain. The second cycle consists of the reactions (6)–(16). It concerns transfer reactions which take place spontaneously or in the presence of both hydrogen and cocatalyst as transfer agents. The reactions with hydrogen as the transfer agent are given by dotted lines.

With respect to the different reactions formulated in *Figure 1*, the following should be considered.

(1) Before the monomer molecule can react, it must be fixed to the active centre as described by reaction (1). Such complex formations between transition metals and α-olefins are well known[19,20]. Reaction (1) is assumed to be reversible.

(2) The most important reaction to form a polymer molecule is the propagation or insertion reaction (2). According to Arlman and Cossee[21] this should be a reaction with a 4-centre cyclic transition state.

(3) Alternative to reaction (2), there may be a reaction (3) with a six-centre cyclic transition state to eliminate a H atom from the β-position of the polymer chain and to transfer this H atom to the monomer molecule. By this process a vinyl group at one end of the polymer chain is

formed. As this vinyl group is formed at the active centre it is assumed that this group remains complexed.

(4) This complexed vinyl group undergoes further reactions. (i) The double bond can be reinserted in the polymer chain according to reaction (4). This leads to an ethyl group branched polymer chain (Markovnikov rule). Such side groups can be detected by i.r. analysis[22,23] for example in polyethylene. (ii) The high molecular weight polymer chain supporting a vinyl group can desorb from the active centre according to reaction (5). Then a polymer chain with a vinyl end-group appears and a coordination site remains at the active centre. In contrast to reaction (1) this reaction is assumed to be irreversible, since it seems unlikely that such a vinyl group will be able to diffuse to the same or another active centre. If recomplexation of such a vinyl group were followed by an insertion reaction, this would lead to the formation of a long chain branching.

(5) A ligand of the organoaluminium compound can be fixed at the free coordination site of an active centre, corresponding to reaction (6). This reaction should be reversible. In such a complex the different ligands can exchange[9,14,16]. If there is a bridge structure as established for dimer organoaluminium compound[24], both ligands are equivalent. The complex can dissociate in two different ways. Either the primary organoaluminium compound is released, or the polymer chain is transferred to the dissociating organoaluminium compound as described by reaction (7). This means that a transfer process has taken place. This reaction is assumed to be irreversible, because it seems unlikely that the organoaluminium compound with a high molecular radical will recombine with the same or another active centre. This process, as well as reaction (6), depends on the nature of the cocatalyst.

(6) In accordance with reaction (8) the polymer chain can terminate spontaneously to form a Cat–H bond and a vinyl group. This reaction corresponds to the displacement reaction discovered by Ziegler and coworkers[25]. As to the reasons discussed in (3) above, it is assumed that the vinyl group is bound to the active centre, and can desorb in an irreversible reaction (9). Reaction (9) is nearly identical to reaction (5). The vinyl group can also be inserted into the Cat–H bond and thus disappear (Markovnikov rule).

(7) The active centre with a Cat–H bond resulting from the reaction sequence (8) and (9) can form an ethylene complex by the reversible reaction (10), followed by the insertion reaction (11) to transform the Cat- H bond into a Cat–C bond.

(8) Another possible way to transform the Cat–H bond into a Cat–C bond is given by the reactions (12) and (13). Similar to reaction (6), the first step is the formation of a complex with an organoaluminium compound by reaction (12). According to the processes (12) or (13), the organoaluminium compound can dissociate from this complex in two ways to form the primary compounds or to transfer an alkyl group to the active centre with the formation of an aluminium hydride. The second process is assumed to be irreversible because there is only a small concentration of this aluminium hydride compound, and because this hydride can be transformed to a al–C bond by insertion of a monomer molecule.

(9) If hydrogen is used as a transfer agent, the reaction model has to be extended to the reactions (14) to (16). In the reversible process (14) a hydrogen molecule is bound at the active centre. This hydrogen molecule can be inserted into the Cat–C bond to form a methyl group at the polymer chain as shown by reaction (15). The polymer chain then dissociates immediately from the active centre.

(10) In the presence of hydrogen, it is possible that the active centre Cat–H may be complexed by a hydrogen molecule. This is shown by reaction (16). Then the active centre is blocked by hydrogen. In catalysis this is called a competitive inhibition.

