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Highly active three-component catalytic systems based on dialkylzirconocenes, triisobutylaluminum, and perfluorophenyl borates for synthesis of low-molecular-weight polyethylene

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The catalytic properties of the zirconium complex with "constrained geometry" $Me_2SiCp^*NBu^tZrX_2$ (Cp^* = C_5Me_4, X = Cl (**1a**), Me (**1b**)) and bridged bis(cyclopentadienyl)zirconocene $Me_2SiCp_2ZrX_2$ (X = Cl (**2a**), Me (**2b**)) during their activation with triisobutylaluminum/perfluorophenyl borates (TIBA/$LB(C_6F_5)_4$, L = CPh_3 (**3**), Me_2HNPh (**4**)) in ethylene polymerization under a monomer pressure of 2—20 atm were studied by comparison. Both dichloride complexes exhibit moderate activity under the action of the combined TIBA/**3** activating agent and give linear high-molecular-weight polyethylene (PE). The interaction of the dimethyl complexes with TIBA/**3**(**4**) afford active sites in which the growing polymeric chain is intensely transferred to the monomer, due to which low-molecular-weight PE is formed. The dichloride complexes affected by TIBA/**4** also afford low-molecular-weight PE. Analysis of the structure of the polymeric products (^1H NMR spectrometry, IR spectroscopy), molecular-weight parameters of the PE samples (gel permeation chromatography (GPC)), and kinetics of polymerization suggested that the active site contains $AlBu^i_3$ as a heteronuclear bridged cationic complex. The influence of various basic substrates (the products of chain transfer with the terminal vinyl groups, the dimethylaniline fragment of borate **4** or other amine specially introduced into the reaction mixture) on the catalytic properties of the Zr—Al site was revealed. The polymerization rate and molecular-weight parameters of PE as functions of the reaction temperature, ethylene pressure, and modifying additives were studied.

Key words: metallocene catalysts, ethylene polymerization, ethylene oligomerization, polymerization kinetics, active site, perfluorophenyl borates, triisobutylaluminum, polyethylene.

Metallocene complexes of Group IVB elements in combination with polymethylalumoxane (MAO) are known as highly efficient catalysts of olefin polymerization and copolymerization. Polymers obtained in the presence of these catalytic systems are usually characterized by a very narrow molecular-weight distribution ($M_w/M_n \approx 2$) and rather high molecular weights. Cationic complexes active in olefin polymerization are also formed by the reaction of perfluorophenyl boranes (or borates) with dimethyl derivatives of metallocenes.[1—4] Another approach to the synthesis of catalytically active complexes from metallocene dichlorides has recently been developed[5—7]: *in situ* alkylation of metallocene dichlorides by trialkyl derivatives of aluminum followed by the formation of a cationic complex by treatment with perfluorophenyl borates (or boranes). This approach makes it possible to prepare active catalytic systems at low concentrations of metallocene, a slight excess of the organoaluminum component, and the stoichiometric ratio transition metal/borate. Triisobutylaluminum (TIBA), which does not participate in chain transfer reactions, unlike lower linear aluminum alkyls,[8—11] is often used as the organoaluminum component. However, only very limited published data are available[8,9,11,12] on the nature of the cationic complexes, influence of the organoaluminum compound on their formation, and effect of various substrates on the catalytic activity of the ternary systems (metallocene dichloride/aluminum alkyl/perfluorophenyl borate (or borane)).

In this work, we studied the catalytic properties of the "constrained geometry catalysts" $Me_2SiCp^*NBu^tZrX_2$ (Cp^* = C_5Me_4, X = Cl (**1a**), Me (**1b**)) and bridged bis(cyclopentadienyl)zirconocenes $Me_2SiCp_2ZrX_2$ (X = Cl (**2a**), Me (**2b**)) in ethylene polymerization activated by TIBA/$LB(C_6F_5)_4$ (L = CPh_3 (**3**), Me_2HNPh (**4**)).

