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Determination of the Number of Active Centres and Growth Rate Constants in the Catalytic Polymerisation of α-Alkenes

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The reliability of different methods for determining the number of active centres (n) and calculating the growth rate constants (k_g) in the catalytic polymerisation of α-alkenes is discussed. The values of n and k_g obtained for different catalytic systems are given. Information on the dependence of the number of growth centres and the rate constants of the separate steps (primarily the growth rate constants) on the composition of the catalyst, its method of preparation, and the conditions of polymerisation can yield important conclusions regarding the mechanism of polymerisation and the composition of the active centres. The bibliography contains 113 references.

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I. INTRODUCTION

In the study of radical polymerisation, the rate constants of the elementary steps are now being measured. The problem of determining the kinetic characteristics of the elementary steps of catalytic polymerisation is only just being tackled. The complexity of the study of the elementary steps in this instance is associated with the fact that the separate reactions involved in catalytic polymerisation are not in general elementary steps in the sense in which this term is used in the theory of absolute reaction rates, but consist of many elementary steps. The study of the kinetics of polymerisation in the presence of homogeneous and heterogeneous catalysts is still at the stage where the rate constants of the separate reactions making up the overall process (chain growth, chain transfer, etc.) are being determined.

Since in the description of catalytic polymerisation, slight differences are noted in the interpretation of a number of terms, it is appropriate to explain the terminology used in the present paper.

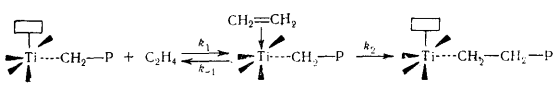
Catalytic polymerisation can be defined as a process in which a catalyst takes part in the formation of the activated complexes for the elementary steps of growth. The growth centre in catalytic polymerisation can be defined as the active bond between the catalyst and the growing polymer molecule, through which the monomer molecule is brought into the chain growth reaction, together with those atoms of the catalyst which take part in the formation of the activated complexes during growth. In heterogeneous catalysts, the growth centre is a surface compound.

In contrast to the situation in heterogeneous-catalytic reactions involving the production of non-polymeric products, the concept of active centres acquires particular

importance in heterogeneous catalytic polymerisation. All stages in the polymerisation involve the participation of localised growth centres; the rates of the elementary steps should thus be influenced primarily by the local properties of the growth centre—the properties of the active bond and the atom or group of atoms joined to the terminal atom of the growing polymer chain and the properties of the immediate environment of the growth centre. Early suggestions[1,2] regarding the mechanism of heterogeneous catalytic polymerisation, in which it was assumed that the end of the growing polymer chain is able, during growth, to move over the surface, which was assumed to have a regular structure, were not confirmed by detailed study of the mechanism of polymerisation on heterogeneous catalysts.

For homogeneous polymerisation, in some instances it is difficult to draw a clear distinction between a catalytic process and a process taking place by an ionic polymerisation mechanism. In general, the reactivity of the growth centre and the structure of the polymer are influenced by the composition of the catalytic complex; a free-ion mechanism may be realised in polymerisation in polar media[3].

A characteristic feature of catalytic polymerisation, which distinguishes it from radical polymerisation, is that the individual reactions are generally complex and consist of several successive elementary steps (in other words, more than one activated complex is formed in the reaction). For example, it is usually postulated that in the catalytic polymerisation of alkenes, growth takes place in two stages: in the first, an unstable π-complex of the alkene with a metal with variable valency is formed, and in the second a *cis*-insertion reaction takes place; for the polymerisation of ethylene on Ziegler–Natta catalysts, this scheme can be represented as follows (the rectangle represents a vacant coordination position, and P the polymer chain):



The catalytic polymerisation of alkenes has been most extensively studied for the determination of the kinetic parameters of the individual steps. The rate constants obtained for the individual reactions, however, are usually not the absolute rate constants of the elementary steps, and their physical significance depends on the way in which the individual reaction takes place. For example, for a growth reaction in which two activated complexes are formed (see above scheme), the growth rate constant k_g depends on the rate constants of these steps:

$$k_g = \frac{k_1 k_2}{k_2 + k_{-1} + k_1 \cdot [M]} \qquad (1)$$

where [M] is the concentration of the monomer, and k_1, k_{-1}, and k_2 the rate constants of the corresponding elementary steps.

In this connection, care must be taken when applying the theory of absolute reaction rates to the interpretation of the rate constants of the separate stages of catalytic polymerisation, and also when examining various correlations between these constants and the physical characteristics of the catalyst. Despite this, however, the determination of the rate constants of the separate reactions in polymerisation is of considerable importance in connection with the problem of predicting catalytic activity.

The activity A of a polymerisation catalyst is proportional to the number of growth centres n and the growth rate constant k_g:

$$A \sim k_g \cdot n$$

In catalytic polymerisation it is possible and necessary to distinguish clearly two factors influencing the catalytic activity: a) the number of growth centres, which is determined by the original state of the catalyst and the reactions taking place in the formation of the growth centres (separated from possible reactions involving subsequent deactivation of the growth centres by reaction with components of the reaction medium); and b) the growth rate constants, that is the reactivity of a single growth centre.

To develop methods for controlling catalyst activity, it is necessary to study the influence of these factors separately. The determination of the rate constants of reactions limiting the growth of a polymer chain is related to the problem of controlling the molecular weight of the polymer.

The determination of the kinetic characteristics of the growth centres also makes it possible to reach a number of important conclusions regarding the mechanism of catalytic polymerisation. The direct use of such quantities as the rate of polymerisation (V) and the degree of polymerisation ($\bar{P}$), cannot give unambiguous information regarding the nature of the individual elementary reactions, since V and $\bar{P}$ are complex quantities which depend on the ratio of the rates of initiation, growth, transfer, and termination of the chains.

The results of the determination of the number of growth centres in catalytic polymerisation have been reviewed briefly by Boor[4]. At the Budapest Symposium on Macromolecular Chemistry (August 1969), Kern[5] described the determination of the number of growth centres for Ziegler–Natta catalysts (chiefly by a method involving the termination of the polymerisation by a radioactive alcohol), but this paper similarly does not contain a sufficiently complete review of the results obtained in the important field of the determination of the kinetic characteristics of growth centres in catalytic polymerisation.

It is possible to distinguish three basic groups of methods used for the determination of the kinetic characteristics of growth in catalytic polymerisation.

1. Methods based on the determination of the dependence of V and $\bar{P}$ on the duration and conditions of the reaction. These will subsequently be referred to conditionally as kinetic methods.
2. The inhibition method, in which the number of growth centres is calculated from the quantity of added inhibitor which brings about complete termination of polymerisation.
3. Methods based on the labelling of the growing polymer molecule.

II. KINETIC METHODS

These methods are based on the study of the dependence of the rate of polymerisation and the molecular weight of the polymer on the conditions of polymerisation. For processes in which the number of growth centres is independent of time (steady-state polymerisation), methods based on the use of the dependence of V on the concentrations of the reagents and the dependence of $\bar{P}$ on time and the concentrations of the reagents have been proposed for the calculation of the rate constants. For processes in

which the number of growth centres changes with time (non-steady-state polymerisation), the time dependence of V is also used in the calculation of rate constants.

1. Steady-state Polymerisation Kinetics

The method of calculating the rate constants of the separate reactions from the dependence of V and $\bar{P}$ on the concentrations of the reagents has been described by Chirkov and coworkers [6] and Natta and coworkers [7]. These authors used a comparatively simple kinetic scheme, based on the following assumptions: a) the total number of active centres remains constant throughout the process; b) the initiation involves the attachment of the first monomer molecule to the active centre; c) transfer takes place with the participation of the monomer, impurities, components of the catalyst, and spontaneously; d) transfer is followed by regeneration of the active centre.

