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The Mechanism of the Catalytic Polymerisation of Olefins Based on the Number of Active Centres and the Rate Constants for Individual Stages

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New data on the numbers of active centres and rate constants for individual stages in the catalytic polymerisation of olefins in the presence of two-component catalysts, obtained by the method of selective radioactive inhibitors, are considered. Certain general aspects of the mechanism of the catalytic polymerisation of olefins are examined on the basis of these data as well as the results of the study of one-component organometallic catalysts and quantum-chemical investigations of the propagation reaction.
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I. INTRODUCTION

One of the main problems arising in the study of the kinetics and mechanism of catalytic polymerisation involves the determination of the number of active centres (AC). The active centre (propagation centre) is understood as a transition metal compound containing metal–carbon alkyl-type σ-bond whereby the monomer is inserted in this bond via repeated addition steps:

$$L_xM-CH_2\sim\sim + CH_2=CH_2 \rightarrow L_xM-CH_2-CH_2-CH_2\sim\sim, \quad (I)$$

where M is the metal, L_x are ligands, and $CH_2\sim\sim$ is the polymer chain.

For solid catalysts, the active centre is an organometallic surface compound. Information about the influence of the composition and conditions of the preparation of the catalyst, the polymerisation conditions, and the nature of the monomer on the number and reactivity of the AC constitutes the basis of the study of processes involving the formation of AC, their composition, and the polymerisation mechanism.

The difficulty of determining the number of AC arises from the fact that this quantity constitutes as a rule a small fraction of the total number of transition metal atoms in the catalyst. Studies designed to determine the number of AC in the catalytic polymerisation of olefins were begun by Natta[1,2], Chien[3], and Feldman and Perry[4]. Subsequently numerous investigations were devoted to this problem and have been considered in a number of reviews[5–9]. The greatest difficulties in the determination of the number of AC arise for polymerisation in the presence of two-component Ziegler–Natta catalysts, since in this case the reaction medium contains, apart from the active titanium–polymer bonds, also inactive aluminium–polymer bonds, formed as a result of the transfer of the polymer chain with the organoaluminium compound. It has therefore been suggested that selective radioactive inhibitors, which interact, like the olefin, with the active transition metal–polymer bond but not with aluminium–polymer bonds, be used to determine the number of AC in two-component systems[10,11]. This approach to the determination of the number of AC has been used recently to investigate catalytic systems based on titanium chlorides. A series of new data were obtained concerning the influence of the composition of the catalyst and the polymerisation conditions on the number of AC and the rate constants for the individual stages; together with the results of the study of polymerisation mechanism in the presence of one-component organometallic catalysts and individual organometallic compounds as well as quantum-chemical investigations of the mechanism of the propagation reaction, these data make it possible to consider certain general aspects of the mechanism of the propagation reaction in catalytic polymerisation.

II. DETERMINATION OF THE NUMBER OF PROPAGATION CENTRES USING SELECTIVE RADIOACTIVE INHIBITORS

1. General Remarks Concerning the Method

The determination of the number of AC by the method of radioactive inhibitors is based on the introduction of a radioactive label into the growing polymer chain when the inhibitor interacts with the active metal–polymer bond:

$$L_xM-CH_2\sim\sim + RO^3H \rightarrow L_xM-OR + {}^3HCH_2\sim\sim. \quad (IIa)$$

Calculations of the number of AC (c_p = mol per mol of transition metal) and the propagation rate constant (k_p) are performed using the following equations:

$$c_p = Ag/aQ, \quad (1)$$

$$k_p = v/3{,}6c_p c_m M, \quad (2)$$

where A is the radioactivity of the polymer (c g^{-1}), g the amount of the polymer (g), a the amount of the catalyst (mol of transition metal), Q the specific radioactivity of the inhibitor (c mol^{-1}), k_p the propagation rate constant (litre mol^{-1} s^{-1}), v the rate of polymerisation at the instant of the introduction of the inhibitor (g per mmol of transition metal per hour), c_m the concentration of the monomer (M), and M the molecular weight of the monomer.

The principal criteria for the quantitative determination of c_p are as follows: (1) agreement between the values of c_p and k_p obtained using different inhibitors, interacting with

the metal–polymer active bond via different mechanisms; (2) the independence of the k_p determined with the aid of the same inhibitor of the polymerisation termination conditions, for example, of the concentration and specific radioactivity of the inhibitor, its residence time in the reaction medium after the cessation of polymerisation, the rate of polymerisation at the instant of the introduction of the inhibitor, etc.

Table 1. The values of c_p and k_p for the polymerisation of ethylene in the presence of $TiCl_2$ at 75 °C with $c_m = 0.33$ M (residence time of ^{14}CO in the reaction medium 20 min).

Inhibitor	Q, μc mol^{-1}	c_i, mol/mol Ti	v, s/mmol Ti h	$10^5 c_p$, mol/mol Ti	$10^{-4}k_p$, litre mol^{-1} s^{-1}	Refs.
^{14}CO	1210	0.01	9.2	2.3	1.2	10
$^{14}CO_2$	2760	0.04	14.5	3.4	1.25	10,16
$^{14}C_3H_7I$	450	0.85	7.5	2.2	1.0	10,15
$^{35}SO_2$	2230	0.02	20	4.5	1.35	16
$CH_3O^{32}H$	2680	0.14	37	3.6	31	16

Note. Q is the specific activity of the inhibitor, c_i the concentration of the inhibitor, and γ the kinetic isotopte effect.

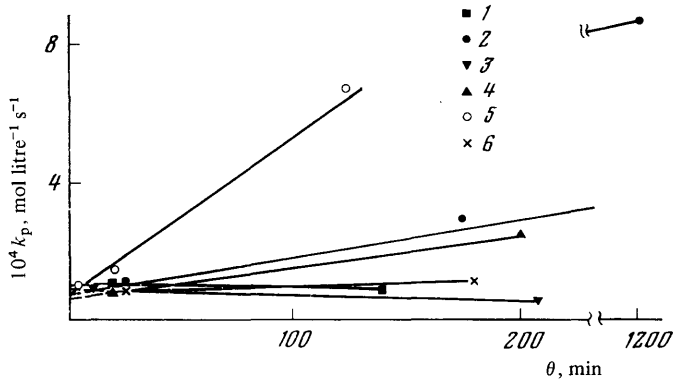


Figure 1. Dependence of the calculated quantity $1/k_p$ on the residence time of inhibitors of various types in the reaction medium after the cessation of polymerisation at 75 °C; $[C_2H_4] = 0.33$ M;[18] 1)–3) $TiCl_2$ catalyst; 4)–6) $TiCl_2$ + $AlEt_2Cl$ catalyst (Al/Ti = 1); 1) and 4) $^{14}CO_2$; 2) and 5) ^{14}CO; 3) and 6) $^{35}SO_2$. $1/k_p$ is proportional to the number of radioactive labels in the polymer.

^{14}CO and $^{14}CO_2$ have been suggested as selective inhibitors[10,11]. Labelled carbon dioxide can be used to determine the number of active bonds (for example Ti–C) in the presence of organoaluminiumhalogeno-compounds:

$$L_xTi{-}CH_2{\sim\!\sim} + {}^{14}CO_2 \rightarrow L_xTi{-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim}. \qquad \text{(IIb)}$$

It is known that, in contrast to trialkyl derivatives of aluminium, CO_2 does not interact with the Al–C bond when even one alkyl group at the aluminium atom is substituted by a halogen[12]. The use of ^{14}CO as the selective inhibitor is based on the familiar reaction involving the insertion of carbon monoxide in the transition metal–carbon bond[13]:

$$L_xM{-}R + CO \rightleftarrows L_xM(\overset{\downarrow}{CO}){-}R \rightarrow L_xM{-}\overset{\overset{O}{\|}}{C}{-}R. \qquad \text{(IIc)}$$

This reaction proceeds via the preliminary coordination of CO to the transition metal ion, as has been suggested for the olefin in the polymer chain propagation reaction[14].

2. The Use of Radioactive Inhibitors for One-Component Catalysts

The possibility of using ^{14}CO and $^{14}CO_2$ for the quantitative determination of c_p has been tested[10,14,16] on the one-component $TiCl_2$ catalyst active in the absence of an organoaluminium cocatalyst. The propagation rate constants in the polymerisation of ethylene in the presence of $TiCl_2$, determined with the aid of various inhibitors, are similar (Table 1). A more convenient inhibitor for the above catalytic system is $^{14}CO_2$, since, unlike the system with ^{14}CO, in this case there is no accumulation of the labels in the polymer as a function of the residence time of the inhibitor in the reaction medium (Fig.1). Quantiative data for the interaction of $^{14}CO_2$ with the propagation centre in the polymerisation of ethylene in the presence of $TiCl_2$ have been obtained[16] in experiments where the polymerisation termination conditions were varied (the concentration of the inhibitor, its specific radioactivity, the rate of polymerisation at the instant of termination, the yield of polymer, etc).

3. The Use of Selective Inhibitors for Two-Component Catalysts

A preliminary study of the possibility of determining c_p with the aid of ^{14}CO and $^{14}CO_2$ in the presence of organoaluminium compounds was made in the presence of the $TiCl_2$ + $AlEt_2Cl$ catalytic system[9,10]. With increased residence time of these inhibitors in the reaction medium after the cessation of polymerisation, an increase in the number of labels in the polymer is observed, and hence a decrease of the calculated k_p (Fig.1). The increase of the number of labels in the $TiCl_2$ + $AlEt_2Cl$ + $^{14}CO_2$ system (Fig.1, curve *4*) can apparently be accounted for by the regeneration of the active centre by the organoaluminium compound:

$$L_xTi{-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim} + AlEt_2Cl \rightarrow L_xTi{-}Et + EtAl(\underset{Cl}{|}){-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim}. \qquad \text{(IId)}$$

The involvement of $AlEt_2Cl$ in this process is indicated by the finding that the number of labels in the polymer in the presence of the $TiCl_2$ + $^{14}CO_2$ system (in the absence of $AlEt_2Cl$) is almost independent of the residence time of $^{14}CO_2$ in the reaction medium (Fig.1, curve *1*).

In the $TiCl_2$ + $AlEt_2Cl$ + ^{14}CO system the increase of the number of labels in the polymer with the residence time of ^{14}CO (Fig.1) can be attributed to the slow copolymerisation of carbon monoxide with the olefin, apart from a reaction analogous to (IId). The possibility of this reaction was demonstrated in the polymerisation of ethylene in the presence of the $TiCl_2$ one-component catalyst, for which there is no reaction (IId). It was found that, for a sufficiently long residence time of ^{14}CO (more than 20 min), the number of labels in the polymer exceeds the number of propagation centres determined using other inhibitors[14].

The possibility of a quantitative determination of the number of propagation centres with the aid of ^{14}CO has been tested in detail on the $TiCl_2$ + $AlEt_2Cl$ [10] and $TiCl_3.0.3AlCl_3$ +

$AlEt_3$ [17] catalytic systems in the polymerisation of ethylene and on the $TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$ system[11,17,18] in the polymerisation of propene and the following data were obtained.