Experimental

Procedures of purification of solvents, methods for preparation of reagents for polymerization, experimental procedures, and methods of analysis of polyethylene (PE) have been described previously.[13] Zirconocenes **1** and **2** available from

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Boulder Sci. Co. were used in the work. The content of branchings and terminal vinyl groups in the samples was determined by IR spectroscopy[14,15] and ^{1}H NMR spectrometry.[16]

Results and Discussion

Comparison of the catalytic effect of the series of substituted biscyclopentadienyl zirconocenes activated by MAO[17] and combined activating agent TIBA/**3** has previously been performed and showed[13] that the three-component systems exhibit, as a whole, a lower specific activity and result in the formation of polyethylene with a high molecular weight. Based on the analysis of the reaction rate as a function of the TIBA concentration, we supposed that the active site contains TIBA, and the heteronuclear [Zr—Al]$^+$-cationic complex is formed under the action of borate. The equilibrium formation of complexes of this type has repeatedly been reported[18,19] for the reaction of the cationic complexes $L_2M^+(CH_3)...B^-(C_6F_5)_4$ (L is the η-bound ligand; M = Zr, Hf) with AlR_3 (R = Me, Et).

Studying the influence of the temperature of ethylene polymerization on the reaction rate and parameters of PE formed in the presence of the catalytic system **1a**/TIBA/**3**, we found an unusual effect (Table 1, entries *A1—A3*). Ethylene consumption at 30 and 70 °C occurred at a low and stable rate. The temperature increase from 70 to 90 °C resulted in a considerable increase in the initial reaction rate with simultaneous sharp decrease in the molecular weight of PE that formed. The integral activity of the system (in kg PE ((mol Zr) h atm)$^{-1}$) at 90 °C is higher by 3—5 times. This increase in the initial reaction rate is hardly the result of an increase in the number of active sites. The substantial decrease in the molecular weight of PE indicates that active sites of different type are formed under these conditions.

It can be supposed that at 30 and 70 °C the reaction of complex **1a** and TIBA (in an excess of the latter) leads to the formation of the monoalkyl monochloride heteronuclear complex, which under the action of perfluorophenyl borate forms a heteronuclear cationic complex (**5**) containing the halogen-type ligand in the outer coordination sphere. An increase in the reaction temperature in an excess of TIBA can result in the exchange of the chloride ligand by the alkyl ligand and transformation of complex **5** into complex **6**. Thus, the observed effects can be explained by the indirect influence of the σ-bound ligand on the particular stages of polymerization (chain growth, chain transfer, and deactivation):

$$\mathrm{Me_2SiCp^*NBu^tZrR...(ClAlBu^i_2)]^{+}...[B(C_6F_5)_4]^-},\ k_{p1},\ k_{tr1},$$

5

$$\mathrm{Me_2SiCp^*NBu^tZrR...(RAlBu^i_2)]^{+}...[B(C_6F_5)_4]^-},\ k_{p2},\ k_{tr2},$$

6

where k_p are the effective rate constants of polymerization, and k_{tr} are the rate constants of chain transfer. It can be expected that complex **5** is less active than complex **6** due to the presence of the chloride ligand in the external coordination sphere of the active site.

The differences in the structure of polyethylene obtained at different temperatures of the reaction is additional evidence favoring the assumption that active sites of different types are formed. It is known that the MAO-activated "constrained geometry catalysts" give branched PE.[20] The appearance of branchings occurs through coordination and insertion of short polymeric chains with terminal vinyl groups (chain transfer products) into the growing polymeric chain. Comparison of the fragments of the IR spectra of PE samples obtained in the three-component catalytic system **1a**/TIBA/**3** at 70 and 90 °C (Fig. 1) showed that in the spectrum of the first sample the absorption band at

Table 1. Catalytic properties of the three-component catalytic systems **1a,b(2a,b)**/TIBA/$CPh_3B(C_6F_5)_4$ and molecular-weight parameters of PE with different types of the σ-bound ligand and polymerization temperatures[a]

Entry	Catalyst	$[Zr] \cdot 10^6$ /mol mol^{-1}	Al/Zr[b]	T/°C	A[c]	M_w[d]	M_w/M_n
A1	**1a**/TIBA/**3**	2.7	260	30	275	>2000000[e]	
A2	**1a**/TIBA/**3**	2.9	260	70	184	1830000[e]	
A3	**1a**/TIBA/**3**	4.9	260	90	897	127000[e]	
A4	**2a**/TIBA/**3**	6.0	500	30	71	>2000000[e]	
A5	**1b**/TIBA/**3**	3.5	260	20	3971	2050	2.2
A6	**1b**/TIBA/**3**	3.6	260	40	6913	2500	2.5
A7	**1b**/TIBA/**3**	3.5	260	60	9480	2430	2.7
A8	**2b**/TIBA/**3**	5.7	500	30	1320	34600	5.4

[a] Ethylene pressure 11 atm.

