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# Mechanism of Olefin Polymerization on Supported Ziegler–Natta Catalysts Based on Data on the Number of Active Centers and Propagation Rate Constants

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**Abstract**—The number of active centers ($C_g$) and propagation rate constants ($k_g$) for the polymerization of propylene and ethylene on highly active titanium–magnesium catalysts (TMCs) of different compositions at 70°C were determined using the method of $^{14}$CO inhibition of polymerization. In the polymerization of propylene on the $TiCl_4/D_1/MgCl_2–AlEt_3/D_2$ system ($D_1$ is dibutyl phthalate or 2,2'-diisobutyl-1,3-dimethoxypropane; $D_2$ is a silane), the effects of $D_1$ and $D_2$ donors on the values of $C_g$ and $k_g$ were studied. It was found that the donors decreased the values of $k_g$ for nonstereospecific centers, had no effect on the values of $k_g$ for stereospecific centers, and increased the fraction of stereospecific centers, as well as the fraction of "sleeping" centers regardless of their stereospecificity. The rate constants of isotactic-chain transfer with $C_3H_6$, $AlEt_3$, $H_2$, and $ZnEt_2$ were determined. In the polymerization of ethylene, a number of TMCs exhibited strong diffusion limitations, which manifested themselves in a dramatic decrease in the determined values of $k_g$. It was demonstrated that diffusion limitations can be removed by decreasing the particle size and the concentration of active centers and by performing prepolymerization with propylene. The values of $k_g$ in ethylene polymerization were similar for stereospecific and nonstereospecific centers.

## INTRODUCTION

Supported Ziegler–Natta catalysts are predominant in the manufacture of polyolefins. Almost all polypropylene (PP) and most high-density polyethylene (PE) and linear low-density PE are manufactured with the use of these catalysts. The supported catalyst for ethylene polymerization is titanium chloride supported on highly dispersed magnesium chloride (titanium–magnesium catalysts (TMCs)). Simplistically, the composition of this catalyst can be represented as $TiCl_4/MgCl_2$. The TMCs used for the stereospecific polymerization of propylene contain electron-donor organic compounds (stereoregulating additives). These compounds are used in the course of preparation of a supported TMC; they enter into the composition of this catalyst as an internal electron donor $D_1$. In the activation of this catalyst by trialkylaluminum, an additional electron-donor compound (external donor $D_2$) is added to the reaction medium in order to increase stereospecificity. In the general case, two electron-donor compounds are constituents of the catalytic system, and it can be represented as $TiCl_4/D_1/MgCl_2–AlR_3/D_2$.

The electron-donor compounds $D_1$ and $D_2$ are of paramount importance for the high stereospecificity of TMC systems [1]. Phthalates and alkylalkoxysilanes are commonly used as internal and external donors, respectively, in current catalytic systems [1, 2]. In the past decade, new highly efficient internal donors (1,3-diethers) were found, which are responsible for the high activity and high stereospecificity of TMCs in the absence of an external donor [3, 4].

A number of publications [1–14] have been devoted to studies on the mechanism of the effect of donors on the activity and stereospecificity of TMCs. It is believed that this effect consists in the deactivation of nonstereospecific centers, an increase in the number of stereospecific centers, an increase in the propagation rate constant for stereospecific centers, etc. However, data on the effect of donors on the number and reactivity of centers with different stereospecificity are scarce [13, 15–17].

Previously, we developed a method for the determination of the number of active centers ($C_g$) and the rate constants of growth ($k_g$) with the use of $^{14}$CO for centers with different stereospecificity (for low-stereoregularity PP fractions) [18]. We found [15, 18] that it is of fundamental importance for the correct determination of $k_g$ to perform polymerization in the presence of hydrogen. In this case, the fraction of "sleeping" centers that resulted from the 2,1-insertion of propylene [19] was insignificant; therefore, the calculated values of $k_g$ were most correct. At the same time, the ratio between the values of $k_g$ obtained in experiments without hydrogen and in the presence of hydrogen can be used for evaluating the fraction of sleeping centers with different stereospecificity.

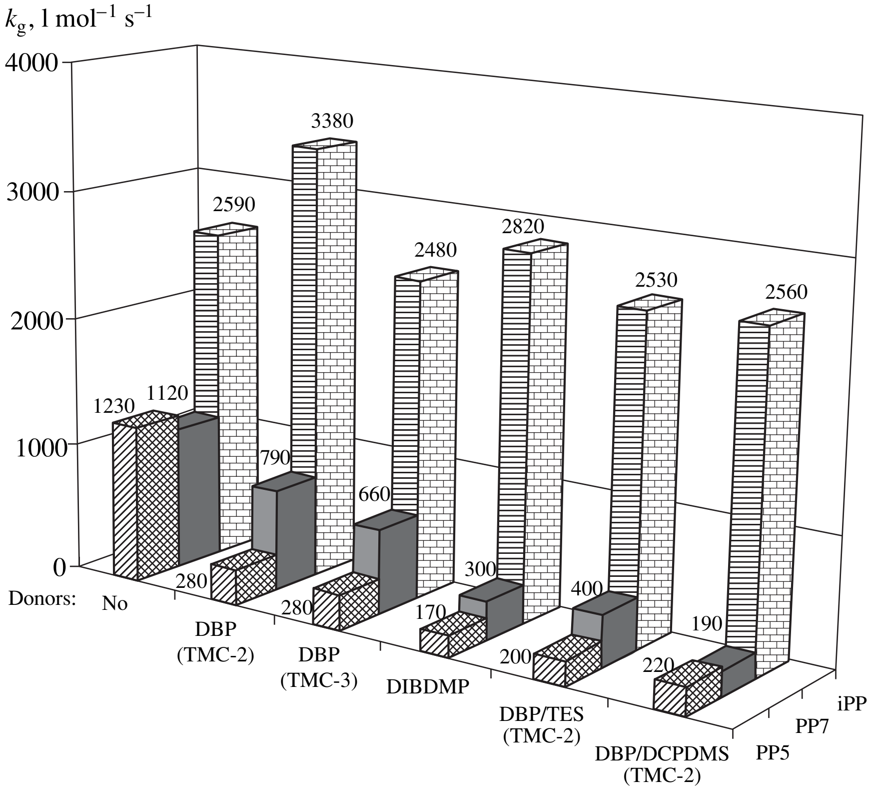

**Fig. 1.** Propagation rate constants for TMCs with various donors and three PP fractions.

In this work, we studied the effects of electron-donor compounds as TMC constituents on the number of active centers and the propagation rate constants for stereospecific and nonstereospecific centers in the polymerization of propylene on supported TMCs. For this purpose, we determined the number stereospecific and nonstereospecific active centers and, correspondingly, propagation rate constants for a number of catalytic systems that differed in the presence and composition of internal and external electron-donor compounds $D_1$ and $D_2$, respectively, and exhibited different stereospecificity. In particular, we studied the following catalytic systems:

(1) $TiCl_4/MgCl_2$–$AlEt_3$ (without donors);

(2) $TiCl_4/D_1/MgCl_2$–$AlEt_3$ ($D_1$ is dibutyl phthalate (DBP) or the 1,3-diether 2,2'-diisobutyl-1,3-dimethoxypropane (DIBDMP));

(3) $TiCl_4/DBP/MgCl_2$–$AlEt_3/D_2$ ($D_2$ is tetraethoxysilane (TES) or dicyclopentyldimethoxysilane (DCPDMS)).

The values of $C_g$ and $k_g$ for each of these catalytic systems were determined during polymerization in the absence and in the presence of $H_2$ for three PP fractions, which were soluble in the following sequence: (1) in boiling pentane (PP5), (2) in boiling heptane (PP7), and (3) insoluble in boiling heptane (isotactic PP (iPP)).

With the use of data on the molecular weight of iPP for various polymerization conditions and the values of $k_g$, the rate constants of various polymer-chain-transfer reactions were determined, and the contribution of these chain-transfer reactions to the molecular weight of the polymer was evaluated.

With the use of data on the values of $C_g$ and $k_g$, the possibility of diffusion limitations appearing in ethylene polymerization on a number of modifications of highly active supported catalysts was discussed.

## EXPERIMENTAL

The TMC-1 catalyst (2.5% Ti) was prepared by supporting $TiCl_4$ on a highly dispersed $MgCl_2$ carrier, which was prepared by the reaction of phenylmagnesium chloride with $CCl_4$ in accordance with the patent [20]. TMC-2 (2.5% Ti) was synthesized by the reaction of the complex $MgCl_2 \cdot 0.2EB \cdot 3ROH$ with $TiCl_4$ in the presence of DBP according to the patent [21]. The TMC-3 catalysts (1.8–2.6% Ti) were prepared by the reaction of $TiCl_4$ and DBP with a carrier prepared by the interaction of phenylmagnesium chloride with tetraethoxysilane according to the patent [22]. TMC-4 (2.8% Ti) was synthesized analogously to TMC-3, but DIBDMP was used in place of DBP. The $TiCl_4/MgCl_2$ catalyst (0.1% Ti) was prepared by supporting a required portion of $TiCl_4$ on $MgCl_2$, which was prepared by the reaction of magnesium with butyl chloride according to the inventor's certificate [23]. The proce-

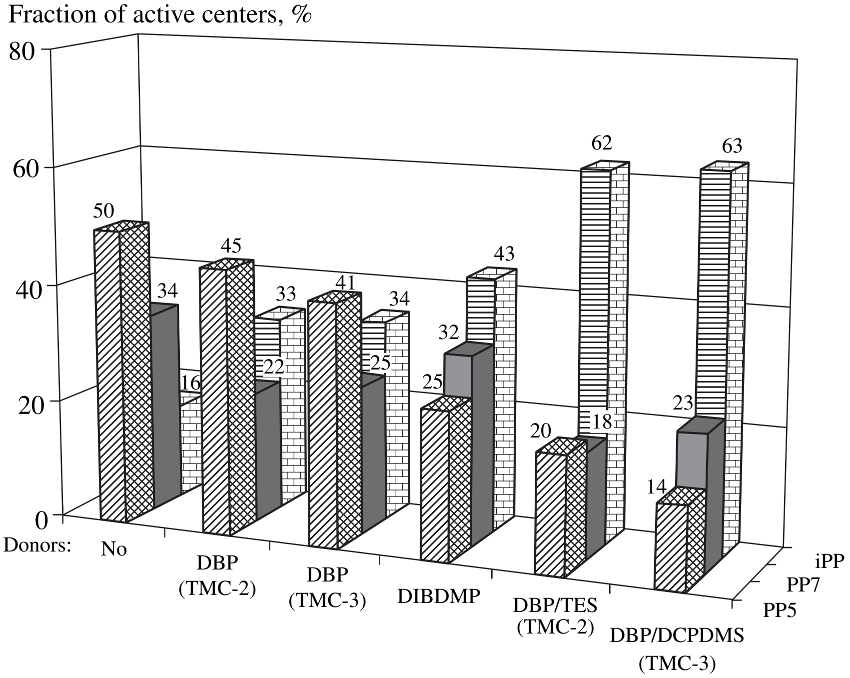

**Fig. 2.** Fraction of active centers for TMC with various donors and three PP fractions.

dures used for propylene polymerization, the determination of $C_g$ and $k_g$, and the purification of PP fractions for the removal of labeled by-products were described previously [18].

## RESULTS AND DISCUSSION

### *Propylene Polymerization*

Table 1 summarizes the values of $C_g$ and $k_g$ for various PP fractions. These data were obtained with the use of $^{14}$CO on the following catalytic systems: TMCs without donors (experiment nos. 1, 2), TMCs with internal donors of DBP (experiment nos. 3–8) and DIBDMP (experiment nos. 9–11), and TMCs with DBP as an internal donor in the presence of external donors of TES (experiment nos. 12–14) and DCPDMS (experiment nos. 15–17). The experiments in each particular catalytic system were performed in the absence and in the presence of hydrogen. As mentioned above, the values of $k_g$ determined with the use of $^{14}$CO in the presence of $H_2$, when the fraction of sleeping centers was insignificant, are true (in contrast to the values of $k_g$ found in experiments without $H_2$). The values of $k_g$ as averaged data from two experiments with $H_2$ for each particular catalytic system, are given in Table 2 and Fig. 1. The average values of the fractions of active centers with different stereospecificity (in various PP fractions) found from the above experiments are given in Table 2 and Fig. 2.