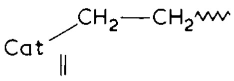
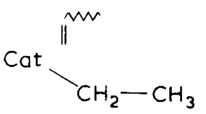
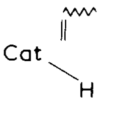
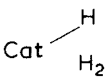
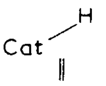
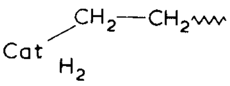
The task is now to express such dependent variables as the reaction velocity and the number-average molecular weight as functions of such independent variables as reaction time and the concentrations of monomer, cocatalyst and hydrogen. These calculations are given in the next section.

MATHEMATICAL FORMULATION OF THE REACTION MODEL

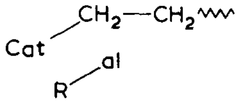
The differential equations used to describe the change of the different complexes with time as given by the reaction model in *Figure 1* cannot be written using concentrations, as is done in the case of homogeneous reactions. It is indeed possible to give the concentration of the catalyst by correlating the amount of catalyst to the volume of the reaction medium; however, it is impossible to obtain significant equations. The probability for the occurrence of the different monomolecular reactions, as given in *Figure 1*, is only proportional to the number of the different complexes. Therefore, it is appropriate to formulate all equations with the number or the quantity of the different complexes. The sum of the amount of substance of the different complexes yields the quantity of all catalytic active centres, which again is proportional to the quantity of the transition metal compound.

It is assumed that the Bodenstein steady state principle holds for all complexes which are regarded as intermediates. A further assumption is that all rate constants are independent of the degree of polymerization. This assumption does not hold for the propagation rate constant k_p [15,16] in the case of very small degrees of polymerization. But as this value levels out rapidly it is possible to make this assumption.

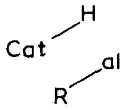
In the calculations the following symbols will be used:

n^*	quantity of all active centres Cat. For a catalyst, n^* is proportional to the amount of catalyst or to the surface area of the heterogeneous catalyst	
n_0^*	quantity of active centres	Cat—CH$_2$—CH$_2$〰
n_a^*	quantity of active centres	
n_b^*	quantity of active centres	
n_c^*	quantity of active centres	
n_d^*	quantity of active centres	Cat—H
$n_{d,\mathrm{H}}^*$	quantity of active centres	
n_e^*	quantity of active centres	
n_H^*	quantity of active centres	

$n^*_{\mathrm{al},1}$ quantity of active centres



$n^*_{\mathrm{al},2}$ quantity of active centres



The rate constants are defined in *Figure 1*. All processes are monomolecular except for the bimolecular adsorption processes.

t	time,
n_K	quantity of catalyst used, expressed in moles of the transition metal compound,
m_p	amount of the polymer formed,
n_m	quantity of the monomer which was polymerized,
M_m	molecular mass of the monomer,
$[\mathrm{M}]_0$	concentration of the monomer in the solvent at the surface of the catalyst,
$[\mathrm{H}_2]_0$	concentration of hydrogen in the solvent at the surface of the catalyst,
$[\mathrm{al}]_0$	concentration of the monomeric organoaluminium compound in the solvent at the surface of the catalyst,
P_n	number-average degree of polymerization,
M_n	number-average of molecular weight,
n	number of macromolecules which dissociate from the active centres during polymerization expressed as 1/2 quantity of end-group,
R_p	reaction velocity which gives g polymer/mole transition metal compound (sec). R_p is proportional to the reaction velocity which gives g polymer/m^2 sec, thus related to the surface of the catalyst,
KA	catalyst yield.

