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Kinetics of Olefin Polymerization and Active Sites of Heterogeneous Ziegler–Natta Catalysts

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Abstract Kinetic investigations of olefin polymerization with Ziegler–Natta (ZN) catalysts provide information for understanding the mechanism of these reactions and are also necessary for development of industrial productions of polyolefins. In this chapter, the main kinetic features of olefin polymerization with heterogeneous ZN catalysts are considered as well as problems such as a deviation from the linear dependence of the rate of polymerization on monomer concentration, the hydrogen effect in ethene and propene polymerizations, and the comonomer effect, the natures of which are not yet completely clear and are discussed in the literature. For analysis of the kinetics and mechanism of olefin polymerization, data on the number of active centers and propagation rate constants are important. The main methods for determination of these kinetic parameters are discussed in this chapter. Data on the number of active centers in ZN catalysts of different composition are presented. On the base of these kinetic data, the hydrogen effect and the heterogeneity of active centers at propylene polymerization over ZN catalysts are analyzed.

Keywords Active site number · Kinetic features · Mechanism · Metallorganic catalysts · Olefin polymerization

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Contents

Kinetic investigations of olefin polymerization with Ziegler–Natta (ZN) catalysts provide information for understanding the mechanism of these reactions. Knowledge of kinetic regularities is also necessary for development of industrial productions of polyolefins.

The complex nature of ZN catalysts, the chemical interaction between the components of the catalyst during polymerization, the decay in activity during polymerization, and the heterogeneity of active centers make it difficult to study the kinetics of olefin polymerization processes and to interpret the results.

For analysis of the kinetics and mechanism of olefin polymerization it is important to know the number of active centers, which depends on the structure and composition of the catalyst and on the polymerization conditions. Properties of catalysts are also determined by the characteristics of the main reactions of the polymerization process, including initiation of active centers, propagation of polymer chain, transfer of the growing polymer chain with the subsequent reactivation of active centers, and deactivation of active centers.

In this review, the conventional heterogeneous ZN catalysts and modern highly active $MgCl_2$-supported catalysts, modified by electron donor stereoregulating compounds, are considered.

The review includes two parts, in which the main features of the kinetics of olefin polymerization with heterogeneous ZN catalysts (Sect. 1) and data on the number of active centers and the propagation rate constants depending on the nature of these catalysts (Sect. 2) are considered.

1 Kinetics of Olefin Polymerization

Olefin polymerization kinetics are considered and discussed in many reviews [1–6]. In this section, the influence of the main parameters such as the concentrations of catalysts and cocatalysts and time of polymerization on polymerization rate, and the main reactions in the olefin polymerization process will be briefly reviewed. We also consider the problems of deviation from the linear law of polymerization rate with changing monomer concentration, the effect of hydrogen in the ethene and propene polymerizations, as well as the nature of the comonomer effect, which are under discussion in the literature and the natures of which are not yet completely clear.

To describe the kinetics of olefin polymerization with heterogeneous catalysts, kinetic models based on adsorption isotherm theories have been proposed [7–10]. The most accepted two-step mechanism of ZN polymerization, proposed by Cossee [10–12], includes olefin coordination and migratory insertion of coordinated monomer into a metal–carbon bond of the growing polymer chain.

1.1 Influence of Catalyst and Cocatalyst Concentrations

The olefin polymerization rate with heterogeneous catalysts is directly proportional to catalyst concentration [5, 13–15]. The concentration of metallorganic cocatalyst does not affect the polymerization rate with $TiCl_3$ unless a too-high Al-alkyl concentration is used [15, 16]. The catalysts based on VCl_3 are more sensitive to the concentration and type of AlR_3 [17]. According to many observations, in the case of $MgCl_2$-supported catalyst, increasing the Al-alkyl concentration leads to an increase in the maximum rate of polymerization and an increase in the polymerization rate decay [5, 18, 19].

1.2 Main Reactions of Olefin Polymerization

Chain propagation:

$Mt–CH_2–CH(CH_3)–Polymer + CH_2{=}CH(CH_3) \rightarrow Mt–CH_2–CH(CH_3)–CH_2–CH(CH_3)–Polymer$

Polymer chain termination occurs mainly through the following reactions:

1. Transfer with monomer:
   $Mt–CH_2–CH(CH_3)–Polymer + CH_2{=}CH(CH_3) \rightarrow Mt–CH_2–CH_2CH_3 + CH_2{=}C(CH_3)–Polymer$

2. Transfer with cocatalyst:
   $\text{Mt–CH}_2\text{–CH(CH}_3\text{)–Polymer} + \text{AlR}_3 \rightarrow \text{Mt–R} + \text{R}_2\text{Al–CH}_2\text{–CH(CH}_3\text{)–Polymer}$
3. β-Hydride elimination:
   $\text{Mt–CH}_2\text{–CH(CH}_3\text{)–Polymer} \rightarrow \text{Mt–H} + \text{CH}_2\text{=C(CH}_3\text{)–Polymer}$
4. Transfer with hydrogen:
   $\text{Mt–CH}_2\text{–CH(CH}_3\text{)–Polymer} + \text{H}_2 \rightarrow \text{Mt–H} + \text{CH}_3\text{–CH(CH}_3\text{)–Polymer}$

1.3 Kinetic Profile of Polymerization Reactions

The kinetic profile of the polymerization reaction depends on many factors, including the nature of monomer, pre-catalyst (transition metal compound), and cocatalyst (aluminum organic compound), their concentrations and molar ratios, the temperature, and the presence of modifying agents. The polymerization process can occur at a constant rate for a long time after an initial acceleration period [15, 20, 21], which may continue from several minutes to some hours and is increased at lower temperatures, or the polymerization can proceed with a decay of activity with time. The latter type of kinetics is characteristic for propene polymerization with highly active $MgCl_2$-supported catalysts [18, 22]. The rate of catalyst decay depends on the catalyst type and usually increases with temperature. One of the possible reasons for catalyst deactivation is the reduction of active Ti^{3+} to Ti^{2+} (or V^{3+} to V^{2+}) [17, 18]. According to [22, 23], in the case of $MgCl_2/TiCl_4$ catalysts, the deactivation can be connected to the formation of complexes between electron donors and the active site, and with their chemical interaction. As shown [18, 24], the rate decay is not associated with diffusion limitation of monomer to the active sites of a heterogeneous catalyst.

1.4 Dependence of Polymerization Rate Order on Monomer Concentration

One of the most important characteristics of the polymerization process is the dependence of the polymerization rate on monomer concentration. A number of investigations have shown a first order reaction rate with respect to monomer concentration for ethene, propene, and other olefins over a broad concentration range, and the overall rate of olefin polymerization is generally described by the equation:

$$R_{\mathrm{p}} = k_{\mathrm{p}} C_{\mathrm{p}} C_{\mathrm{M}} \tag{1}$$

where k_{p} is the propagation rate constant, C_{p} the number of active sites, and C_{M} the monomer concentration.

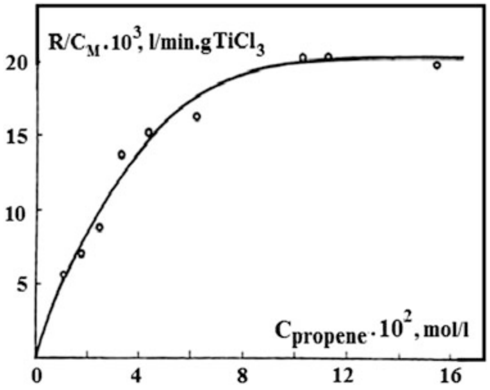


Fig. 1 Dependence of specific stationary rate of propene polymerization on the monomer concentration with $TiCl_3$–$Be(C_2H_5)_2$ in *n*-heptane at 70°C [29]

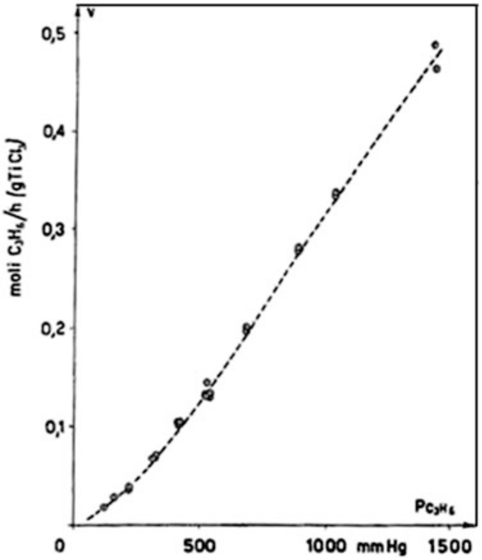


Fig. 2 Dependence of stationary rate of propene polymerization on the monomer pressure with $TiCl_3$–$Al(C_2H_5)_3$ in toluene at 72°C [30]

However, there are now many observations that show a higher rate law order dependence on monomer concentration (up to 2) for ethene [2, 25–27], propene [2, 28–39], styrene [40], and diene [41] using heterogeneous ZN catalysts as well as homogeneous and supported metallocene systems of different kinds.

This was first detected in 1962 by Firsov et al. [28, 29] and Natta at al. [30] in studies of propene polymerization with $TiCl_3$ at low propene concentrations (propene pressure <1 atm). Polymerization proceeded with an initial acceleration to a constant rate, and the effect of propene concentration on the polymerization rate was tested during the steady state phase of the process. It was shown that the dependence of polymerization rate order on monomer concentration increases from first order to some intermediate between first and second order with a reduction in monomer concentration (Figs. 1 and 2).