The values of $k_g$ determined in the absence of $H_2$ (Table 1) are lower because of the formation of “sleeping” Ti–polymer bonds. We used these bonds for evaluating the fraction of sleeping centers ($P$), which was calculated as

$$P = \frac{1 - k_g(\text{without } H_2)}{k_g(\text{with } H_2)} \times 100\%. \qquad (1)$$

These data for centers with different stereospecificity (various PP fractions) depending on the composition of the catalytic system are given in Table 2 and Fig. 3.

Henceforth, we will designate values of $C_g$ and $k_g$ for the PP5 fraction as the values for nonstereospecific centers, for the iPP fraction as the values for stereospecific centers, and for the PP7 fraction as the values for low-stereospecificity (or stereoblock) centers. Note that, in reality, the PP5 fraction is not strictly atactic, but contains short isotactic and syndiotactic sequences [24].

**Catalytic system without donors.** In the TMC-1 catalyst, the values of $k_g$ for stereospecific centers (iPP fraction) were higher than the values for nonstereospecific centers (PP5 fraction) by a factor of 2 (Table 2, Fig. 1). However, the fraction of stereospecific centers was lower than the fraction of nonstereospecific centers by a factor of ~3 (Table 2, Fig. 2). As a result, the yield of the PP5 fraction was higher than the yield of the iPP fraction by a factor of 1.5 (Table 1, experiment no. 2).

The fraction of sleeping centers under the test conditions in the absence of $H_2$ was ~50% for both stereospecific and nonstereospecific centers (Table 2, Fig. 3). Consequently, the ratio between the rates of change of active centers to a sleeping state (because of

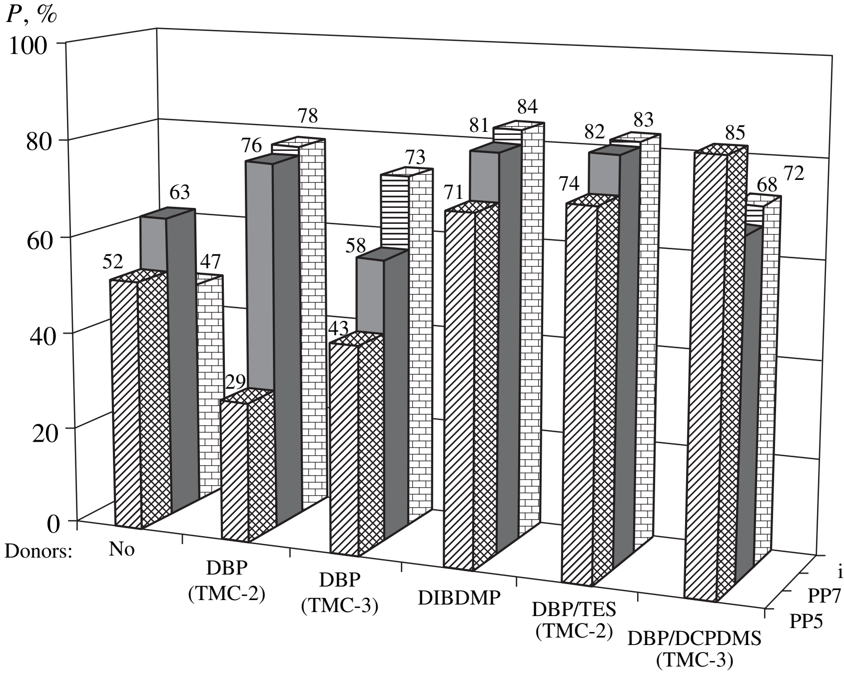

**Fig. 3.** Fraction of sleeping centers (*P*) for TMC with various donors and three PP fractions.

2,1-insertion) and reactivation of Ti–polymer bonds does not depend on the steric environment of titanium ions in the active center.

**Effect of an internal donor on the values of $C_g$ and $k_g$.** Upon the introduction of an internal donor as a constituent of TMCs (TMC-2, TMC-3, and TMC-4 catalysts), the values of $k_g$ remained practically unchanged for stereospecific centers and dramatically decreased for nonstereospecific centers (from 1230 to 280 and 170 l mol$^{-1}$ s$^{-1}$ in the case of DBP and DIBDMP, respectively) (Table 2, Fig. 1). The values of $k_g$ for low-stereospecificity centers also decreased considerably (PP7 fraction: from 1120 to 300 l mol$^{-1}$ s$^{-1}$ in the case of DIBDMP, Fig. 1). It is likely that an internal donor blocks $MgCl_2$ surface regions (for example, (110) faces) at which $TiCl_4$ is adsorbed in the absence of electron donors to form highly active low-stereospecificity and nonstereospecific centers [25, 26]. An internal donor may also have a steric effect on the growth of an atactic chain at the neighboring ion of titanium to decrease its reactivity.

The fraction of stereospecific centers increased by a factor of ~2 or ~3 upon the addition of DBP or DIBDMP, respectively, whereas the fraction of nonstereospecific centers in these cases decreased only slightly (DBP) or by a factor of 2 (DIBDMP) (Fig. 2).

Thus, with the use of DBP as an internal donor, the isotacticity of PP increased mainly because of a dramatic decrease in the reactivity of nonstereospecific centers and an increase in the fraction of stereospecific centers. These effects were more pronounced in the case of DIBDMP as an internal donor. The lower efficiency of DBP, as compared with that of DIBDMP, can be partially related to the partial removal of DBP from the catalyst surface in the reaction with $AlEt_3$ [6].