In accordance with the foregoing:

$$n_0 = n_g + n_i \qquad (2)$$

where n_0 is the total number of active centres in the catalyst, n_g the number of active centres joined to a growing polymer molecule, and n_i the number of centres in a state of temporary deactivation. The steady-state conditions for this scheme gave the dependence of V and $\bar{P}$ on the concentrations of the reagents:

$$\frac{[M]}{V} = \frac{1}{k_g \cdot n_0} + \frac{k_M}{k_g \cdot k_i \cdot n_0} + \frac{\sum_{j-1} k_j \cdot c_j^a}{k_g \cdot k_i \cdot n_0} \cdot \frac{1}{[M]} \qquad (3)$$

$$\frac{1}{\bar{P}_n} = \frac{V_0}{V_g} = \frac{k_M}{k_g} + \frac{\sum_{j-1} k_j \cdot c_j^a}{k_g} \cdot \frac{1}{[M]} \qquad (4)$$

where V_g is the rate of growth, V_0 the rate of transfer, k_j the rate constant for transfer involving the agent j, k_M the rate constant for transfer involving the monomer, k_i the initiation rate constant, c_j the concentration of transfer agent j; [M] the concentration of monomer, and n_0 the total number of active centres.

The experimental dependence of V and $\bar{P}$ on the concentrations of the reagents can be used to calculate products of the rate constants of the separate reactions and the concentrations of the active centres, but this method does not yield absolute values of the rate constants. This method has been used to study the polymerisation of propene on heterogeneous catalytic systems based on $TiCl_3$ and VCl_3 combined with various organometallic components [3-17] (see Table 1). It should be noted that the correct application of this method requires the use of the experimental values of the number-average degree of polymerisation ($\bar{P}_n$). In the calculations, however, the weight-average factor ($\bar{P}_w$) is usually employed, with the assumption that the polydispersion factor γ ($\gamma = \bar{P}_w/\bar{P}_n$) remains constant over the range of values of the parameters studied. The applicability of this assumption will be discussed below. Because of the assumptions made in the derivation of the kinetic equations and the calculation, the results of the calculation are approximate and suitable only for the comparative estimation of the efficiency of chain transfer agents for catalytic systems with similar compositions.

A method for calculating the rate constants of the separate reactions for steady-state polymerisation, based on an analysis of the dependence of the molecular weight

Table 1. Determination of the kinetic parameters of growth for the catalytic polymerisation of propene.

Catalytic system	Temp. of reaction, °C	$10^2 n$, mole per mole of M[a]	k_g, litre mole^{-1} s^{-1}	Method of calculation[b] and remarks	References
$TiCl_3+AlEt_2Cl$	50	1.35	4.7	II-2. Maximum values of n given;	18
	70	2.8	7.5		
	90	9	11.5	E_g = 5.0 kcal mole^{-1}[c]	
$TiCl_3+AlEt_3$	70	0.3	48	III-2. AMP = amide hexamethyltriphosphoric acid	19
$TiCl_3+AlEt_2Cl$	70	0.1	40		
$TiCl_3+AlEtCl_2+AMP$	70	0.02	50		
α-$TiCl_3+AlEt_2Cl$	50	—	1.2	I-4	20
α-$TiCl_3+AlEt_3$					
α-$TiCl_3+AlEt_2Cl$	50	2.3—7.0	3—0.48[c]	III-2. k_g changes with change in the duration of polymerisation	20
α-$TiCl_3+AlEt_3$	50	1.1—4.5	5.9—0.48[c]		
$TiCl_3+AlEt_2Cl$	70	0.19	5.5	I-4	21
$TiCl_3+AlEt_2Cl$		1.9	7.5	I-3. Parallel values of n and k_g obtained for different $TiCl_3$ specimens	22
	60	0.57	6.2		
$TiCl_3+AlEt_2Cl$	60	0.3*	26*	III-2.	
	60	0.45**	18**	*I_2 used as stopper	5
				**CH_3O^3H used as stopper	
$TiCl_3+AlEt_2Cl$	30	5.1	0.8[c]	III-2. Initial values of n and k_g given; n increases with increase in the duration of polymerisation, and k_g decreases;	23
	50	4.4	2.5[c]		
	70	3	7.0[c]		
				E_g = 8.0 ± 1 kcal mole^{-1}	24
$TiCl_3+AlEt_2Cl$	30	9.5	0.10	III-1.	
	50	7.6	0.42	E_g = 13.0 kcal mole^{-1}	
	70	5.5	1.25		
	90	3.3	3.50		
$Al_xTi_yCl_2+(C_5H_5)_3N$	50	0.0007—0.0012	1.1—0.28	III-2. n increases with increase in the duration of polymerisation, and k_g decreases	25
$TiCl_3+AlEt_3$	70	1.0	2.5[c]	III-1.	26
$TiCl_3+AlEt_2Cl$	70	0.4	5.6[c]		
$TiCl_3+AlEt_3$	70	1.16—1.40	4.3	I-3.	27
	35	4	1.0[c]	I-3.	28
$TiCl_3+AlEt_3$	60	25	0.3[c]		
$TiCl_3+AlEt_3$	70	0.54	—	II	29
$TiCl_3+AlEt_2Cl$	60	0.40	10[c]	II	30
	20	1.0	—	III-1. Parallel values of n obtained for $TiCl_3$ specimens with different activities	31
	46	1.1	—		
$TiCl_3+AlEt_3$	70	1.1—0.7	2.9[c]		
	100	0.3	—		
	70	1.7	2.8[c]		15
$VCl_3+Al(i\text{-}Bu)_3$	60	0.8	23	I-1 and I-2.	32
$VCl_3+Al(i\text{-}C_7H_9)_3$	70	0.8	46.5	I-2, E_g = 12.9 kcal mole^{-1}	32, 33
α-$TiCl_3+AlEt_3$	70	0.54	3.8		
α-$TiCl_3+Al(C_3H_7)_3$	70	0.54	5.2	I-2, II	
α-$TiCl_3+Al(i\text{-}Bu)_3$	70	0.54	2.9	E_g = 13.5 kcal mole^{-1}	34
α-$TiCl_3+Al(CH_3)_3$	25	—	$1\cdot10^3$—$1\cdot10^6$	IV.	

[a] M represents the transition metal compound.

[b] Arbitrary symbols for methods of determining n and k_g.
I—Kinetic methods:
I-1—calculation from the dependence of V and $\bar{P}_n$ on the concentrations of the reagents for steady-state kinetics;
I-2—calculation from the dependence of V on the conditions of polymerisation for non-steady-state kinetics;
I-3—calculation from the dependence of $\bar{P}_n$ on the duration of polymerisation for steady-state kinetics;
I-4—calculation from the dependence of V and $\bar{P}_n$ on the duration of polymerisation for non-steady-state kinetics;
II—Inhibition method
III—Methods based on the labelling of the polymer:
III-1—labelled catalysts;
III-2—stopper method
IV—Calculation from the results of an electron-microscope study of the morphology of the polyalkene formed in the initial stage of the polymerisation.

[c] Calculated by us from published data.

on the duration of polymerisation, was proposed by Natta and coworkers [8,9,31,35]. This method uses the following expression for the number-average degree of polymerisation:

$$\overline{P}_n = \frac{Q}{N} = \frac{\int_0^\tau k_g \cdot n \cdot [M] \cdot d\tau}{n + \int_0^\tau \sum_j k_j \cdot n \cdot c_j^a \, d\tau} \qquad (5)$$

where N is the number of polymer molecules formed in polymerisation for time τ, Q the yield of polymer, k_j the rate constant for transfer involving agent j, and [M] the concentration of monomer.

