

## Effect of substituents on the catalytic properties of bis(cyclopentadienyl) zirconocene dichlorides in polymerization of ethene

N. M. Bravaya,\* V. V. Strelets, Z. M. Dzhabieva, O. N. Babkina, and V. P. Maryin

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,  
142432 Chernogolovka, Moscow Region, Russian Federation.  
Fax: +7 (096) 515 3588*

Comparative analysis of catalytic activity of substituted bis(cyclopentadienyl)zirconium dichlorides with the general formula  $(R_n\text{Cp})_2\text{ZrCl}_2$  ( $\text{Cp}_2\text{ZrCl}_2$ ,  $(\text{MeCp})_2\text{ZrCl}_2$ ,  $(\text{Pr}^i\text{Cp})_2\text{ZrCl}_2$ ,  $(\text{Pr}^i\text{Cp})_2\text{ZrCl}_2$ ,  $(\text{Bu}^n\text{Cp})_2\text{ZrCl}_2$ ,  $(\text{Bu}^i\text{Cp})_2\text{ZrCl}_2$ ,  $(\text{Bu}^t\text{Cp})_2\text{ZrCl}_2$ ,  $\text{Cp}^*\text{ZrCl}_2$  ( $\text{Cp}^* = \text{Me}_5\text{C}_5$ ),  $(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2$ ,  $(\text{cyclo-C}_6\text{H}_{11}\text{Cp})_2\text{ZrCl}_2$ , and  $\{(\text{cyclo-C}_6\text{H}_{11})_2\text{Cp}\}_2\text{ZrCl}_2$ ) in ethene polymerization using polymethylalumoxane as the cocatalyst was performed. The molecular mass characteristics of the polyethylene samples obtained were determined. A linear correlation of the specific activity of the catalysts and the turnover number with the electronic and steric characteristics of substituents at the Cp ring of the complexes was established for the first time. Analysis of the polymerization kinetics and the obtained correlation between the specific activity of the complexes and molecular mass characteristics of the polyethylene samples suggest that alkyl substituents participate in reactions responsible for the restriction of the polymer chain growth and regeneration of the active center. These interactions most likely involve associates of  $\text{AlMe}_3$  with polymethylalumoxane molecules.

**Key words:** metallocene complexes, bis(cyclopentadienyl)zirconium dichlorides, effect of substituents, ethene polymerization.

Many experimental and calculation works are devoted to the effect of substituents on the reactivity of substituted zirconium and titanium bis(cyclopentadienyl) complexes in olefin polymerization in the presence of the cocatalyst, polymethylalumoxane (MAO). However, it is difficult to compare the catalytic properties of the metallocene dichloride—MAO systems described by different authors, because these very efficient catalysts are very sensitive to experimental conditions (purity of reagents, concentration and order of introducing components of the catalytic system, pressure of the monomer,  $\text{Al/Zr}$  ratio, etc.). The effect of substituents was analyzed in most detail in the recent review.<sup>1</sup>

As for cyclopentadienyl complexes, an increase in the catalytic activity of the catalyst and molecular mass of the polymer when alkyl substituents are introduced into the ring was mentioned in several works.<sup>2–6</sup> Data on the effect of substituents are discussed at the qualitative level, as a rule, in terms of the electronic and steric effects of substituents. However, analyses of experimental results are often contradictory. For example, the explanation of the effect of electron-donor substituents in the cyclopentadienyl ring on the activity of the  $\text{M—C}$  bond in Ref. 1 is reduced, in particular, to the fact that "these substituents decrease the positive charge on the metal, thus weakening bonds of the metal with other ligands, including the  $\text{M—C}$  bond" at which olefin is

inserted during polymerization. At the same time, the cyclotron-resonance mass spectrometric study of the ion-molecular reactions of  $\text{L}_2\text{ZrCH}_3^+$  with  $\text{H}_2$  and  $\text{C}_2\text{H}_4$ , where  $\text{L}_2 = \text{CpCp}$ ,  $\text{CpInd}$ ,  $\text{Ind}_2$ , and  $\text{Flu}_2$  ( $\text{Cp}$  is cyclopentadienyl,  $\text{Ind}$  is indenyl, and  $\text{Flu}$  is fluorenyl) are substituents, whose donating capability increases in the series indicated, showed<sup>7</sup> that the reaction rate constants decrease in the same series. This corresponds to weakening of the electrophilic properties of the central metal atom and contradicts the experimental data on ethene polymerization under the action of the corresponding dichloride complexes activated by MAO.

An increase in the volume of the substituent results in a decrease in the activity due to difficulties in coordination and insertion of olefin. For example, it has been established<sup>8</sup> that the catalytic activity in ethene polymerization of a series of symmetrically and unsymmetrically  $\text{Me-}$  and  $\text{Bu-}$ substituted zirconocenes depends on the geometric parameters of the complex providing accessibility for the olefin to the central metal ion. The size of substituents can also affect the chain transfer reaction and regeneration of the active center. Steric factors can affect the conformation mobility of metallocene complexes, especially when several bulky substituents are introduced in the ring, and in this case, it is difficult to predict their effect on all stages of the polymerization reaction.