Upon the introduction of an internal donor, the fraction of sleeping centers increased from 50 to 70–85% for all types of active centers (Fig. 3). This may be indicative of the presence of the internal donor near active centers and of the effect of this donor on an increase in the ratio between the rate of change of active centers to a sleeping state (due to 2,1-insertion) and the rate of reactivation of sleeping Ti–polymer bonds. It is likely that the donor decreases the rate of reactivation of centers and, hence, increases the rate of the 2,1-insertion of propylene. Note that, in the case of DBP, a decrease in the fraction of sleeping centers (from 52 to 29–43%; Table 2, Fig. 3) was observed for nonstereospecific centers. In this case, an increase in the rate of reactivation of centers relative to the rate of the 2,1-insertion of propylene can be due to the partial removal of DBP from TMCs upon the interaction with $AlEt_3$. In the case of the unremovable DIBDMP donor, this effect of a decrease in the fraction of sleeping centers was absent.

**Effect of an external donor on the values of $C_g$ and $k_g$.** Upon the addition of an external donor (TES or DCPDMS) to the catalytic system containing an internal donor, the values of $k_g$ remained unchanged for stereospecific centers and decreased to a small extent for nonstereospecific centers (Table 2, Fig. 1). The value of $k_g$ decreased more noticeably only for low-stereospecificity centers (PP7 fraction).

**Table 1.** The values of $C_g$ and $k_g$ in propylene polymerization on various TMCs

| Experiment no. | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Internal donor* | | – | | DBP | | | DBP | | | DIBDMP | | | DBP | | | DBP | | |
| External donor* | | – | | – | | | – | | | – | | | TES | | | DCPDMS | | |
| TMC | | TMC-1 | | TMC-2 | | | TMC-3 (2.6% Ti) | | | TMC-4 | | | TMC-2 | | | TMC-3 (2% Ti) | | |
| $H_2/C_3H_6$ (in a gas phase) | | 0 | 0.15 | 0 | 0.1 | 0.15 | 0 | 0.15 | 0.15 | 0 | 0.1 | 0.15 | 0 | 0.1 | 0.15 | 0 | 0.15 | 0.15 |
| $R$**, kg $C_3H_6$ (g Ti)$^{-1}$ h$^{-1}$ atm$^{-1}$ | | 8.8 | 16.8 | 6.8 | 19.2 | 16.3 | 13.8 | 25.3 | 26.7 | 6.4 | 25.4 | 25.9 | 4.9 | 20.8 | 21.0 | 11.9 | 37.8 | 36.7 |
| Concentration of PP fractions, wt % | PP5 | 48 | 43 | 13.2 | 9.6 | 8.0 | 18.5 | 11.6 | 9.5 | 3.0 | 3.0 | 3.2 | 4.9 | 2.6 | 2.0 | 2.0 | 2.1 | 1.6 |
| | PP7 | 16 | 27 | 18.7 | 12.8 | 11.3 | 17.5 | 14.6 | 14.9 | 5.2 | 6.5 | 7.4 | 5.0 | 4.0 | 4.1 | 3.6 | 3.4 | 2.0 |
| | iPP | 36 | 30 | 68.1 | 77.6 | 80.7 | 64.0 | 73.8 | 75.6 | 91.8 | 90.5 | 89.4 | 90.1 | 93.4 | 93.9 | 94.4 | 94.5 | 96.4 |
| $k_g$, l mol$^{-1}$ s$^{-1}$ | PP5 | 590 | 1230 | 200 | 300 | 250 | 160 | 270 | 280 | 49 | 180 | 160 | 52 | 200 | 190 | 32 | 235 | 195 |
| | PP7 | 410 | 1120 | 190 | 740 | 830 | 280 | 570 | 740 | 57 | 300 | 300 | 72 | 370 | 420 | 61 | 230 | 155 |
| | iPP | 1370 | 2590 | 740 | 3030 | 3720 | 660 | 1910 | 3050 | 460 | 3240 | 2390 | 420 | 2230 | 2830 | 720 | 2400 | 2710 |
| $C_g$, mmol/(mol Ti) | PP5 | 6.8 | 5.7 | 4.4 | 6.0 | 5.0 | 15.1 | 10.6 | 8.8 | 3.8 | 4.1 | 5.1 | 4.4 | 2.6 | 2.2 | 7.2 | 3.3 | 2.9 |
| | PP7 | 3.3 | 3.9 | 6.4 | 3.2 | 2.1 | 8.4 | 6.2 | 5.2 | 5.7 | 5.3 | 6.1 | 3.2 | 2.2 | 2.0 | 6.8 | 5.4 | 4.6 |
| | iPP | 2.2 | 1.9 | 6.0 | 4.7 | 3.3 | 12.8 | 9.4 | 6.4 | 12.4 | 6.8 | 9.3 | 10.0 | 8.4 | 6.7 | 15.0 | 14.3 | 12.6 |
| | Total | 12.3 | 11.5 | 16.8 | 13.9 | 10.4 | 36.3 | 26.2 | 20.4 | 21.9 | 16.2 | 20.5 | 17.6 | 13.2 | 10.9 | 29.0 | 23.0 | 20.1 |
| Fraction of active centers, % | PP5 | 55 | 50 | 26 | 43 | 48 | 42 | 40 | 43 | 17 | 25 | 25 | 25 | 20 | 20 | 25 | 14 | 14 |
| | PP7 | 27 | 34 | 38 | 23 | 20 | 23 | 24 | 26 | 26 | 33 | 30 | 18 | 17 | 18 | 23 | 24 | 23 |
| | iPP | 18 | 16 | 36 | 34 | 32 | 35 | 36 | 31 | 57 | 42 | 45 | 57 | 63 | 62 | 52 | 62 | 63 |

* DBP is dibutyl phthalate, DIBDMP is 2,2'-diisobutyl-1,3-dimethoxypropane, TES is tetraethoxysilane, and DCPDMS is dicyclopentyldimethoxysilane.