For steady-state systems (n = const), the rate constants can be calculated from the linear dependence of $1/\overline{P}_n$ on $1/\tau$, which follows from Eqn.(5). With values of the polymerisation factor $\overline{P}_V$, calculated from measurements of the characteristic viscosity, the authors cited [8,9] used the equation

$$\frac{1}{\overline{P}_V} = \frac{1}{k'_g[M]} \cdot \frac{1}{\tau} + \frac{\sum_j k_j \cdot c_j^a}{k'_g \cdot [M]} \qquad (6)$$

where k'_g is the viscosimetric-average rate constant for chain growth, taken as a measure of the activity of one growth centre, and $k'_g = k_g/\gamma$, where γ is the polydispersion factor. The method based on Eqn.(5) makes it possible in principle to determine the absolute values of the kinetic parameters of growth.

Table 2. Determination of the kinetic parameters of growth for the catalytic polymerisation of α-butene at 0° (method of calculation I-3, see Table 1).

Catalytic system	k'_g[M], s^{-1}	E^*_g, kcal mole^{-1}	Catalytic system	k'_g[M], s^{-1}	E^*_g, kcal mole^{-1}
VCl_3 + $AlEt_3$ / $BeEt_2$	3100	2.3	$TiCl_3$ + $AlEt_3$	280	—
α-$TiCl_3$ + $BeEt_2$ / $AlEt_3$ / $AlEt_2Cl$ / $AlEt_2I$ / Al(*i*-Bu)·Cl	275	4.5	β-$TiCl_3$ + $AlEt_2Cl$ / $AlEt_2Cl + AlCl_3 \cdot (C_5H_5)_3N$	54	—

*E_g is the activation energy of growth, calculated from the temperature dependence of k_g.

This method has been used [8,9] to determine k_g for the polymerisation of α-butene on catalytic systems based on VCl_3 and different crystalline modifications of $TiCl_3$ (see Table 2). The dependence of P_V on τ was determined for comparatively small polymerisation times (30–600 s). The value of k_g depended on the form of the compound of the metal with variable valency, but was almost independent of the organometallic co-catalyst, although the replacement of the co-catalyst influenced the overall rate of the process, the stereoregularity, and the molecular weight of the polymer.

The Italian authors [9] used the same method to study the polymerisation of propene into a syndiotactic polymer on the VCl_4 + $AlEt_2Cl$ catalytic system in the presence of anisole. The graphs giving the dependence of the stereospecificity of the catalysts and the rate of polymerisation on the concentration of anisole showed maxima; the value of k'_g decreased considerably when anisole was added and was independent of its concentration in the system. The Italian authors [9] introduced into the expression for the "viscosimetric-average" growth rate constant a coefficient making allowance for the change in the number of growth centres during the polymerisation, but the choice of value for this coefficient was somewhat arbitrary.

Table 3. Determination of the kinetic parameters of growth for the catalytic polymerisation of ethylene.

Catalytic system	Temp. of reaction, °C	$10^2 n$, mole per mole of M[a]	k_g, litre mole^{-1} s^{-1}	Method of calculation[b] and remarks	References
$TiCl_4$ + $AlEt_3$	39	4.8	52	III-2.	38
	54	1.1	127	E_g = 12 ± 2.5 kcal mole^{-1}	
	57	23	175		
α-$TiCl_3$ + $AlEt_2Cl$	40	1.5	76.5	I-1 and I-3	37
α-$TiCl_3$ + $AlEt_2Cl$ + H_2	40	0.6	80		
VCl_3 + Al-*i*-Bu_3	60	0.3	266	I-1 and I-2	39
VCl_4 + Al-*i*-Bu_3	0	4	1900	I-4	40
$VOCl_3$ + $AlEt_3$	0	0.82	1200	I-4. Maximal value of n given	41
$(C_5H_5)_2TiCl_2$ + $Al(CH_3)_2Cl$	0	40	1.50	III-2. Values of n given for one	42
	15	5	5.13	of several series of experiments;	
	30	78	13.6	the values depend on the condi-	
	45	98.0	39.0	tions of polymerisation.	
				E_g = 12.2 kcal mole^{-1}	
$(C_5H_5)_2TiCl_2$ + $Al(CH_3)_2Cl$	20	$1 \cdot 10^{-4}$	$1 \cdot 10^6$	n calculated from data on the dissociation of the original catalytic complex	43
$(C_5H_5)_2TiCl_2$ + $AlEt_2Cl$	15	10	1.5	I-4	44
CrO_3/aluminosilicate (3% Al_2O_3)	75	0.85	97	II	45
ditto	60	—	140	I-4. Values of $\gamma.k_g$ given, where γ	46
	70	—	137	is the polydispersion factor	
	120	—	55		
	140—	—	39		
»	50	1.10	280	I-2	18
CrO_3/SiO_2, reduced with CO	75	—	2600	IV	47
α-$TiCl_3$ + $AlEt_3$	70	0.54	410	I-1,	32
α-$TiCl_3$ + Al(*i*-Bu)$_3$	70	0.54	380	II, E_g = 12 kcal mole^{-1}	
α-$TiCl_3$ + $AlEt_2Cl$	70	0.54	80		
$V(AcAc)_3$ + Al(*i*-Bu)$_2$Cl	—10°	—	30	I-4, E_g = 4.4 kcal mole^{-1}	32
$(C_5H_5)TiCl_2$ + $Al(Et)_2Cl$	20	—	4	I-4	32
$TiCl_2$	75°	0.003	$1.5 \cdot 10^4$	III-2	48, 49

[a] M represents the transition metal compound.
[b] Arbitrary symbols for methods of calculation; see footnote to Table 1.

A method for determining the kinetic parameters for steady-state catalytic systems, based on an analysis of the dependence of $\overline{P}_V$ on τ, was used [36,37] for the polymerisation of ethylene (the γ-$TiCl_3$ + $AlEt_2Cl$ system) in the presence and absence of hydrogen (see Table 3). After the initial non-steady-state period, the duration of which was not correlated with any of the parameters of the reaction, the rate of polymerisation remained stable for a prolonged period. Determination of the polydispersion of several polymers obtained under different conditions showed that the value of γ varies from 7 to 16. A constant value of γ equal to 10 was taken for the calculations. It was recognised [37] that the numerical values obtained for the rate constants are only approximate, because of the assumptions made and the limited accuracy of the measurement of the characteristic viscosity for polymers with high molecular weight. This method was also used [27,28] for the polymerisation of propene in the presence of the α-$TiCl_3$ + $AlEt_3$ system, although this system is not a steady-state system: the rate of polymerisation in the initial period increased until a constant value was established. The calculation based on the dependence of $\overline{P}_V$

and $\bar{P}_n$ on τ showed a decrease in the concentration of active centres during the polymerisation. The probable reason for this contradiction is that in this instance the condition for applicability of the method used to calculate the rate constants (n = const) was not satisfied.

2. Non-steady-state Kinetics

A number of authors have examined methods for calculating n and k_g for catalytic systems with variable activity from the dependence of the rate of polymerisation and the yield of polymer (Q) on time (τ). The dependence of V and Q on τ for one of the possible kinetic schemes for non-steady-state polymerisation has been derived[50]. For the interpretation of the time dependence of the number of growth centres in the kinetic scheme, the deactivation of the active centres in their reactions with monomers, with one another, and spontaneously were examined. The rate constants for the separate reactions involved in the polymerisation of propene were calculated[17] from the dependence of V on τ for the VCl_3 + AlR_3 system. In the interpretation of the non-steady-state behaviour of the system at elevated temperatures and high Al/V ratios, the kinetic scheme for steady-state polymerisation, examined earlier[14-16], was supplemented by deactivation of the catalyst, which, in the opinion of the authors cited, is associated with the extensive reduction of vanadium by the organoaluminium compound. By assuming that the period of accelerating rate of polymerisation is due to slow initiation with rate constant k_i, the product $k_i k_g n$ was calculated. Comparison of this quantity with the values of $k_i n$ and $k_g n$ found under conditions of steady-state behaviour of the system[16], made it possible to calculate n and the values of the rate constants for the separate reactions (Table 1) with an accuracy equal to that of γ.