(1) The nature of the variation of the number of labels in the polymer with the residence time of ^{14}CO after the cessation of polymerisation indicates a sharp alteration of the rate of accumulation of labels in the first minutes after the termination of polymerisation (Fig.2).[18] Apparently there is initially a fairly rapid insertion of the first ^{14}CO molecule in the Ti–C bond, after which a slow increase of the number of labels in the polymer is observed as a result of the copolymerisation of ^{14}CO with the olefin. It is noteworthy that the processes involving the accumulation of labels in the polymer as a function of the inhibitor residence time are fairly slow when either ^{14}CO or $^{14}CO_2$ are used. Extrapolation of the number of labels to the initial instant, when the influence of side processes leading to the accumulation of radioactivity has been reduced to a minimum, shows (Fig.1) that, regardless of the inhibitor employed, the constant k_p in the polymerisation of ethylene in the presence of $TiCl_2$ lies within a fairly narrow range of values [$(1.5 \pm 0.5) \times 10^4$ litre mol^{-1} s^{-1}].

(2) the insertion of ^{14}CO in the Ti–C bond is an irreversible process (there is no decarboxylation reaction), which is indicated by the conservation of the number of labels in the polymer after the removal of ^{14}CO from the reaction medium, despite the restoration of the activity of the catalytic system under these conditions[18].

(3) The copolymerisation process can be stopped by adding phosphine to the reaction medium. The constant k_p, determined from the number of labels in experiments with the addition of PH_3 for long reaidence times of the ^{14}CO + PH_3 mixture in the reaction medium, is close to the value of k_p found for short residence times of ^{14}CO.[11]

(4) The constant k_p calculated from the number of labels after a short residence time of ^{14}CO is independent of the polymerisation termination conditions—the inhibitor concentration, the yield of the polymer, the surface concentration of the propagation centres, etc.[17]

(5) As for the catalysts based on $TiCl_2$, the value of k_p found using ^{14}CO for the $TiCl_3$ + $AlEt_2Cl$ + C_3H_6 system is close to that found with the aid of another inhibitor—$^{14}CO_2$.[11]

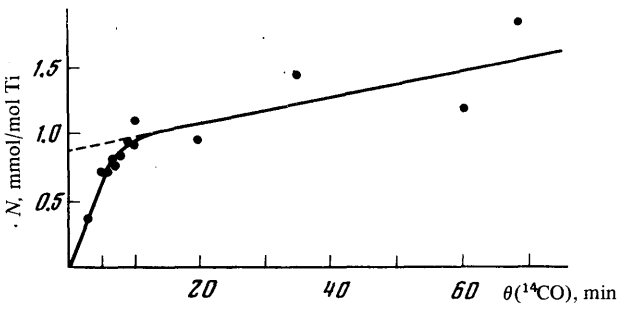


Figure 2. Dependence of the number of labels (N) in non-atactic polypropylene on the residence time of ^{14}CO in the reaction medium after the cessation of polymerisation[18]; catalyst—δ-$TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$; 70 °C; [Ti] = (1–2) × 10^{-3} M; [$AlEt_2Cl$] = 3×10^{-3} M; [C_3H_6] = 1 M; molar ratio ^{14}CO/Ti = 0.5–1.0.

Thus a quantitative determination of c_p and k_p in the polymerisation of olefins in the presence of two-component catalysts is possible when the ^{14}CO and $^{14}CO_2$ selective catalysts are used. ^{14}CO is preferable, since $^{14}CO_2$ is a less effective inhibitor (at the same concentrations) than ^{14}CO and can be used only in two-component systems containing a halogen-substituted cocatalyst.

4. The Use of an Alcohol RO^3H as an Inhibitor

The use of an alcohol RO^3H as an inhibitor in two-component catalysts is possible, as stated previously[19], when the following factors are taken into account. Firstly, in the case of non-stationary polymerisation kinetics, where c_p varies with the reaction time, the number of propagation centres must be determined from the dependence of the total number of metal–polymer bonds on the yield of the polymer but not on the polymerisation time. Secondly, the use of an alcohol for the determination of c_p is possible when the number of inactive metal–polymer bonds differs comparatively little from c_p. This can be observed either for very low yields of the polymer or under conditions and for catalytic systems such that the rate of formation of inactive metal–polymer bonds is fairly low, for example, in the polymerisation of 4-methylpent-1-ene in the presence of VCl_3 + $Al(iso\text{-}Bu)_3$.[20] Thirdly, in the study of the influence of polymerisation conditions and catalyst composition on the number of propagation centres, account must be taken of the fact that, when these parameters are varied, there is a possibility also of a change in the rate of formation of metal–polymer bonds.

Table 2. The values of ν_{max}, c_p^{max}, and k_p for "massive" and deposited catalysts based on titanium chlorides.

Catalyst	Cocatalyst [(3–10) × 10^{-3} M]	ν_{max}, g/polymer/mmol Ti h atm	$10^4 c_p^{max}$, mol/mol Ti	$10^{-2}k_p$, litre mol^{-1} s^{-1}
Polymerisation of ethylene, 75 °C				
$TiCl_2$	—	8.0	1.1	120[10,16]
$TiCl_2$	$AlEt_2Cl$	5.5	0.75	120[10]
α-$TiCl_3$	$AlEt_3$	35.0	4.0	140[17]
δ-$TiCl_3$·0.3 $AlCl_3$	$AlEt_3$	72.0	9.7	120[17]
δ-$TiCl_3$·0.3 $AlCl_3$	$Al(iso\text{-}Bu)_3$	96.0	11.2	140[17]
$TiCl_3$ on SiO_2	$AlEt_3$	960	110	140[23]
α-$TiCl_3$·0.5 $AlCl_3$ on polyethylene	$AlEt_3$	720	89	130[23]
$TiCl_4$ on R_xMgCl_y	$AlEt_3$	29 000	3600	130[23]
Polymerisation of propene, 70 °C				
$TiCl_2$	—	0.005	0.013	0.76[10]
$TiCl_2$	$AlEt_2Cl$	0.004	0.0085	0.94[10]
α-$TiCl_3$	$AlEt_2Cl$	0.11	0.33	0.71[17]
δ-$TiCl_3$·0.3 $AlCl_3$	$AlEt_2Cl$	7.7	17	0.90[11,17]
δ-$TiCl_3$·0.3 $AlCl_3$	$AlEt_3$	28	58	1.00[17]
δ-$TiCl_3$·0.3$AlCl_3$	$Al(iso\text{-}Bu)_3$	36	80	0.90[17]
α-$TiCl_3$·0.5$AlCl_3$ on polyethylene	$AlEt_2Cl$	10	20	1.0

Note. In the case of the polymerisation of propene data are given for the polymer fractions insoluble in boiling ether (for $TiCl_3$) and n-heptane (for $TiCl_2$).

The correct application of a radioactive alcohol as an inhibitor enabled some workers to obtain values of k_p = 20–50 litre mol^{-1} s^{-1} in the polymerisation of propene in the presence of the $TiCl_3$ + organoaluminium cocatalyst system[21,22], differing comparatively little from the corresponding k_p obtained with the aid of ^{14}CO and $^{14}CO_2$ (Table 2).

III. THE NUMBER OF PROPAGATION CENTRES AND PROPAGATION RATE CONSTANTS FOR CATALYSTS BASED ON TITANIUM CHLORIDES

1. The Number and Composition of Propagation Centres

The number of AC depends significantly on the catalyst preparation and polymerisation conditions (for example, the purity of the reactants). When problems concerning the composition of the AC and the mechanism of their formation are considered, data concerning the maximum number of AC (c_p^{max}) for the system investigated are important. The quantity c_p^{max} can be calculated from the maximum observed rate of polymerisation and k_p for the given catalytic system.

Table 2 presents the values of c_p^{max} for different catalytic systems based on titanium chlorides[24]. Evidently the conditions in the preparation of titanium chlorides and the catalyst composition as well as the nature of the organoaluminium cocatalyst and the monomer influence significantly the number of AC. In the case of the $TiCl_2$ one-component catalyst (specific surface 25 $m^2\ g^{-1}$) the maximum number of propagation centres (approximately 10^{-4} mol per mol of titanium) does not exceed approximately 0.3% of the number of surface titanium atoms[16], which is apparently associated with the fact that the alkylation of titanium ions by ethylene takes place only on surface defects of the $TiCl_2$ crystals with a high degree of coordination unsaturation. Naturally, the fraction of such surface atoms cannot be large. For $TiCl_2$ and $TiCl_3$ 0.1–1 μm crystals (specimens which are not specially activated by grinding), the fraction of surface titanium atoms having one or two chlorine vacancies is 10^{-2}–10^{-3} and 10^{-4}–10^{-6} mol/mol Ti respectively. The latter value agrees with the number of propagation centres for $TiCl_2$ (Table 2).

In typical Ziegler–Natta catalysts based on $TiCl_3$, the number of propagation centres depends significantly on the preparation conditions and composition of titanium trichloride. The maximum number of propagation centres in catalysts based on $TiCl_3$ is 1×10^{-2} mol/mol Ti, i.e. 1% of the total content of titanium ions in the catalyst (Table 2). In estimating the surface concentration of propagation centres, account must be taken of the possibility of a change in the specific surface as a result of the comminution of the catalyst by the crystalline polymer in the polymerisation process; experimental evidence for this has been obtained in a number of studies[25,26]. Comminution of the catalyst in the polymerisation process apparently constitutes the physical basis of the correlation observed[27,28] between the size of the primary crystallites, determined by X-ray diffraction, and the activity in the polymerisation of propene. In this case the number of propagation centres must be referred to the surface area of the primary crystallites (calculated from their dimensions), which is formed in the polymerisation process as a result of the comminution of the catalyst and can be significantly greater than the surface area of the initial catalyst.

When titanium chloride is deposited on silica gel or powdered polyethylene, it is possible to increase the number of propagation centres in the polymerisation of ethylene approximately by an order of magnitude and to attain the same values as in the polymerisation of propene in the presence of massive $TiCl_3$ (Table 2). A finely dispersed $TiCl_3$ phase is formed as the active component on the surface of silica gel and polyethylene[29,30]. The use of these carriers hardly influences the number of propagation centres in the polymerisation of propene (Table 2).

Titanium–magnesium catalysts, obtained by depositing $TiCl_4$ on magnesium chloride or alkylmagnesium chloride, exhibit a maximum activity among all known catalytic systems[31]. In this case the number of AC can reach approximately 40% of the total number of titanium atoms in the catalyst (Table 2). The activity of the above catalysts probably reaches a limiting value for catalytic systems based on titanium chlorides. Strong binding of titanium tetrachloride to magnesium chloride is achieved by the insertion of titanium ions in defect sites of the disordered crystal structure of magnesium chloride[32]. This type of the interaction ("structural" binding) ensures a high degree of utilisation of titanium ions and their stability under the polymerisation conditions[33].

The difference between the activities of catalytic systems based on titanium chlorides, reaching four orders of magnitude (Table 2), is also caused by the change of the number of AC; the reactivity of a single propagation centre for a given olefin hardly changes. These data show that the AC in Ziegler catalysts are monometallic, i.e. their composition includes only one transition metal ion.