CALCULATIONS

The sum of the quantity of all complexes is equal to the total quantity of all active centres:

$$n^* = n_0^* + n_a^* + n_b^* + n_c^* + n_d^* + n_e^* + n^*_{\mathrm{al},1} + n^*_{\mathrm{al},2} \tag{1}$$

The formation and the disappearance of the different intermediates are described by the following differential equations. According to the assumption that for all intermediates the Bodenstein steady state principle holds, all differential equations are equal to zero:

$$\frac{\mathrm{d}n_a^*}{\mathrm{d}t} = k_a[\mathrm{M}]_0 n_0^* - (k_p + k_d + k_\beta)n_a^* = 0 \tag{2}$$

$$\frac{\mathrm{d}n_b^*}{\mathrm{d}t} = k_\beta n_a^* - (k_p + k_d)n_b^* = 0 \tag{3}$$

$$\frac{\mathrm{d}n_c^*}{\mathrm{d}t} = k_{\beta,0} n_0^* - (k_s + k_d)n_c^* = 0 \tag{4}$$

$$\frac{\mathrm{d}n_d^*}{\mathrm{d}t} = k_d n_c^* + k_d n_e^* + k_{d,\mathrm{al}} n^*_{\mathrm{al},2} - (k_a[\mathrm{M}]_0 + k_{a,\mathrm{al}}[\mathrm{al}]_0)n_d^* = 0 \tag{5}$$

$$\frac{\mathrm{d}n_e^*}{\mathrm{d}t} = k_a[\mathrm{M}]_0 n_d^* - (k_s + k_d)n_e^* = 0 \tag{6}$$

$$\frac{\mathrm{d}n^*_{\mathrm{al},1}}{\mathrm{d}t} = k_{a,\mathrm{al}}[\mathrm{al}]_0 n_0^* - (k_{d,\mathrm{al}} + k_t)n^*_{\mathrm{al},1} = 0 \tag{7}$$

$$\frac{\mathrm{d}n^*_{\mathrm{al},2}}{\mathrm{d}t} = k_{a,\mathrm{al}}[\mathrm{al}]_0 n_d^* - (k_{d,\mathrm{al}} + k_t)n^*_{\mathrm{al},2} = 0 \tag{8}$$

The quantities of different complexes as shown in *Figure 1* are given by the following expressions:

$$n_a^* = \frac{k_a[\mathrm{M}]_0}{k_p + k_d + k_\beta}\, n_0^* \tag{9}$$

$$n_b^* = \frac{k_\beta k_a[\mathrm{M}]_0}{(k_p + k_d)(k_p + k_d + k_\beta)}\, n_0^* \tag{10}$$

$$n_c^* = \frac{k_{\beta,0}}{k_s + k_d}\, n_0^* \tag{11}$$

$$n^*_{\mathrm{al},1} = \frac{k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}\, n_0^* \tag{12}$$

with

$$n_0^* = \frac{n^*}{a + b + c} \tag{13}$$

and

$$a = \frac{k_p + k_d + k_a[\mathrm{M}]_0}{k_p + k_d} \tag{14a}$$

$$b = \frac{k_{\beta,0}}{k_s + k_d}\left\{1 + \frac{k_d + \dfrac{k_d k_a[\mathrm{M}]_0}{k_s + k_d} + \dfrac{k_d k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}}{\dfrac{k_s k_a[\mathrm{M}]_0}{k_s + k_d} + \dfrac{k_t k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}}\right\} \tag{14b}$$

$$c = \frac{k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_t + k_{d,\mathrm{al}}} \tag{14c}$$

The rate of polymer formation or the consumption of monomer is given by equation (15):

$$-\frac{\mathrm{d}n_m}{\mathrm{d}t} = \frac{1}{M_m}\frac{\mathrm{d}m_p}{\mathrm{d}t} = k_p(n_a^* + n_b^*) + k_s n_e^* \tag{15}$$

If $k_s n_e^*$ is very small in comparison to $k_p(n_a^* + n_b^*)$ this part of equation (15) can be neglected. The rate of polymer formation can be calculated using equations (9), (10), (13), and (14):

$$\frac{1}{M_m}\cdot\frac{\mathrm{d}m_p}{\mathrm{d}t} = \frac{k_p k_a[\mathrm{M}]_0}{k_p + k_a} \times \frac{n^*}{a + b + c} \tag{16}$$