A variant of the kinetic method of determining the constants of the elementary steps in non-steady-state catalytic polymerisation from the dependence of the rate of polymerisation on the conditions of the process was described by Ermakov and coworkers[51]. Its unique feature is that the description of the kinetics is not taken as far as the overall kinetic equation in integral form, which either includes a considerable number of variables, or requires for its simplification a large number of assumptions, but is represented in the form of a system of differential equations, derived from the kinetic scheme adopted for the process. This mathematical description is studied by means of an electronic computer. The mathematical description of the polymerisation of ethylene on a chromium oxide catalyst, compiled on the basis of a kinetic scheme involving initiation, growth, transfer, and deactivation of the catalyst was studied[51]. This kinetic scheme was proposed on the basis of data obtained in a study of the kinetics of the process[52]. The rate constants for the separate reactions were adjusted to obtain a dependence of V on time, the concentration of the catalyst, and the monomer which agreed with experiment. The chief limitations of this method are the indefinite nature of the choice of kinetic scheme and the ambiguous nature of the numerical solution of the system of equations. Considerable difficulties also arise in the selection of the initial conditions: the concentrations of the active component, the chain transfer agent, and the catalyst deactivator.

A method for determining the rate constants of the separate reactions from the dependence of $\bar{P}_V$ on τ for non-steady-state polymerisation was proposed by Matkovskii[41]. In order to apply this method it is necessary to establish, in a reaction vessel with ideal mixing, a constant concentration of active centres by selection of the rates of supply of catalyst and removal of polymer and catalyst. Under steady-state conditions, the rate constants can in principle be calculated by the methods proposed for steady-state catalytic systems[6,7,13]. For one of the probable kinetic schemes, equations relating V to the rate constants of the separate reactions, the concentrations of the reagents, and the amount of material exchange with the external medium, and also equations relating the mean time (τ_{mean}) for which the reaction mixture is in the reaction vessel to the concentration of the active centres and the rate constants of the deactivation processes, were derived. For a certain intensity of mass exchange, a linear relationship is observed between τ_{mean} and $\bar{P}_V$; this dependence was used to calculate n and k_g for the polymerisation of ethylene in the presence of the $VOCl_3$ + $Al(i\text{-}Bu)_3$ system (see Table 3).

An approach to the determination of the rate constants of the separate reactions on the basis of data on the dependence of V, Q, and $\bar{P}_n$ on the duration of polymerisation has been described[46,53,54]. For non-steady-state polymerisation, when chain transfer involving the monomer and spontaneous chain transfer take place, Eqn.(3) can be rewritten in the form[53]

$$\frac{1}{\bar{P}_n} = \frac{1}{k_g \cdot [M]} \cdot \frac{V}{Q} + \frac{k_M}{k_g} + \frac{k_S}{k_g \cdot [M]} \qquad (7)$$

(k_S is the rate constant for the spontaneous transfer).

Expression (7) has a relatively simple form, since it does not include the rate constants for initiation and deactivation of the growth centres. The change in the number of growth centres with time as a consequence of these reactions is included in implicit form in the ratio V/Q. Thus Eqn.(7) gives the dependence of the molecular weight on the duration of polymerisation, resulting from the change in the number of growth centres. This method can be used to determine the values of k_g (with an accuracy equal to that of the coefficient γ), k_M, and k_S. When this method was used to study the polymerisation of ethylene on a chromium oxide catalyst[46,53], a decrease in the quantity $\gamma . k_g$ with decrease in the temperature of polymerisation was observed, and this was attributed to a decrease in the polydispersion of the polymer (data on the possibility of narrowing the molecular weight distributation of a polymer by decreasing the temperature of polymerisation on oxide catalysts have been published[55]). This method is also used for the polymerisation of ethylene in the presence of a soluble catalytic system[44].

3. Applicability of Kinetic Methods

The following possible sources of error in the determination of the absolute values of n and k_g by kinetic methods may be noted.

1. Lack of correspondence between the kinetic scheme adopted and the actual mechanism of the process. For non-steady-state polymerisation, when a method based on the analysis of the dependence of V and $\bar{P}$ on τ is used, the choice between different mechanisms of chain transfer and termination is somewhat arbitrary; different authors have

proposed different transfer and termination reactions for catalytic systems with similar compositions [13,18,24,30,42,56-60]. For steady-state polymerisation, k_g can be calculated on the basis of the linear dependence of $1/\bar{P}_V$ on $1/\tau$ if the catalytic system is suitable from the start of polymerisation. Most authors who have used this method, however, do not give kinetic curves justifying the assumption that the number of active centres is constant in the initial period of polymerisation for which the dependence of $\bar{P}_V$ on τ is determined. When methods based on the analysis of the dependence of $\bar{P}_V$ on τ are used, errors may arise because processes involving the temporary deactivation of active centres, not associated with rupture of the active chain, are not taken into account in the derivation of the equations (6) and (7) used in the calculations. When these processes take place, the growth of an individual molecule is interrupted periodically; the temporary interruption of growth ("falling asleep") leads to a decrease in the overall rate of polymerisation, but does not increase the number of polymeric molecules.

2. Use of $\bar{P}_V$ instead of $\bar{P}_n$. Most authors who have used kinetic methods have calculated the number-average polymerisation factor ($\bar{P}_n$) from the results of the measurement of the characteristic viscosity (η). In this instance, errors may arise as a consequence of errors in the determination of η for polymers with high molecular weight, and also because of the arbitrary nature of the selection of the method for calculating $\bar{P}_V$ from η. It is known that even for narrow fractions of linear polyethylene [61], the equations proposed by different authors, for the same values of the viscosity, give molecular weight values which differ considerably. Moreover, it appears that one of the fundamental assumptions which is usually made when kinetic methods are used—the assumption that the polydispersion of the polymer (the factor $\gamma = \bar{P}_V/\bar{P}_n$) is independent of the conditions of the process—is not always satisfied. It should be noted that the experimental determination of the quantity γ for polyalkenes with high molecular weight involves considerable difficulty, and published data on this topic are somewhat contradictory. For soluble catalytic systems, a narrower molecular weight distribution is observed, but even for these systems, the values of γ given by different authors [20,62-64] vary from 1.5 to 6, and Chien [62] points out that the quantity γ shows a complex dependence on τ, increases with decrease in temperature, and changes with change in the catalyst concentration and the Ti/Al ratio. It has been noted [63,64] that γ depends on the concentration of the catalyst and monomer, and the nature of the solvent. For heterogeneous catalysts, the polymers obtained have a wider molecular weight distribution; according to the data of various authors [20,27,37,62,65,66], the value of γ may vary for a given catalytic system with change in the duration and conditions of polymerisation. A change in the width of the molecular weight distribution is even more probable with change in the chemical composition of the catalyst (either the metal with variable valency [66,67] or the organometallic component [68]). According to some authors [69], the polydispersion decreases considerably when hydrogen is used to control the molecular weight of polyethylene obtained on Ziegler–Natta catalysts.

Thus the absolute values of the rate constants of the separate reactions and the number of active centres determined by kinetic methods cannot be taken as sufficiently reliable. Particularly large errors may arise when catalysts with different chemical compositions are compared.

III. INHIBITION METHOD

A number of authors [29,30,45,70], for the estimation of a number of active centres on heterogeneous catalytic systems in the polymerisation of α-alkenes, have used the inhibition method, which is often used for radical polymerisation. In this method, the concentration of growth centres is estimated from the quantity of inhibitor required for the complete or partial termination of polymerisation.