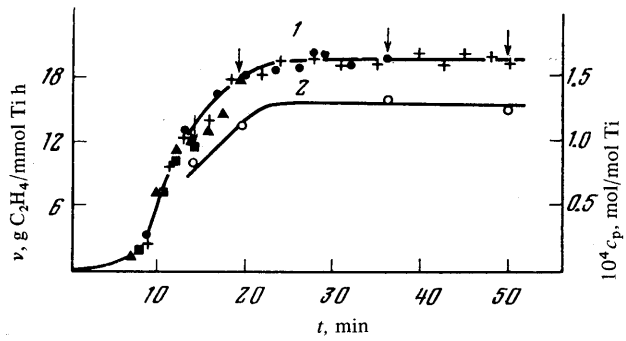


Figure 3. Dependence of the rate (v) of polymerisation of ethylene (curve *1*) and of the number of propagation centres (c_p) (curve *2*) on the polymerisation time *t*; $TiCl_2$ catalyst; 60 °C; $[C_2H_4] = 0.2$ M.[16] The arrows indicate the instants of the introduction of the $^{14}CO_2$ inhibitor in individual experiments where the number of propagation centres was determined.

2. Description of the Kinetics on the Basis of the Number of Propagation Centres

Data have been obtained[16,17,34,35] for the influence of polymerisation conditions (time, monomer concentration, and temperature) on the rate of polymerisation, the number of propagation centres, and the propagation rate constant in the polymerisation of ethylene and propene in the presence of the $TiCl_2$, δ-$TiCl_3.0.3AlCl_3$ + $AlEt_3$, and δ-$TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$ catalysts. The variations of the rate of polymerisation of ethylene and of the number of propagation centres with the reaction time are compared in Fig.3 for $TiCl_2$. Evidently the rate of polymerisation and the number of AC vary in parallel. Similar relations have been obtained also for other catalysts[17]. These results show that the propagation rate constant being determined is independent of the polymerisation time and of the yield of the polymer. Consequently the

hypotheses, occasionally encountered in the literature, concerning the influence on k_p of the length of the polymer chain or diffusion-dependent limitations in the polymer formed in the presence of such catalysts are not well founded. The constant k_p is independent of the monomer concentration[17,34]; the number of AC , which determines the steady-state reaction rate, is also independent of the monomer concentration.

On the basis of data for the variation of the steady-state rate of polymerisation, k_p, and c_p with the reaction temperature, it is possible to calculate the corresponding effective activation energies E_{eff}, the activation energies for the propagation step E_p, and the temperature coefficient of the change in the number of active centres ($E_{c_p} = E_{eff} - E_p$).

The energies obtained (kcal mol^{-1}) for the polymerisation of ethylene and propene in the presence of titanium trichloride[35] are listed below:

Catalyst	Monomer	E_{eff}	E_p	E_{c_p}
$TiCl_3$+$AlEt_3$	ethylene	6.0	3.0	3.0
$TiCl_3$+$AlEt_2Cl$	propene	11.0	5.5	5.5

Evidently appreciable differences between E_p and E_{eff} are observed for two-component catalysts. This is caused by the increase of the number of propagation centres with increase of polymerisation temperature, which is associated with the reversible adsorption of the organoaluminium cocatalyst on the propagation centres[10,35,36].

The values of E_p found for titanium chlorides are low compared to the activation energy in radical polymerisation (Table 3).

Table 3. The coefficients of the equation $k_p = 10^5 A_p \cdot \exp(-E/RT)$ for the catalytic polymerisation of olefins.

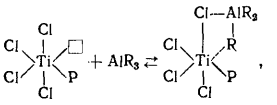
Catalyst	Monomer	A_p, litre mol^{-1} s^{-1}	E_p, cal mol^{-1}	Refs.
CrO_3/SiO_2	C_2H_4	4.5	4 500	37
$TiCl_3$+$AlEt_3$	C_2H_4	8.0	3 000	35
$TiCl_3$+$AlEt_2Cl$	C_3H_6	3.0	5 500	35
$AlEt_3$	C_3H_6	0.02	12 000	62
Radical initiator	C_2H_4	67	5 000	38

3. The Role of the Organometallic Cocatalyst

Comparative study of the one-component $TiCl_2$ catalyst and $TiCl_n$ + AlR_xCl_y two-component systems gives rise to new possibilities for the elucidation of the role of the organometallic cocatalyst in the regulation of the activity and stereospecificity of Ziegler–Natta catalytic systems.

The stereospecificity of the active centres. The data obtained for the polymerisation of propene in the presence of $TiCl_2$ concerning the stereoregular structure of the polymer (60% of X-ray-amorphous atactic polymer and 25% of the highly crystalline fraction)[10,36] show that at least two types of active centres exist on the surface of titanium chloride—non-stereospecific centres leading to the formation of the atactic polymer and isospecific centres giving rise to the stereoregular polymer. The difference between them apparently consists in the number and steric dispositions of the chloride ions surrounding the titanium ion (in conformity with the ideas of Cossee and Arlman[39,40]).

Adsorption of the organoaluminium catalyst on the active centre. It has been shown[9,10] that the rate of polymerisation of ethylene and propene decreases following the addition of $AlEt_2Cl$ to $TiCl_2$. Under these conditions, there is mainly a decrease in the number of non-stereospecific polymerisation centres. This explains the higher stereospecificity of the $TiCl_2$ + $AlEt_2Cl$ system compared with $TiCl_2$ alone. When the organoaluminium cocatalyst (OAC) is added to $TiCl_2$, it apparently undergoes equilibrium adsortion on the AC:



(III)

(P is the polymer chain and □ a free coordination site), as a result of which the propagation centre passes temporarily from the active to the inactive state.

Ideas concerning the possibility of the reversible adsorption of the OAC on the active centres of the VCl_3 + AlR_3 catalyst were also formulated by Tait and coworkers[41].

Analogous processes can occur during chain propagation also in the presence of $TiCl_3$. The adsorption of the OAC on the propagation centres formed on the $TiCl_3$ surface can explain the experimentally observed decrease of c_p with decrease of temperature, i.e. $E_{c_p} > 0$, and with increase of the OAC concentration[42]. The equilibrium constant for the adsorption of $AlEt_3$ on the AC (K_A) of the $TiCl_3.0.3AlCl_3$ + $AlEt_3$ catalytic system was calculated from the temperature variation of c_p. It amounts to $3.9 \times 10^{-10} e^{18\,500/RT}$ litre mol^{-1} [42] and the effective heat of adsorption of $AlEt_3$ on the active centre is approximately 10 kcal mol^{-1} after the subtraction of the heat of dissociation of the dimeric molecule $[AlEt_3]_2$.

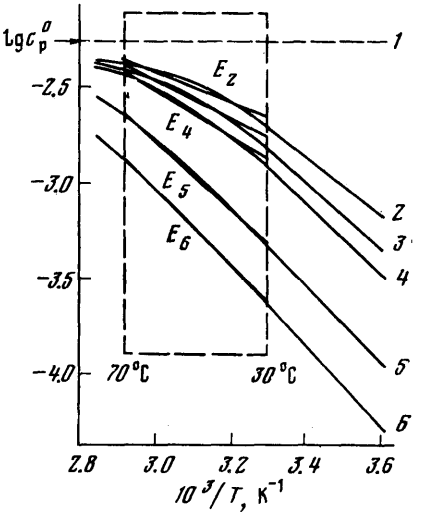


Figure 4. Calculated relations between the number of propagation centres (c_p) and the polymerisation temperature at different $AlEt_3$ concentrations[42]: 1) 0; 2) 6×10^{-3}; 3) 1.5×10^{-2}; 4) 3×10^{-2}; 5) 3×10^{-1}; 6) 1.5; corresponding activation energies (kcal mole^{-1}): $E_2 = 2.8$; $E_4 = 5.0$; $E_5 = 8.3$; $E_6 = 9.2$.

The number of AC (and correspondingly the rate of polymerisation) can be calculated from K_A at different temperatures and $AlEt_3$ concentrations (Fig.4). The temperature coefficient of the change in the number of propagation centres E_{c_p}, characterising the slope of the curves in Fig.4, varies both with polymerisation temperature at the same $AlEt_3$ concentration and as the OAC concentration is varied for the same temperature range. In the range 30–70 °C, which is most commonly investigated, the quantity E_{c_p} varies only slightly with temperature at the same $AlEt_3$ concentration (within the limits of experimental error). More appreciable changes in E_{c_p} in the above temperature range are observed as the $AlEt_3$ concentration is varied (Fig.4, cf. curves *2* and *6*). Thus, at a fairly high OAC concentration, amounting to 1.5 M, calculation leads to the expectation of an increase in the effective activation energy for the polymerisation of ethylene and propene up to 12 and 14.5 kcal mol^{-1} respectively, which is close to the experimental values of E_{eff} obtained under these conditions[42].

It follows from the data in Fig.4 that at low temperatures a change in the OAC concentration can influence c_p appreciably. Indeed at 30 °C in the $AlEt_3$ concentration during the experiment leads to a significant alteration of the rate of polymerisation, which is reversible and agrees satisfactorily with calculated data[42].

The influence of the nature of the organoaluminium cocatalyst on activity and stereospecificity. Since the OAC does not enter into the composition of the propagation centres, the influence of the type of OAC on the catalytic properties can be due to a change in the total number of propagation centres and the ratios of the numbers of centres of different types. In the polymer chain propagation stage this can occur as a result of the adsorption of the OAC on the AC. The influence of the nature of the OAC on the nature and heat of chemisorption can be determined by two factors: the Lewis acidity and the size of the OAC molecule.

Accordingly, in the case of the $TiCl_2 + AlR_xCl_y$ catalyst one should expect a decrease of activity in the sequence $AlEt_3 > AlEt_2Cl > AlEtCl_2$, which has been confirmed by experimental data[36]. The decrease of the degree of isotacticity of polypropylene in the same sequence can apparently be accounted for by the influence of the size of the OAC on adsorption on centres with different steric environments. Evidently, in adsorption on isospecific propagation centres, which are least accessible, the influence of the size of the OAC molecule is greater than in adsorption on non-stereospecific centres. With decreased size of the OAC molecule, one should expect a decrease in the fraction of isospecific propagation centres in the active state.

For $TiCl_3$, the heat of adsorption also depends on the type of OAC. Among the organoaluminium cocatalysts investigated by the present authors[35], $Al(iso\text{-}Bu)_3$ shows the least tendency towards complex formation and there is correspondingly an insignificant temperature variation of the number of propagation centres in its presence (E_{c_p} = 1.5 kcal mol^{-1}). When $AlEt_2Cl$, with the smallest size and highest Lewis acidity among the cocatalysts employed, is used as a cocatalyst, an appreciable decrease of the number of propagation centres with decrease of polymerisation temperature is observed (E_{c_p} = 5.5 kcal mol^{-1}). For $AlEt_3$, we have E_{c_p} = 3 kcal mol^{-1}.

For two-component catalytic systems based on $TiCl_3$, the influence of the OAC is manifested to a large extent in the stage involving the formation of propagation centres (alkylation of surface titanium ions). For all such catalysts, the nature of the OAC can therefore influence both the total number of AC and the ratios of the propagation centres of different stereospecificity already in the initiation stage and hence can determine the activity and stereospecificity of the catalytic system as a whole. The nature of the transition metal compound can play a significant role in this process. Hence, whereas for one transition metal compound it is possible to observe a particular series based on the changes in stereospecificity as a function of the type of organometallic cocatalyst, for another transition metal compound the series may be completely different[43]. However, despite this, the stereospecific propagation centres for catalysts of different compositions can have the same structure. The ^{13}C NMR data indicating the identical structures of the most stereoregular polymer fraction, insoluble in boiling n-heptane (or octane), for catalysts with different transition metal compounds ($TiCl_2$, δ-$TiCl_3$, β-$TiCl_3$, $CrCl_3$, and $ZrCl_4$) can serve as experimental confirmation of this[44,45].