For an explanation of this effect, authors of works [28–30] proposed similar kinetic models in which the chain propagation includes two reactions of the active site with monomer molecules that differ in the value of the rate constant. The slower reaction is the insertion of the first monomer molecule (the initiation/activation of the active site), the faster reactions are the subsequent insertions of monomer molecules into activated sites (chain propagation). For a description of the stationary rate of polymerization, Eq. (2) was proposed, which takes into account the reactions of initiation (re-initiation after the chain terminations), propagation, and termination:

$$R = \frac{k_{\mathrm{p}} k_{\mathrm{i}} C^* C_{\mathrm{M}}^2}{k_{\mathrm{i}} \mathrm{C}_{\mathrm{M}} + k_{\mathrm{tM}} C_{\mathrm{M}} + \sum_j k_{\mathrm{t}j} C_j^{\alpha j}} \tag{2}$$

or in form (3):

$$R = \frac{k_{\mathrm{p}} C^* C_{\mathrm{M}}}{1 + k_{\mathrm{tM}}/k_{\mathrm{iM}} + \sum_j \left(k_{\mathrm{t}j} C_{\mathrm{t}j}/k_{\mathrm{i}j} C_{\mathrm{M}}\right)} \tag{3}$$

where C^* is the total number of active sites and is equal to the sum of initiation sites (C_{i}) and propagation sites (C_{p}), $k_{\mathrm{i}j}$ is the constant rate of active center initiation and re-initiation after termination by agent j, C_{M} is the monomer concentration, $k_{\mathrm{t}j}$ is the constant rate of termination with agent j (metallorganic cocatalyst, hydrogen, β-hydride elimination), and C_j is the concentration of appropriate termination agent.

According to these equations, depending on the conditions of polymerization, one can observe a first order rate, an intermediate between first and second order, or a second order rate with respect to the monomer concentration.

On the base of this kinetic scheme, Novokshonova et al. [17] proposed equations for the description of polymerization rate as a function of time, including the initial period of rate acceleration (4) and the possible deactivation of active sites (5):

$$R = \frac{k_{\mathrm{p}} k_{\mathrm{i}} C^* C_{\mathrm{M}}^2}{k_{\mathrm{i}} \mathrm{C}_{\mathrm{M}} + \sum_j k_{\mathrm{t}j} \mathrm{C}_{\mathrm{t}j}} \left(1 - \mathrm{e}^{-(k_{\mathrm{i}} C_{\mathrm{M}} + \sum_j k_{\mathrm{t}j} \mathrm{C}_{tj})t}\right) \tag{4}$$

$$R = \frac{k_{\mathrm{p}} k_{\mathrm{i}} C^* C_{\mathrm{M}}^2}{k_{\mathrm{i}} \mathrm{C}_{\mathrm{M}} + \sum_j k_{\mathrm{t}j} \mathrm{C}_{tj}} \left(1 - \mathrm{e}^{-(k_{\mathrm{i}} C_{\mathrm{M}} + \sum_j k_{\mathrm{t}j} \mathrm{C}_{tj})t}\right) \mathrm{e}^{-k_{\mathrm{d}} \mathrm{C}_{\mathrm{A}} t} \tag{5}$$

where k_{d} is the rate constant of active site deactivation by cocatalyst, and C_{A} is the cocatalyst concentration.

Experimental data obtained for the stationary rate of polymerization with $\mathrm{VCl_3}$–Al*i*$\mathrm{Bu_3}$ [17, 31, 32] both for propene and ethene, depending on monomer concentration, support Eqs. (2) and (3): there was an increase in the reaction order

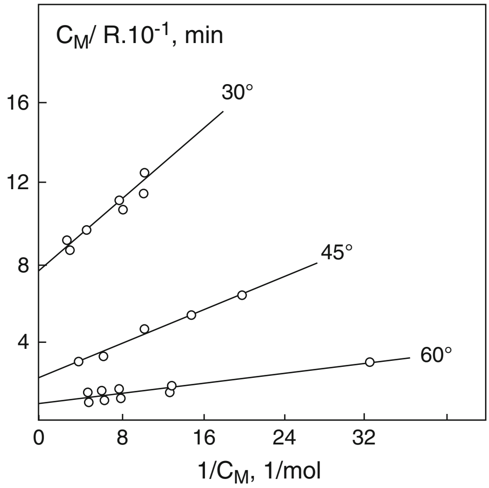


Fig. 3 Dependence of specific stationary rate of propene polymerization on the monomer concentration with VCl_3–Al(i-Bu)$_3$ in n-heptane at temperatures of 30°C, 45°C and 60°C. The graph plots C_M/R against $1/C_M$, where C_M is the monomer concentration [31]

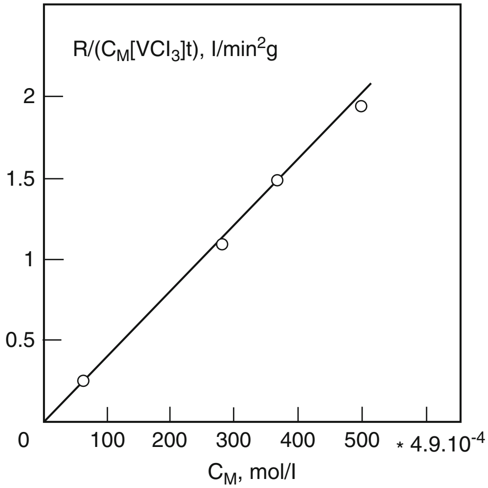


Fig. 4 The rate at initial acceleration period of propene polymerization as a function of the monomer concentration. Catalyst is VCl_3–Al(i-Bu)$_3$, temperature 60°C [17]

with respect to monomer with lowering the monomer concentration, and a linear relationship of C_M/R with $1/C_M$ (Fig. 3).

The series expansion of the exponent in Eq. (4) gives at small times t the Eq. (6), which describes the acceleration period on the kinetic curve for polymerization without deactivation of catalyst:

$$R = k_p k_i C^* {C_m}^2 t \tag{6}$$

According to experimental data (Fig. 4) [17], the rate of polymerization at the acceleration stage of propene polymerization is second order with respect to monomer concentration, which fits Eq. (6). It was found from the kinetic results for propene polymerization [17], that the rate constant of initiation is several orders

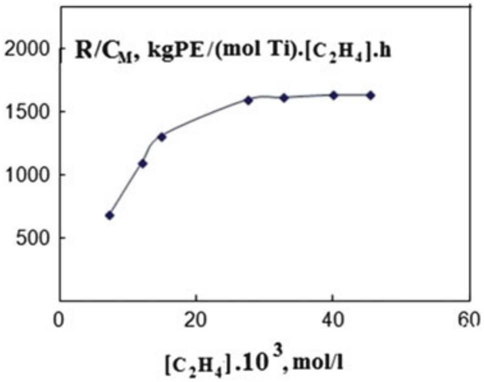


Fig. 5 The specific rate of ethene polymerization at steady state as a function of the monomer concentration with $MgCl_2/D_1/TiCl_4/Al(C_2H_5)_3$ at 50°C [26]

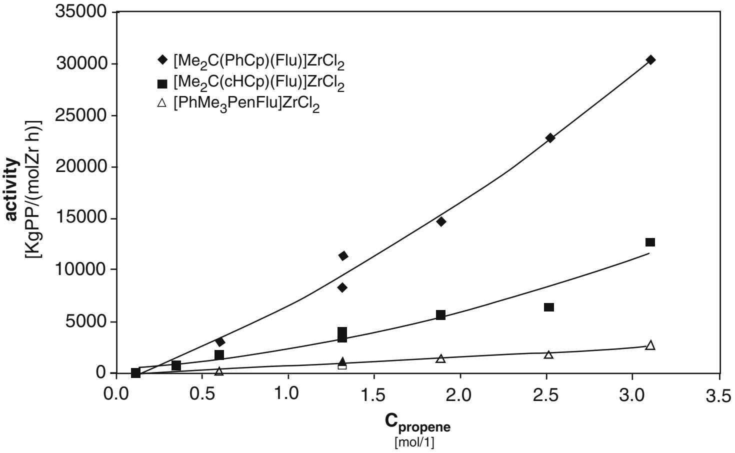


Fig. 6 Activity of metallocene catalysts in propene polymerization as a function of the monomer concentration [39]

of magnitude lower than the propagation rate constant, and that the activation energy of initiation (slow monomer insertion stage) is much higher than the activation energy of chain propagation (fast monomer insertion stage).

A reaction rate order higher than one has also been reported for olefin polymerization with $MgCl_2/TiCl_4$ [26, 38] (Fig. 5) and with homogeneous and supported metallocene catalysts of different types [27, 35–37, 39, 42] (Fig. 6).

At the steady state, the change in the specific rate of polymerization with an alteration of monomer concentration is fully reversible, as has been shown in studies performed during the course of a single experiment for propene polymerization with $MgCl_2/TiCl_4$ catalyst [26] (Fig. 7).

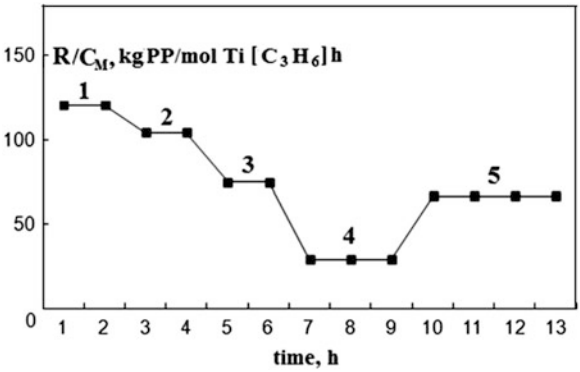


Fig. 7 The specific rate of propene polymerization with an alteration of the monomer concentration in the course of single experiment at steady state with $MgCl_2/D_1/TiCl_4/D_2–Al(C_2H_5)_3$ at 50°C [26]. Monomer concentration, mol/l: 1 – 0.12; 2 – 0.10; 3 – 0.073, 4 – 0.028; 5 – 0.065

It should be noted that when comparing the polymerization rates at different monomer concentrations, the complicated change of rate with time is not always taken into account, so the appropriate concentration range is not always chosen.

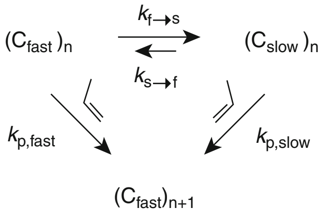
To date, besides the above kinetic model, a number of other approaches have been proposed in the literature to explain the deviation from a linear law of olefin polymerization rate with changing monomer concentration. Most recent studies have been carried out on metallocene catalysts.