** $R$ is the rate of polymerization at the instant $^{14}CO$ was added.

**Table 2.** Effect of donors on the values of $k_g$ and the fraction of active centers for PP fractions with different stereoregularity

| Internal donor | | – | DBP | DBP | DIBDMP | DBP | DBP | – |
|---|---|---|---|---|---|---|---|---|
| External donor | | – | – | – | – | TES | DCPDMS | – |
| Catalyst | | TMC-1 | TMC-2 | TMC-3 (2.6% Ti) | TMC-4 | TMC-2 | TMC-3 (2% Ti) | $TiCl_3$ |
| $k_g^*$, l mol$^{-1}$ s$^{-1}$ | PP5 | 1230 | 280 | 280 | 170 | 200 | 220 | 220 |
| | PP7 | 1120 | 790 | 660 | 300 | 400 | 190 | 280 |
| | iPP | 2590 | 3380 | 2480 | 2820 | 2530 | 2560 | 1560 |
| Fraction of active sites*, % | PP5 | 50 | 45 | 41 | 25 | 20 | 14 | 51 |
| | PP7 | 34 | 22 | 25 | 32 | 18 | 23 | 23 |
| | iPP | 16 | 33 | 34 | 43 | 62 | 63 | 26 |
| Fraction of sleeping centers**, % | PP5 | 52 | 29 | 43 | 71 | 74 | 85 | 0 |
| | PP7 | 63 | 76 | 58 | 81 | 82 | 68 | 54 |
| | iPP | 47 | 78 | 73 | 84 | 83 | 72 | 59 |

* Average values from the experiments in the presence of hydrogen.

** Calculated from Eq. (1), in which the values of $k_g$ (without $H_2$) from Table 1 and $k_g$ (with $H_2$) from Table 2 were used.

Upon the addition of an external donor, the fraction of stereospecific centers considerably increased (by a factor of ~2), whereas the fraction of nonstereospecific centers significantly decreased (by a factor of 2–3) (Fig. 2). This change in the ratio between active centers with different stereospecificity (as compared with the decrease in $k_g$ for nonstereospecific and low-stereospecificity centers) is primarily responsible for an increase in the isotacticity of PP under the action of an external donor. Because the total number of active centers in this case changed only slightly (Table 1), it is believed that the external donor is responsible for a higher yield of stereospecific centers with reference to nonstereospecific centers; for example, it converts the latter into stereospecific centers. Another reason for the effect of an external donor is considered below. DBP, as well as DIBDMP, is responsible for the high stereospecificity of a catalyst. Note that, according to Keii *et al.* [27], even a monoester (ethyl benzoate) as an internal donor provided a high isotacticity of PP (~90%) without an external donor in propylene polymerization at a very low $AlEt_3$/Ti ratio. However, at a commonly used $AlEt_3$/Ti ratio, the removal of DBP from the catalyst by the reaction with $AlEt_3$ can result in a decrease in the stereospecificity of the catalyst. An external donor replaced DBP in the interaction of a catalyst with a cocatalyst [28] and retained the high stereospecificity of the catalyst, which was close to that of a catalyst with only DIBDMP (without an external donor); this high stereospecificity is not removed by the reaction of the TMC with $AlEt_3$. Close values of $k_g$ (Fig. 1) and the fractions of active centers (Fig. 2) in corresponding PP fractions in both of the catalysts are consistent with this assumption.

In the presence of an external donor, the fraction of sleeping centers $P$ was 70–85% for centers with different stereospecificity, as in the case of TMCs with DIBDMP (Fig. 3). Note that silanes increased the fraction of sleeping nonstereospecific centers. As mentioned above, in the presence of DBP only, this fraction decreased (from 52 to 29–43%, Table 2), as compared with TMCs without donors, because of the partial removal of DBP. In the presence of an external donor, silane replaced DBP and an increase in the fraction of sleeping centers to the same level as in the case of unremovable DIBDMP was observed in place of a decrease in this fraction. These changes in the fraction of sleeping centers suggest that both an internal donor (DBP or DIBDMP) and an external donor (silane) are adsorbed near active centers to affect their reactivity.

Figure 4 illustrates the overall effect of the values of $k_g$ and the fraction of active centers on the yields of particular PP fractions. It can be seen that an internal donor increased the yield of the isotactic PP fraction because of a dramatic decrease in the reactivity of nonstereospecific centers and an increase in the fraction of stereospecific centers. An external donor (TES or DCPDMS) increased the yield of the isotactic fraction because of a further decrease in $k_g$ and the fraction of active centers for nonstereospecific and low-stereospecificity centers.

**Comparative data on $C_g$ and $k_g$ for TMCs and $TiCl_3$.** It is of interest to compare highly active TMCs with titanium trichloride, a traditional Ziegler–Natta catalyst for propylene polymerization. Table 2 summarizes the averaged values of the fraction of active centers and $k_g$, which were obtained previously in the $TiCl_3$–$AlEt_3$ catalytic system [18]. These values are more clearly compared with data for TMCs in Fig. 4. It can be seen that the PP-fraction distribution of the values of the fraction of active centers and $k_g$ for $TiCl_3$ was noticeably different from that in the less stereospecific TMC (without donors) or the most stereospecific TMC