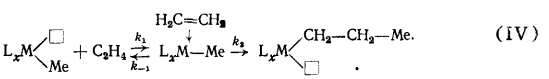
IV. THE MECHANISM OF THE PROPAGATION REACTION

1. One-Stage and Two-Stage Mechanisms

Two main mechanisms of the propagation reaction are considered in the literature.

(1) The one-stage mechanism, in which the propagation reaction takes place as a result of the interaction of a bulk-phase olefin molecule directly with the metal–carbon bond[5,7,46]; in this case the rate of the propagation reaction corresponds to the rate of the insertion reaction.

(2) The two-stage mechanism proposed by Natta[47] and analysed in greater detail by Cossee[48]. According to this mechanism, the propagation reaction includes a preliminary stage, in which the olefin is adsorbed on the transition metal ion with subsequent insertion of the adsorbed olefin in the metal–carbon bond:



(IV)

In this case the experimental constant k_p is defined by the following expression:

$$k_p = k_1k_2/(k_2 + k_{-1} + k_1c_m). \quad (3)$$

Depending on the ratios of the rate constants for the individual elementary stages, the following instances can be observed:

$$\text{(a)}\ k_2 \gg k_{-1} + k_1c_m,\ k_p = k_1; \quad (4)$$

$$\text{(b)}\ k_{-1} \gg k_2 + k_1c_m,\ k_p = k_2k_1/k_{-1}; \quad (5)$$

$$\text{(c)}\ k_1c_m \gg k_{-1} + k_2;\ k_p = k_2/c_m. \quad (6)$$

The observed first order kinetics of the propagation reaction with respect to the monomer can correspond to either the one-stage mechanism or to cases (a) and (b) of the two-stage mechanism.

Table 3 presents the experimental quantities E_p, k_p, and pre-exponential factors for the polymerisation of ethylene and propene in the presence of catalysts of different composition. The table includes for comparison the propagation rate constants in the radical polymerisation of ethylene and the rate contants for the addition of propene to the aluminium–carbon bond in triethylaluminium.

The experimental pre-exponential factors can be compared with the calculated values for the elementary stages, which may constitute the propagation reaction (Table 4). The experimental data for different types of catalysts (the chromium oxide catalyst, titanium trichloride) are consistent with

the two-stage mechanism, which can include as the limiting stage the adsorption of the olefin on the transition metal ion with formation of a π-complex. At the same time, low values of the pre-exponential factor can also be observed for the one-stage mechanism, which involves direct interaction of the olefin with the metal–carbon bond, leading to the formation of a four-centre transition state. Thus the pre-exponential factor cannot serve as a criterion which would permit a differentiation between one- and two-stage mechanisms. For this purpose, one must use other experimental data. We shall enumerate briefly the experimental evidence available hitherto, which confirms the two-stage mechanism of the propagation reaction.

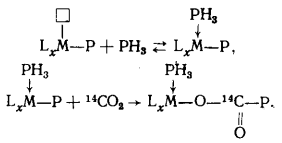
Table 4. The calculated pre-exponential factors of the rate constants for the possible elementary reactions constituting the propagation reaction in the catalytic polymerisation of olefins.

Elementary stage	Method of calculation	$10^{-5}A$, litre mol^{-1} s^{-1}
Adsorption of ethylene on a titanium ion	collision theory (Ref.34)	10^3 (7–70)
Adsorption of ethylene on a transition metal ion with formation of a π-complex	activated complex method (Ref.34)	0.3–3
Bimolecular impact interaction between bulk-phase ethylene and the metal–carbon bond	collision theory (Ref.7)	10^5
Interaction of bulk-phase propene with the metal–carbon bond to form a four-centre activated complex	activated complex method	0.1–1

1. In a study of the relative reactivities of different styrene derivatives in copolymerisation reactions, Natta[47] established that the rate of the propagation reaction is independent of the nature of the terminal unit of the polymer chain linked to the titanium ion. These data suggest that the reaction proceeds in two stages and that the adsorption of the monomer on the titanium ion is rate-limiting.

2. In the catalytic polymerisation of olefins the propagation reaction is usually first order with respect to the monomer. For certain types of Ziegler catalysts, a transition of the propagation reaction from first to zero order with respect to the monomer was observed[49–51]. This is possible in the two-stage mechanism of the propagation reaction, where virtually all the centres are "complexed" by the adsorbed monomer and the insertion of the coordinated olefin in the metal–carbon bond constitutes the rate-limiting stage.

3. An important condition, necessary for the operation of the two-stage mechanism of the propagation reaction, is coordination unsaturation of the metal ions on the active centre, which in the given instance is understood to be the ability of the transition metal ion to increase its coordination number in the adsorption of the olefin. Direct experimental evidence for coordination unsaturation was obtained in a study of the interaction of radioactive inhibitors of different types with the propagation centres. In particular, when compounds such as phosphine are introduced into the polymerisation medium, the polymerisation ceases, but metal–polymer bonds (M–P) are preserved [reaction (V)]. This can be demonstrated on the basis of the radioactivity of the polymer formed by the subsequent decomposition of the metal–polymer bonds by radioactive alcohol or carbon dioxide; the number of labels in the polymer in experiments with preliminary introduction of PH_3 corresponded to the number of propagation centres[14]:



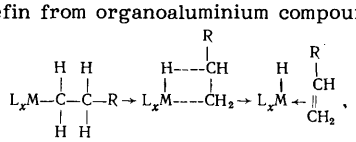
(V)

(VI)

Data showing a preliminary coordination of ethylene on the metal ion in the active centre were also obtained in EPR studies of a number of deposited organometallic catalysts[52,53]. In particular, it has been shown that at low temperatures the benzyl and hydride titanium(III) and zirconium(III) complexes, fixed on the carrier surface, adsorb ethylene, while, following an increase of temperature, ethylene is bound irreversibly, which corresponds to the insertion of the adsorbed ethylene in the metal–hydrogen and metal–benzyl bonds.

2. The Rate-Limiting Stage of the Propagation Reaction

The observed first order of the polymerisation reaction with respect to the monomer can correspond to cases (a) and (b) of the two-stage mechanism [Eqns.(4) and (5)]. It is possible to estimate the pre-exponential factor (A_p) for the propagation rate constant in case (b). For a single unimolecular desorption reaction, a normal value $A_{-1} = 10^{13}$–10^{14} s^{-1} is to be expected. At the same time, in the case of a unimolecular reaction involving the insertion of the adsorbed olefin, proceeding with a low activation energy via an involved four-centre activated complex, one may expect a pre-exponential factor significantly lower than the theoretical value. Pre-exponential factors of 10^8–10^{10} s^{-1} have been quoted in the literature[54,55] for reactions proceeding via the formation of a four-centre activated complex, for example, for the β-elimination of an olefin from organoaluminium compounds:



(VII)

Low-pre-exponential factors for the insertion rate constant (A_2) compared with A_{-1}, i.e. $A_2 \ll A_{-1}$, can also be expected for the insertion of a coordinated olefin, which proceeds via a similar transition state. Consequently in case (b) [Eqn.(5)] we have $A_p = A_1A_2/A_{-1} \ll A_1$. The closeness of the experimental values of A_p to the calculated pre-exponential factor associated with the rate constant for the adsorption of the olefin on the metal ion (Tables 3 and 4) suggests that the rate-limiting stage of the propagation reaction is the adsorption of the olefin on the active centre [case (a), Eqn.(4)].

Low activation energies for the propagation reaction (3–6 kcal mol^{-1}) (Table 3), which do not exceed E_p for radical polymerisation, are characteristic of the catalytic polymerisation of olefins in the presence of transition metal compounds. On passing from transition metal compounds to those of non-transition elements, the activation energy for the propagation reaction (the addition of the olefin to the metal–carbon bond) increases appreciably (see the next Section).

The energy diagram for the two-stage propagation reaction has been examined[56] on the assumption of a linear relation between the change in the activation energy ΔE and in the heat of reaction Δq, of the type

$$\Delta E = \alpha \Delta q \quad (0 < \alpha < 1). \qquad (7)$$

It follows from this diagram that an increase in the heat of adsorption of the olefin on the metal ion can lead to a

decrease of the activation energy for the propagation reaction in both case (a) [Eqn.(4)] and case (b) [Eqn.(5)].

We may note that, whereas the donor–acceptor interaction makes the main contribution to the metal–olefin bond, which is entirely likely for Group IV metals in the highest oxidation states and has been confirmed by quantum-chemical calculations (see subsection 4 of this Section), following a decrease of electron density on the metal ion, a decrease of the activation energy for the propagation reaction is to be expected.

3. The Mechanism of Reactions Involving the Addition of Olefins to Aluminium–Carbon and Aluminium–Hydrogen Bonds

The catalytic oligomerisation of ethylene in the presence of triethylaluminium, which includes reactions involving the addition of the olefin to aluminium–carbon and aluminium–hydrogen bonds, can be represented as follows[12]:

$$R_2Al{-}R + CH_2{=}CH_2 \rightarrow \underset{(A)}{R_2Al{-}CH_2{-}CH_2{-}R}, \qquad (VIII)$$

$$A \xrightarrow{(CH_2=CH_2)} \underset{(B)}{R_2Al\,(CH_2{-}CH_2)_{n+1}{-}R}, \qquad (IX)$$

$$B \rightarrow R_2AlH + CH_2{=}CH{-}(CH_2{-}CH_2)_n{-}R, \qquad (X)$$

$$R_2AlH + CH_2{=}CH_2 \rightarrow R_2Al{-}CH_2CH_3. \qquad (XI)$$

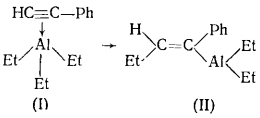
Depending on the process conditions (pressure and temperature), it is possible to obtain α-olefins ranging from C_4 to C_{20}. The interaction of aluminium trialkyls with higher α-olefins takes place as a rule under conditions where the addition of the first olefin molecule is followed by the β-elimination reaction [as in reactions (VII) and (X)]. In this case the process can be catalytic in relation to dialkylaluminium hydride, since the insertion of the α-olefin in the Al–H bond under these conditions is followed again by the β-elimination reaction with formation of a new α-olefin[12].

The catalytic olefin polymerisation processes in the presence of transition metal compounds and processes leading to the formation of higher α-olefins in the presence of organoaluminium compounds are based on reactions involving the addition of olefins to metal–carbon and metal–hydrogen bonds. The observed quantitative differences between the rates of the processes and between the degrees of polymerisation can be attributed to the differences between the rate constants for the chain propagation and termination reactions involving the above groups of catalysts, provided that all these reactions have a single mechanism. Thus reactions involving the addition of olefins to aluminium–hydrogen and aluminium–carbon bonds can be regarded as models for reactions of this type.