Some authors have postulated that the active centers can coordinate two monomer molecules [33, 43]. Ystenes [44, 45] suggested the "trigger mechanism" according to which the insertion of coordinated monomer is triggered by a second monomer molecule. The main assumptions of this mechanism are as follows: the active site is never free because a new monomer enters the site at the same time as the first monomer is inserted; the insertion of the first monomer will not proceed (or will proceed very slowly) if no new monomer is available; in the transition state, two monomer molecules interact with each other and with the central metal atom. Brintzinger et al. [46] analyzed the consistency of "trigger mechanism" by DFT studies.

Resconi et al. [34, 47–49]' proposed a model in which, at the steady state, the active site can exist in two active states, having different propagation rate constants (a faster propagation state and a slower one), that can interconvert without monomer assistance. The monomer insertion transforms a slow center into a fast one (see Scheme 1 [47]).

According to this kinetic scheme, the propagation rate R_p can be presented as:

$$\frac{R_p|}{[C]} = \frac{\left(k_{f\to s}\frac{k_{p,fast}k_{s\to f}}{k_{p,slow}}\right)[\mathrm{M}] + k_{p,fast}[\mathrm{M}]^2}{\left(\frac{k_{f\to s}+k_{s\to f}}{k_{p,slow}}[\mathrm{M}]\right)} \qquad (7)$$



Scheme 1 Transformation of a slow center into a fast one

In this case, a reaction rate order with respect to monomer concentration higher than 1 is due to the decrease in the concentration of the slower state as the monomer concentration increases. The authors suggest that the distinction between the fast and slow states of the active center is in the conformation of the growing chain. Some theoretical calculations show that the kinetic product of monomer insertion is a γ-hydrogen agostic intermediate, whereas the resting (slow) state has the β-hydrogen agostic interaction.

Busico et al. [50–52] proposed a microstructural approach to propene polymerization. It is stated that the regioirregular 2,1-insertion slows chain propagation. The active center with a secondary growing chain enters into a dormant state because of higher steric hindrance for subsequent monomer insertion. However, this approach cannot be considered general because an order higher than 1 is also observed in ethene polymerization.

The physical reasons (mass and heat transfer) for the deviation from a linear law of polymerization rate with changing monomer concentration in propene polymerization have been analyzed and outlined by Mülhaupt et al. [37]. Some aspects of chain propagation steps are also considered in other works [53–55].

Thus, the nature of the two states of active center responsible for the slow and fast insertions of monomer, leading to the nonlinear relationship between activity and monomer concentration, is not yet fully clarified.

1.5 Concentration of Monomer Near the Active Centers

For the calculation of the rate constants of olefin polymerization as well as the constants of copolymerization, it is necessary to know the actual concentration of monomer near the active centers [56]. According to the known schemes [57–59], polyolefin is formed on the surface of the catalyst particles as a polymer shell, and monomer access to the active centers is by diffusion through this polymer shell. As shown [60], the crystallites in polyethylene are impenetrable and are randomly distributed on a macroscopic scale with respect to the diffusion and dissolution processes; the amorphous phase of polymer behaves as a homogeneous liquid. That is, monomer access to the active centers occurs by monomer dissolution in

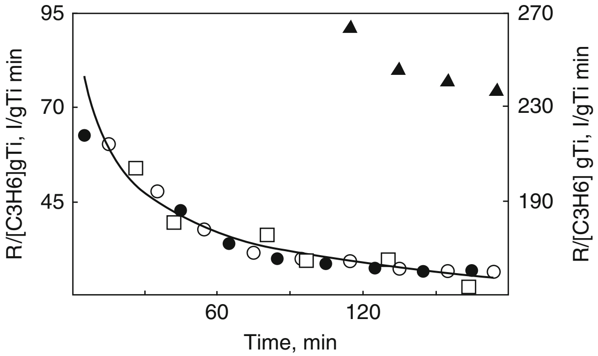


Fig. 8 Kinetic curves of propene polymerization with $MgCl_2/D_1/TiCl_4/D_2$–$AlEt_3$, 70°C. (*Open circles*) polymerization of propylene in *n*-heptane $p_{C_3H_6} = 2.5\,\text{atm}$, $K_H = 0.325$ mol/(l atm); (*closed circles*) polymerization in liquid propene $[C_3H_6] = 10.5$ mol/L; (*open squares*) gas-phase polymerization of propylene, $p_{C_3H_6} = 2.5\,\text{atm}, K_H^{C_3H_6/PP} = 0.13\,\text{mol}/(1\ \text{atm})$; (*closed triangles*) gas-phase polymerization of propylene, $p_{C_3H_6} = 2.5\,\text{atm}$, $[C_3H_6] = p_{C_3H_6}/RT\,\text{mol/L}$ [61]

Table 1 Reactivity ratios of ethene and propene in gas-phase and suspension copolymerizations with $MgCl_2/TiCl_4$ catalyst at 70°C [61]

Copolymerization mode	r_1^*	r_1	r_2^*	r_2
Gas phase	2.26 ± 0.04	7.3 ± 0.2	0.55 ± 0.04	0.141 ± 0.004
Suspension in *n*-heptane	–	7.3 ± 0.2	–	0.141 ± 0.004

Copolymerization constants were determined by kinetic method [63] and calculated by the Fineman–Ross equation [64]

r_1^* and r_2^* were calculated using the concentrations of comonomers in the gas phase; r_1 and r_2 were calculated using the concentrations of comonomers in the polymer shell

the amorphous regions of polymer shells for polymerization in both the slurry and gas phase. This means that for estimation of monomer concentration near the active centers, the solubility constants in the polymer should be used. Use of the monomer concentration in the gas phase for the calculation of the specific rate of polymerization and of the copolymerization constants in the gas-phase processes gives incorrect (anomalous) results. As shown in Fig. 8 [61], the specific rates of propene polymerization in *n*-heptane, in bulk, and in the gas phase on $MgCl_4/TiCl_4$ under identical conditions are the same, using the monomer solubility constants in polymer. Use of the monomer concentration in the gas phase for the calculation of gas-phase homopolymerization specific rate and calculation of reactivity ratios (r_1 and r_2) in gas-phase copolymerization gives the higher value for the specific rate and values of r_1 and r_2 that are not typical for ZN catalysts [61, 62] (see Table 1).

The temperature dependence of solubility constants for ethene and propene in nascent UHMWPE and isotactic PP (in dry powder-like state and swollen in heptane) were determined in the range of 20–70°C [61]. Solubility constants (Henry constants, K_H) were calculated taking into account the fact that the solubility of gases in the semicrystalline polymers is directly proportional to the content of the amorphous phase: $K_H = 20\times10^{-3}\ e^{730/RT}$, $2.5\times10^{-3}\ e^{1,700/RT}$, $25\times10^{-3}\ e^{1,330/RT}$, and $1.3\times10^{-3}\ e^{3,100/RT}$ for ethene in PE, ethene in PP, propene in PE, and propene in PP, respectively. The constants for ethene and propene solubility in PE and PP, and swollen in *n*-heptane, are close to the constants for their solubility in *n*-heptane [65–67].

1.6 Hydrogen Effect

Hydrogen is the most used molecular weight regulator in polyolefin production. There are many publications describing the effect of hydrogen on olefin polymerization. The dependence of catalyst activity on the presence of hydrogen varies with the nature of the monomer and catalyst.

Usually, hydrogen significantly reduces the activity of the catalyst in the ethene polymerization [22, 68–71]. The character of the kinetic curves of ethene polymerization in the presence of hydrogen is practically unchanged [71, 72]. It is also noted [73, 74] that the effect of hydrogen is reversible. The removal of hydrogen from the reaction medium is accompanied by recovery of the original activity level. These facts indicate that the hydrogen does not affect the stability of the active centers. According to Natta [68] and Grieveson [75], the reason for the reduction in the rate of ethene polymerization in the presence of hydrogen is connected to the slower insertion of monomer into the Ti–H bonds, which are formed by reaction of active centers with H_2:

$$\mathrm{Mt-CH_2-CH_2-Pol + H_2 \rightarrow\ Mt-H + CH_3-CH-Pol} \qquad (8)$$

Kissin et al. [72, 73, 76, 77] explain the reduction in activity by the formation of $Ti–CH_2–CH_3$ structures after the insertion of ethene into Ti–H bonds, and these structures are the low-activity (or dormant) centers in polymerization because of the β-hydrogen agostic interaction.

Published data [78–81] show that a first order rate of chain transfer to hydrogen in the polymerization of ethylene with a ZN catalyst is usually observed; on the other hand, a number of studies [82] show a rate order of 0.5.

In propylene polymerization, the activating effect of hydrogen, i.e., an increase in initial polymerization rate as well as in overall activity, is observed [83–90] (Fig. 9). This activation is reversible and the polymerization rate decreases after the removal of hydrogen from the reaction zone [89, 90]. The degree of increase in the activity and change of the polymerization rate with time, in comparison with polymerization without hydrogen, depend on the catalyst nature and the hydrogen concentration.