Carbon tetrachloride [45] and allyl alcohol [70] have been used to inhibit polymerisation on chromium oxide catalysts; the inhibiting action of CCl_4 was found to be much stronger. The inhibition method has also been used [29] to determine the concentration of active centres in the polymerisation of propene on an α-$TiCl_3$ + $AlEt_3$ catalyst. Before the polymerisation, the titanium trichloride was treated with ethanol, and this led to the production of an induction period during polymerisation. Comparison of the initial rates of polymerisation in the "pure" experiments and the experiments in the presence of different quantities of alcohol and catalyst makes it possible, in the opinion of the authors cited, to calculate the concentration of growth centres (Table 1). As in the work with CCl_4, [45] it is assumed that the inhibition of one active centre requires one molecule of alcohol, and allowance is not made for the consumption of alcohol in possible side reactions or as a result of adsorption on the surface of the catalyst, not associated with the catalytic activity. This may lead to high values for the measured number of active centres.

In general it may be noted that the inhibition method in catalytic polymerisation provides only limited possibilities, since it is difficult to select an inhibitor which is used up only in deactivation of the growth centres and which is not used up in reaction with the surface of the catalyst or with components of the reaction system.

IV. METHODS BASED ON LABELLING OF THE POLYMERIC MOLECULE

A tracer can be introduced into a polymeric molecule either at the initiation stage (the use of labelled catalyst components) or during the termination of growth (the stopper method). In the formation of a polymer with high molecular weight, in order to attain the necessary sensitivity in the determination of the number of labelled polymer molecules, it is best to use radioactive isotopes as tracers. Iodine has been used as a non-radioactive tracer for the termination of catalytic polymerisation [6,30,71]. Compounds labelled with carbon-14 and tritium are most frequently used in the study of catalytic polymerisation. Chlorine-36, iodine-131, and zinc-65 have also been used.

1. Use of Labelled Catalyst Components as Tracers

Natta's school [26,31,78] and Chien [24,42] determined the kinetic parameters of growth and initiation from the radioactivity of a polymer obtained in the presence of a labelled catalyst. For heterogeneous systems based on $TiCl_3$, the number of active centres [26,31,72] was determined by two methods: a) by adsorption of labelled alkylaluminium on $TiCl_3$ with subsequent analysis of the reaction products for radioactivity; and b) by carrying out the polymerisation in the presence of labelled trialkylaluminium.

The use of the adsorption method made it possible to establish that the number of labelled alkyl groups on the

surface of titanium trichloride depends on the temperature of adsorption, the conditions of the subsequent washing of the catalyst with a hydrocarbon solvent, and the nature of the organometallic compound. The radioactivity of polypropene obtained on a catalyst treated with labelled alkylaluminium was used to calculate the number of alkyl groups transferred to the polymer; this was taken to be equal to the number of active centres. The value found in this way for the number of active centres was less than or equal to the number of alkyl groups initially combined with the $TiCl_3$ surface. The adsorption method gives the number of active centres initially present on the catalyst surface (n_0). It may not correspond to the steady-state value of the concentration of active centres; this may change after the start of polymerisation and reach a certain constant steady-state value. To estimate the steady-state number of growth centres, use has been made of a method [31] based on the determination of the number of labelled ethyl groups in a polymer, obtained after polymerisation for different periods of time in the presence of free triethylaluminium labelled with ^{14}C. The calculation of the number of active centres from the concentration of labelled ethyl groups in the polymer was based on the assumption that the rate of chain transfer by triethylaluminium and the rate of growth are independent of the duration of polymerisation. Table 1 gives data on the determination of the kinetic parameters of growth [26,31] obtained by both methods.

In an evaluation of the results obtained by the two methods for determining n with a labelled catalyst, it was assumed [31] that the results obtained by the introduction of a labelled co-catalyst into the polymerisation system are more accurate, since when this method is used the influence of foreign radiochemical contamination is smaller and more effective allowance is made for the effect of transfer processes.

A labelled catalyst was also used by Chien [24] to study the kinetics of the polymerisation of propene. Before the reaction, titanium trichloride was treated with diethylaluminium chloride labelled with ^{14}C. An increase in the number of active centres with increase in the $TiCl_3$ concentration at a constant ratio of the titanium and aluminium components was observed; the number of active centres increased with increase in the concentration of $AlEt_2Cl$ at constant concentration of $TiCl_3$, and decreased with increase in temperature in the range 30–90°. Change in the pressure of the monomer had no influence on the concentration of the active centres. The calculated values of k_g were constant in experiments with different concentrations of the monomer, titanium trichloride, and diethylaluminium chloride, and for different yields of polymer (see Table 1).

2. Introduction of Tracers on Termination of Polymerisation

This method is based on the introduction, into the reaction system, of substances (stoppers) which terminate the polymerisation in such a way that a molecule of the substance, or part of it, is attached to the growing polymer chain. If the stopper reacts quantitatively with the growing polymer chains, the number of growth centres can be calculated from the concentration of tracer in the polymer. If however the polymerisation takes place in the kinetic range, the growth rate constants can be calculated from data on the number of growth centres, the rate of polymerisation, and the concentration of monomer.

The stoppers which have been used in anionic and anionic-coordination polymerisation include carbon dioxide labelled with ^{14}C, [73–76] acetic acid in which the active hydrogen was replaced by tritium [77,78], alcohols labelled with tritium in the hydroxyl group [18,19,23,25,38,73,74,79,80], and radioactive iodine [42]. Alcohols labelled with ^{14}C in the alkoxy group [73,81] have been used for cationic polymerisation.

The stopper method has been widely used to determine the number of growth centres in the polymerisation of α-alkenes on complex organometallic catalysts. In most instances, alcohols in which the hydroxyl hydrogen was replaced by tritium were used. This was first done by Feldman and Perry [38] in a study of the polymerisation of ethylene in the presence of the $TiCl_4 + AlEt_3$ system. This work was based on the assumption that if the active catalyst–carbon bond is polarised in such a way that the carbon atom carries a negative charge, as should be the case for a metal–carbon bond, the hydroxyl group should combine with the negatively charged carbon on rupture of the active bond, and the polymer should become radioactive:

$$\text{Cat.}^{+\delta} - - - \overset{-\delta}{\underset{|}{\overset{|}{C}}}\text{—P} + \text{ROT} \rightarrow \text{Cat.—OR} + \text{T—}\underset{|}{\overset{|}{C}}\text{—P}$$

where P represents the polymer chain.

Quantitative reactions of this kind are known for organotitanium compounds of low molecular weight [82]. When CH_3OT is introduced in the polymerisation of alkenes on Ziegler–Natta catalysts, a radioactive polymer is obtained, whereas when methanol $^{14}CH_3OH$ is used as inhibitor, radioactivity is not detected in the polymer [38]. These results indicate that growth takes place at a catalyst–carbon bond, polarised as follows:

$$(\text{catalyst})^{+} \cdots {}^{-}\text{CH}_2\text{—P}$$

This result corresponds to the anionic-coordination mechanism of the polymerisation of α-alkenes, accepted for Ziegler–Natta catalysts.

The method involving the introduction of a tracer into a polymer on termination of the polymerisation by stoppers (chiefly by alcohols labelled with tritium in the hydroxyl group [19,23,25,38,42,79,80] and less frequently by radioactive or non-radioactive iodine [30,42,71]) has been used to obtain the kinetic characteristics of growth in the polymerisation of α-alkenes on many Ziegler–Natta catalytic systems; the results are given in Tables 1 and 3.

The method involving termination by radioactive alcohol has been used to study the polymerisation of ethylene on oxide catalysts [83–89]. In the termination of polymerisation by alcohol in which the hydroxyl hydrogen was replaced by tritium, radioactivity was not detected in the polymer. A radioactive polymer was obtained when methanol labelled with ^{14}C was used for the termination. From these results it was concluded [83,84] that in oxide catalysts the terminal atom of the growing polymer chain carries a positive charge:

$$(\text{catalyst})^{-} \cdots {}^{+}\text{CH}_2\text{=P}$$

Thus polymerisation on oxide catalysts can be classified as belonging to the "cationic-coordination" type of catalytic polymerisation. To explain the nature of the polarisation of the active bond, it was suggested that in this bond the carbon is joined to a more electronegative element; for oxide catalysts, this element may be oxygen [83,86]. The possibility that an active M–C bond with an unusual type of polarisation is formed cannot however be excluded.