Numerous kinetic studies of the addition of olefins to the aluminium–carbon bond in trialkylaluminium[57–63] have shown convincingly that the active centre is the monomeric form of the trialkylaluminium molecule, which is as a rule present in solution in the associated form as Al_2R_6 dimers. The addition of the monomeric coordination-unsaturated form of the organoaluminium compound in the addition reaction ensures the possibility of a preliminary interaction of the olefin with the free *p* orbitals of the aluminium ion to form a π-complex before the step involving the insertion of the olefin in the aluminium–carbon bond[57,58].

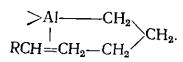
The first order with respect to the monomer[57–59,63–66] suggests that the concentration of π-complexes relative to the monomeric form of the OAC is low and they cannot therefore be detected by physical methods at elevated temperatures under the reaction conditions. With decrease of temperature, one may expect an increase in the concentration of these complexes, but under these conditions the dimerisation of the OAC molecules predominates, the dimer being incapable of coordinating with the olefin.

On the other hand, in many special cases data have been obtained concerning the possibility of the formation of π-complexes of olefins with the monomeric form of the OAC. For example, the formation of π-complexes in the reaction of phenylacetylene with triethylaluminium has been demonstrated[67] by ^{1}H NMR. The heat of this reaction is 0.7 ± 0.2 kcal mol^{-1}. When account is taken of the heat of dissociation of the Al_2Et_6 molecule, amounting to 17 kcal mol^{-1},[68] the strength of the π-bond between phenylacetylene and the aluminium ion is estimated as 9 kcal mol^{-1}. The insertion of phenylacetylene in the aluminium–ethyl bond is of first order with respect to π-complex (I), in conformity with the reaction equation



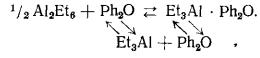
(XII)

The formation of intramolecular π-complexes in aluminium trialkenyls has been established[69–71] by infrared spectroscopy and ^{1}H NMR:



In contrast to their alkyl analogues, the alkenyl compounds of aluminium exist in the monomeric form. The energy of formation of the π-complex should be in this case more than 2–5 kcal mol^{-1} in order to stabilise them in the monomeric form[71].

The necessity for a free coordination site in the trialkylaluminium molecule for the addition of the olefin to take place has received significant confirmation by data concerning the influence of electron-donating compounds on the kinetics of this reaction. The kinetics of the addition of oct-1-ene to triethylaluminium in diphenyl ether, which reduces sharply the rate of this reaction, have been studied by ^{1}H NMR.[72] Under the given conditions, there is a system of equilibria



(XIII)

It has been established[72] that only the monomeric form of triethylaluminium is active in the olefin addition reaction, while the complex $Et_3Al.Ph_2O$ is inactive.

The rate constants for the addition of olefins to the Al–C and Al–H bonds. Table 5 presents the activation energies and the pre-exponential factors associated with the rate constants for the addition of olefins of different structures to triethylaluminium. Some uncertainty in the determination of the rate constants for this reaction is associated with the possibility of using in the calculations of the concentration of the monomeric form of triethylaluminium of different dissociation constants K_d of the dimeric molecule Al_2Et_6 obtained in different investigations[60,62,68,74]. The results presented in Table 5 have therefore been grouped in accordance with the values of K_d used in the calculations. In the series from propene to oct-1-ene the activation energies increase from 12.2–15.4 to 16.6–19.4 kcal mol^{-1}. The pre-exponential factors also tend to increase in this series by about an order of magnitude.

The addition of olefins to $Al(Me)_3$ is much slower than the addition of $AlEt_3$, which is associated, firstly, with the higher heat of dissociation of the $[AlMe_3]_2$ molecule[74,75] and with the higher activation energy for the addition reaction (Table 6).

The interaction of ethylene with triethylaluminium has been studied in the gas phase under the conditions of the preferential formation of α-butylene[66,76]. The kinetic characteristics obtained for this reaction are listed in Table 6. One must bear in mind that, in the calculation of the rate constants for the addition reaction, a number of addition assumptions were introduced in this instance concerning the concentrations of different forms of the OAC and the ratio of the rate constants for different reactions. Apparently not all the assumptions are valid and the activation energies for the addition of ethylene in Table 6 are too high. In this connection one should note that Ziegler[12,77] established the following series based on the variation of the reactivity in the addition of olefins to organoaluminium compounds: $CH_2{=}CH_2 > CH_2{=}CHR > CH_2{=}CR_2$.

Table 5. The activation energies E (kcal mol^{-1}) and the pre-exponential factors A of the rate constants for the addition of olefins to triethylaluminium.

Monomer	From data in Refs. 59, 60, 65, and 73		From data in Refs. 62 and 63			
	E^*	$\lg A^*$	E^{**}	$\lg A^{**}$	E^{***}	$\lg A^{***}$
Propene	15.5	5.5	12.1	3.3	14.4	4.2
But-1-ene	16.4	5.8	13.2	3.6	15.4	4.5
Pent-1-ene	18.5	6.8	15.1	4.6	17.8	5.5
Hex-1-ene	17.2	6.2	15.0	4.8	17.3	5.6
Oct-1-ene	18.4	6.6	16.5	5.0	19.6	6.3
Cyclohexene	17.8	4.6				
Methylpent-1-ene	17.0	5.8				
3-Methylpent-1-ene	18.8	6.5				
3,3-Dimethylbut-1-ene	25.4	9.4				

*K_d from Hay et al.[60], ΔH_d = 10.2 kcal mol^{-1}, ΔS_d = 14.9 cal mol^{-1} K^{-1}.

**K_d from Smith[68,74], ΔH_d = 17 kcal mol^{-1}, ΔS_d = 3.2 cal mol^{-1} K^{-1}.

***K_d from Allen and Byers[62], ΔH_d = 12.2 kcal mol^{-1}, ΔS_d = 27.8 cal mol^{-1}K^{-1}.

Table 6. The activation energies E (kcal mol^{-1}) and the pre-exponential factors A of the rate constants for the addition of olefins to different OAC.

OAC	E	$\lg A$	E	$\lg A$
	Oct-1-ene (Ref.61)		Ethylene (Refs.66,76)	
$AlEt_3$	18.4	6.6	16.8	6.2
$AlMe_3$	20.5	6.7	22.7	7.2

On passing from metal–carbon to metal–hydrogen bonds, there is a sharp increase of reactivity for the addition of olefins due to the decreased activation energy (Table 7). The activation energy for the addition to the Al–H bond is virtually the same for different monomers and for a single monomer increases in the sequence $R_2AlH < R_2GaH < R_2BH$.

The data examined above are in best agreement with the hypothesis that the addition of olefins to the metal–carbon bond takes place via a single two-stage mechanism for compounds of both transition and non-transition metals. The reaction proceeds with participation of coordination-unsaturated metal alkyls via the intermediate formation of π-complexes. The pre-exponential factors associated with the rate constant for this reaction are close for active centres of different compositions and the higher reactivity of transition metal compounds compared with organoaluminium compounds is determined mainly by the low activation energy for this process. Many facts show that the polarity of the bonds does not determine the reactivity of the metal alkyls in the addition of olefins. Presumably the most significant factor is the ability of metal alkyls to form π-complexes with the possibility of interaction with the metal–carbon bond via a concerted mechanism.

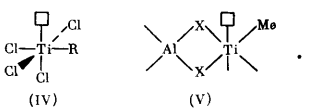
Table 7. The activation energies for the addition of olefins to the metal–hydrogen bond in the organometallic compound $(iso\text{-}C_7H_9)_2MH$.

Monomer	M	E, kcal mol^{-1}	Refs.
Ethylene	Al	5.0—6.0	78,79
But-1-ene	Al	5.0—6.0	78,79
2-Methylpropene	Al	5.0—6.0	78,79
2-Methylpropene	Ga	8.8	80
2-Methylpropene	B	12	81

4. Quantum-Chemical Analysis of the Mechanism of the Propagation Reaction†

The first studies on the quantum-chemical analysis of the propagation reaction in the polymerisation of olefins were carried out by Cossee[82,83]. The ideas developed in these investigations have been widely accepted. Later a further series of studies were carried out[84–89], including some using improved computational methods[85–89].

The AC models. The AC model proposed by Cossee[82,83], incorporating an octahedral titanium(III) complex which exists on the surface of the titanium trichloride crystal [complex (IV)], is fully consistent with the experimental data discussed above. The titanium ion in this complex contains an alkyl group and a chlorine vacancy. This AC model has been used in many computational studies[82–84,89]. AC models of more complex composition, for example the Ti_2Cl_{10} cluster[90], and simplified models containing either no metal–alkyl bond or a free vacancy[91–94] have also been analysed.



(IV) (V)

The AC model proposed for soluble catalytic systems has been analysed[85,86]. In this case the AC consists of a titanium(IV) complex linked to an organoaluminium compound [complex (V)].

The metal–alkyl bond and the influence of the coordination of the olefin on its strength. The Ti–C bond is predominantly covalent with $Ti^{\delta+}$–$C^{\delta-}$ polarisation[89]. The titanium–carbon bond length changes only slightly on passing from the methyl to the ethyl complex, i.e. the properties of this bond are presumably independent of the chain length. On

† This Section was written together with V.I.Avdeev and I.I.Zakharov.

formation of a π-complex with ethylene, an appreciable proportion of the electron density is transferred to the titanium ion (~0.25e).

The metal–olefin bond is formed as a result of the donor–acceptor and dative interactions[95,96]. Fig.5 illustrates the variation of the energy ΔE of transition from the σ_R orbital, involved in the formation of the metal–alkyl bond, to the half-filled or vacant d_π orbital of the metal on coordination of the olefin to the titanium ion. Presumably the lower the value of ΔE, the higher the probability of the $\sigma_R \rightarrow d_\pi$ transition and hence the more effective is the electron transfer from the metal–carbon bond to the metal. This process leads to an increased electron density on the metal and to a decrease in the M–C bond strength. If only the donor–acceptor interaction between the AC and the ligand is taken into account (Fig.5*a*), then the energy of the $\sigma_R \rightarrow d_\pi$ transition increases on complex formation ($\Delta E' > \Delta E$) and the M–C bond is strengthened. When account is taken of both the donor–acceptor and the dative interactions (Fig.5*b*), it is possible to obtain $\Delta E' > \Delta E$ or $\Delta E' < \Delta E$ depending on their relative contributions ($\Delta\varepsilon$ and $\Delta\varepsilon'$ respectively). In the first case the coordination of the olefin strengthens the M–C bond, while in the second it destabilises it.

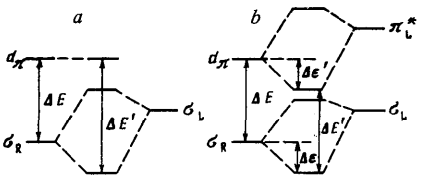
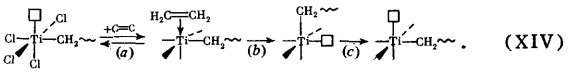


Figure 5. A simplified scheme of the changes in the one-electron levels of the AC (σ_R, d_π) in the interaction with the donor (σ_L) and acceptor (π^*_L) orbitals of the coordinating ligand[89]: *a*) allowance for the donor–acceptor interaction of the AC and the ligand; *b*) allowance for the donor–acceptor and dative interactions.