It is noteworthy that MAO (cocatalyst of polymerization usually used in a high excess with respect to the activated complex) contains<sup>9,10</sup> an insignificant amount (~30%) of partially bound  $\text{AlMe}_3$ . It is assumed that MAO can also contain other active admixtures capable of affecting the catalytic activity<sup>11,12</sup> (e.g., associated water molecules or fragments with OH groups). The structure and composition of MAO change in time, and it is difficult to analyze them. Some authors believe that this is precisely  $\text{AlMe}_3$  which is the alkylating agent in the composition of the cocatalyst.<sup>11,13</sup> However, these difficultly controllable factors are not taken into account, as a rule, in analysis of the effect of substituents on the catalytic activity and chain transfer reactions.

These circumstances impede the separation "in the pure form" of the effect of substituents on the state of the active metal-carbon bond. Therefore, in this work, we attempted to analyze the factors determining the overall effect of substituents in the cyclopentadienyl rings on the catalytic properties of active centers and polymeric products formed in the reactions of zirconium dichloride complexes with MAO during the ethene polymerization. The polymerization processes were carried out under rigidly similar conditions. For this purpose, we compared the catalytic properties of unsubstituted  $\text{Cp}_2\text{ZrCl}_2$  (1) and ten monosubstituted zirconium cyclopentadienyl complexes:  $(\text{MeCp})_2\text{ZrCl}_2$  (2),  $(\text{Pr}^i\text{Cp})_2\text{ZrCl}_2$  (3),  $(\text{Pr}^i\text{Cp})_2\text{ZrCl}_2$  (4),  $(\text{Bu}^n\text{Cp})_2\text{ZrCl}_2$  (5),  $(\text{Bu}^i\text{Cp})_2\text{ZrCl}_2$  (6),  $(\text{Bu}^t\text{Cp})_2\text{ZrCl}_2$  (7),  $\text{Cp}^*\text{ZrCl}_2$  ( $\text{Cp}^* = \text{Me}_5\text{C}_5$ ) (8),  $(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2$  (9),  $(\text{cyclo-C}_6\text{H}_{11}\text{Cp})_2\text{ZrCl}_2$  (10), and  $[(\text{cyclo-C}_6\text{H}_{11})_2\text{Cp}]_2\text{ZrCl}_2$  (11).

## Results and Discussion

Titanium, zirconium, and hafnium metallocene dichlorides react with MAO to form coordinately unsaturated 14-electron cationic complexes\* (or ion pairs) with the metal-methyl bond (see, e.g., Refs. 16–18). Olefin is inserted very rapidly in the M–C bond *via* the stage of coordination of the olefin by the metal atom. The formation of a new M–C bond is preceded by weakening and cleavage of the M–C bond and the double bond in olefin. The growth of the polymeric chain is mainly restricted by the elimination of the  $\beta$ -hydrogen atom of the growing polymer chain, although processes of activation of the C–H bond in  $\sigma$ -coordinated olefin<sup>19</sup> and chain transfer to the organoaluminum compound can also be substantial.<sup>2</sup> Evidently,

substituents in the  $\eta^5$ -bound ligand (cyclopentadienyl, indenyl, and fluorenyl) can exert a substantial effect on all these elementary acts of the polymerization process in the coordination sphere of the transition metal due to both the electron density redistribution in the complex and steric factors. The capability of the electron-deficient cationic active center of entering the agostic interaction with hydrogen atoms of adjacent functional groups affects the occurrence of all stages of the reaction.<sup>20–23</sup> Transalkylation of the active center or addition of olefin to the hydride complex results in the regeneration of the active center. Evidently, substituents in *hapto*-bound ligands can exert a substantial effect on these processes.