A number of explanations of this effect have been proposed. The most accepted hypotheses for the activation effect are based on the capability of active centers of ZN and metallocene catalysts for regioirregular 2,1-insertion of propene into

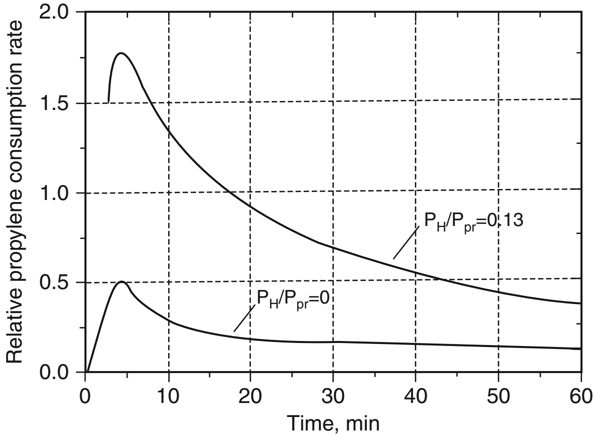


Fig. 9 Kinetics of propene polymerization at 70°C with $MgCl_2$/dibutylphtalate/$TiCl_4$/PhSi$(OEt)_3$–$AlEt_3$ without hydrogen (p_H/p_{pr}=0) and in the presence of hydrogen (p_H/p_{pr}=0.13) [76]

the growing chain, resulting in the formation of the low-activity or dormant active centers, Mt–CH(CH_3)–CH_2–Pol:

$$\begin{aligned}&\mathrm{Mt-CH_2-CH(CH_3)-Pol+CH(CH_3)=CH_2\rightarrow}\\&\mathrm{Mt-CH(CH_3)-CH_2-CH_2-CH(CH_3)-Pol}\end{aligned}\tag{9}$$

Chain transfer in the presence of hydrogen reactivates such dormant centers:

$$\begin{aligned}&\mathrm{Mt-CH(CH_3)-CH_2-CH_2-CH(CH_3)-Pol+H_2}\\&\rightarrow\ \mathrm{Mt-H+CH_3-CH_2-CH_2-CH_2-CH(CH_3)-Pol}\end{aligned}\tag{10}$$

The presence of *n*-butyl end groups in polymer chains formed during propene polymerization in the presence of hydrogen supports this hypothesis [85, 91–93]. The possibility of formation of the inactive centers Mt–CH$(CH_3)_2$ by the reaction of chain transfer with the monomer in a secondary 2,1-orientation or by a secondary insertion in the Mt–H bond, formed as a result of chain transfer to hydrogen, has been considered [76]:

$$\begin{aligned}&\mathrm{Mt-CH_2-CH(CH_3)-Pol+CH(CH_3)=CH_2}\\&\rightarrow\ \mathrm{Mt-CH(CH_3)_2+CH_2=C(CH_3)-Pol}\end{aligned}\tag{11}$$

$$\mathrm{Mt-H+CH(CH_3)=CH_2\rightarrow\ Mt-CH(CH_3)_2}\tag{12}$$

The chain transfer with hydrogen reactivates inactive centers Mt–CH$(CH_3)_2$ with the formation of a Ti–H bond, followed by a primary propene insertion. Another explanation is related to the reactivation of Ti^{2+} sites, which are inactive in propene polymerization, by hydrogen oxidative addition [94]; indeed, the concentration of active sites is noticeably increased in the presence of hydrogen [87, 95] due to hydrogenation of inactive Ti-allyl centers [95].

Thus, the mechanism of the activating action of hydrogen in propene polymerization, as well as the mechanism of reduction of catalyst activity in ethene polymerization in the presence of hydrogen, are still not completely clear and need further confirmation.

1.7 Heterogeneity of Active Centers

The distinctive property of heterogeneous ZN catalysts is a heterogeneity of active centers. This influences the kinetics of olefin polymerization and the characteristics of the polymers obtained. The multicenter nature of heterogeneous catalysts manifests itself in broadening of molecular weight distribution (MWD), formation of polymer fractions of different stereoregularity, compositional non-uniformity of copolymers of ethene and propene with α-olefins, and the complicated order of catalyst deactivation reactions. Non-uniformity of active sites is related, obviously, to the chemical, structural, and energy non-uniformity of the catalyst surface. The presence on the catalyst surface of active centers of various types, differing in the magnitude of propagation rate constants, has been reported in a number of publications [18, 96–98]. This fact has been proposed [99] as a cause of MWD broadening. Floyd et al. [100] found that the unimodal MWD curves for polypropylene obtained with heterogeneous ZN catalysts can be simulated only by assuming the presence of at least three or four types of active sites, each of which follows Flory's most probable distribution. The MWD of the polymer depends on the type of heterogeneous catalyst, nature of the donors in $MgCl_2$-supported catalysts, comonomer presence, and the conditions of polymerization.

For investigation of active site non-uniformity, a method was proposed [101, 102] based on mass-spectrometric study of temperature-programmed desorption (TPD) products from the catalyst surface at the most initial stage of olefin polymerization (up to 10–15 monomer units in chain). The method allows one to obtain information concerning the energy non-uniformity of active sites in terms of a distribution of active sites over the activation energy of active Mt–C bond thermal destruction in active sites. So, it was shown for ethene polymerization with $SiO_2/TiCl_4/AlEt_2Cl$ and $SiO_2/AlEt_2Cl/TiCl_4$ catalysts that there are at least two groups of active sites in these catalysts, varying in the activation energy of thermal destruction of active Ti–C bonds (Fig. 10), and that the distribution depends on the catalyst type.

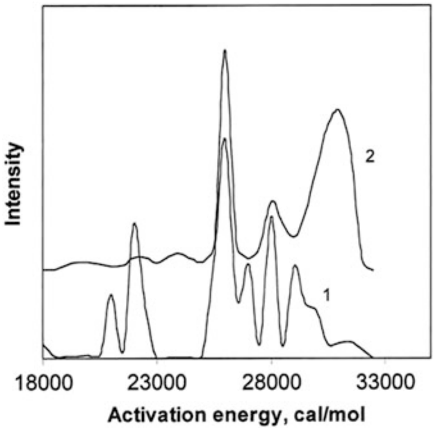


Fig. 10 Energy spectra of active sites for $SiO_2/TiCl_4/Al(C_2H_5)_2Cl$ (*1*) and $SiO_2/Al(C_2H_5)_3/TiCl_4$ (*2*) catalysts calculated on the basis of TPD experiments in the terms of active site distribution over activation energy of thermal destruction of Ti–C bonds [102]

1.8 Copolymerization

Processes of ethene/α-olefin copolymerization are of great practical importance. Copolymerization of ethene with small amounts of highest α-olefins (1-butene, 1-hexene, 1-octene) allows one to produce linear low density polyethylene (LLDPE), which is one of the most widely used large-scale polyolefin products. Polypropylene, modified with small amounts of ethene, exhibits higher impact strength compared to isotactic homopolypropylene. Copolymerization of propene with large amounts of ethene and terpolymerization of ethene/propene/diene result in amorphous elastomer materials (rubbers) [103].

The properties of olefin copolymers depend on the nature and content of comonomer and on the comonomer distribution in the polymer chain. If monomers are distributed as long sequences, crystalline copolymers are formed. The random distribution of comonomers gives amorphous polymer materials. The conventional ZN systems, such as heterogeneous Ti- or V-based catalysts and homogeneous V-based catalysts, are used for industrial production of olefin copolymers. The application of metallocene catalysts [104] has allowed an increase in the comonomer content in copolymers, more uniform comonomer distribution in the polymer chains, and broadening of the range of comonomers used [104–106]. Several examples of reactivity ratios r_1 and r_2 and their product r_1r_2 for ethene/propene copolymerization are given in Table 2. For most heterogeneous titanium catalysts, the product r_1r_2 is usually close to 1 or greater, which corresponds to the tendency for this catalysts to form copolymers with long crystallizable ethene sequences. In the case of V-based systems, the r_1r_2 value is lower and they give a more random comonomer distribution in the chain [107–109, 112]. For metallocene catalysts, the product r_1r_2 is smaller than 1, which is reflected in the alternation of ethene and propene units in copolymer chains [110, 111].

Table 2 Reactivity ratios of ethene/propene copolymerization

Catalyst	Temperature (°C)	r_1	r_2	r_1r_2	References
δ-$TiCl_3-Al(C_2H_5)_2Cl$	70	11.6	0.35	4.1	[107]
$VCl_3-Al(n\text{-}C_6H_{13})_3$	25	5.6	0.15	0.81	[108]
$VOCl_3-Al(n\text{-}C_6H_{13})_3$	25	18	0.07	1.2	[108]
$MgCl_2/TiCl_4$/ethylbenzoate/$Al(C_2H_5)_3$	70	5.5	0.36	2.0	[107]
$MgCl_2/TiCl_4/Al(i\text{-}C_4H_9)_3$	70	15.8	0.03	0.5	[109]
$MgCl_2/VCl_4/Al(i\text{-}C_4H_9)_3$	70	3.4	0.06	1.9	[109]
$EBIZrCl_2$/MAO	50	6.61	0.06	0.4	[110]
$EBIZrCl_2$/MAO	25	6.26	0.11	0.69	[110]
$Me_2C(Cp)(Flu)ZrCl_2$/MAO	25	1.3	0.2	0.26	[111]

1.9 Comonomer Effect in Olefin Copolymerization Reactions

One of the features of olefin copolymerization kinetics is the effect of comonomer on the rate of ethene or propene polymerization during ethene/α-olefin or propene/α-olefin copolymerization, i.e., the so-called comonomer effect (CEF). The rate enhancement of ethene or propene polymerization in the presence of a comonomer is observed for conventional ZN catalysts [80, 113–123] and for homogeneous [124–133] and supported metallocenes [134–136] and post-metallocenes catalysts [137–140]. The increase in activity was remarked in the presence of such comonomers as propene, 2-methylpropene, 1-butene, 3-methylbutene, 4-methylpentene-1, 1-hexene, 1-octene,1-decene, cyclopentene, styrene, and dienes.

Numerous studies have shown that the magnitude of effect depends on the catalyst nature, the comonomer type, and the experimental conditions. Examples of the comonomer effect for various catalysts and comonomers are shown in Tables 3, 4, and 5 as the ratio of copolymerization rate to the ethylene (or propylene) homopolymerization rate.

The effect is generally higher for heterogeneous catalysts, and for supported metallocenes it is higher than for homogeneous catalysts. The length of the α-olefin chain is also important. The higher the comonomer chain length, the smaller the effect. The negative effect of comonomer on the rate was found for ethylene/norbornene copolymerization [126] and for copolymerization of propene with 1-octene for metallocene catalysts [136].

For understanding the nature of the comonomer effect, it is also very important that the rate enhancement takes place in the sequential processes of homo- and copolymerization, i.e., when the ethene homopolymerization is carried out after the α-olefin homopolymerization or ethene/α-olefin copolymerization [122, 123] (Table 6).