The nature of the metal–olefin bond. In the early studies[82–84] no estimates were made of the relative contributions of these interactions. The hypothesis[83] of the dominant role of the dative interaction does not appear convincing, since the metal ions in the highest oxidation states [for example the d^1 configuration for titanium(III)] can hardly transfer effectively the electron density from the d_π orbitals (which are actually unoccupied) to the antibonding π* orbitals of ethylene. It is therefore not surprising that Armstrong[85] arrived at the opposite conclusion for titanium(IV) complexes on the basis of calculations by the CNDO method, namely that the contribution of the donor–acceptor interaction predominates. This conclusion has been confirmed by calculations on the π-complexes $Ti^{3+}F_5.C_2H_4$ and $Ti^{3+}Cl_5.C_2H_4$ carried out by the Slater–Johnson method[91,92]. According to these calculations, the contribution of the dative interaction does not exceed 12% for the fluoride complexes and is significantly lower for the chloride complex. Thus the calculated data suggests that the metal–olefin bond in the AC incorporating titanium(III) ions is formed mainly as a result of the donor–acceptor interaction.

The monomer insertion stage. Cossee[82,83] was the first to analyse this reaction theoretically, assuming that it is the rate-limiting stage of the propagation reaction [stage (b) in reaction (XIV)]:

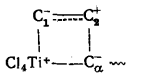


(XIV)

After the *cis*-insertion of the monomer, the geometry of the active centre is restored but with an interchange of the vacant site and the alkyl. Analysis of the orbital contributions to the molecular orbital localised at the Ti–C bond shows that the metal–alkyl bond persists along the entire reaction pathway. The vacant d_{xy} orbital of titanium plays an important role in this process. The energy losses on passing from the Ti–C_α bond to the Ti–C_1 bond do not exceed 20% of the bond strength and are fully compensated by the formation of a new C_2–C_α bond [reaction (XVII)].[89] Cossee[83] classified such reactions as concerted and characterised by a synchronous redistribution of electron density in the ruptured and reformed bonds, which is the reason for the low activation energies for these reactions.

On the basis of calculated data demonstrating a marked destabilisation of the σ_R and d_π orbitals and an increase of ΔE (Fig.5) in the monomer insertion process, Cossee[83] proposed a relation between the activation energy for the propagation reaction and ΔE. The same conclusion was reached by Begley and Penella[84] using the same computational methods, on the basis of estimates of ΔE for the series of complexes CH_3TiCl_3, $CH_3TiCl_4.\square$ (octahedron with a vacancy), and $CH_3TiCl_4.C_2H_4$. They postulated that $\Delta E'$ (Fig.5) represents the energy barrier which is overcome when the coordinated olefin is introduced into the metal–carbon σ-bond and $\Delta E'$ can therefore be compared with the activation energy for the chain propagation reaction. However, this conclusion was not confirmed in calculations by the more effective CNDO method[85,86,89]. It has been shown[89] that $\Delta E'$ depends greatly on the metal–alkyl and metal–ethylene bond lengths chosen, it is therefore important to determine the equilibrium lengths of these bonds by minimising the total energy. This factor was not taken into account by Cossee et al.[83] and Begley and Penella[84] and the attempt to relate the activation energy for the insertion reaction to $\Delta E'$ is therefore unjustified.

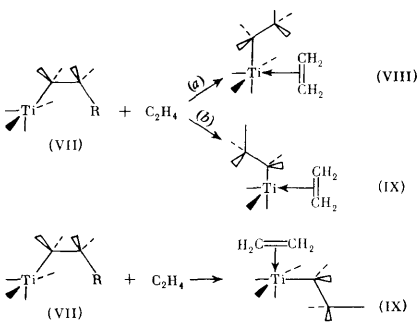
The insertion reaction for the AC [complex (V)] in a homogeneous catalyst has been analysed[85,86] by the CNDO method. It was observed that the behaviour of the one-electron levels following the insertion of ethylene is analogous to that found earlier by Cossee and the process is activated but the total energy of the system decreases along the reaction coordinate. Hence the authors[85,86] concluded that the insertion stage does not have an activation energy. In contrast to earlier workers[83–86], Avdeev et al.[89] attemped to determine the optimum reaction pathway in the insertion of ethylene taking into account the mutual influence of the metal–olefin and metal–alkyl bonds. We may note certain characteristic features of the insertion stage, which follow from the results of this study. In the initial stage of the process a four-centre complex (VI) of the type



is formed, its polarisation ensuring its energetic suitability compared with the initial complex. The transition to the final stage, where the *cis*-opening of the double bond is completed, requires that an insignificant energy barrier be overcome (approximately 1 kcal mol^{-1}), which is consistent with

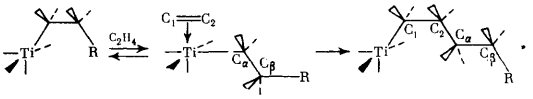
the results of Armstrong et al.[85] and Novaro et al.[86] However, Avdeev et al.[89] found that the stable state of the AC corresponds to structure (VII) [Eqns.(XV) and (XVI)], in which the Ti–C bond occupies a position intermediate between the octahedral sites and the propyl group has the *cis*-configuration.

Coordination of the olefin. Armstrong[85] was the first to note that the total energy of the AC decreases when the structure is deformed to a trigonal bipyramid. Formally there is no vacancy in such a deformed AC, so that it is necessary that in the adsorption of ethylene the octahedral geometry of the AC should be restored. Such a rearrangement requires energy, which can be identified as the activation energy for the adsorption stage. Avdeev et al.[89] analysed in detail, within the framework of the CNDO method, the stage involving the coordination of ethylene on the active centre, having structure (VII), which they showed to correspond to the free energy minimum. There are several ways in which ethylene can be incorporated in the coordination sphere of the metal ion:



A characteristic feature of the first case [reaction (XV)] is that the olefin and the alkyl change places in the coordination sphere of the metal ion during the chain propagation process. The second case [reaction (XVI)] corresponds to the adsorption of the monomer to the same coordination site in repeated propagation steps. Calculation of the potential surfaces for coordination of ethylene in relation to reaction (XV) shows that it involves the overcoming of an energy barrier [approximately 25 kcal mol^{-1} for reaction (XV*a*) and 65 kcal mol^{-1} for reaction (XV*b*)]. The coordination of etheylene via reaction (XVI) is also activated, but with a much smaller activation energy (approximately 4 kcal mol^{-1}). The low activation energy in the latter case is due to the fact that the energy evolved on coordination of the monomer compensates for the energy expended in the migration of the alkyl group and its transition to the *trans*-configuration. On the other hand, in reaction (XV) the rearrangement of the AC must take place before the energy compensation due to the adsorption of ethylene begins. The conclusions reached on the basis that the monomer is adsorbed at the same site in the coordination sphere of titanium provide a more natural explanation of the isospecificity of the addition of the monomer in the polymerisation of α-olefins in the presence of titanium chlorides. The need to introduce a special alkyl migration stage, proposed in some investigations[48,82] [reaction (XIV*c*)], is eliminated.

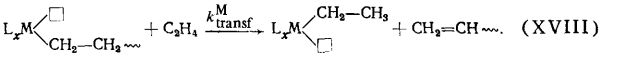
Comparison of the one-stage and two-stage mechanisms. The potential energy surface has been calculated[89] for the one-stage mechanism of the propagation reaction; the results obtained were compared with data for the adsorption reaction and the insertion of the coordinated olefin. It was found that the insertion of ethylene in the metal–polymer bond directly from the gas phase requires that a considerably larger energy barrier be overcome than in its insertion via preliminary coordination. Consequently the two-stage mechanism of the propagation reaction is preferable, and according to Avdeev et al.[89] it can be represented as follows:


(XVII)

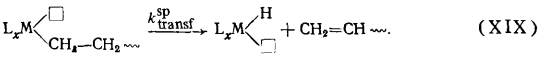
V. POLYMER CHAIN TRANSFER REACTIONS

In the catalytic polymerisation of olefins the following main reactions which limit the propagation of the polymer chain take place.

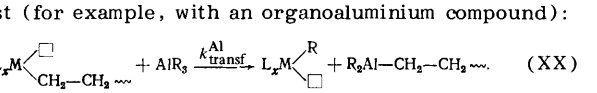
1. Transfer with the monomer:


(XVIII)

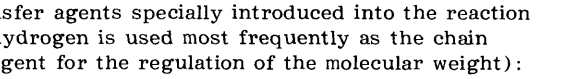
2. Spontaneous chain transfer reaction:


(XIX)

3. Reaction involving chain transfer with the organometallic cocatalyst (for example, with an organoaluminium compound):


(XX)

4. Reactions involving chain termination by impurities or chain transfer agents specially introduced into the reaction medium (hydrogen is used most frequently as the chain transfer agent for the regulation of the molecular weight):


(XXI)

All the reactions enumerated above are polymer chain transfer reactions, after which the kinetic chain is preserved and a new polymer molecule is formed on the AC. In the catalytic polymerisation of olefins a large number of polymer molecules (from tens to thousands) are therefore formed as a rule on a single AC.

The equation proposed by Natta is usually employed to calculate the chain transfer rate constants:

$$\frac{1}{\bar{P}_W} = \frac{k^{M}_{transf}}{k_p\omega} + \left(\frac{k^{sp}_{transf}}{k_p\omega} + \frac{k^{Al}_{transf}[Al]^n}{k_p\omega} + \frac{k^{X}_{transf}[X]^m}{k_p\omega} \right) \frac{1}{c_M}, \qquad (8)$$

where $\bar{P}_W$ is the weight-average degree of polymerisation, k^{M}_{transf}, k^{sp}_{transf}, k^{Al}_{transf}, and k^{X}_{transf} are the rate constants for the corresponding transfer reactions [see schemes (XVIII)–(XXI)], c_M, [Al], and [X] are the concentrations of the monomer, the organoaluminium cocatalyst, and the chain transfer agent X, for example, hydrogen, and ω is the coefficient of the polydispersity of the polymer. The ratios of the chain transfer rate constants to the chain propagation rate constant (k^{i}_{transf}/k_p) can be calculated by Eqn.(8) from the experimental relations between the molecular weight of the polymer and the concentrations of the chain transfer agents[97,98]. The values of k_p, determined independently by the method of radioactive inhibitors (see Sections II and III), were used[16,34,99,100] for the subsequent calculation of the absolute rate constants, listed in Table 8, for chain transfer with the monomer and hydrogen as well as spontaneously. The rate constants for chain transfer with the organoaluminium cocatalyst, listed in Table 8,[19,100] were calculated from

the experimental relations between the number of metal–polymer bonds (q) and the yield of the polymer (G) in accordance with the expression[2,6,19]:

$$[q]=c_p+\frac{k^{Al}_{transf}[Al]^n G}{k_p c_m}, \qquad (9)$$

where $[q]$ is the total number of aluminium–polymer and titanium–polymer bonds, determined by a method involving the termination of the polymerisation by a radioactive alcohol RO^3H. In the calculation of k^{Al}_{transf} the values of k_p determined independently by a method involving the termination of polymerisation by ^{14}CO were also used[17,23].