Data on the number of growth centres and the growth rate constants for the polymerisation of ethylene on oxide catalysts with different compositions, obtained by terminating the polymerisation by the introduction of $^{14}CH_3OH$, are given in Table 4.

Table 4. Determination of the kinetic parameters of growth for the polymerisation of ethylene on deposited oxide catalysts, by the radioactive stopper method [81-89].

Composition of catalyst	Conditions of activation	Temp. of polymerisation, °C	$10^2 n$, mole per mole of M	k_g, litre mole^{-1} s^{-1}	E_g, kcal mole^{-1}
Cr/SiO_2	Vacuum activation at 400°	75	0.45	695	—
Cr/aluminosilicate (3% Al_2O_3)	То же	75	0.39	350	—
Cr/TiO_2	»	75	0.11	195	—
Cr/ZrO_2	»	75	0.023	133	—
Cr/Al_2O_3	»	75	1.50	47	—
Cr/aluminosilicate (3% Al_2O_3)	»	75	0.255	262	—
ditto	Vacuum activation at 710°	75	0.260	680	—
»	Vacuum activation at 400°	75	0.39	350	—
»	Activated by reduction with SO_2	75	0.47	208	—
»	Ditto CO	75	0.50	1390	—
»	» H_2	75	0.056	695	—
»	» NH_3	75	0.046	2640	—
»	» HCN	75	0.065	2910	—
Cr/Al_2O_3	Activated by reduction with H_2	75	0.043	103	—
Mo/Al_2O_3	ditto	75	0.04	15.3	—
W/Al_2O_3	»	75	0.11	4.7	—
Cr/aluminosilicate	Activated by reduction with CO	75	0.50	1390	—
V/aluminosilicate	ditto	75	0.0057	28	—
Cr/SiO_2	Vacuum activation at 400°	90	0.27	—	—
ditto	ditto	75	0.24	670	—
»	»	60	0.16	468	4.2±0.5
»	»	50	0.130	412	—
»	»	40	0.060	334	—
Cr/Al_2O_3	Vacuum activation at 400°	90	0.86	—	—
ditto	ditto	75	0.65	61	5.4±1.0
»	»	50	0.216	33	—
Cr/Al_2O_3	Activated by reduction with CO	90	0.58	—	—
ditto	ditto	75	0.59	139	—
»	»	60	0.62	103	4.7±1.0
»	»	50	0.45	83	—
»	»	40	0.44	56	—

Evaluation of methods based on the introduction of a tracer. One of the chief difficulties in the quantitative determination of the number of growth centres by the introduction of a tracer into a polymer when complex organometallic catalysts are used is associated with the formation of inactive metal-polymer bonds (MPB) during polymerisation. These bonds arise as a result of chain transfer involving the organometallic co-catalysts. The reaction of inactive MPB with a stopper (alcohol or iodine) also leads to the introduction of a tracer into the polymer, as with active catalyst–carbon bonds. A direct indication of the formation of inactive MPB in a polymerisation system was obtained, for example, by Kohn and coworkers [18], who found that with increase in the duration of polymerisation the number of labelled polymer chains gradually increased, whereas the rate of polymerisation decreased (polymerisation of propene in the presence of $TiCl_3 + AlEt_2Cl$). A sharp increase in the number of labelled chains at constant rate of polymerisation was observed by Coover and coworkers [19].

Different authors have used different methods to introduce corrections for the formation of inactive MPB. The assumptions regarding the mechanism of polymerisation on which these calculations have been based have not always been sufficiently well-founded. According to the results obtained by Coover and coworkers [19], the rate of formation of MPB does not remain constant during the polymerisation—it is much greater in the initial stage than in later stages. In the opinion of the authors cited [19], this result casts doubt on data on the number of growth centres obtained by Natta and coworkers [31], Kohn and coworkers [18], and Chien [42], where the rate of transfer involving the organometallic compound was assumed to be constant, and the analysis for the concentration of tracer was carried out with a polymer obtained after polymerisation for a considerable period of time, as a result of which high values were obtained for the calculated number of active centres. In the calculation of the number of inactive MPB, [18,19] it was assumed that tracers enter all the polymeric molecules; the possibility that polymeric molecules are formed as a result of transfer involving the monomer or spontaneous termination was not taken into account. Coover and coworkers [19] recognise that, because of the difficulty of making allowance for inactive MPB, the accuracy of the determination of n and k_g is insufficient to permit the comparison of catalytic systems with different compositions.

The results obtained by Bier and coworkers [20,80] in a study of the polymerisation of propene on the catalytic system α-$TiCl_3 + AlEt_2Cl$ (or $AlEt_3$) with termination of the reaction by labelled alcohol, differ in many respects from the results of the study of analogous catalytic systems published by other workers [18,19,24,26,31]. In the opinion of Bier and coworkers, reactions involving transfer and termination of the chain with the formation of inactive MPB play a very small role for these catalytic systems, since they found that the molecular weight of the polymer was not influenced by the concentration of organoaluminium compound. The number of growth centres was therefore calculated directly from the concentration of tritium in a polymer obtained after termination of the polymerisation by butanol-^{3}H. These results were criticised by Kohn [30] and Medvedev and coworkers [90], who found for the same catalytic systems that the molecular weight of the polymer depends on the concentration of organometallic co-catalyst, indicating chain transfer, in which the formation of inactive MPB is possible.

The difficulties associated with the formation of inactive MPB can apparently be avoided by using catalytic systems which do not contain free metal alkyls. Youngman and Boor [25] tried to use this system as a model for the determination of the kinetic characteristics of the growth centres (see Table 1), but the results of the determination of k_g obtained by these workers cannot be regarded as unambiguous, since an increase in the number of metal–polymer bonds with time was observed, together with a decrease in the rate of polymerisation.

Oxide catalysts have been found to be more convenient when the method of radioactive stoppers is used, since these catalysts are one-component catalytic systems, which exhibit activity without the addition of organometallic compounds. All the catalyst–polymer bonds present in the system are active, and this makes it possible to calculate the number of growth centres directly from the radioactivity of the polymer [86,88]. For catalysts with the same chemical composition, within the limits of possible experimental error, the value of k_g was not affected by the quantity of inhibitor introduced, the concentration of catalyst in the solvent, the duration of polymerisation up to the moment of termination, the rate of polymerisation, and the porosity and original particle size of the catalyst. The value of k_g was also found to be independent of whether the polymerisation was carried out with or without

a solvent. The fact that the values of k_g were found to be constant provides evidence that the number of growth centres for this catalytic system is determined quantitatively, and that there is no diffusion retardation under these conditions.

The unsatisfactory features of methods in which tritium is used as a tracer include the difficulty of making allowance for the kinetic isotope effect. The magnitude of the isotopic effect in work in which alcohols labelled with tritium were used as stoppers has been estimated from the change in the radioactivity of the polymer on termination of the polymerisation by different quantities of stopper [18,80] or by altering the time interval within which the stopper is introduced into the reaction medium [38]. Considerable differences were observed in the values found for the kinetic isotope effect, the values obtained by different authors [18,19,38,79,80,91] varying from 1 to 4.5.

When iodine is used as stopper, the results of the determination of the number of active centres may be distorted by side reactions leading to a change in the concentration of the tracer in the polymer. One such reaction may be, for example, the formation of terminal vinylidene groups in polypropene with the liberation of hydrogen iodide [15].