The nature of this phenomenon is widely discussed in the literature. Several reasons (physical and chemical) have been proposed:

1. Monomer access to active centers through the polymer film becomes easier with higher amorphous phase content in the copolymer [116, 119, 121–123] or with dissolving of the polymer in the reaction medium [126, 130, 131]

Table 3 Comonomer effect in ethene/α-olefin copolymerization using heterogeneous and supported ZN catalyst systems

Catalyst	Comonomer	CEF (R_{cop}/R_{pol})	References
δ-$TiCl_3$ × 0.33 $AlCl_3$ + $AlEt_3$	4-MP-1	15.8–4.7	[113]
	1-Hexene	14–10	
$TiCl_4/MgCl_2$ + $AlEt_3$	1-Hexene	2–4	[114]
$TiCl_4/MgCl_2$/EB + Al(*n*-oct)$_3$	4-MP-1	6.9–9.5	[113]
$TiCl_4/MgCl_2$/DIBP + $AlEt_3$	Propene	2.0	[116]
VCl_3(THF)/SiO_2 + $AlEt_3$	Propene	5.8	[141]
	1-Butene	3.4	
	1-Hexene	2.0	

CEF – comonomer effect, Rcop – rate of ethene insertion in ethene/α-olefin copolymerization Rpol –rate of ethene homopolymerization

Table 4 Comonomer effect in ethene/α-olefin copolymerization using homogeneous metallocene catalysts

Catalyst	Comonomer	Temperature (°C)	CEF (R_{cop}/R_{pol})	References
Cp_2ZrCl_2/MAO	Propylene	30	1.65	[124]
	1-Hexene	30	2.30	
Cp_2ZrCl_2/MAO	1-Hexene	50	2.3	[127]
		95	Not observed	
Et(IndH$_4$)$_2$ZrCl$_2$/MAO	Propene	40	2	[129]
	1-Hexene	40	1.8	
*i*Pr(Cp)(Flu)ZrCl2	Propene	40	Not observed	[129]
	1-Hexene	40	Not observed	
(*tert*-Butanamide)Me(Me$_4$-η^5-Cp) silane-TiCl$_2$/MAO	Poly(propylene) macromonomer	40	3.2	[130]
		90	Not observed	
*i*Pr[FluCp]ZrCl$_2$/MAO	1-Hexene	25	6	[126]
Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	1-Hexene	25	2.6	[126]

2. The increase in the number of active centers can be achieved as a result of heterogeneous catalyst fragmentation [122, 123], deagglomeration of the growing polymer particles during copolymerization with homogeneous catalysts [126, 130, 131], or by activation of dormant active centers [113]
3. Modification of active centers by comonomer, with variation in the propagation rate constant [118, 119, 124, 125, 127, 132, 141]
4. Diffusion effects and the related increase in monomer concentration near the active site [134, 145]

Due to the diversity and complexity of the considered polymerization processes, the different causes for manifestation of the comonomer effect or their combination may appear, depending on conditions.

Table 5 Comonomer effect in propene/α-olefin copolymerization using heterogeneous ZN catalyst and homogeneous and supported metallocene catalyst systems

Catalyst	Comonomer	Copolymerization conditions	CEF $(Q_{cop}/Q_{pol})^a$	References
$MgCl_2$/DIBP/$TiCl_4$ + $AlEt_3$ + D_2 with no external donor	1-Hexene	60°C, in *n*-heptane, 30 min	1.2	[142]
$MgCl_2$/DIBP/$TiCl_4$ + $AlEt_3$ + D_2 with PTES (triethoxyphenylsilane)			1.02	
$MgCl_2$/DIBP/$TiCl_4$ + $AlEt_3$ + D_2 with DTBDMS(dimethoxydi-*tert*-butylsilane)			1.63	
rac-$Me_2Si(Ind)_2ZrCl_2$/MAO	1-Hexene	30°C, in toluene, 120 min	2.38	[143]
rac-Me_2Si(4-Ph-2Me-Ind)$_2$ $ZrCl_2$/MAO			1.60	
Ph_2C(Cp)(Flu)$ZrCl_2$/MAO			0.21	
rac-Me_2Si(4-Ph-2Me-Ind)$_2$ $ZrCl_2$/MAO	1-Butene	60°C, in liquid propene, 10/11 min	4.87	[144]
rac-Me_2Si(4-Ph-2Me-Ind)$_2$ $ZrCl_2$/MAO	1-Octene	60°C, in liquid propene, 40/29 min	0.57	[136]
SiO_2/MAO/*rac*-Me_2Si (4-Ph-2Me-Ind)$_2ZrCl_2$/Al*i*Bu_3	1-Octene	60°C, in liquid propene, 50 min	1.69	[136]

$^a Q_{cop}$ and Q_{pol} are polymer and copolymer yields

Table 6 Comonomer effect in the two-step process of homo- and copolymerization of ethene and α-olefin using different types of catalyst [133]

Catalyst	Process	R_2/R_1
$TiCl_4/MgCl_2/D_1{}^a$–$D_2{}^b$–$AlEt_3$	$C_3 \to C_2$	3.0
$VCl_3/Al(OH)_3$–$Al(i\text{-}Bu)_3$	$C_2 + C_3 \to C_2$	3.3
Cp_2ZrCl_2–MAO	$C_3 \to C_2$	1.5
$Et(Ind)_2ZrCl_2$–ZSM-5(H_2O)–$AlMe_3$	$C_3 \to C_2$	5.3

R_1 is the specific rate of ethene homopolymerization and R_2 the specific rate of ethene homopolymerization on the second step of the two-step process

[a] Mixture of dibutylphthalate and ethylbenzoate

[b] Phenyltriethoxysilane

2 Number of Active Centers and Propagation Rate Constants for Olefin Polymerization on ZN Catalysts

For catalytic olefin polymerization on heterogeneous ZN catalysts, it is accepted that surface alkyl compounds of transition metals should be considered as the active centers. These species contain a growing polymer chain as an alkyl group. For analysis of the kinetics and mechanism of polymerization on ZN catalysts, it is all-important to have data on the number of active centers (C_p). The number of active centers depends on the composition and conditions of preparation of the catalysts and on the conditions of polymerization and is usually a small fraction of the total number of surface transition metal compounds in the catalyst. Thus, the rate of polymerization, which is equal to the rate of propagation of the olefin polymer chain, is defined by a simple equation (1).

The problem of determination of the number of active centers as the number of titanium–polymer bonds was formulated for the first time in the pioneering works of Natta [15, 146] for propylene polymerization on catalyst $TiCl_3 + AlEt_3$. He used for this purpose cocatalyst $AlEt_3$ labeled by a radioactive isotope ^{14}C in the ethyl group. Active centers of type $Cl_xTi{-}^{14}CH_2CH_3$ are formed in this case and polymer with a radioactive label obtained on these centers. The number of active centers can be calculated from these data.

In this review, data on the number of active centers and values of propagation rate constants (k_p) for olefin polymerization on traditional ZN catalysts (mainly $TiCl_3/AlEt_xCl_y$) and highly active supported ZN catalysts containing titanium chlorides on activated magnesium dichloride will be presented.

Different methods for determination of the number of active centers during catalytic olefin polymerization are proposed. There are two basic groups of method applied to determine the kinetic characteristics of propagation reactions and transfer reactions of polymer chains (values of C_p, k_p, and K_{tr}) for catalytic olefin polymerization.

1. Methods based on the analysis of dependences of polymerization rate and molecular weight on the time and conditions of polymerization. We will name them conditionally “kinetic methods.”
2. Methods based on introduction of a radioactive label in the growing polymer molecule.

2.1 Kinetic Methods

The method of calculation of rate constants of the separate reactions proceeding in the course of polymerization and based on the analysis of dependences of polymerization rate (R_p) and polymerization degree (P_n) on the concentration of reagents was used for the first time in the works of Natta [15, 146] and Chirkov [28, 29]. This method allows calculation of values for the products of rate constants of separate reactions and the number of active centers, but does not allow calculation of separate values for rate constants and the number of active centers.

Another kinetic method has been proposed [17]. This method allows one to determine the k_p value and the number of active sites using the dependence on monomer concentration of the stationary polymerization rate and of the polymerization rate during the acceleration period of the kinetic curve, according to Eqs. (2) and (6). The method has been applied for determination of these kinetic parameters in the polymerization of propylene and ethylene with $VCl_3/Al(i\text{-}Bu)_3$ catalyst.

Calculation of rate constants of separate reactions for the stationary phase of polymerization, when the number of the active centers does not change with polymerization time, is possible by use the dependence of the molecular weight of polymer (polymerization degree) on polymerization time [147, 148]:

$$\frac{1}{P_{\mathrm{n}}}=\frac{1}{k_{\mathrm{p}}C_{\mathrm{m}}}\cdot\frac{1}{\tau}+\frac{\sum k_{\mathrm{tr}}^{i}\cdot C_{\mathrm{i}}^{i}}{k_{\mathrm{p}}C_{\mathrm{m}}} \tag{13}$$

where P_{n} is the average polymerization degree, k_{p} is the propagation rate constant, C_{m} is the concentration of monomer, τ is polymerization time, K_{tr}^{i} is the rate constant for the transfer of polymer chain reaction with a component i, and C_{i} is the concentration of component i.

This method has been used [147, 148] for determination of k_{p} values for polymerization of butene-1 on a ZN catalyst based on $TiCl_3$ and VCl_3. The k_{p} value greatly increases at transition from $TiCl_3$ to VCl_3. The same method has also been used [149, 150] for study of propylene polymerization on the catalyst α-$TiCl_3$ + $AlEt_3$, and also for study of ethylene polymerization on the catalyst γ-$TiCl_3$ + $AlEt_3Cl$ [151, 152]. However, in the latter cases the condition of polymerization stability was not met. It is necessary to notice also that in works [147–152], P_{n} values were calculated from polymer viscosity data in the assumption that polydispersity of the polymer does not depend on polymerization time. These assumptions are not always met and therefore reduces the reliability of results obtained by this method.

A new and more effective and reliable variant of the kinetic method is the stopped flow method (SF method), which has been offered by Keii and Terano [153] for determination of the number of active centers and the propagation rate constant in olefin polymerization on ZN catalysts. The main feature of this method is determination of C_{p} and k_{p} values in conditions of quasi-living polymerization, when transfer reactions of a polymer chain practically do not proceed and linear dependences of molecular weight of formed polymer and yield of polymer on polymerization time are observed. It has been shown that these conditions are obtained for propylene polymerization on supported titanium-magnesium catalysts (TMC) at low temperature (30°C) and at times of polymerization less than 0.2 s; in these cases, values of C_{p} and k_{p} can be calculated from Eqs. (14) and (15):

$$M_{\mathrm{n}}=M_0k_{\mathrm{p}}C_{\mathrm{m}}\tau \tag{14}$$

$$Y=k_{\mathrm{p}}C_{\mathrm{p}}C_{\mathrm{m}}\tau \tag{15}$$

where M_{n} is the average number molecular weight of polymer, M_0 the molecular weight of monomer, C_{m} the concentration of monomer, Y the polymer yield, and τ the polymerization time.