Chain transfer with the monomer and spontaneous chain transfer are the main chain transfer processes in the case of one-component catalysts. Chain transfer with the monomer predominates at temperatures below 90 °C,[16,101] whilst spontaneous transfer predominates above 120 °C.[101] For two-component catalysts based on $TiCl_3$ chain transfer with the monomer predominates at 70–80 °C.[99,100] Experimental data concerning the molecular structure of the polymers {vinyl unsaturation for polyethylene and vinylidene unsaturation for polypropylene arising via reactions (XVIII) and (XIX)} confirm the occurrence of these processes under the conditions investigated[99,100].

Table 8. The rate constants for chain transfer in the catalytic polymerisation of olefins[16,19,34,99,100].

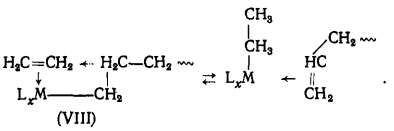
Catalyst	k^{M}_{transf}/ω, litre mol^{-1} s^{-1}	k^{Al}_{transf}, litre$^{0.5}$ mol$^{-0.5}$ s^{-1}	$k^{H_2}_{transf}/\omega$, litre$^{0.5}$ mol$^{-0.5}$ s^{-1}	$\bar{\tau}\cdot\omega$, s*
CrO_3/SiO_2**	$1.2\cdot10^5\exp(-11\,700/RT)$; 0.0064	—	—	60
$TiCl_3$	$0.8\cdot10^5\exp(-9000/RT)$; 0.2	—	—	12
$TiCl_3+AlEt_3$	0.084	2.3	2.3	25
$TiCl_3+AlEt_3$***	0.004	0.045	0.59	160
$TiCl_4/MgCl_2+AlEt_3$	0.22	1.7	—	10

*The average polymer chain propagation time $\bar{\tau}$ was calculated from the relation $\bar{\tau}=\bar{P}_W/\omega k_p c_m$ with $c_m = 0.5$ M at 80 °C for ethylene and at 70 °C for propene.

**k^{sp}_{transf}/ω, $c^{-1} = 2.2\times10^5\exp(-13\,500/RT)$.

***Monomer—C_3H_6; the rate constants for 70 °C are indicated; in the remaining cases the monomer is C_3H_4 and the rate constants for 80 °C are indicated.

The pre-exponential factors associated with the rate constant for chain transfer with the monomer (Table 8) are close to the calculated pre-exponential factor of the rate constant for the adsorption of monomer on the metal ion with formation of a π-complex (Table 4) or to the pre-exponential factor of the propagation rate constant (Table 3). Presumably chain transfer with the monomer, like the propagation reaction, proceeds via a stage in which the monomer is adsorbed on the metal ion in the AC [reactions (XV) and (XVI)]. Depending on the steric disposition of the adsorbed olefin and the alkyl group, either the insertion reaction takes place in this instance [after the formation of complex (IX) via reaction (XVI)] or reaction (XXII), involving the transfer of hydrogen from the β-carbon atom of the alkyl group to the adsorbed monomer [provided that complex (VIII) is formed via reaction (XVa)]:



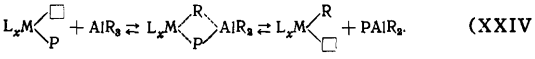
(VIII) (XXII)

As mentioned in the previous Section, the formation of a π-complex of type (VIII) via reaction (XVa) is energetically less favourable than the formation of complex (IX) via reaction (XVI), which is apparently due to the higher activation energy for chain transfer with the monomer compared with the propagation reaction.

The spontaneous chain transfer process (XIX) is a reaction involving the β-elimination of the olefin with formation of a metal hydride complex. This reaction is well known for organoaluminium compounds[12]. The low pre-exponential factors of the rate constants for the unimolecular spontaneous transfer process (Table 8) and the reactions involving the β-elimination of olefins from aluminium alkyls[54,55] are apparently caused by the fact that the process proceeds via an involved activated complex [reaction (VII)] the formation of which requires a specific steric disposition of the alkyl group, favourable for the migration of a hydrogen atom to the transition metal ion. When this reaction takes place in the coordination sphere of the metal, the C–H bond is dissociated with a relatively low activation energy [13.5 kcal mol^{-1} for the chromium oxide catalyst (Table 8) and 26–30 kcal mol^{-1} for organoaluminium compounds[54,55]].

Chain transfer with the organoaluminium cocatalyst plays a notable role in two-component catalysts. This reaction consists in essence of the exchange of the alkyl ligands between the OAC and the AC and apparently includes the following stages: dissociation of the dimeric OAC molecule and adsorption of the monomeric form of the OAC on the AC followed by desorption of the OAC molecule, in which the alkyl group is replaced by the polymer chain[19,102]:

$$[AlR_3]_2 \rightleftarrows 2\,AlR_3, \qquad (XXIII)$$



(XXIV)

Within the framework of this mechanism, it is possible to account for the experimental data[19,32] concerning the influence of the nature of the OAC [$AlEt_3$ and $Al(iso\text{-}Bu)_3$] and the monomer on k^{Al}_{transf}. For steric reasons, the adsorption of $Al(iso\text{-}Bu)_3$ on the AC via reaction (XXIV) should be hindered. This reduces the rate constant for chain transfer from $Al(iso\text{-}Bu)_3$ compared with $AlEt_3$. In the polymerisation of propene the presence of methyl substituents in the polymer chain, bound to the metal ion in the AC, gives rise to greater difficulties in the adsorption of the OAC compared with the polymerisation of ethylene. The rate constant for chain transfer from $AlEt_3$ in the polymerisation of propene is therefore significantly lower than in the polymerisation of ethylene (Table 8).

VI. CONCLUSION

The data obtained for the influence of the composition of catalysts and polymerisation conditions on the number of AC and the propagation rate constant constitute the experimental basis for the analysis of kinetic data and for the discussion of problems concerning the composition of the AC and the mechanism of the propagation reaction.

The basic cause of the comparatively low activity of the usual Ziegler–Natta catalysts is the small number of AC, not exceeding 0.01 mol per mol of the transition metal. In practice this quantity is considerably lower in most instances. A

sharp increase of the number of centres has been achieved using deposited catalysts. The employment of carriers such as polyethylene and silica gel, on the surfaces of which the active component exists as a finely dispersed titanium chloride phase, makes it possible to increase the number of AC in the polymerisation of ethylene approximately by an order of magnitude. The maximum number of propagation centres is attained as a result of the "structural" binding of titanium chloride by anhydrous highly dispersed magnesium chloride having a disordered structure.

The most important characteristic of the catalytic polymerisation, which to a large extent determines the process kinetics, is the influence of the polymerisation conditions and the composition of the reaction medium on the number of AC. Observations such as the influence of the polymerisation temperature and the nature and concentration of the OAC on the number of AC were explained in this connection by an adsorption mechanism for the reversible interaction of the OAC with the monometallic AC.

Numerous data, particularly those concerning the absence of an effect of the nature of the OAC on k_p, are consistent with the monometallic composition of the AC.

Increasing amounts of experimental data have been accumulated at the present time concerning the preliminary coordination of the monomer to the metal ion before the step involving the insertion of the olefin either into the transition metal–carbon bond in the far-reaching polymerisation of olefins or into the aluminium–carbon bond in the oligomerisation of the olefins. Kinetic as well as calculated data suggest that in many instances this stage can be rate-limiting in the propagation reaction.

The high reactivity of the AC containing a transition metal is determined by the low activation energy for the propagation reaction, which is comparable to the activation energy for radical polymerisation. The insertion of the olefin in the transition metal–carbon and aluminium–carbon bonds proceeds via the same two-stage mechanism, but in the case of a transition metal a significant decrease of the activation energy for the propagation reaction is achieved.

The method based on the inhibition of the polymerisation by a radioactive alcohol is useful for the direct determination of the rate constant for the transfer of the polymer chain from the OAC. This constant depends on the nature of the OAC and the structure of the polymer chain, which is due to the adsorption mechanism of this reaction. The rate constants for other chain transfer processes have been determined from the k_p.

Further development of ideas concerning the elementary stages in the propagation and polymer chain termination reactions can be achieved by using quantum-chemical and physical methods in the study of these reactions. In the formulation of investigations using physical methods it is as a rule necessary to employ catalysts in which the number of AC constitutes an appreciable fraction of the content of the transition metal in the catalyst; it is then necessary to estimate this value quantitatively. As a result of the selection of the optimum composition and preparation conditions for the catalyst (particularly in the deposition of a transition metal compound on a carrier), it is possible to increase sharply the number of AC and to obtain highly active one- and two-component catalysts. These catalysts are widely used nowadays and are at the same time convenient for the investigation of the composition of the AC and the polymerisation mechanism by physical methods. The results obtained by physical research methods together with the determinations of the rate constants for individual stages can serve as a basis for the establishment of relations between the composition of the AC, the state of the transition metal in the AC, and their reactivity in chain propagation and transfer reactions.

REFERENCES

1. G.Natta and I.Pasquon, Chim.e Ind.(Milano), **40**, 556 (1958).
2. G.Natta and I.Pasquon, Adv.Catal., **11**, 1 (1959).
3. J.W.C.Chien, J.Amer.Chem.Soc., **81**, 86 (1958).
4. G.F.Feldman, and E.Perry, J.Polymer Sci., **46**, 217 (1960).
5. J.Boor, Makromol.Rev., **2**, 115 (1967).
6. H.Schnecko and W.Kern, Chem.Ztg.Chem.Appar., **94**, 229 (1970).
7. N.M.Chirkov, "Proceedings of the IUPAC International Symposium on Macromolecular Chemistry, Budapest", Akad.Kiado, 1971, p.365.
8. Yu.I.Ermakov and V.A.Zakharov, Uspekhi Khim., **41**, 377 (1972) [Russ.Chem.Rev., No.3 (1972)].
9. Yu.I.Yermakov and V.A.Zakharov, "Coordination Polymerization" (Edited by J.C.W.Chien), Acad.Press, New York–London, 1975, p.91.
10. Yu.I.Yermakov, V.A.Zakharov, and G.D.Bukatov, "Proccedings of the Vth International Congress on Catalysis", Amsterdam–New York, 1973, Vol.1, p.399.
11. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Yermakov, React.Kinet.Catal.Letters, **1**, 247 (1974).
12. K.Ziegler, Symposium, "Khimiya Metalloorganicheskikh Soedinenii" (The Chemistry of Organometallic Compounds) (Translated into Russian), Izd.Mir, Moscow, 1964, p.231.
13. J.P.Candlin, K.A.Taylor, and D.T.Thompson, "Reactions of Transition-Metal Complexes" (Translated into Russian), Izd.Mir, Moscow, 1970.
14. V.A.Zakharov, G.D.Bukatov, Yu.I.Ermakov, and E.A.Demin, Dokl.Akad.Nauk SSSR, **207**, 857 (1972).
15. V.A.Zakharov, G.D.Bukatov, and Yu.I.Ermakov, Kinetika i Kataliz, **12**, 263 (1971).
16. V.A.Zakharov, G.D.Bukatov, V.K.Dudchenko, and Yu.I.Ermakov, Kinetika i Kataliz, **16**, 417 (1975).
17. N.B.Chumaevskii, V.A.Zakharov, G.D.Bukatov, G.I.Kuznetsova, and Yu.I.Yermakov, Makromol. Chem., **177**, 747 (1976).
18. G.D.Bukatov, V.A.Zakharov, and Yu.I.Yermakov, Makromol.Chem., **179**, 2097 (1978).
19. G.D.Bukatov, N.B.Chumaevskii, V.A.Zakharov, G.I.Kuznetsova, and Yu.I.Yermakov, Makromol. Chem., **178**, 953 (1977).
20. D.R.Burfield, P.J.T.Tait, and J.McKenzie, Polymer, **13**, 321 (1972).
21. H.W.Coover, Jr., J.E.Guillet, R.L.Combs, and F.B.Joyner, J.Polymer Sci., **58**, 2583 (1966).
22. K.A.Jung and H.Schnecko, Makromol.Chem., **154**, 227 (1972).
23. V.A.Zakharov, N.B.Chumaevskii, S.I.Makhtarulin, G.D.Bukatov, and Yu.I.Yermakov, React.Kinet.Catal. Letters, **2**, 329 (1975).
24. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Ermakov, Kinetika i Kataliz, **18**, 848 (1977).
25. V.M.Buls and T.L.Higgins, J.Polymer Sci., **A1**, 8, 1025 (1970).
26. W.R.Carradine and H.F.Rase, J.Appl.Polymer Sci., **15**, 889 (1971).
27. Z.W.Wilshinsky, R.W.Looney, and G.M.Tornqvist, J.Catal., **28**, 351 (1973).