It is noteworthy that it is difficult to study reactions of metallocene dichloride complexes with MAO at concentrations providing maximum activity of the complexes ( $10^{-6}$ – $10^{-5}$  mol  $\text{L}^{-1}$ ). Only few published data exist that indicate the participation of substituents in the ligand ring in the reactions occurring in the coordination sphere of the central metal ion. The anomalously high activity of  $\text{Pr}^i\text{Cp}_2\text{ZrCl}_2$ –MAO in the propylene oligomerization is assumed to be the result of the formation of zirconium hydride complexes involving hydrogen atoms at the  $\alpha$ -carbon atom of the substituent.<sup>24</sup> The studies of the decomposition of the  $\text{RCp}_2\text{ZrX}_2$  complexes ( $\text{R} = \text{Alk}$ ;  $\text{X} = \text{Cl}, \text{Me}$ ) on heating<sup>25</sup> or under electron impact<sup>26</sup> indicate possible rearrangements involving the alkyl groups of substituents. The coordination of methoxy groups  $[4,7-(\text{MeO})_2\text{Ind}]_2\text{Zr}(\text{CH}_2\text{Ph})$  by polymethylalumoxane, which is revealed by NMR data and results in enhancement of the induction effect and weakening of the resonance effect of the indenyl system,<sup>27</sup> is the reason for the decrease in the catalytic activity and molecular mass of the polyethylene formed when the substituted zirconocene complex is used (as compared to the unsubstituted analog). It is mentioned in one of the early Collins's works<sup>28</sup> that the nonbridged  $[5,6-\text{MeOInd}]_2\text{ZrCl}_2$  complex is inactive in ethene polymerization after preliminary contact with MAO. The same complex is active when added in a toluene solution to a dilute solution of MAO saturated with the monomer. The polydispersity coefficient of the polyethylene obtained with this complex is considerably higher (~3) than that of the samples obtained with other complexes that are in preliminary contact with MAO. The reactions involving the central metal atom and ligands can lead to a change in the structure of the active center. In the literature the catalytic complexes formed in the interactions of sandwich complexes of Group IV metals with MAO are called active centers of the *mono*-type ("single site catalysts"). In fact, polyolefins obtained with these complexes are characterized, as a rule, by a very low polydispersity coefficient ( $\bar{M}_w/\bar{M}_n \leq 2$ ), although sufficiently wide molecular mass distributions are known.<sup>2</sup> In this connection, it was of interest to compare the catalytic behavior of a series of substituted zirconium cyclopentadienyl complexes and to analyze the polymeric complexes obtained.

\* The concept of cationic complexes active in olefin polymerization and formed during the reactions of titanium metallocene dichloride complexes with  $\text{AlR}_2\text{Cl}$  has been formulated and experimentally confirmed by A. E. Shilov and coworkers<sup>14,15</sup> in the early sixties and then it gained wide recognition and development in studying the mechanism of formation and action of active centers of homogeneous metallocene catalysts of olefin polymerization.

**Table 1.** Activity of the series of substituted bis(cyclopentadienyl)zirconium dichlorides in ethene polymerization and molecular mass parameters of the polymer samples obtained<sup>a</sup>

Catalyst	<i>A</i> <sup>b</sup>	<i>M</i> <sub>n</sub>	Turnover number	<i>M</i> <sub>w</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>
Cp <sub>2</sub> ZrCl <sub>2</sub> (1)	959	40900	23	213600	5.2
(MeCp) <sub>2</sub> ZrCl <sub>2</sub> (2)	6470	133800 <sup>c</sup>	48	345500	2.6
		49600	130		7.0
(Pr <sup>i</sup> Cp) <sub>2</sub> ZrCl <sub>2</sub> (3)	4555	67000	68	291200	4.3
(Pr <sup>i</sup> <sub>2</sub> Cp) <sub>2</sub> ZrCl <sub>2</sub> (4)	3500	28440	123	131400	4.6
(Bu <sup>n</sup> Cp) <sub>2</sub> ZrCl <sub>2</sub> (5)	2235	59600	38	323300	5.4
(Bu <sup>i</sup> Cp) <sub>2</sub> ZrCl <sub>2</sub> (6)	1658	68700	24	272900	4.0
(Bu <sup>t</sup> Cp) <sub>2</sub> ZrCl <sub>2</sub> (7)	706	114200	6	271700	2.4
Cp* <sub>2</sub> ZrCl <sub>2</sub> (8)	1418	9400	150	72400	7.7
(Me <sub>3</sub> Si) <sub>2</sub> ZrCl <sub>2</sub> (9)	2049	101100	20	654700	6.5
(cyclo-(C <sub>6</sub> H <sub>11</sub> )Cp) <sub>2</sub> ZrCl <sub>2</sub> (10)	1265	74900	17	196600	2.6
(cyclo-(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> Cp) <sub>2</sub> ZrCl <sub>2</sub> (11)	628	52800	12	257200	4.9

Note. Polymerization conditions: MAO is cocatalyst, 30 °C, toluene, ethene pressure 0.54 atm, [Zr] = 2 · 10<sup>-7</sup> mol L<sup>-1</sup>, Al/Zr = 2000). <sup>a</sup> Determined by gel permeation chromatography. <sup>b</sup> Activity in kg PE · (mol Zr h)<sup>-1</sup>. <sup>c</sup> Bimodal sample.