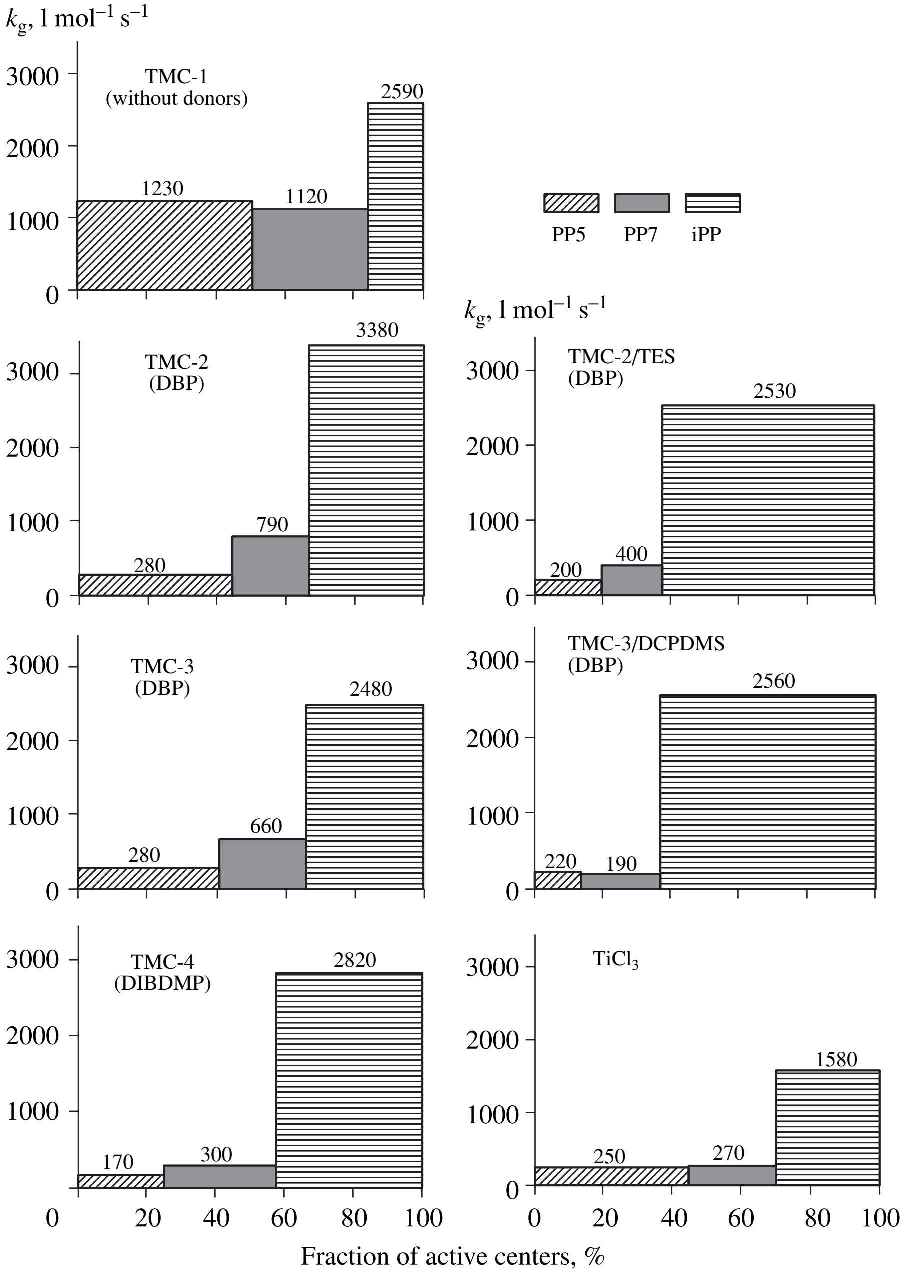

**Fig. 4.** Yields of PP fractions with different stereoregularity for various catalytic systems from the found values of $k_g$ and the fraction of active centers.

(with $D_1$ and $D_2$ donors). It was closest to the distribution of the values of the fraction of active centers and $k_g$ for the $TiCl_4/DBP/MgCl_2$ catalyst without an external donor. Note that the stereoregularity distribution of PP fractions for $TiCl_3$ is also closest to an analogous distribution for the $TiCl_4/DBP/MgCl_2$ catalyst. The similar behaviors of these catalysts may be nonrandom. In TMCs without donors, titanium chlorides (isolated ions, dimers, or clusters) protruded on the surface of $MgCl_2$, and they were more sterically accessible. This resulted in the formation of systems with low stereospecificity. The internal donor DBP, adsorbing on the surface of $MgCl_2$ between titanium chlorides, seemingly flattened the catalyst surface and made the titanium ions sterically less accessible, similarly to surface titanium ions in the lattice of $TiCl_3$ (these titanium ions are surrounded by adjacent titanium ions and chloride ions).

In general, the values of $k_g$ for nonstereospecific centers of TMC and $TiCl_3$ catalysts were similar (Table 2). The values of $k_g$ for stereospecific centers in both of the catalysts were much higher (by a factor of 7–12), and they differed for TMCs and $TiCl_3$ by a factor of no more than 2. We can conclude that the reac-

**Table 3.** The values of $k_g$ in ethylene polymerization on catalytic systems with different stereospecificity

| Catalytic system | | Rate of polymerization, kg PE (g Ti)$^{-1}$ h$^{-1}$ atm$^{-1}$ | $C_g$, mol/(mol Ti) | $k_g$, l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| composition | stereospecificity*, % | | | |
| $TiCl_4/MgCl_2$ (0.1% Ti)–$AlEt_3$ | 10 | 250 | 0.18 | 11500 |
| $TiCl_4/DBP/MgCl_2$ (2.4% Ti)<br>$AlEt_3$/DCPDMS | 96 | 100** | 0.063 | 12100 |

* The fraction of isotactic PP obtained on the catalytic system in propylene polymerization.

** The experiment was performed with the prepolymerization of propylene (see p. 191).

tivities of corresponding centers in supported and unsupported catalysts differ only slightly from one another. This is likely due to the fact that the nearest environments of titanium ions in active centers are identical: titanium ions in an octahedral environment of chloride ions, a polymer chain, and chloride ion vacancies (one or two for stereospecific or nonstereospecific centers, respectively).