To make these calculations, some conditions are necessary:

1. Active centers should be formed instantly at interaction of the catalyst with cocatalyst and the time necessary for formation of the active centers should be less than the time of quasi-living polymerization
2. The number of active centers and polymerization rate should be constant at the stage of quasi-living polymerization

2.2 Radiochemical Methods

In these methods, the number of active centers is defined by introduction of a radioactive label in a growing polymeric chain. The label can be entered at an initiation stage by use of an organoaluminum cocatalyst, containing alkyl group with a radioactive label. This method has been used Natta [15, 146] and Chien [154] in a study of propylene polymerization on the $TiCl_3$ catalyst in a combination with cocatalysts $Al(Et)_3$ or $Al(Et)_2Cl$ labeled by radioactive isotope ^{14}C.

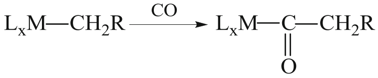
Another method is based on introduction into polymerization of compounds (quenching agents) labeled by a radioactive isotope and by termination of polymerization in such a manner that this compound or its part joins a growing polymer chain (QR method). In the case of olefin polymerization on ZN catalysts, alcohol labeled with ^3H in the hydroxyl group was used as a quenching agent (QR RO^3H method):

$$\mathrm{Cl}_x\mathrm{Ti}-\mathrm{CH_2R}+\mathrm{RO^3H}\rightarrow\mathrm{Cl}_x\mathrm{Ti}-\mathrm{OR}+{}^3\mathrm{HCH_2R} \qquad (16)$$

For the first time, this method was used [155] for study of ethylene polymerization on catalyst $TiCl_4 + AlEt_3$. Further, a number of works on definition of C_p and k_p values have been published for olefin polymerization on ZN catalysts using this method [156–162]. The basic difficulty of quantitative definition of the number of active centers at polymerization on ZN catalysts by this method is connected with the formation of inactive aluminum–polymer bonds during the course of polymerization. These bonds appear as a result of transfer reaction of a growing polymer chain with organoaluminum cocatalyst. The presence of this reaction was shown in the early works of Natta [15, 146] and confirmed experimentally for all ZN catalysts. For this reason, an increase in the number of metal–polymer bonds is observed with increasing polymerization time although polymerization rate can decrease [162] or remain constant [156]. To account for the effect of inactive aluminum–polymer bonds, the number of active centers is defined by extrapolation of the total number of metal–polymer bonds to zero time of polymerization. However, according to Coover et al. [156], the rate of formation of aluminum–polymer bonds sharply decreases during the course of polymerizations and this effect should be accounted for in calculation of the number of active centers. The authors [156] believe that this effect is connected with a reduction in the concentration of organoaluminum compound on a surface of the catalyst owing to its slow diffusion through a layer of formed polymer.

More reliable data on the number of active centers can be obtained by this method for cases where the contribution of the transfer reaction with organoaluminum cocatalyst is very small. Such a case is the polymerization of 4-methylpentene-1 on catalyst $VCl_3/Al(i\text{-}Bu)_3$ [163].

Later, for definition of the number of active centers at polymerization on ZN catalysts, it was suggested that the “selective” quenching agent (^{14}CO), interacting only with titanium–polymer bonds [164–166], (QR ^{14}CO method) be used. The use of carbon monoxide for this purpose is based on the well-known metallorganic chemistry reaction of CO insertion into δ-bond transition metal-alkyl:



$$L_xM\text{—}CH_2R \xrightarrow{CO} L_xM\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_2R \tag{17}$$

Examples of irreversible CO insertion into a titanium-alkyl bond are described [167] for CO reaction with a complex Cp_2TiClR, with formation of acyl complex $Cp_2Ti(Cl)COR$. There are examples of CO insertion into vanadium-alkyl and titanium-alkyl bonds, formed in ZN catalysts [168, 169]. In particular [168], it is shown that CO is attached irreversibly with “living” polypropylene molecules formed during propylene polymerization on soluble catalyst $V(acac)_3/AlEt_2Cl$ at a temperature of −78°C. Introduction of CO terminates polymerization and after that each polymer molecule contains one terminal group $R(C{=}O)H$. Thus, CO interacts quantitatively with growing polymer molecules by insertion into active vanadium–polymer bonds. Similar research [169] has been performed for ethylene polymerization on TMC catalysts in the conditions of “living” polymerization, with the subsequent interaction of growing polymer chains with CO. It was also confirmed that CO insertion into titanium–polymer bonds results mainly in formation of structures $R\,(CO)R'$.

Details of the interaction of ^{14}CO with ZN catalysts during olefin polymerization and the use of this technique for definition of the number of active centers are presented in works [166, 170–173] and the review [174]. In particular, it is necessary to note the necessity of additional clearing of polymer from the low molecular weight by-products containing a radioactive label [173]. These by-products are formed through interaction of ^{14}CO with titanium-alkyl bonds like the Ti–Et present in the catalyst as a result of alkylation of titanium chlorides by AlR_3 and transfer reactions of the growing polymer chain with $AlEt_3$ cocatalyst or with monomer.

We have listed the advantages and some limitations of the SF method. In the case of QR, it is possible to study polymerization kinetics at a wide variation of composition and morphology of the catalysts, leading to change in the rates of formation and deactivation of the active centers during the course of polymerization. It is also possible to study polymerization with more reactive monomers like ethylene, and in the presence of an additional effective chain transfer agent such as hydrogen.

Data on the number of active centers and propagation rate constants for olefin polymerization on traditional ZN catalysts and highly active supported ZN catalysts, obtained by use of SF and QR methods, will be presented and discussed below.

2.3 Number of Active Centers in Ethylene and Propylene Polymerization on Traditional ZN Catalysts and Supported Titanium–Magnesium Catalysts

It is known that the activity of catalysts changes very much depending on their composition, preparation and activation methods, and polymerization conditions. The most plausible reason for this is a change in the number of active centers. From the data obtained using a QR RO^3H method [155, 157, 161, 162] or using labeled cocatalyst $Al(^{14}C_2H_5)_3$ [15, 146, 154] for ethylene and propylene polymerization on $TiCl_3/AlR_xCl_y$ catalysts, the number of active centers is $(1–10) \times 10^{-2}$ mol/mol Ti. However, in work [156] it has been shown that the rate of transfer reaction of polymer chain with AlR_3 decreases sharply with increasing polymerization time (polymer yield). Taking into account this effect, it was found [156] that the C_p values for propylene polymerization on $TiCl_3/AlEt_2Cl$ ($AlEt_3$) catalyst are lower and only $(0.1–0.3) \times 10^{-2}$ mol/mol Ti. This value is close to the number of active centers, $(0.1–0.5) \times 10^{-2}$ mol/mol Ti, found later with use of the QR ^{14}CO method for ethylene and propylene polymerization on similar catalysts, $TiCl_3/AlEt_2Cl$ ($AlEt_3$, $Al\mathit{i}Bu)_3$ [21, 165, 166, 174, 175]. Thus, the number of active centers for traditional ZN catalysts based on $TiCl_3$ is very low and, according to works [21, 59, 166, 175] (QR methods), makes up no more than 0.8 mol% of the total content of Ti in catalysts. By estimation [174], this value can correspond to the number of titanium chlorides located on the lateral sides of crystals, making microparticles of δ-$TiCl_3$ with a surface of 70–100 m^2/g.

A great increase in activity of ZN catalysts is reached by supporting $TiCl_4$ on “activated” magnesium dichloride, having a high surface and disordered crystal structure (supported TMC catalysts) [176, 177]. The activity of these catalysts in ethylene and propylene polymerization is usually 30–150 kg/g Ti h atm, which exceeds the activity of traditional ZN catalysts based on δ-$TiCl_3$ by approximately two orders of magnitude. According to works [74, 165, 173, 178–180] (QR ^{14}CO method) and works [181, 182] (QR RO^3H method), such an increase in activity is connected with a great increase in the number of active centers, which for these catalysts is 1–7 mol% of the total Ti content. Further, in works [153, 183–192] with use of the SF method in the case of propylene polymerization on TMC, C_p values of the same order (0.5–11 mol%) have been obtained. It is necessary to notice that the number of active centers changes considerably with variation in the composition and conditions of catalyst preparation. For example, in work [183] for three types of TMC with different activities, C_p values from 0.8 to 9.9 mol% were obtained by the SF method.

Thus, the results of definition of the number of active centers for propylene polymerization on TMC, obtained by independent methods (SF and QR methods), show the following:

1. The great increase in activity of TMC in comparison with traditional ZN catalysts is defined, mainly, by an increase in the number of active centers
2. The number of active centers is less than 10 mol% of the total titanium content in the catalysts (usually in limits from 1% to 10%) and depends on the composition and procedure of TMC preparation; most of the titanium is in the inactive form and does not participate in polymerization

It has been found [80, 193] that a great increase in activity of TMC in ethylene polymerization (from 50–100 kg/g Ti h atm to 400–600 kg/g Ti h atm) is observed with a decrease in titanium content in the catalyst from 1–4 wt% of Ti to values less than 0.1 wt% of Ti. In this case, it is possible to expect that the number of the active centers increases to 30–40 mol% of the total content of titanium [194].

The number of active centers at polymerization on ZN catalysts essentially depends on the conditions of polymerization, in particular on the composition of the organoaluminum cocatalyst and its concentration, the temperature of polymerization, and the presence of additional components added for regulation of activity and the molecular weight of polymer.

Data on the effect of hydrogen on the number of the active centers and propagation rate constants for polymerization of propylene and ethylene on ZN catalysts of various compositions will be presented and discussed in the next section.