If equation (16) is divided by n_K, the total quantity of the catalyst used, it is possible to obtain an equation for the reaction velocity. As n_K is proportional to the amount of catalyst, and thus to the catalytic active surface, this velocity can be related to the surface as frequently found in the case of heterogeneous catalytic processes:

$$R_p = \frac{1}{M_m}\frac{\mathrm{d}(KA)}{\mathrm{d}t} = \frac{k_p k_a[\mathrm{M}]_0}{k_p + k_d + k_a[\mathrm{M}]_0}\,\frac{1}{1 + \frac{b}{a} + \frac{c}{a}}\,\frac{n^*}{n_K} \tag{17}$$

with the catalyst yield KA.

$$KA = \frac{m_p}{n_K} \tag{17a}$$

Equation (17) shows that the velocity of the polymer formation is proportional to the amount of substance of the active centres, and thus to the amount of catalyst. This is a fundamental principle in catalysis which is sometimes called the first law of catalysis. The value $1/[1 + (b/a) + (c/a)]$ describes the extent of inhibition of the polymerization process by the organoaluminium compound.

It can be shown that the equation for the reaction velocity given by Tait and coworkers[14] is involved in equation (17). If $k_{\beta,0} = 0$ and $k_i = k_p$ and if it is assumed that there are equilibria due to the adsorption of monomer and organoaluminium compound, equation (17) becomes identical to the equation given by Tait and coworkers[14].

With the reaction scheme in *Figure 1* it is also possible to calculate the quantity of all polymer molecules, and thus to calculate the number-average degree of polymerization:

$$P_n = \frac{m_p}{M_m(n^* + n)} \tag{18}$$

For this equation there are two limits corresponding to short and long reaction times. If the reaction time is very short it can be assumed that transfer reactions have not taken place and therefore n becomes zero.

$$\lim_{t\to 0} P_n = P_{n,0} \approx \frac{m_p}{M_m n^*} \tag{19}$$

If the reaction time is long the quantity of polymer molecules formed by transfer reaction is greater than the amount of molecules bound to the active centre. Thus equation (18) can be transformed into equation (20):

$$\lim_{t\to\infty} P_n = P_{n,\infty} \approx \frac{m_p}{M_m n} \tag{20}$$

In contrast to the evaluation of the equations referring to polymerization kinetics, it is necessary to perform integrations to correlate the number-average degree of polymerization P_n with the different rate constants and concentrations. If the velocity of the polymerization reaction R_p is constant there is no problem, because in this case it can be assumed that n^* and the different concentrations are constant. For longer reaction times the velocity R_p drops. This can be interpreted in different ways. A possible interpretation is that the active centres are deactivated continuously, or that there is an increasing diffusion control of the monomer transfer towards the active sites. The diffusion barrier is formed by the polymer which precipitates around the heterogeneous catalyst particle. For small reaction times it is assumed that n^* is independent of time and constant. For longer reaction times n^* becomes smaller. If this assumption is made, this does not mean that the steady state principle is invalid. This would only be true if this deactivation process is more rapid than the reactions presented in *Figure 1*, and/or if not all intermediates are decomposed.

Making these assumptions the following equations can be derived:

$$P_{n,0} = \frac{k_p k_a[\mathrm{M}]_0}{k_p + k_d + k_a[\mathrm{M}]_0} \times \frac{t}{1 + \frac{b}{a} + \frac{c}{a}} \tag{21}$$

Equation (21) implies that $P_{n,0}$ is proportional to the reaction time, t, irrespective of the amount of catalyst used.

To calculate $P_{n,\infty}$ from equation (20) it is necessary to express m_p/M_m and n as functions of the reaction time. To obtain m_p/M_m, equation (16) must be integrated:

$$\int_0^{m_p} \frac{\mathrm{d}m_p}{M_m} = \frac{m_p}{M_m} = \frac{k_p k_a[\mathrm{M}]_0}{k_p + k_d} \times \frac{1}{a + b + c}\int_0^t n^*(t)\mathrm{d}t \tag{22}$$

There are three processes listed in *Figure 1* by which a growing chain dissociates from the active centre. Thus the formation of these polymer molecules with time is give by:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = k_d n_b^* + k_d n_c^* + k_t n_{\mathrm{al},1}^* \tag{23}$$