28. V.A.Zakharov, P.A.Zhdan, E.E.Vermel', and S.G.Artamonova, Kinetika i Kataliz, **16**, 1184 (1975).
29. V.A.Zakharov, V.N.Druzhkov, E.G.Kushnareva, and Yu.I.Ermakov, Kinetika i Kataliz, 15, 446 (1974).
30. M.G.Maksimov, E.G.Kushnareva, V.A.Zakharov, V.F.Anufrienko, P.A.Zhdan, and Yu.I.Ermakov, Kinetika i Kataliz, **15**, 738 (1974).
31. V.A.Zakharov and Yu.I.Ermakov, Symposium, "Katalizatory i Kataliticheskie Protsessy" (Catalysts and Catalytic Processes), Inst.Kataliza, Novosibirsk, 1977, p.135.
32. S.I.Makhtarulin, E.M.Moroz, E.E.Vermel, and V.A.Zakharov, React.Kinet.Catal.Letters, **9**, 269 (1978).
33. S.I.Mahtarulin, V.A.Zakharov, and Yu.I.Yermakov, React.Kinet.Catal.Letters, **9**, 137 (1978).
34. G.D.Bukatov, V.A.Zakharov, and Yu.I.Ermakov, Kinetika i Kataliz, **16**, 645 (1975).
35. V.A.Zakharov, N.B.Chumaevskii, G.D.Bukatov, and Yu.I.Yermakov, Makromol.Chem., **177**, 763 (1976).
36. V.A.Zakharov, G.D.Bukatov, and Yu.I.Yermakov, Makromol.Chem., **176**, 1959 (1975).
37. V.A.Zakharov and Yu.I.Yermakov, J.Polymer Sci., **A1**, 9, 3124 (1971).
38. Kh.S.Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd.Nauka, Moscow, 1966.
39. E.J.Arlman and P.Cossee, J.Catal., **3**, 99 (1964).
40. E.J.Arlman, J.Catal., **5**, 178 (1966).
41. P.J.T.Tait, "Coordination Polymerization" (Edited by J.W.C.Chien), Acad.Press, New York–San Francisco–London, 1975, p.155.
42. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Yermakov, Makromol.Chem., **178**, 967 (1977).
43. G.Natta, A.Zambelli, I.Pasquon, and G.M.Giongo, Chim.e Ind.(Milano), **43**, 1307 (1966).
44. C.Wolfsgruber, G.Zannoni, E.Rigamonti, and A.Zambelli, Makromol.Chem., **176**, 2765 (1975).
45. G.D.Bukatov, V.A.Zakharov, Yu.I.Yermakov, and A.Zambelli, Makromol.Chem., **179**, 2093 (1978).
46. T.Keii, Kinetics of Ziegler–Natta Polymerization, Kodansha, Tokyo, 1972.
47. G.Natta, F.Danusso, and D.Sianesi, Makromol.Chem., **30**, 238 (1959).
48. P.Cossee, in "Stereochemistry of Makromolecules", Vol.1, (Edited by A.Ketley), M.Dekker, New York, 1967.
49. A.Zambelli, I.Pasquon, R.Signorini, and G.Natta, Makrmol.Chem., **112**, 160 (1968).
50. N.D.Zavorokhin, V.V.Belyaev, T.A.Vlasova, M.V.Favorskaya, and D.V.Sokol'skii, Dokl.Akad.Nauk SSSR, **215**, 593 (1974).
51. N.V.Bokareva, V.I.Tsvetkova, and F.S.D'yachkovskii, Vysokomol.Soed., **A20**, 2707 (1978).
52. N.G.Maksimov, V.K.Dudchenko, V.A.Zakharov, V.F.Anufrienko, and Yu.I.Ermakov, Teor.Eksper. Khim., **14**, 53 (1978).
53. N.G.Maksimov, G.A.Nesterov, V.A.Zakharov, V.P.Schastnev, V.F.Anufrienko, and Yu.I.Yermakov, J.Mol.Catal., **4**, 167 (1978).
54. W.L.Smith and T.Wartik, J.Inorg.Nuclear Chem., **29**, 629 (1967).
55. A.T.Clocks and K.W.Egger, J.Chem.Soc., Faraday Trans.I, **68**, 423 (1972).
56. Yu.I.Yermakov and V.A.Zakharov, Adv.Catal., **24**, 173 (1975).
57. K.Ziegler, W.R.Kroll, W.Larbig, and O.W.Stendel, Ann., **629**, 53 (1960).
58. K.Ziegler and H.Hoberg, Chem.Ber., **93**, 2944 (1960).
59. N.D.Zavorokhin, V.V.Belyaev, T.A.Vlasova, M.V.Favorskaya, and D.V.Sokol'skii, [No Journal given in Russian (Ed.of Translation)].
60. J.N.Hay, P.C.Hooper and J.C.Robb, Trans.Faraday Soc., **65**, 1365 (1969).
61. J.N.Hay, P.G.Hooper, and J.C.Robb, Trans.Faraday Soc., **66**, 2800 (1970).
62. P.E.M.Allen and A.E.Byers, Trans.Faraday Soc., **67**, 1718 (1971).
63. P.E.M.Allen, J.N.Hay, G.R.Jones, and J.C.Robb, Trans.Faraday Soc., **63**, 1636 (1967).
64. P.E.M.Allen, J.P.Allison, S.R.Majer, and J.C.Robb, Trans.Faraday Soc., **59**, 2080 (1963).
65. J.N.Hay, P.G.Hooper, and J.C.Robb, Trans.Faraday Soc., **66**, 2045 (1970).
66. K.W.Egger, Trans.Faraday Soc., **67**, 2638 (1971).
67. P.E.M.Allen and R.M.Lough, J.Chem.Soc., Faraday Trans.I, **69**, 849 (1973).
68. M.B.Smith, J.Phys.Chem., **71**, 364 (1967).
69. G.Hata, Chem.Comm., 7 (1968).
70. J.St.Dawies, J.P.Oliver, and J.B.Smart, J.Organomet. Chem., **44**, C 32 (1972).
71. T.W.Dobzine and J.R.Oliver, J.Amer.Chem.Soc., **96**, 1737 (1974).
72. P.E.M.Allen, A.E.Byers, and R.M.Lough, J.Chem.Soc., Dalton Trans., 479 (1972).
73. J.N.Hay, P.G.Hooper, and J.C.Robb, J.Organomet. Chem., **28**, 193 (1971).
74. M.B.Smith, J.Organomet.Chem., **46**, 211 (1972).
75. C.H.Henrickson and D.P.Eyman, Inorg.Chem., **6**, 1461 (1967).
76. K.W.Egger and A.T.Cocks, J.Amer.Chem.Soc., **94**, 1810 (1972).
77. K.Ziegler, W.R.Kroll, W.Larbig, and O.W.Steudel, Ann., **629**, 53 (1960).
78. K.W.Egger, J.Amer.Chem.Soc., **91**, 2867 (1969).
79. K.W.Egger, J.Chem.Soc., Faraday Trans.I, **68**, 423 (1972).
80. K.W.Egger, J.Chem.Soc.A, 3603 (1971).
81. A.T.Cocks and K.W.Egger, J.Chem.Soc.A, 3606 (1971).
82. P.Cossee, J.Catal., **3**, 80 (1964).
83. P.Cossee, P.Ros, and J.H.Schachtschneider, "Proceedings of the IVth International Congress on Catalysis (Moscow, 1968)", Acad.Kiado, Budapest, 1971, p.237.
84. J.W.Begley and F.Penella, J.Catal., **8**, 203 (1967).
85. D.R.Armstrong, P.G.Perkins, and J.J.P.Stewart, J.Chem.Soc., Dalton Trans., 1972 (1972).
86. O.Novaro, S.Chow, and P.Magnonat, J.Catal., **41**, 91 (1976).
87. O.Novaro, S.Chow, and P.Magnonat, J.Catal., **42**, 131 (1976).
88. D.R.Armstrong, F.Fortune, and P.G.Perkins, J.Catal., **42**, 435 (1976).
89. V.I.Avdeev, I.I.Zakharov, V.A.Zakharov, G.D.Bukatov, and Yu.I.Ermakov, Zhur.Strukt.Khim., **18**, 525 (1977).
90. D.R.Armstrong, P.G.Perkins, and J.J.P.Stewar, Rev. Roumaine Chim., **19**, 1695 (1974).
91. P.Ros, "Proceedings of the International Symposium on Chemical and Biochemical Reactivity, Jerusalem, 1974", p.207.
92. N.Rösch and K.H.Jonson, J.Mol.Catal., **1**, 395 (1976).
93. D.R.Armstrong, P.G.Perkins, and J.J.Stewart, Rev. Roumaine Chim., **20**, 177 (1975).

94. V.E.L'vovskii and G.B.Erusalimskii, Koord.Khim., **2**, 1221 (1976).
95. M.J.S.Dewar, Bull.Soc.chim.France, **18**, C79 (1971).
96. J.Chatt and L.A.Duncanson, J.Chem.Soc., 2939 (1953).
97. G.Natta, I.Pasquon, J.Svab, and A.Zambelli, Chim.e Ind.(Milano), **44**, 621 (1962).
98. V.I.Tsvetkova, A.P.Firsov, and N.M.Chirkov, Dokl. Akad.Nauk SSSR, **142**, 149 (1962).
99. V.A.Zakharov, N.B.Chumaevskii, Z.K.Bukatova, G.D.Bukatov, and Yu.I.Yermakov, React.Kinet. Catal.Letters, **5**, 429 (1976).
100. V.A.Zakharov, Z.K.Bukatova, S.I.Makhtarulin, N.B.Chumaevskii, and Yu.I.Ermakov, Vysokomol.Soed., **21A**, 496 (1979).
101. Yu.I.Ermakov, L.P.Ivanov, and A.G.Gel'dshtein, Kinetika i Kataliz, **10**, 183 (1969).
102. P.Cossee, Trans.Faraday Soc., **58**, 1926 (1962).

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