2.4 Number of the Active Centers and Propagation Rate Constants in Polymerization in the Presence of Hydrogen

Hydrogen is the most effective chain transfer agent for olefin polymerization on ZN catalysts and is widely used for polyolefin production in industry and in laboratory research for control of molecular weight of polymers. The presence of hydrogen during the polymerization influences the polymerization kinetics. In the case of ethylene polymerization, addition of hydrogen into polymerization usually decreases the polymerization rate. In work [195] for the first time it was shown that addition of hydrogen during propylene polymerization on ZN catalysts leads to an appreciable increase in polymerization rate. This phenomenon has been confirmed in a number of other works [22, 89, 196–198]. To reveal the reasons for the activating effect of hydrogen (the “hydrogen effect”), data on the influence of hydrogen on the number of active centers and propagation rate constants can be the useful. In work [199] it was found that in the presence of hydrogen during propylene polymerization on TMC the number of active centers increases considerably (QR ^{14}CO method). However, according to data presented in [184], the presence of hydrogen at a quasi-living polymerization for 0.2 s does

Table 7 Data on the hydrogen effect on C_p and k_p values for propylene polymerization over ZN catalysts (QR ^{14}CO method) [74, 180]

Catalyst[a]	H_2	Temperature[b] (°C)	R_p[c] (kg/g Ti h atm)	C_p[d] ($\times 10^2$ mol/mol Ti)	k_p[d] (L/mol s)
I	–	70	9.0	1.4	650
I	+[e]	70	20.2	0.72	2,750
III	–	70	1.1	0.27	640
III	+[e]	70	1.6	0.23	1,580
II	–	40	26.0	4.1	350
II	+[e]	40	33.6	1.5	1,200

[a] Catalyst I: $TiCl_4/MgCl_2$/dibutylphtalate + $AlEt_3$/phenyltriethoxysilane; catalyst II: $TiCl_4/MgCl_2$/ethylbenzoate + Al(*i*-Bu)$_3$/ethylanizate; catalyst III: $TiCl_3$ + $AlEt_3$

[b] Polymerization temperature

[c] Polymerization rate at the moment of ^{14}CO addition

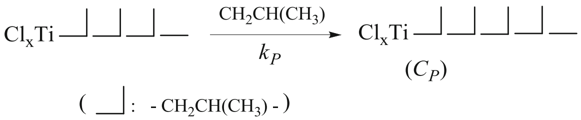
[d] Data for PP insoluble in boiling heptane (isotactic fraction)

[e] The ratio $H_2/C_3H_6 = 0.16$ (in gas phase)

not influence the number of active centers nor the propagation rate constant, and the hydrogen effect is not observed in conditions of quasi-living polymerization. Later [185], it was shown that in these conditions hydrogen does not influence the molecular weight of formed polymer. In works [74, 180], the hydrogen effect on propylene polymerization on TMC of various compositions and titanium trichloride has been studied (using QR ^{14}CO method) for definition of the number of active centers and propagation rate constants. It was found that the hydrogen effect is reversible and that removal of hydrogen from polymerization decreases the polymerization rate to the value observed for polymerization without hydrogen.

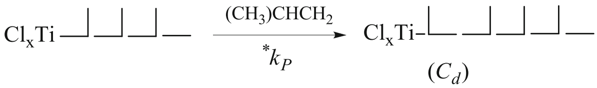
In Table 7, data on the influence of hydrogen on C_p and k_p values at propylene polymerization on catalysts with various compositions are presented. It is seen that hydrogen addition leads to a decrease in the number of active centers and an increase in k_p values calculated from data on the rate of polymerization and C_p. It is necessary to note that data in Table 7 are obtained for the isotactic PP fraction insoluble in boiling heptane. In work [199], with use of the same method (QR ^{14}CO), it was found that the number of active centers (radioactive labels in polymer) increases for polymerization in the presence of hydrogen. These data, unlike those in work [180], were obtained for the total polymer including the fraction soluble in boiling heptane. However, according to works [173, 180], this fraction after quenching polymerization with ^{14}CO contains low molecular weight by-products labeled with ^{14}C, and special techniques are required for their separation from polymer [173, 180]. The presence of these by-products can cause the raised number of radioactive labels in polymer, and accordingly leads to an increase in the calculated C_p value [199]. At the same time, it is improbable to expect an increase in reactivity of the active center (k_p value) after interaction of the active center with hydrogen. In [180], the possibility of formation of "dormant" centers is used to explain the increase in k_p values. These representations have been offered earlier [90, 200]. According to [90, 200], these centers are formed during propylene polymerization as a result of propylene 2,1-addition into an active titanium–polymer bond in the active center. In this case, two types of centers are formed during propylene polymerization on ZN catalysts without hydrogen:

1. Active centers (C_p), functioning in the conditions of 1,2-insertion of propylene into titanium–polymer bonds in the active center



(18)

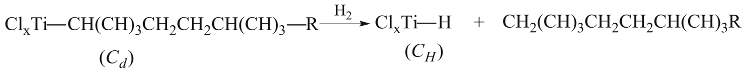
2. Dormant centers (C_d), formed after propylene 2,1-insertion into titanium–polymer bonds



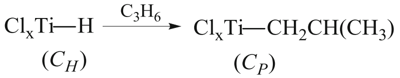
(19)

Dormant centers (C_d), do not attach propylene for steric reasons, but interact with ^{14}CO the same as the active centers C_p. In this case, the QR^{14}CO method can define the total number of the centers ($C_p + C_d$), containing titanium–polymer bonds.

Dormant centers can be transformed to an active state by interaction with hydrogen as a result of reactions (20) and (21):



$$\underset{(C_d)}{Cl_xTi{-}CH(CH)_3CH_2CH_2CH(CH)_3{-}R} \xrightarrow{H_2} \underset{(C_H)}{Cl_xTi{-}H} + CH_2(CH)_3CH_2CH_2CH(CH)_3R \tag{20}$$



$$\underset{(C_H)}{Cl_xTi{-}H} \xrightarrow{C_3H_6} \underset{(C_P)}{Cl_xTi{-}CH_2CH(CH_3)} \tag{21}$$

As a result of reactions (20) and (21) during polymerization in the presence of hydrogen, the share of active centers (C_p) increases, leading to an increase in polymerization rate and, accordingly, to an increase in the calculated values of k_p:

$$k_p = R_p/\left(C_p + C_d\right)C_m \tag{22}$$

The values of k_p concerning reactivity of the active center in the propagation reaction can be calculated if $C_p \gg C_d$, which is reached only for polymerization in the presence of hydrogen.

Surface titanium hydrides ($Cl_xTi–H$) are highly reactive compounds and can be partially deactivated in side reactions by interaction with components of the catalytic system. As a result of these side reactions, the number of active centers for polymerization in the presence of hydrogen is as a rule lower than the total number of the centers containing titanium–polymer bonds ($C_p + C_d$) during polymerization without hydrogen (Table 7). In the case of ethylene polymerization, dormant centers (C_d) are not formed. But, for polymerization in the presence of hydrogen, the centers C_H (surface hydrides of titanium) are deactivated by interaction with components of the catalytic system the same as and at propylene polymerization. These reactions lead to a decrease in the number of active centers (C_p) and to a decrease in ethylene polymerization rate. Thus, the values of the propagation rate constant are the same for ethylene polymerization with hydrogen and without hydrogen [201].

So, in the case of propylene polymerization in the presence of hydrogen, the proportion of the centers participating in the propagation reaction (C_p) is essentially higher than for polymerization without hydrogen, when some of the centers are in a "sleeping" condition, C_d. Therefore, k_p values calculated for experiments in the presence of hydrogen more precisely correspond to the real reactivity of active centers in the propagation reaction. These values (see Table 7) of $(1.6–2.8)\times10^3$ L/mol s at 70°C and $(1.2–1.6)\times10^3$ L/mol s at 40°C are close to the k_p values found for propylene polymerization on TMC by the SF method, $(1.0–5.0)\times10^3$ L/mol s at 30°C [149, 153, 183–185].

2.5 Heterogeneity of Active Centers of ZN Catalysts, Taking into Account Data on the Distribution of Active Centers on Propagation Rate Constants and Their Stereospecificity

It is known that ZN catalysts are multisite catalytic systems containing active centers that differ in their k_p values and stereospecificity. This is apparent in the formation of polymers with broad molecular mass distribution (MMD, $M_w/M_n > 2$) and polyolefins containing separate fractions with varying stereoregularity. Data on the reactivity (k_p values) of separate groups of the active centers and their transformations with the variation in the composition of catalysts and polymerization conditions have an undoubtedly important role in analysis of this phenomenon.

In the literature, various reasons for formation of polymers with broad MMD on heterogeneous ZN catalysts are discussed. Convincing evidence has been obtained using the SF method that the reason is heterogeneity of the active centers on a surface of the catalyst [186]. In conditions of quasi-living polymerization there are no transfer reactions of the growing polymer chain and polymer is formed on the surface of catalyst in very small quantities. This polymer cannot cause diffusion restrictions, but nevertheless polymer with broad MMD ($M_w/M_n = 3.2–4.3$) is formed. The further increase in time of polymerization does not influence the width of MMD ($M_w/M_n = 3.6$).