**Determination of the rate constants of polymer-chain transfer.** The following polymer-chain-transfer reactions can occur in the polymerization of olefins:

(1) with a monomer,

$$L_xTi\text{–}P + C_3H_6 \xrightarrow{k_t^M} L_xTi\text{–}C_3H_7 + CH_2{=}CH(CH)_3\text{–}P_{n-1};$$

(2) with an organoaluminum cocatalyst,

$$L_xTi\text{–}P + AlEt_3 \xrightarrow{k_t^{Al}} L_xTi\text{–}Et + Et_2Al\text{–}P;$$

(3) β-hydride (spontaneous) transfer,

$$L_xTi\text{–}P \xrightarrow{k_t^s} L_xTi\text{–}H + CH_2{=}CH(CH)_3\text{–}P_{n-1};$$

(4) with hydrogen, which is specially introduced into the polymerization medium in the manufacture of polyolefins for controlling the molecular weight of the polymer,

$$L_xTi\text{–}P + H_2 \xrightarrow{k_t^H} L_xTi\text{–}H + H\text{–}P;$$

(5) with $ZnEt_2$, which is occasionally used as a more effective chain-transfer agent than $AlEt_3$,

$$L_xTi\text{–}P + ZnEt_2 \xrightarrow{k_t^{Zn}} L_xTi\text{–}Et + EtZn\text{–}P.$$

In general, the number-average molecular weight of the polymer is determined by the following equation:

$$\frac{42}{M_n} = \frac{k_t^M}{k_g} + \frac{k_t^{Al}[AlEt_3]^{0.5}}{k_g[M]} + \frac{k_t^s}{k_g[M]} + \frac{k_t^H[H_2]^{0.5}}{k_g[M]} + \frac{k_t^{Zn}[ZnEt_2]}{k_g[M]}. \tag{2}$$

Using the experimental dependence of $M_n$ on the concentrations of chain-transfer agents, the values of $k_g$, and Eq. (2), we determined the rate constants of transfer for the corresponding chain-transfer agents. These constants for the isotactic polymerization of propylene (for the iPP fraction) on the $TiCl_4/DBP/MgCl_2$–$AlEt_3$/DCPDMS catalytic system at 70°C are given below.

| $k_g$, l mol$^{-1}$ s$^{-1}$ | $k_t^M$, l mol$^{-1}$ s$^{-1}$ | $k_t^{Al}$, l$^{0.5}$ mol$^{-0.5}$ s$^{-1}$ | $k_t^S$, s$^{-1}$ | $k_t^H$, l$^{0.5}$ mol$^{-0.5}$ s$^{-1}$ | $k_t^{Zn}$, l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 2750 | 0.67 | 5.9 | <0.1 | 33 | 410 |

Note: TMC samples with Ti concentrations of 1.8–2.1% were used for determining the rate constants of chain transfer.

The resulting rate constants of chain transfer allowed us to evaluate the contributions of various transfer reactions under given polymerization conditions. Let us evaluate these contributions for the suspension polymerization of propylene (at 70°C, 7 bar $C_3H_6$); $[AlEt_3] = 2.5$ mmol/l; $H_2/C_3H_6 = 0.04$ in a gas phase; and $ZnEt_2/AlEt_3 = 1$. From Eq. (2) and the above chain-transfer rate constants, we obtain the following equation:

$$\frac{42}{M_n} = 2.43 \times 10^{-4} + 0.47 \times 10^{-4} + 2.37 \times 10^{-4} + 1.6 \times 10^{-4}. \tag{3}$$

Analysis of Eq. (3) allowed us to draw the following conclusions:

(1) In the absence of specially added chain-transfer agents ($H_2$, $ZnEt_2$), the predominant chain-transfer reaction is the chain-transfer reaction with the monomer (the first term in the right-hand side of Eq. (3)).

(2) The contribution of the chain-transfer reaction with $AlEt_3$ is much lower than that with the monomer (by a factor of 5 under the specified conditions). The rate of the chain-transfer reaction with the other cocatalyst ($ZnEt_2$) is higher than that with $AlEt_3$ (by a factor of ~3; cf. the second and fourth terms in the right-hand

side of Eq. (3)); however, it is also lower than the rate of the chain-transfer reaction with the monomer.

(3) Chain transfer with hydrogen is the most effective. Even at a low hydrogen content of the gas phase (a few vol %; $H_2/C_3H_6 = 0.04$), the rates of chain transfer with hydrogen and the monomer are commensurable (the first and third terms in the right-hand side of Eq. (3)).

(4) In the polymerization of propylene in a liquid monomer medium, when the concentration of propylene is higher by a factor of 4, the contribution of chain-transfer reactions with a cocatalyst and hydrogen decreases in accordance with Eq. (2). Therefore, a much higher concentration of hydrogen (higher by more than one order of magnitude) will be required to reach the same molecular weight of PP as in suspension polymerization at a propylene pressure of 7 bar.

### *Ethylene Polymerization*

A number of highly active supported catalysts for propylene polymerization (polymerization rate of ~1000 g PP (g Cat)$^{-1}$ h$^{-1}$ atm$^{-1}$) with low porosity and a particle size greater than 15 μm exhibited a very low rate of ethylene polymerization (~100 g PE (g Cat)$^{-1}$ h$^{-1}$ atm$^{-1}$).

It is believed that the low rate of ethylene polymerization is due to diffusion limitations, which appear within a dense macroparticle because of the high reactivity and high concentration of centers at the initial stage of ethylene polymerization. The results of a mathematical simulation of olefin polymerization [29–32] count in favor of the above hypothesis. Another reason can be a low number of active centers because of diffusion limitations for a cocatalyst, a lower degree of catalyst fragmentation by a polymer, etc. In the case of diffusion limitations for ethylene, the calculated values of $k_g$ ($RC_g^{-1}$ $[C_2H_4]^{-1}$), where $R$ is the rate of polymerization, mol $C_2H_4$, (mol Ti)$^{-1}$ s$^{-1}$, and $[C_2H_4]$ is the concentration of ethylene in heptane, mol/l, are underestimated because the actual concentration of ethylene near the active center within a polymer particle is lower. In this case, the greater the particle size, the stronger the effect of diffusion.

To analyze these effects, we determined the number of active centers in ethylene polymerization on a number of supported TMC with different compositions and particle morphologies.