[b] Molar ratio.

[c] Activity/(kg PE) ((mol Zr) h atm)$^{-1}$.

[d] GPC data.

[e] Viscosimetry data.

1378 cm^{-1} corresponding to symmetric bending vibrations of the methyl groups of the branchings (spectrum *1*) is not pronounced, whereas this band becomes rather intense in the spectrum of the second sample (spectrum *2*). Thus, linear high-molecular-weight PE is formed even at 70 °C by the combined activator TIBA/**3** in the catalytic system involving the dichloride "constrained geometry" complex, which is characterized by the formation of branched PE under the action of MAO. The presence of the chloride ligand in the coordination sphere of the heteronuclear active center explains the lower activity of the metal—carbon bond in both coordination, insertion of ethylene and α-olefin, and chain transfer. The influence of the halogen-type ligand on the activity of the systems $CpTi(Hal)_3$/MAO (Hal = Cl, F) in the synthesis of syndiotactic polystyrene has previously been observed.[21] The trifluoride derivatives of this complex exhibited considerably higher activity than the trichloride derivatives under other similar conditions.

To reveal the role of the σ-bound ligand, we performed a series of experiments on ethylene polymerization by the catalytic system based on the corresponding dimethyl complex **1b**. In fact, the replacement of the chloride ligands by methyl ligands in the initial complex resulted in a considerable change in the catalytic properties of the system (see Table 1, *cf.* entries *A1* and *A5*): a multiple increase in the activity and a sharp decrease in the molecular weights of the PE. It is seen in Table 1 that the catalytic system **1a**/TIBA/**3** at 30 °C possesses an integral specific activity of ~300 kg PE ((mol Zr) h atm)$^{-1}$ and forms PE with a very high molecular weight (~2000000), whereas the **1b**/TIBA/**3** system at 20 °C is characterized by an activity of ~4000 kg PE ((mol Zr) h atm)$^{-1}$ and forms low-molecular-weight PE with an weight-average molecular weight of ~2000. The effective activation energy of polymerization determined from the Arrhenius plot of the initial reaction rates (entries *A5*—*A7*) is 4.3±0.4 kcal mol^{-1}. This is a low value even for catalysis of ethylene polymerization by cationic metallocene complexes of Group IVB elements.

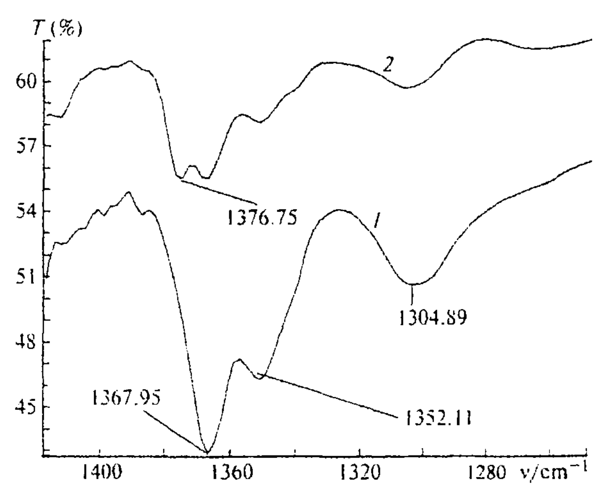


Fig. 1. Fragments of the IR spectra of the PE samples obtained in the presence of the catalytic system **1a**/TIBA/**3** at different temperatures of the reaction: *1*, 70 °C (entry *A2*) and *2*, 90 °C (entry *A3*).