In works [187, 188], using the SF method, the tendency for increased k_p values with increase in stereospecificity of the catalyst has been noted (Table 8, experiments 1–3). It is supposed that an external donor mainly deactivates

Table 8 Data on the effect of internal and external donors on C_p and k_p values for propylene polymerization [183, 187, 188] (SF method)

Experiment number	Catalyst	Isotacticity, mmmm (mol%)	C_p (mol/mol Ti)	k_p (L/mol s)
1	$TiCl_4/MgCl_2 + AlEt_3$ (I)	56	0.1	1,100
2	I + $Me_2Si(OEt)_2$	66	0.064	1,500
3	I + CMDMS[a]	66	0.038	1,600
4	$TiCl_4/MgCl_2 \cdot n$DBP[b] + $AlEt_3$ (II-A)	94	0.008	3,000
5	II-B[c]	85	0.0075	2,500
6	II-C[c]	78	0.0072	2,300

[a] External donor, *CMDMS* cyclohexyl(methyl)dimethoxysilane

[b] Internal donor, *DBP* dibutylphtalate

[c] Catalysts II-B and II-C were prepared by pretreatment of catalyst II-A by $AlEt_3$ at 30°C for 5 and 30 min, respectively, to remove DBP from catalyst II-A

Table 9 Data on the effect of AlR_3 cocatalysts on the C_p and k_p values for propylene polymerization over catalyst $TiCl_4/MgCl_2$/DBP [189] (SF method)

	Cocatalyst				
Parameter	TEA	TNBA	TNHA	TNOA	TIBA
C_p^{tot} (mol/mol Ti)	0.056	0.036	0.027	0.016	0.02
K_p^{tot} (L/mol s)	3,900	4,000	3,700	3,400	2,800
mmmm (mol%)	92.8	92.9	91.8	89.3	87.8
C_p^i (mol/mol Ti)	0.03	0.028	0.016	0.008	0.008
K_p^i (L/mol s)	4,700	4,800	4,900	4,900	4,900

TEA $AlEt_3$, *TNBA* Al(*n*-Bu)$_3$, *TNHA* Al(*n*-hexyl)$_3$, *TNOA* Al(*n*-oktyl)$_3$, *TIBA* Al(*i*-Bu)$_3$

nonstereospecific centers. This leads to an increase in polymer isotacticity and to a decrease in polymerization rate. The k_p value increases because of an increase in the proportion of stereospecific active centers with higher reactivity. A similar effect of the influence of stereospecificity of the catalyst on k_p values has been found [183] using a catalyst containing an internal donor (dibutylphtalate, DBP) (see Table 8, experiments 4–6). In this case, the stereospecificity of the catalyst was changed by its preliminary treatment with triethylaluminum, which leads to partial removal of DBP from the catalyst. It is seen that in this case the k_p values also increase with an increase in stereospecificity of the catalyst (i.e., in the content of *meso*-pentads in polypropylene).

In work [189], data on the influence of the composition of organoaluminum cocatalyst on C_p and k_p values were obtained for propylene polymerization on TMC containing an internal donor (Table 9, SF method). In Table 9, the data both for total polymer and the isotactic fraction insoluble in boiling heptane are presented. The values calculated for total polymer (K_p^{tot}) depend on AlR_3 composition and this dependence correlates with changes in isotacticity of polypropylene (the content of

Table 10 Data on C_p and k_p values for separate fractions of PP with different isotacticity [190–192] (SF method)

Parameter	Catalyst A: $TiCl_4/MgCl_2 + AlEt_3$	Catalyst B: $TiCl_4/MgCl_2 + AlEt_3ED$[a]
Total		
C_p^{tot} (mol/mol Ti)	0.1	0.038
K_p^{tot} (L/mol s)	1,100	1,600
Fraction III[b] (100–110°C by TREF)		
C_p^{III} (mol/mol Ti)	0.0063	0.080
K_p^{III} (L/mol s)	4,170	4,830
Fraction IV[c] (110–140°C by TREF)		
C_p^{IV}(mol/mol Ti)	0.00041	0.00038
K_p^{IV} (L/mol s)	9,300	9,270

[a] *ED* external donor, cyclohexyl(methyl)dimethoxysilane
[b] Fraction III: $M_n \cong 20\times10^3$ g/mol, $M_w/M_n = 1.8$ mmmm ≅ 95 mol% for catalysts A and B
[c] Fraction IV: $M_n \cong 41.5\times10^3$ g/mol, $M_w/M_n = 1.8$ mmmm ≅ 98.5 mol% for catalysts A and B

meso-pentads). At the same time, values calculated for the isotactic fraction (K_p^i), which contains 99% of *meso*-pentads, do not depend on AlR_3 composition. Thus, the composition of AlR_3 does not influence the reactivity of stereospecific active centers but considerably influences both the total number of active centers (C_p^{tot}), and the number of stereospecific active centers (C_p^i).

New important information on the distribution of the active centers was obtained using a combination of the SF method and temperature rising elution fractionation (TREF) [190–192]. According to the TREF data, polypropylene obtained for 0.15 s on catalysts $TiCl_4/MgCl_2 + AlEt_3$ (catalyst A) and $TiCl_4/MgCl_2 + AlEt_3/ED$ (catalyst B) contains four fractions liberated at temperatures of approximately 20°C (I), 20–100°C (II), 100–110°C (III), and 110–140°C (IV). Fraction I is atactic polymer, fraction II is polymer with low isotacticity, fractions III and IV are isotactic polymers, and fraction IV has the highest isotacticity (98.5 mol% of *meso*-pentads). Table 10 presents data on the number of the active centers making fractions III and IV (C_p^{III} and C_p^{IV}) and the propagation rate constants for these centers (K_p^{III} and K_p^{IV}). It is seen that the isospecific centers III and highly isospecific centers IV have higher propagation rate constants in comparison with the average propagation rate constant for the total polymer. However, the proportion of isospecific active centers is insignificant and is only 6% for the centers III and 0.4% for the centers IV of the total number of active centers of catalyst A. In the case of catalyst B, the share of the isospecific active centers III and IV is considerably higher and is 21% for the centers III and 1% for the centers IV of the total number of active centers. It is necessary to notice that fractions III and IV have narrow MMD ($M_w/M_n \cong 2$), but various molecular weights. A difference in M_n for these fractions (approximately twofold) is defined

Table 11 Data on C_p and k_p values for different fractions of PP prepared with ZN catalysts of different composition [202] (QR ^{14}CO method)

Parameter		$TiCl_3$	TMC-1	TMC-2	TMC-3	TMC-4
R_p[a] (kg/g Ti h atm)		1.6	16.8	26.0	25.7	37.2
Content of PP fraction (wt%)	PP5[b]	17.1	43	10.6	3.1	1.9
	PP7[b]	10.5	27	14.7	6.9	2.7
	IPP[b]	72.4	30	74.7	90	95.4
Total C_p (mmol/mol Ti)		2.34	11.5	23.3	18.4	21.6
Portion of C_p (%) for fraction	PP5	45	50	41	25	14
	PP7	25	34	25	32	23
	IPP	30	16	34	43	63
k_p (L/mol s) for fraction	PP5	250	1,230	280	170	220
	PP7	270	1,120	660	300	190
	IPP	1,580	2,590	2,480	2,820	2,560

Polymerization conditions: 70°C, $AlEt_3$ as cocatalyst, with hydrogen presence at ratio H_2/C_3H_6 = 0.15 in gas phase

TMC-1 $TiCl_4/MgCl_2$, *TMC-2* $TiCl_4/MgCl_2 \cdot n$DBPh, *TMC-3* $TiCl_4/MgCl_2 \cdot n$DBDMP, *TMC-4* $TiCl_4/MgCl_2 \cdot n$DBPh + DCPDMS, *DCPDMS* dicyclopentyldimethoxysilane as an external donor

[a] Polymerization rate at the moment of ^{14}CO addition

[b] *PP5* atactic fraction soluble in boiling pentane, *PP7* stereoblock fraction soluble in boiling heptane, *IPP* isotactic fraction insoluble in boiling heptane

by the twofold increase in k_p values for active centers IV. k_p values for active centers III and IV are similar for catalysts A and B. So, the presence of internal donor in TMC does not affect the k_p values of isospecific active centers III and IV.

Thus, the SF method gives valuable information on the quantity of active centers and their reactivity in the propagation reaction, the influence of catalyst composition on these kinetic parameters, and on the distribution of the active centers and their reactivity for the centers with various isospecificities. Of course, these data only concern the initial stage of polymerization for time of polymerization less than 0.2 s. But, ZN catalysts undergo essential changes in the conditions of the real process of polymerization because of interaction of the components of the catalytic system with each other and with components of the reaction environment. These interactions can lead to changes in the number of active centers and in the distribution of the active centers with different reactivities. Some reversible interactions can also occur between active centers and different components of the catalyst and polymerization environment. These interactions can be studied only for polymerization at different polymerization times. Therefore, it is necessary to also have data on the number of active centers and propagation rate constants at various stages of polymerization. As noted above, such data can be obtained by the QR method. Some results obtained in works [180, 202] by the QR ^{14}CO method for propylene polymerization on ZN catalysts are presented in Table 11. These data were obtained for polymerization on the traditional ZN catalyst based on $TiCl_3$ and on supported titanium–magnesium catalysts with different compositions, i.e., catalyst not containing electron donor stereoregulating additives (TMC-1), catalysts containing internal donors of various structures

(TMC-2 and TMC-3), and catalyst containing an internal and external donor (TMC-4). Polymers obtained with these catalysts have been fractionated into three fractions: PP5, atactic fraction soluble in boiling pentane; PP7, stereoblock fraction soluble in boiling heptane; and IPP, isotactic fraction insoluble in boiling heptane. C_p and k_p values have been calculated for separate fractions to account for the content of every fraction in the total polymer.

Following conclusions can be made from results presented in Table 11:

1. For all catalysts, k_p values increase considerably at transition from aspecific active centers (PP5 and PP7 fractions) to isospecific centers (IPP fraction) and reach values of $(2.5\text{–}2.8)\times10^3$ L/mol s.
2. k_p values for isospecific centers (IPP fraction) are close for TMC of various compositions.

   Conclusions (1) and (2) agree with results obtained by the SF method in works [190–192].
3. The proportion of aspecific and low specificity centers (PP5 and PP7 fractions) in the catalysts that do not contain internal or external donors ($TiCl_3$, TMC-1) is great enough (70–84%).
4. Addition of the external donor to TMC, containing the internal donor, has little effect on the total number of active centers (catalysts TMC-2 and TMC-4). However, the proportion of isospecific active centers increases considerably from 34% to 63%. This is possibly because aspecific centers in TMC-2 (PP5 fraction) transform into isospecific centers (IPP fraction).

The results presented show that data on the number of active centers and the propagation rate constants allow us to explain many questions connected with the role of the separate components of catalysts in the formation of active centers and their transformations during polymerization, revealing the factors that define the activity and stereospecificity of catalysts.

The information about the number of active centers and the propagation rate constants is also important for analysis of some kinetic features of olefin polymerization:

- The causes of heterogeneity of the catalyst active centers
- Exact estimation of activation energy of reactions of propagation and transfer of polymer chain is impossible without data on the effect of temperature on the number of active centers
- The reasons for the widespread comonomer effect in ZN catalysis
- Data on the dependence of active site number on monomer concentration might help in understanding the deviation from the low linear rate of polymerization with changing monomer concentration

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