**Effects of the concentration of active centers and particle size.** We determined the values of $C_g$ and $k_g$ in the polymerization of ethylene on two catalysts with different titanium concentrations and broad particle-size distributions.

| Catalyst | $R$ |  | $C_g$ |  | $k_g$ |
|---|---|---|---|---|---|
|  | kg PE (g Cat)$^{-1}$ h$^{-1}$ atm$^{-1}$ | kg PE (g Ti)$^{-1}$ h$^{-1}$ atm$^{-1}$ | mmol (g Cat)$^{-1}$ | mol (mol Ti)$^{-1}$ | l mol$^{-1}$ s$^{-1}$ |
| $TiCl_4$/DBP/$MgCl_2$ (2.3% Ti) | 0.47 | 20 | 0.034 | 0.07 | 2400 |
| $TiCl_4$/$MgCl_2$ (0.1% Ti) | 0.25 | 250 | 0.0038 | 0.18 | 11500 |

It can be seen that, on both of the catalysts, the rates of polymerization per gram of a catalyst were similar; however, the rates of polymerization per gram of titanium dramatically differed (by a factor of 12.5). The low rate of polymerization on the catalyst with a high titanium content ($TiCl_4$/DBP/$MgCl_2$, 2.3% Ti) was only partly due to a decrease in the number of active centers (by a factor of 2.6); it was primarily due to the effect of diffusion limitations. This manifested itself in a lower calculated value of $k_g$ for this catalyst (by a factor of ~5).

The values of $k_g$ for various PE fractions were determined.

| Catalyst | $TiCl_4$/DBP/$MgCl_2$ (2.3% Ti) |  |  | $TiCl_4$/$MgCl_2$ (0.1% Ti) |  |  |
|---|---|---|---|---|---|---|
| Polymer | Total | Fraction of 1–2 mm | Fraction of 0.09–0.25 mm | Total | Fraction of 1–2 mm | Fraction of 0.09–0.25 mm |
| $k_g$, l mol$^{-1}$ s$^{-1}$ | 2400 | 1800 | 8400 | 11500 | 12000 | 11300 |

It can be seen that, in the case of the catalyst with a high titanium content ($TiCl_4$/DBP/$MgCl_2$, 2.3% Ti), a considerable decrease in the values of $k_g$ for the coarse fraction of PE was observed. This suggests diffusion limitations for the monomer in PE particles as the particle size increased. If the concentration of active centers in a catalyst ($TiCl_4$/$MgCl_2$, 0.1% Ti) was significantly decreased (0.0038 mmol/(g Cat), as compared with 0.034 mmol/(g Cat)), the values of $k_g$ were higher and were independent of the particle size of PE; this suggests an absence of diffusion limitations.

**Effect of prepolymerization.** Preliminary polymerization under mild conditions (prepolymerization) is another procedure that can decrease or eliminate diffusion limitations. The results of two experiments with the use of prepolymerization with ethylene (experiment 1) and propylene (experiment 2) are given below.

| Experiment | Prepolymerization with monomer | R, kg PE (g Cat)$^{-1}$ h$^{-1}$ atm$^{-1}$ | $C_g$, mol/(mol Ti) | $k_g$, l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 1 | $C_2H_4$ | 0.11 | 0.043 | 900 |
| 2 | $C_3H_6$ | 2.3 | 0.063 | 12100 |

Note: Prepolymerization was performed as follows: 0.3 g of a monomer was introduced into the polymerization medium with 9.5 mg of a TMC (2.4% Ti); the mixture was allowed to stand at 40°C for 5 min; next, the temperature was increased to 70°C, and ethylene was added to 2 bar after 10 min.

In the former case, the rate of ethylene polymerization remained low. If the polymerization of ethylene was performed after the prepolymerization of propylene, the rate of ethylene polymerization dramatically increased. Simultaneously, the value of $k_g$ dramatically increased at a small change in the number of active centers. This can be explained by the fact that, in the course of prepolymerization, propylene penetrated more deeply into a catalyst macroparticle than ethylene because of the lower reactivity of propylene. The resulting PP crushed the catalyst within the growing polymer macroparticle into small fragments (to microparticles). As a result, active centers became distributed more uniformly and their bulk concentration in the macroparticle decreased. In this case, catalyst microparticles in the resulting polymer macroparticle became more accessible to the monomer, and diffusion limitations were not observed in the subsequent polymerization of ethylene.

**Data on $k_g$ for TMCs with different stereospecificity.** Table 3 summarizes the values of $k_g$ determined in ethylene polymerization on low-stereospecificity and high-stereospecificity catalytic systems. In both cases, the experiments were performed under conditions that excluded the effect of diffusion limitations. It can be seen in Table 3 that the reactivity of stereospecific and nonstereospecific centers in ethylene polymerization was practically the same.

## CONCLUSIONS

(1) In the polymerization of propylene on stereospecific catalysts (TMCs with donors, $TiCl_3$), the value of $k_g$ for stereospecific centers is higher than that for nonstereospecific centers by one order of magnitude.

(2) In the polymerization of propylene, the effect of an internal donor (DBP, DIBDMP) in TMCs manifests itself in (a) a decrease in the values of $k_g$ for nonstereospecific and low-stereospecificity centers, (b) the absence of an effect of stereospecific centers on $k_g$, (c) an increase in the fraction of stereospecific centers, and (d) an increase in the fraction of sleeping centers regardless of their stereospecificity (from 50 to 70–85%).

(3) In the polymerization of propylene, an external donor (silane) enhances the effect of DBP as an internal donor and makes the DBP/silane system similar to the system with a highly effective internal donor (DIBDMP) in the values of $k_g$ and the fractions of corresponding active centers. The introduction of an external electron donor into the system also retained the stereospecificity of centers, which is provided by DBP and lost because of the partial removal of DBP by the interaction with $AlEt_3$. In general, the effects found suggest that both external and internal donors are adsorbed on $MgCl_2$ near active centers, and they affect the reactivity of these active centers.

(4) In the polymerization of propylene, the values of $k_g$ for corresponding active centers are similar in supported TMCs and $TiCl_3$.

(5) The rate constants of isotactic-chain transfer with propylene, hydrogen, $AlEt_3$, and $ZnEt_2$ were determined. These constants allow us to evaluate the contributions of various chain-transfer reactions depending on polymerization conditions.

(6) In the polymerization of ethylene, strong diffusion limitations are observed in the dense and coarse particles of highly active supported catalysts. Diffusion limitations can be eliminated with the use of catalysts with particles smaller than 10 μm, by decreasing concentration of active centers, or by performing prepolymerization with propylene.

(7) The values of $k_g$ in ethylene polymerization are similar for stereospecific and nonstereospecific centers.

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