Comparison of the catalytic activity of the series of substituted complexes showed that under similar conditions, the activity of the complexes changes in the sequence: 2 > 3 > 4 > 5 > 9 > 6 > 8 > 10 > 1 > 7 > 11 (Table 1). The complexes with alkyl substituents in the pentadienyl ring (MeCp, Pr<sup>i</sup>Cp, and Pr<sup>i</sup><sub>2</sub>Cp) are the most active. It is noteworthy that MAO-activated complex 2 exhibits<sup>24</sup> the maximum activity in ethene polymerization. The following activity rows of the complexes have been found: 9 > 1 > 7,<sup>29</sup> 2 > 1 > 8,<sup>30</sup> and 9 > 3 > 1 > 7.<sup>3,4</sup> In the presence of polyethylalumoxane as the cocatalyst, the ratio of activities changes substantially: 7 > 9 > 3 > 2 ≈ 1,<sup>5</sup> 3 > 2 > 7 > 1.<sup>31</sup> The value of efficiency per time unit (as a rule, per h) in mass units of polymer referred to a mole of the transition metal is accepted as the characteristic of the catalytic properties of complexes. The molecular mass parameters of polymers are not always analyzed. The presented examples of differences in the activity rows of substituted bis(cyclopentadienyl) zirconocenes indicate that the effect of substituents on all stages of polymerization, including stages of chain transfer, regeneration of the active center, and others, should be analyzed in more detail.

The authors of almost all works discuss the effect of electronic and steric factors of substituents on polymerization; however, attempts at quantitative correlation are few. In particular, for the quantitative estimation of the influence of electronic and steric effects of substituents (six complexes, polyethylalumoxane as the cocatalyst), the Hammett functions of substituents (*F*) tabulated in

**Table 2.** Electronic (inductive Taft constants σ\*) and steric (steric Pal'm constants *E*<sub>s</sub>) characteristics of substituents<sup>33,34</sup>

Substituent	-Σσ*	-Σ <i>E</i> <sub>s</sub>
H	0	0
Me	0.49	0.25
Pr <sup>i</sup>	0.68	1.1
Pr <sup>i</sup> <sub>2</sub>	1.36	2.2
Bu <sup>n</sup>	0.75	1.9
Bu <sup>i</sup>	0.6	1.78
Bu <sup>t</sup>	0.79	2.39
Cp*	2.45	3.85 <sup>a</sup>
cyclo-C <sub>6</sub> H <sub>11</sub>	0.64	1.44
cyclo-(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	1.28	2.88
SiMe <sub>3</sub>	0.75	3.7

<sup>a</sup> The *E*<sub>s</sub><sup>0</sup> value for the permethylated complex is shown<sup>34</sup> to be substantially greater than the simple sum of five *E*<sub>s</sub><sup>0</sup> for Me groups, which agrees with structural data for permethylated complexes with different (depending on the orientation) deviations of Me groups from the cyclopentadienyl ring plane (from 2 to 18°).<sup>35</sup>

the review<sup>32</sup> were used,<sup>5</sup> and the Tolman angle with the basis on the metal atom (Θ<sub>1</sub>) or on the Cp-centroid (Θ<sub>2</sub>) were used as the steric characteristic of substituents. However, no satisfactory correlation of the activity of the complexes in ethene polymerization with these characteristics was obtained. In the three-dimensional dependences of the activity of the complexes studied on *F* and Θ<sub>1</sub>, an increase in both the donating ability of substituents and their size is accompanied by an increase in the activity of the complexes, which seems improbable for the polymerization reaction in which bulky substituents should prevent approach of the olefin to the active center.

A sufficiently wide set of complexes made it possible to obtain a correlation of the activity of the complexes with electronic and steric constants of substituents. We used the values of the electronic Taft functions (σ\*) and steric Pal'm constants (*E*<sub>s</sub>)<sup>33</sup> presented in Table 2. A good correlation of these parameters with potentials of the electrochemical reduction of the complexes has been established previously<sup>34</sup> for several zirconocene dichlorides studied in this work.

Attempts at correlating the activity of complexes with different substituents or only to electronic, to the Hammett constants of substituents, to the induction Taft substituents, or to steric constants were unsuccessful. The values of specific activity of different complexes are well described by the biparametric equation using the induction Taft constants (σ\*) and the steric Pal'm constants (*E*<sub>s</sub><sup>0</sup>).

$$\frac{A^R - A^H}{A^H} = \rho^* \Sigma \sigma^* + \delta \Sigma E_s^0$$

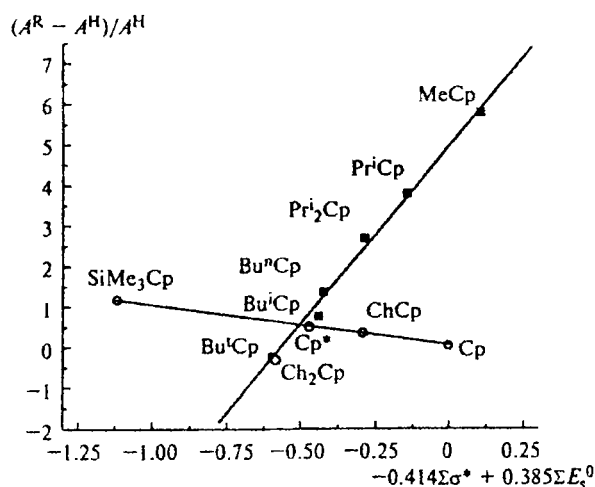


Fig. 1. Dependences of the reduced specific activity in ethene polymerization of several substituted zirconium bis(cyclopentadienyl) dichloride complexes on inductive and steric effects of substituents (Ch = *cyclo*-C<sub>6</sub>H<sub>11</sub>).