In a number of instances, the possibility that the results of the determination of the number of active centres and the calculation of k_g may be distorted because of the influence of the rate of diffusion of the stopper and monomer to the growth centres cannot be excluded. The possibility that the formation of solid polymer during the reaction affects the kinetic relationships has been examined by many authors [23,80,92,93] in studies of the kinetics of the polymerisation of alkenes on Ziegler–Natta catalysts. Coover and coworkers [19] regarded the decrease in the concentration of aluminium alkyl on the catalyst surface due to slow diffusion through the layer of polymer formed as the reason for the decrease in the rate of formation of metal–polymer bonds during polymerisation. Youngman and Boor [25] attributed the decrease in the calculated value of k_g during polymerisation to an increase in the diffusion retardation of the transport of monomer as result of the formation of polymer on the surface of the catalyst. The possibility that the values of k_g found from the results of analysing a radioactive polymer may be distorted by diffusion retardation was also noted by Feldman and Perry [38]. Diffusion retardation was not observed in the polymerisation of ethylene on oxide catalysts when a loose porous polymer powder was formed [94]. When the polymerisation is carried out above 90° in a solvent, a decrease in the concentration of monomer at the surface of the catalyst particles is possible as a consequence of the resistance to diffusion through the layer of partly soluble polyethylene fraction with low molecular weight. This leads to a decrease in the rate of polymerisation on going from 75° to 90° with a constant number of growth centres [88], so that the calculated value of k_g decreases.

V. MECHANISM OF CATALYTIC POLYMERISATION BASED ON MEASUREMENT OF n AND k_g

The value of k_g provides a measure of the reactivity of the active centres with respect to growth. The conclusions which may be drawn from data on the change in n and k_g are more reliable than those obtained by comparing catalysts with respect to the rates of polymerisation relative to unit weight or surface area of the catalyst. We can consider some examples of the use of data on the kinetic parameters of growth to reach conclusions regarding the mechanism of the catalytic polymerisation of alkenes.

1. Number of Growth Centres and Degree of Utilisation of the Metal with Variable Valency

By determining the relative fraction of the metal with variable valency taking part in the formation of the growth centres it is possible to reach certain conclusions regarding the state of the transition element necessary for the manifestation of catalytic activity. In the examination of the mechanism of action of catalysts based on $TiCl_3$, two contradictory viewpoints have been put forward on the question as to which of the surface titanium atoms are potential active centres. Cossee and Arlman [10–12,95–97] formulated a theory, according to which catalytic activity is exhibited by coordinatively unsaturated titanium atoms, with chlorine vacancies, situated on the lateral faces of the $TiCl_3$ crystal; according to this theory, the titanium atoms adjoining the (001) basal plane do not take part in the formation of growth centres. Rodriguez and Van Looy [91] observed the formation of patches of polymer on the surface of a $TiCl_3$ crystal, the positions of which coincided with the points of emergence of spiral dislocations. In their opinion, these results confirm the view that the active centres arise only on the lateral faces of the $TiCl_3$ crystals; active centres are not formed on the basal plane, which makes up 95% of the total surface area of the $TiCl_3$ crystal.

Chirkov and coworkers [17,39] determined the number of growth centres by a kinetic method for a system based on VCl_3 (specific surface $\sim 5\ m^2\ g^{-1}$) and found that the maximum number of active centres amounts to $\sim 5 \times 10^{14}$ centres per cm^2, the order of magnitude of which corresponds to that of the total number of surface vanadium atoms. Thus according to these results, active centres should form on the basal plane of the crystals of the halides of the metals with variable valency.

It should be noted that when the fraction of the metal with variable valency taking part in the formation of growth centres is compared with the total number of surface atoms of the transition metal halides, it is necessary to consider the possibility that reversible deactivation (transfer processes) and irreversible poisoning of the growth centres take place. In general, the following relationship applies for catalytic polymerisation:

$$N = n_g + n_x + n_y \qquad (8)$$

where N is the total number of transition metal atoms capable of taking part in the formation of growth centres ("potentially active centres" or "active component" of the catalyst), n_g the centres joined by an active bond to the growing polymer molecule (actual growth centres), n_x the centres in a state of reversible deactivation as a result of transfer processes ("initiation centres"), and n_y the irreversibly deactivated centres.

Data on the value of n_g, which usually depends markedly on the purity of the polymerisation system and the conditions of preparation of the catalyst, cannot provide an unambiguous basis for obtaining information as to the number of potentially active transition metal ions (the value of N). Analysis of data on the fraction n_g relative to the total number of transition metal atoms in Ziegler–Natta catalysts is made difficult by the fact that most authors do not give data on the surface area of the heterogeneous component of the catalytic system. It may be noted that most papers on catalysts based on $TiCl_3$

($AlEt_2Cl$ and $AlEt_3$ co-catalysts) give similar values for n_g ($0.5\times10^{-2}-5\times10^{-2}$ mole per mole $TiCl_3$ for temperatures in the range 50–70°, which for $TiCl_3$ specimens with a surface area of 5–25 $m^2\,g^{-1}$ corresponds to 10–100% of the surface atoms). Some authors [28] have obtained values of n_g which are clearly greater than the number of titanium atoms adjoining the surface. For systems based on $TiCl_4$ and VCl_4, used for the polymerisation of ethylene (see Table 3), a higher fraction n_g is observed, probably due to the high degree of dispersion of the heterogeneous component.

For oxide catalysts, the fraction of growth centres relative to the total concentration of deposited metal with variable valency depends on the composition of the catalyst (see Table 4). The maximum degree of utilisation of the metal with variable valency, observed for a chromium oxide catalyst on an Al_2O_3 base, amounted to 1.5%. It should however be noted that these results were obtained for comparatively low rates of polymerisation. By decreasing the concentration of impurities in the reaction medium, in particular by carrying out the polymerisation in the gaseous phase, when there is no deactivation of the growth centres by impurities in the solvent, a high rate of polymerisation is achieved on chromium oxide catalysts (up to 1.5×10^5 g polyethylene per g of chromium per hour). Under these conditions, up to 25% of the deposited chromium is present in growth centres. From these results it was concluded [98] that all the chromium with oxidation state +6, present in the deposited oxide catalysts in the form of surface compounds of the chromate type [99], can act as active centres. The formation of growth centres is accompanied by the reduction of Cr^{6+} to compounds of chromium in one of its lower oxidation states (Cr^{2+} and Cr^{3+}). The decrease in the number n_g relative to N is due both to reversible deactivation [100] as a result of transfer involving impurities such as CO, CO_2, and C_2H_2, and to irreversible poisoning (for example as a result of the action of water [51,52]).

The dependence of the number of growth centres on the conditions of polymerisation can give information on the mechanism of their formation. The most detailed results have been obtained by studying the dependence of the number of growth centres on the temperature of polymerisation. If the number of growth centres changes with change in temperature, the total activation energy (E_{form}), determined from the temperature dependence of the rate of polymerisation, differs from the activation energy of growth (E_g), which can be determined from the temperature of k_g. A large amount of published information indicates that the number of growth centres depends on the temperature of the catalytic polymerisation [18,23,24,31,38,42,80,101]. It has been shown [81,101,102] that for systems based on $TiCl_3$ the number of growth centres is inversely proportional to the temperature of the process. The explanation is that the reaction involved in their formation, which takes place when $TiCl_3$ reacts with the metal alkyl, is reversible and reaches equilibrium under the conditions of polymerisation. A characteristic feature is the marked scatter in the values of E_{form} obtained by different authors for catalytic systems with similar compositions [36,38,103–105]. Data on the dependence of E_{form} on the composition of the catalyst are equally contradictory [65,103,105–109].

There is comparatively little published information on the direct determination of E_g from the change in k_g with temperature for complex organometallic catalysts (see Tables 1–3). The values of E_g differ considerably from the values of E_{form} [5,8,18,53,38].