By insertion of n_b^*, n_c^* and $n_{\mathrm{al},1}^*$ as given by equations (9)–(12), and integration, equation (24) is obtained:

$$\int_0^n \mathrm{d}n = n = \left\{\frac{k_d k_\beta k_a[\mathrm{M}]_0}{(k_p + k_d)(k_p + k_d + k_\beta)} + \frac{k_d k_{\beta,0}}{k_s + k_d} + \frac{k_t k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}\right\}$$

$$\times \frac{1}{a + b + c}\int_0^t n^*(t)\mathrm{d}t \tag{24}$$

The formation of polymer molecules by spontaneous deactivation of active sites is not considered in equation (24) as this process must be slow in comparison to the transfer processes, if the assumption of a steady state for all intermediates in *Figure 1* should hold.

By combining equations (20), (22) and (24), equation (25) can be derived:

$$\frac{1}{P_{n,\infty}} = A + B\frac{1}{[\mathrm{M}]_0} + C\frac{[\mathrm{al}]_0}{[\mathrm{M}]_0} \tag{25}$$

with

$$A = \frac{k_d k_\beta}{k_p(k_p + k_d + k_\beta)} \tag{26a}$$

$$B = \frac{k_d k_{\beta,0}(k_p + k_d)}{(k_d + k_s)k_p k_a} \tag{26b}$$

$$C = \frac{k_t k_{a,\mathrm{al}}(k_p + k_d)}{(k_{d,\mathrm{al}} + k_t)k_p k_a} \tag{26c}$$

If $k_{\beta,0}$ is equal to zero, that is, if reaction (8) in *Figure 1* does not occur, and if the reaction time is very long ($t \to \infty$), equation (25) is identical to an equation given by Tait and coworkers[14].

From equation (18) it is possible to obtain an equation in which the number-average molecular weight, M_n, is correlated to the catalyst yield KA, using n as given by equation (24) and eliminating

$$\int_0^t n^*(t)\mathrm{d}t/(a + b + c)$$

with equation (22):

$$\frac{KA}{M_n} = \frac{n^*}{n_K} + \frac{1}{M_{n,\infty}} KA \tag{27}$$

where $M_{n,\infty} = P_{n,\infty} M_m$

This is an important equation which shows how to determine the number of catalytic active centres, n^*. To obtain n^*/n_K it is necessary to measure the number-average molecular weight M_n as a function of catalyst yield KA, and to plot these data in accordance to equation (27); n^*/n_K is taken as intercept. This method of determination of the number of catalytic active sites was first pointed out by Natta and Pasquon[26].

If hydrogen is used to control molecular weight, the reaction scheme has to be expanded by the reactions (14) to (16). To obtain equations for the reaction rate R_p and $P_{n,\infty}$, calculations are performed in the same way as presented above. The only difference is that there are two additional intermediates (see the reactions given as dotted lines in *Figure 1*). Therefore equations (1) and (5) have to be extended:

$$n^* = n_0^* + n_a^* + n_b^* + n_c^* + n_d^* + n_e^* + n_\mathrm{H}^* + n_{d,\mathrm{H}}^* + n_{\mathrm{al},1}^* + n_{\mathrm{al},2}^* \tag{28}$$

$$\frac{\mathrm{d}n_d^*}{\mathrm{d}t} = k_d n_c^* + k_d n_e^* + k_{d,\mathrm{al}} n_{\mathrm{al},2}^* + k_\mathrm{H} n_\mathrm{H}^* + k_{d,\mathrm{H}} n_{d,\mathrm{H}}^*$$

$$- (k_a[\mathrm{M}]_0 + k_{a,\mathrm{al}}[\mathrm{al}]_0 + k_{a,\mathrm{H}}[\mathrm{H}_2]_0) = 0 \tag{29}$$

The following equations describe the steady state quantities of the two intermediates formed by complexation with hydrogen:

$$\frac{\mathrm{d}n_\mathrm{H}^*}{\mathrm{d}t} = k_{a,\mathrm{H}}[\mathrm{H}_2]_0 n_0^* - (k_{d,\mathrm{H}} + k_\mathrm{H})n_\mathrm{H}^* = 0 \tag{30}$$

$$\frac{\mathrm{d}n_{d,\mathrm{H}}^*}{\mathrm{d}t} = k_{a,\mathrm{H}}[\mathrm{H}_2]_0 n_d^* - k_{d,\mathrm{H}} n_{d,\mathrm{H}}^* = 0 \tag{31}$$