The values of the  $\rho$  and  $\delta$  coefficients were determined by multiple regression analysis with minimization of the root-mean-square deviation of the activity of the whole series of complexes under study. The optimum values of the parameters are  $\rho = -0.414$  and  $\delta = 0.385$  (Fig. 1). The root-mean-square error is not greater than 4%.

Analysis of the dependences of the specific activity of the complexes with different substituents on the sum of the electronic and steric factors showed that all the complexes studied can be divided into two groups. The first group contains the complexes with alkyl substituents in the Cp ring. Their specific activity increases linearly as the total effect of substituents increases ( $\text{tg}\alpha \approx 9$ ). The activity of the second group of complexes decreases linearly as the total electronic and steric effect of substituents increases ( $\text{tg}\alpha \approx -1$ ). Since the  $\sigma^*$  and  $E_s^0$  values are negative, at  $\rho < 0$  the reaction rate should increase as the electron density on the active center increases, and an increase in the substituent volume at  $\delta > 0$  should result in a decrease in the reaction rate. However, for the group of  $\text{Cp}_2\text{ZrCl}_2$ , (*cyclo*-C<sub>6</sub>H<sub>11</sub>)Cp<sub>2</sub>ZrCl<sub>2</sub>, and SiMe<sub>3</sub>Cp<sub>2</sub>ZrCl<sub>2</sub> complexes, an inverse tendency for an increase in the specific activity is observed. For the group of complexes with alkyl substituents in the cyclopentadienyl ring, the specific activity of the complex increases as the total effect of substituents increases, but the Bu<sup>i</sup>Cp<sub>2</sub>ZrCl<sub>2</sub> complex is the initial point rather than the unsubstituted analog Cp<sub>2</sub>ZrCl<sub>2</sub>.

If the specific activity of the complexes reflects only the ability of the M—C bond to insert an olefin molecule, the total effect of substituents should result in a decrease in the efficiency of the complex as compared to the unsubstituted analog. The dependences observed allow us to consider alkyl substituents in the cyclopentadienyl ring

as active functional groups capable of affecting the polymer chain transfer and regeneration of the active center rather than the addition of the monomer.

As can be seen in Table 1, no pronounced dependence is observed between the activity of the complex and numerical-mean molecular masses of the polymers obtained. For example, the specific activity of the Pr<sup>i</sup>Cp<sub>2</sub>ZrCl<sub>2</sub> complex (3) is approximately threefold higher than that of Bu<sup>i</sup>Cp<sub>2</sub>ZrCl<sub>2</sub> (5), whereas the molecular masses of the polyethylene samples are approximately equal. The molecular mass of PE obtained using Bu<sup>i</sup>Cp<sub>2</sub>ZrCl<sub>2</sub> (7) is ~2 times higher than that of the polymer formed in the case of complex 3, and the activity of the catalytic system is 6.5-fold lower. At the same time, the numerical-mean molecular mass of PE obtained using Pr<sup>i</sup>Cp<sub>2</sub>ZrCl<sub>2</sub> is ~2 times lower than that of PE formed in the case of the complex with one isopropyl substituent. The curve of the molecular mass distribution of PE obtained using MeCp<sub>2</sub>ZrCl<sub>2</sub> is bimodal. The  $M_n$  value of the low-molecular fraction is 49600 g mol<sup>-1</sup>, which is ~5-fold higher than  $M_n$  of PE formed in the presence of the permethylated complex. It is noteworthy that the polydispersity coefficients of the polymers are sufficiently high; polyethylene obtained using complex 7 has the lowest value  $M_w/M_n = 2.4$ . All these observations and the differences between the numerical-mean molecular masses for mono- and poly-substituted complexes (3 and 4, 10 and 11, 2 and 8) were reasons for introducing an additional parameter for the analysis of the results. This parameter is the catalytic turnover number, which can be defined as the ratio of the specific activity of the complex ((g polymer) · (mol Zr h)<sup>-1</sup>) to the numerical-mean molecular mass of the polymer obtained using this catalytic system. The values of the turnover numbers are presented in Table 1. It can be seen that this value for the complexes with alkyl substituents depends on the substituent nature more strongly than that for the complexes of the second group.