For oxide catalysts it has been shown by the radioactive stopper method that the number of growth centres changes with change in the temperature of polymerisation [88,101]. The nature of this dependence (and hence the value of E_{form}) varies with the composition of the catalyst. From data on the influence of preliminary reduction of the catalyst on the temperature dependence of the number of growth centres, it was concluded that the formation of growth centres in chromium oxide catalysts involves the reduction of sexavalent chromium and is irreversible.

2. Composition of Growth Centres

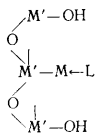
Data on the influence of the composition of a catalyst and the conditions of its preparation on the value of k_g can be used to reach a number of conclusions regarding the composition of the active centres. Unfortunately, for Ziegler–Natta catalysts, different methods for determining k_g for a given catalytic system give values which differ considerably (for example, by a factor of 30 at 70° for the simplest system studied—the polymerisation of propene in the presence of $TiCl_3$ + $AlEt_2Cl$) (see Table 1). There is little published information on the comparison of catalysts with different compositions using values of k_g obtained by the same method. Natta and coworkers [8,35] compared the "viscosity-average" growth rate constants (k_g) for the polymerisation of but-1-ene in the presence of different catalytic systems. They found (Table 2) that k_g is independent of the form of organometallic compound used, but depends on the compound of the metal with variable valency. On the basis of these results, it was concluded [8,35] that for systems based on the same transition metal halide, the growth centres are kinetically equivalent, and their reactivity is independent of the alkylating compound. The difference in the rate of polymerisation for different organometallic components, which in some instances amounts to more than two orders of magnitude, is due entirely to the difference in the number of active centres. Change in the metal with variable valency leads to a change in both the growth rate constant and the number of active centres. The stereoregularity of the polymer was found to depend on the type of metal alkyl, from which it was concluded [8,35] that the active centres are "bimetallic" (include both the metal with variable valency and the metal of the alkylating compound). Cossee and Arlman [10,95–97] formulated the theory that the active centres of the Ziegler–Natta catalysts are "monometallic". Unfortunately, the change in k_g for catalysts not containing alkyls [25], prevents unambiguous results on the influence of the organometallic compound on the kinetic properties of the growth centre being obtained.

Data have been published on the change in the kinetic properties of the growth centres when electron-donor additives are introduced into a catalytic system [9], when hydrogen is introduced into the system [110], and with change in the ratio of the organometallic co-catalyst to the compound of the metal with variable valency [9,38,42,111].

Interesting results were obtained [31] by comparing the radioactivity of the atactic and isotactic fractions of polypropene with their concentration in the polymer; from these results it was concluded that the rate constant for the centres on which the atactic polymer is formed is smaller by a factor of 6 than that for the centres on which the stereoregular polymer is formed.

In a study of the effect of the composition and conditions of preparation of oxide catalysts on the value of k_g, it was

established that k_g is influenced by change in the metal with variable valency (M), the cation of the oxide carrier (M'), the agent used for the preliminary reduction of the catalyst, and the temperature of activation of the catalyst. On the basis of these results, the following scheme[89], giving the composition of the immediate environment of the metal with variable valency in the growth centre of oxide catalysts was proposed:



Here, L represents the ligand which forms part of the growth centre after treatment of the catalyst with an agent capable of forming coordination compounds. The rate constants for transfer (involving the monomer and the spontaneous process), determined from the dependence of the molecular weight on the conditions of polymerisation, depend on the same factors as the value of k_g.[112]

3. Mechanism of Growth

The number of growth centres for different concentrations of monomer has been measured, and it has been shown that the reaction involved in growth is first order with respect to the monomer for catalysts based on transition metal halides[8,18,24,35] and for chromium oxide catalysts[88].

In most schemes proposed to explain the mechanism of the catalytic transformation of alkenes in the presence of transition metal compounds, it is considered that a necessary stage is preliminary complex formation by the alkene (the so-called coordination mechanisms[109,113]), as a result of which the double bond is weakened and its reactivity increases. For a two-stage mechanism of polymerisation, including as first stage the formation of a π-complex[9-12], the first order kinetics of the reaction with respect to monomer may correspond to case 2 [see Eqn. (1)]:

1. $k_g = k_1$; in this instance, E_g corresponds to the activation energy of the formation of the π-complex;
2. $k_g = K_a.k_2$; in this instance, $E_g = E_2 - Q$, where E_2 is the activation energy of the introduction of ethylene at the active bond; Q the heat of formation of the π-complex, and $K_a = k_1/k_{-1}$ the equilibrium constant for the formation of the π-complex.

In the opinion of Natta and coworkers[8], the limiting stage in the polymerisation of alkenes on catalysts based on transition metal halides is the first stage (the formation of the π-complex). In a number of instances, low values were found for E_g (2.5 kcal mole^{-1} for a catalyst based on VCl_3; 4.5 kcal mole^{-1} for a catalyst based on $TiCl_3$; and 4–5 kcal mole^{-1} for chromium oxide catalysts). In these instances the pre-exponential factors have anomalously low values (10^5–10^6 litre mole^{-1} s^{-1}). A possible reason is that the formation of the surface π-complexes is accompanied by a marked decrease in entropy. At the present time, however, there are no unambiguous data which exclude the possibility that for the catalytic polymerisation of alkenes the second situation is realised ($k_g = K_a.k_2$), and the value found for E_g is not the activation energy of the elementary stage.

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After the present review had been written, a number of new papers were published[32-34,47-49], giving results of the determination of the number of growth centres and the growth rate constants for the catalytic polymerisation of alkenes. These results are included in Tables 1 and 3.

Papers[32,33] based on previously developed kinetic methods and the inhibition method give new data on the values of n and k_g for the polymerisation of alkenes in the presence of complex catalysts based on $TiCl_3$ and VCl_3. The values obtained for n correspond to almost complete coverage of the catalyst surface, from which it follows that the active centres are situated chiefly on the basal planes of the $TiCl_3$ and VCl_3 crystals. These results were used to provide a basis for a model of a stereospecific active centre, which is localised on the basal plane and which has two vacancies per transition metal ion in the growth centre.

Radioactive inhibitors have been used[48,49] to determine the kinetic parameters of growth in the polymerisation of ethylene on titanium dichloride, which is active in the polymerisation of alkenes without the addition of organometallic compounds. In addition to the labelled alcohol which is usually employed for this purpose, $^{14}CO_2$, ^{14}CO, and $^{14}CH_3CH_2CH_2I$ were used. For this one-component heterogeneous catalytic system, since there are no inactive aluminium–polymer bonds, the method of radioactive inhibitors makes it possible to determine reliably the number of growth centres. The results obtained show that the value of n amounts to not more than ~0.1% of the number of surface titanium atoms in the $TiCl_2$ specimens used. The probable explanation is that the alkylation of titanium by ethylene under mild conditions takes place on surface defects of the $TiCl_2$ crystals. The value of k_g found in these experiments is greater by about two orders of magnitude than the values of k_g obtained for the polymerisation of ethylene on catalysts based on $TiCl_3$.[32,37,38]

The use of radioactive inhibitors of different types to study one-component heterogeneous catalysts (chromium oxide and titanium dichloride) also gave results[49] confirming the coordination mechanism of growth in the catalytic polymerisation of alkenes.

A number of papers published in recent years have been devoted to the study of the morphology of polyalkene crystals formed directly during polymerisation ("primordial morphology"). These results can be used to reach an understanding of the mechanism of formation of a solid polymer on the surface of a solid catalyst. In particular, values of the growth rate constants have been calculated[34,47] from the results of an electron-microscope study of polyalkene crystals produced in the initial stage of polymerisation. The value of k_g found[47] for the polymerisation of ethylene on a chromium oxide catalyst is close to the value of k_g obtained for catalysts with the same composition by the radioactive inhibitor method. The value of k_g obtained[34] for the polymerisation of propene on the $TiCl_3 + Al(CH_3)_3$ catalytic system is smaller by two orders of magnitude than the values given above for analogous systems (see Table 1).

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