The equations (9) to (12) hold as well. To obtain an equation for $P_{n,\infty}$, it is necessary to express n_H^* as:

$$n_\mathrm{H}^* = \frac{k_{a,\mathrm{H}}[\mathrm{H}_2]_0}{k_{d,\mathrm{H}} + k_\mathrm{H}} n_0^* \tag{32}$$

On the other hand, equation (13) does not hold in this case, and has to be extended in the following way:

$$n_0^* = \frac{n^*}{a + b + c + d} \tag{33}$$

with a, b and c as given by equations (14a, b and c) and:

$$\mathrm{d} = \frac{k_{a,\mathrm{H}}[\mathrm{H}_2]_0}{k_{d,\mathrm{H}} + k_\mathrm{H}} \times \left\{ 1 + \frac{k_\mathrm{H} + \dfrac{k_\mathrm{H} k_a[\mathrm{M}]_0}{k_s + k_d} + \dfrac{k_d k_{\beta,0}(k_{d,\mathrm{H}} + k_\mathrm{H})}{k_{d,\mathrm{H}}(k_s + k_d)} + \dfrac{k_\mathrm{H} k_{a,\mathrm{H}}[\mathrm{H}_2]_0}{k_{d,\mathrm{H}}} + \dfrac{k_\mathrm{H} k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}}{\dfrac{k_s k_a[\mathrm{M}]_0}{k_s + k_d} + \dfrac{k_t k_{a,\mathrm{al}}[\mathrm{al}]_0}{k_{d,\mathrm{al}} + k_t}} \right. \tag{34}$$

As the rate of polymer formation is again given by equation (15), R_p is similar to equation (17):

$$R_p = \frac{k_p k_a[\mathrm{M}]_0}{k_p + k_d + k_a[\mathrm{M}]_0} \times \frac{1}{1 + \dfrac{b}{a} + \dfrac{c}{a} + \dfrac{d}{a}} \frac{n^*}{n_K} \tag{35}$$

The term d in equation (35) describes the extent of inhibition of the polymerization process by hydrogen.

To obtain an equation for $P_{n,\infty}$, equation (23) has to be extended by a further term to describe the transfer process with hydrogen as given by the reaction (15) in *Figure 1*:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = k_d n_b^* + k_d n_c^* + k_t n_{\mathrm{al},1}^* + k_\mathrm{H} n_\mathrm{H}^* \tag{36}$$

Making the same assumptions as described above the following equation can be derived:

$$\frac{1}{P_{n,\infty}} = A + B\frac{1}{[\mathrm{M}]_0} + C\frac{[\mathrm{al}]_0}{[\mathrm{M}]_0} + D\frac{[\mathrm{H}_2]_0}{[\mathrm{M}]_0} \tag{37}$$

where A, B and C are given by equations (26a, b and c) and:

$$D = \frac{k_\mathrm{H} k_{a,\mathrm{H}}(k_p + k_d)}{(k_{d,\mathrm{H}} + k_\mathrm{H})k_p k_a} \tag{38}$$

Using the reaction model in *Figure 1* it is also possible to derive equations for the yield of cocatalyst–polymer bond formation and the yield of vinyl and ethyl group formation at the polymer.

DISCUSSION

By summarizing previous results[1–5], an attempt has been made to develop a kinetic scheme for homogeneous and heterogeneous Ziegler–Natta polymerization processes. In both cases the reactants which participate in this process must interact with the catalytic active species by complexation as pointed out by Cossee[7] and Henrici-Olivé and Olivé[8]. For a heterogeneous catalyst the polymerization process can be interpreted according to Rideal[18], who assumed the substrate molecules to be bound in a van der Waals trough at the surface of the catalyst.

The reaction scheme is formulated in a comprehensive way, including equilibria due to complexation or adsorption as well. The equations which are given in this paper only hold if the following conditions are fulfilled.

(A) The rate constants must be constant, independent of the degree of polymerization.