We observed the dependence of the catalytic turnover number referred to the number of substituents in the cyclopentadienyl ring on the total effect of substituents with coefficients  $\rho$  and  $\delta$  determined for the correlation dependence of the specific activity of the complexes in order to show that these are the processes related to the restriction of the polymer chain growth and regeneration of the active center which determine the observed correlation of the specific activity to the total effect of substituents (Fig. 2). For the estimation of the ratio of the turnover number to the number of substituents of the complex with the methyl substituent, we used the  $M_n$  value corresponding to the low-molecular fraction of the molecular mass distribution, since this is the fraction which reflects the process of restriction of the polymer chain growth and regeneration of the active center involving the alkyl substituent. It is seen in Fig. 2 that the catalytic turnover number increases ~50-fold faster for the complexes with alkyl substituents ( $\text{tg}\alpha =$

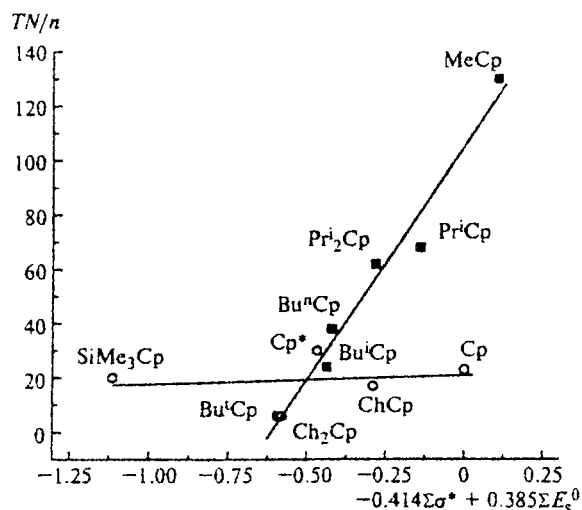


Fig. 2. Dependences of the catalytic turnover number (TN) referred to the number of substituents ( $n$ ) in ethene polymerization by substituted zirconium bis(cyclopentadienyl) dichloride complexes on inductive and steric effects of substituents (Ch = cyclo-C<sub>6</sub>H<sub>11</sub>).

172.2) than that for the complexes of the second group ( $\text{tg}\alpha = 3.4$ ). This observation allows us to consider the alkyl substituent in the cyclopentadienyl ring as the functional group capable of affecting the stages of the polymerization process related to the chain transfer and regeneration of the active center.

The more or less pronounced exponential decrease in the polymerization rate is a characteristic feature of the catalytic behavior of metallocene catalysts under the action of activators. The mechanism of deactivation of the complexes is unclear yet, but it is assumed<sup>36</sup> that binuclear complexes (Zr—Zr or Al—Zr) containing methyl or methylene bridges are the main products of deactivation. Analysis of the kinetics of ethene polymer-

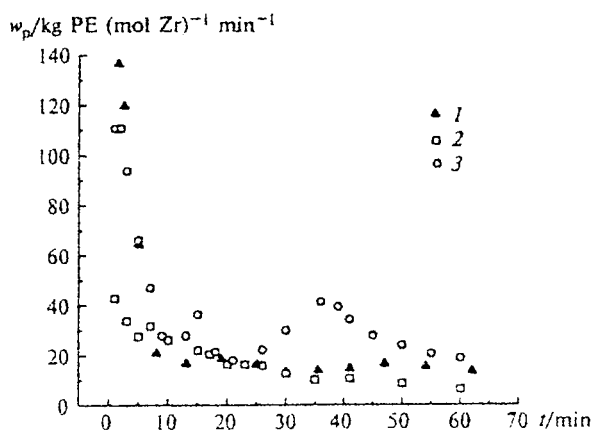


Fig. 3. Time dependences of the ethene polymerization rate ( $w_p$ ) for catalytic systems Cp<sub>2</sub>ZrCl<sub>2</sub> (1); Cp\*<sub>2</sub>ZrCl<sub>2</sub> (2); and SiMe<sub>3</sub>Cp<sub>2</sub>ZrCl<sub>2</sub> (3). Polymerization conditions are presented in Table 1.

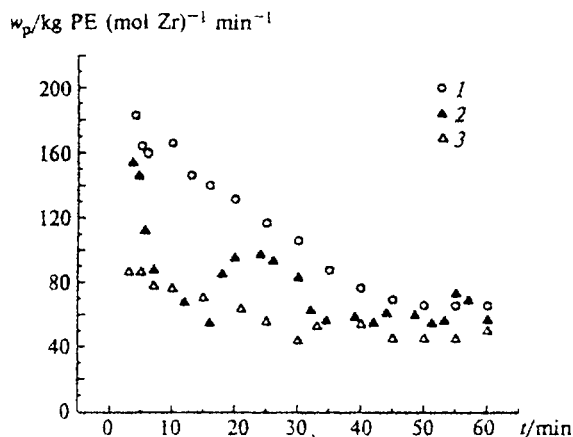


Fig. 4. Time dependences of the ethene polymerization rate ( $w_p$ ) for catalytic systems MeCp<sub>2</sub>ZrCl<sub>2</sub> (1); PrCp<sub>2</sub>ZrCl<sub>2</sub> (2); and Pr<sub>2</sub>Cp<sub>2</sub>ZrCl<sub>2</sub> (3). Polymerization conditions are presented in Table 1.

ization in the series of the complexes studied showed that the exponential decrease in the polymerization rate in time is observed in fact for some complexes (Fig. 3, curves 1 and 2). At the same time, we observed a more complicated time dependence of the polymerization rate (Fig. 3, curve 3; Fig. 4) for several complexes, a linear decrease or acceleration of the polymerization process. These specific features are most pronounced for the group of complexes with alkyl substituents in the cyclopentadienyl ring. It is noteworthy that similar time dependences of the polymerization rate were observed for several catalytic 1-AlkInd<sub>2</sub>ZrCl<sub>2</sub>—MAO systems during ethene polymerization.<sup>37</sup>

Since the participation of alkyl substituents in the reactions within the coordination sphere of the central metal ion resulting in a change in the catalytic center during polymerization was not mentioned in the literature, we analyzed the polymer samples obtained using the same complex at different polymerization times (Table 3). It is seen in Table 3 that a tendency to form polymer chains with high average molecular masses is observed during the polymerization process, and the

Table 3. Dependence of molecular mass characteristics of polyethylene samples obtained with the catalytic PrCp<sub>2</sub>ZrCl<sub>2</sub>—MAO system on the polymerization time

$t/\text{min}$	$M_w$	$M_n$	$M_w/M_n$
2.5	277052	133455	2.08
5	296661	141670	2.09
10	331585	138063	2.40
15	420916	171725	2.45
30	495116	195305	2.54
60	556042	173282	3.21

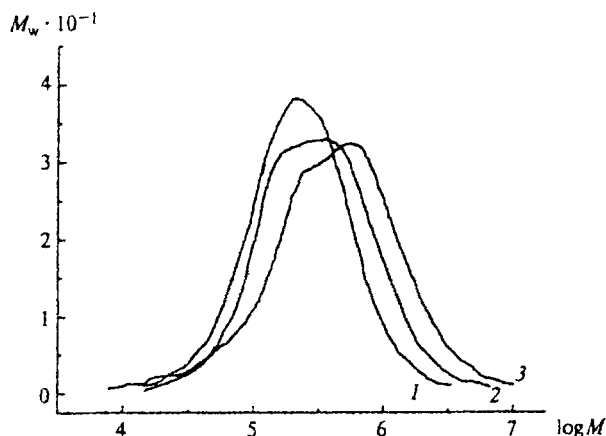


Fig. 5. Curves of the molecular mass distribution of polyethylene samples obtained using the catalytic  $\text{Pr}^i\text{Cp}_2\text{ZrCl}_2$ —MAO system at polymerization times 2.5 (1), 15 (2), and 60 (3) min.

polydispersity increases as well. The additional mode in the curve of the molecular mass distribution for the polymer samples obtained at long polymerization times is clear evidence for the transformation of the complexes during polymerization (Fig. 5).

At present it is difficult to determine the sequence of reactions resulting in the transformation of the active center and a change in its structure during the polymerization process. It is difficult to study these processes directly, because an increase in the concentration of the metallocene complex and a decrease in the Al/Zr ratio are accompanied by a sharp decrease in the rate of the polymerization process, a change in the direction of the reactions leading to the formation and deactivation of electron-unsaturated cationic complexes, and the shift of equilibria during the formation of intermediates in the catalytic system. It can only be assumed that  $\text{AlMe}_3$ , which is contained in MAO in a considerable amount, is the main component capable of affecting the stages of the polymerization process through the interaction with the alkyl groups of substituted complexes. Our experiments with MAO containing different amounts of  $\text{AlMe}_3$  are now in progress.

Thus, the catalytic activity of substituted cyclopentadienyl zirconocene dichlorides in ethene polymerization (and, possibly, in other polymerization processes) depends on the steric factors of the substituents rather than on polar factors. The contribution of these factors can be separated, and the catalytic activity of the complexes and their turnover numbers can be described by a biparametric equation of the Taft type. This makes it possible to predict the catalytic properties of zirconium metallocene dichloride complexes, which are as yet unstudied in polymerization.

This work was financially supported by Exxon Chemical Company (Division Exxon Corporation) and the Russian Foundation for Basic Research (Project Nos. 97-03-32243a and 95-03-08840a).