(B) If an integration has been performed to obtain an equation, it has been assumed that the concentrations of the different substrates in the reaction medium at the surface of the catalyst are constant and time independent.

(C) It has been assumed that only the amount of substance of active sites, n^*, is time dependent and that n^* decreases slowly.

If these assumptions do not hold the calculations must be performed in a different way. ,

The equations given in this paper are also applicable to homogeneous Ziegler–Nata processes. In this case, the quantities of different intermediates have to be replaced by concentrations. Thus it is possible to obtain comparable results whether the polymerization is homogeneous or heterogeneous. For homogeneous polymerization processes, the concentrations at the surface of the catalyst must be replaced by the concentrations in the bulk.

As the polymers build up by a Ziegler–Natta polymerization process have relatively broad molecular weight distributions as first pointed out by Wesslau[27], the possibility that there are different species of catalytically active sites cannot be excluded (see Clark and Bailey[28]).

Therefore, the validity of the equations given in this paper must be checked for this case. Indeed, if the fraction of the different species is constant during the polymerization process, the equations do hold, although the constants are much more complex. This is shown in the Appendix.

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APPENDIX

If there are k different species of active sites whose fractions x_i are constant, then equations (17), (21), and (25, 26), for example, hold as well:

$$R_p = [\mathrm{M}]_0 \frac{n^*}{n_k} \sum_{i=1}^{k} \frac{k_{p,i}k_{a,i}}{k_{p,i} + k_{d,i} + k_{a,i}[\mathrm{M}]_0} \times$$

$$\frac{x_i}{1 + \dfrac{b_i}{a_i} + \dfrac{c_i}{a_i}} \qquad 0 < x_i \leqslant 1 \qquad \text{(A1)}$$

$$P_{n,0} = [\mathrm{M}]_0 t \sum_{i=1}^{k} \frac{k_{p,i}k_{a,i}}{k_{p,i} + k_{d,i} + k_{a,i}[\mathrm{M}]_0} \times$$

$$\frac{x_i}{1 + \dfrac{b_i}{a_i} + \dfrac{c_i}{a_i}} \qquad 0 < x_i \leqslant 1 \qquad \text{(A2)}$$

$$\frac{1}{P_{n,\infty}} = \bar{A} + \bar{B}\frac{1}{[\mathrm{M}]_0} + \bar{C}\frac{[\mathrm{al}]_0}{[\mathrm{M}]_0} \qquad \text{(A3)}$$

where

$$\bar{A} = \frac{\displaystyle\sum_{i=1}^{k} \frac{k_{d,i}k_{\beta,i}k_{a,i}}{(k_{p,i} + k_{d,i})(k_{p,i} + k_{d,i} + k_{\beta,i})} \times \frac{x_i}{a_i + b_i + c_i}}{\displaystyle\sum_{i=1}^{k} \frac{k_{p,i}k_{a,i}}{k_{p,i} + k_{d,i}} \times \frac{x_i}{a_i + b_i + c_i}} \tag{A3a}$$

$$\bar{B} = \frac{\displaystyle\sum_{i=1}^{k} \frac{k_{d,i}k_{a,i}}{k_{p,i} + k_{d,i}} \times \frac{x_i}{a_i + b_i + c_i}}{\displaystyle\sum_{i=1}^{k} \frac{k_{p,i}k_{a,i}}{k_{p,i} + k_{d,i}} \times \frac{x_i}{a_i + b_i + c_i}} \tag{A3b}$$

$$\bar{C} = \frac{\displaystyle\sum_{i=1}^{k} \frac{k_{t,i}k_{a,\mathrm{al},i}}{k_{d,\mathrm{al},i} + k_t} \times \frac{x_i}{a_i + b_i + c_i}}{\displaystyle\sum_{i=1}^{k} \frac{k_{p,i}k_{a,i}}{k_{p,i} + k_{d,i}} \times \frac{x_i}{a_i + b_i + c_i}} \tag{A3c}$$

It is important to point out that equation (A3) can only be considered as a first approximation because $\bar{A}, \bar{B}$ and $\bar{C}$ are not constants but depend on concentrations via a_i, b_i, and c_i. It can also be shown that similar equations can be derived starting from the equations (35) and (37).