## References

1. P. C. Möhring and N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
2. J. C. W. Chien and B.-P. Wang, *J. Polym. Sci., A, Polym. Chem.*, 1990, **28**, 15.
3. V. P. Maryin, L. A. Nekhaeva, L. I. Vyshinskaya, B. A. Krentsel', and N. I. Ivanova, *Metalloorg. Khim.*, 1990, **3**, 474 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
4. L. A. Nekhaeva, B. A. Krentsel', V. L. Khodzhaeva, S. V. Rykov, S. D. Artamonova, Yu. M. Antipov, S. I. Ganicheva, and A. A. Boitsov, *Vysokomol. Soedin., Ser. A*, 1992, **34**, 84 [*Russ. Polym. Sci., A*, 1992, **34** (Engl. Transl.)].
5. P. C. Möhring and N. J. Coville, *J. Mol. Catal.*, 1992, **77**, 41.
6. P. C. Möhring, N. Vlachakis, N. E. Grimmer, and N. J. Coville, *J. Organomet. Chem.*, 1994, **483**, 159.
7. N. G. Alameddini, M. F. Ryan, J. R. Eyler, A. R. Siedle, and D. E. Richardson, *Organometallics*, 1995, **14**, 5005.
8. C. Janiak, K. C. H. Lange, U. Versteeg, D. Lentz, and P. H. M. Budzelaar, *Chem. Ber.*, 1996, **129**, 1517.
9. J. Bliemeister, W. Hagendorf, A. Harder, B. Heitmann, I. Scimmel, E. Schemedt, W. Schnuchel, H. Sinn, L. Tikwe, N. von Thienen, K. Urlass, H. Winter, and O. Zarncke, in *Ziegler Catalysts*, Eds. G. Fink, R. Mülhaupt, and H. H. Brintzinger, Springer, New York—London—Paris, 1995, p. 57.
10. I. Tritto, M. C. Sacchi, P. Locatelli, and S. X. Li, *Macromol. Chem. Phys.*, 1996, **197**, 1537.
11. E. A. Fushman, A. D. Margolin, S. S. Lalayan, and V. E. L'vovskii, *Vysokomol. Soedin., Ser. B*, 1995, **37**, 1589 [*Russ. Polym. Sci., B*, 1995, **37** (Engl. Transl.)].
12. A. D. Margolin, E. A. Fushman, S. S. Lalayan, and V. E. L'vovskii, *Vysokomol. Soedin., Ser. A*, 1996, **38**, 1812 [*Russ. Polym. Sci., A*, 1996, **38** (Engl. Transl.)].
13. D. Cam and U. Giannini, *Makromol. Chem.*, 1992, **193**, S. 1049.
14. A. K. Zefirova and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 599 [*Dokl. Chem.*, 1961, **136** (Engl. Transl.)].
15. F. S. Dyachkovskii, A. K. Shilova, and A. E. Shilov, *J. Polym. Sci., Part C*, 1967, **16**, 2333.
16. J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe, and F. L. Lee, *J. Am. Chem. Soc.*, 1985, **107**, 7219.
17. R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.
18. C. Sishta, R. M. Hathorn, and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 1112.
19. T. K. Woo, L. Fan, and T. Ziegler, *Organometallics*, 1994, **13**, 2252.
20. M. Brookhart and L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
21. H. H. Brintzinger, D. Fischer, R. Mülhaupt, R. Reiger, and R. Waymouth, *Angew. Chem.*, 1995, **107**, 1255.
22. R. Grubbs and G. W. Coates, *Acc. Chem. Rev.*, 1996, **29**, 85.
23. J. A. Støvneng and E. Rytter, *J. Organomet. Chem.*, 1996, **519**, 277.
24. L. A. Nekhaeva, B. A. Krentsel', V. P. Maryin, I. M. Khrapova, V. L. Khodzhaeva, A. I. Mikaya, and S. I. Ganicheva, *Neftekhimiya*, 1991, **31**, 209 [*Petroleum Chem.*, 1991, **31** (Engl. Transl.)].
25. V. P. Maryin, L. I. Vyshinskaya, and O. N. Druzhkov, *Metalloorg. Khim.*, 1991, **4**, 546 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
26. Yu. A. Andrianov and V. P. Maryin, *J. Organomet. Chem.*, 1992, **441**, 419.

27. N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, and M. Moret, *Organometallics*, 1990, **9**, 3098.
28. I.-M. Lee, J. Gauthier, J. M. Ball, B. Iyengar, and S. Collins, *Organometallics*, 1992, **11**, 2115.
29. L. A. Nekhaeva, G. N. Bondarenko, S. V. Rykov, A. I. Nekhaev, B. A. Krentsel', V. P. Maryin, L. I. Vyshinskaya, I. M. Khrapova, A. V. Polonskii, and N. N. Korneev, *J. Organomet. Chem.*, 1991, **406**, 139.
30. J. A. Ewen, *Stud. Surf. Sci. and Catal.*, 1986, **25**, 271.
31. G. P. Belov, H. R. Gyulumyan, I. M. Khrapova, V. P. Maryin, and N. N. Korneev, *J. Mol. Catal., A: Chemical*, 1997, **115**, 155.
32. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
33. V. A. Pal'm, *Osnovy kolichestvennoi teorii organicheskikh reaktsii* [Fundamentals of the Quantitative Theory of Organic Reactions], Khimiya, Leningrad, 1977 (in Russian).
34. G. L. Soloveichik, A. B. Gavrilov, and V. V. Strelets, *Metalloorg. Khim.*, 1989, **2**, 431 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
35. T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.
36. M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
37. N. M. Bravaya, Z. M. Dzhabieva, V. P. Maryin, and V. V. Strelets, *Polymers*, 1997, **42**, 591.

Received April 30, 1997;  
in revised form November 21, 1997