A similar effect of the replacement of the chloride ligand with the methyl ligand in the initial complex was observed for the catalytic system involving zirconocene **2** (see Table 1, entries *A4* and *A8*). The dimethyl derivative of complex **2b** also exhibits a very high activity, but the molecular weight of the PE that formed is much lower than that formed in the case of complex **2a**. At the same time, the more hindered complex **2b** possesses a lower specific activity than **1b** and the PE formed on it has a higher molecular weight (*cf.* entries *A5* and *A8*). These facts indicate the parallel influence of the steric factors on both chain growth and transfer at active sites of this type. It is of interest that the corresponding zirconocene **2a** affected by the combination activator TIBA/**3** is also approximately fourfold less active than complex **1a**, although the PE formed on it is of high molecular weight, M_w > 2000000 (entries *A1* and *A4*).

It was of interest to reveal the route *via* which chain transfer occurs during ethylene polymerization in these three-component catalytic systems. The most probable reactions restricting chain growth are the transfer to an organoaluminum compound, transfer of the H_β atom to the metal, or transfer to the monomer. As mentioned above, some experimental data indicate that in the catalytic systems with TIBA the latter is not the agent of chain transfer.[8—13] The increase in the Al/Zr ratio from 150 to 500 in the homogeneous system based on bridged bis(indenyl)zirconocene *rac*-$Me_2SiInd_2ZrCl_2$/TIBA/**3** (Ind = inden-1-yl) was accompanied by a simultaneous increase in the yield and molecular weight of polypropylene.[8] The considerable increase in the activity for ethylene polymerization in the three-component homogeneous system $Me_2SiInd_2ZrCl_2$/TIBA/**4** with an increase in the Al/Zr ratio from 20 to 200 has also been observed previously.[9]

The main peaks of the ^1H NMR spectrum (Fig. 2, *a*) are presented by signals of the terminal methyl groups (δ 0.8—1.1) and methylene groups of the oligomeric chain (δ 1.3) and signals from protons at the tertiary carbon atom of the branchings in the chain (δ 1.9—2.2) and terminal vinyl groups (δ 4.85—5.09 and δ 5.69—5.96). Under some reaction conditions, the spectra sometimes contain signals from protons of the terminal isobutyl groups (δ 1.6), whose intensity is low as compared to those attributed to other terminal groups. The presence of branchings and terminal vinyl groups is also confirmed by the IR spectra of the polymers (Fig. 2, *b*): absorption bands at 1378 cm^{-1} (symmetric bending vibrations of the methyl groups) and 909, 991 cm^{-1} (bending vibrations of the $=CH-$, $=CH_2$ groups).

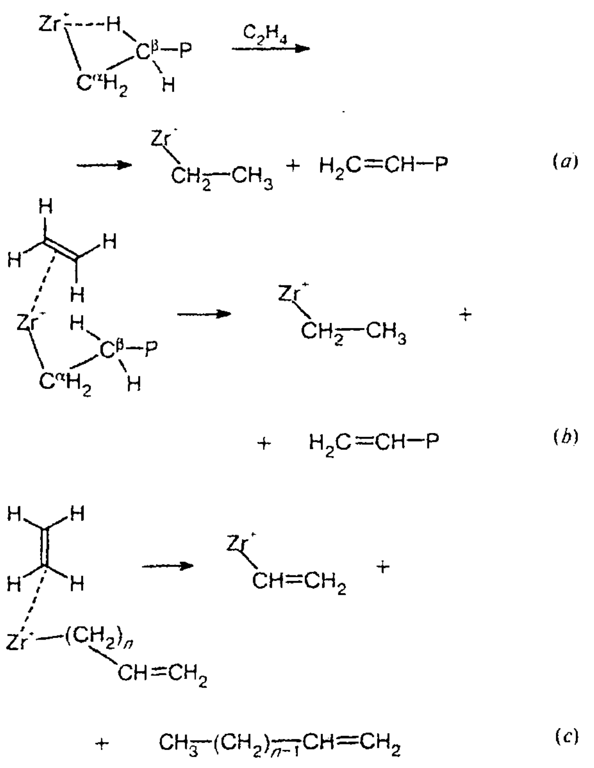
The formation of the polymer with terminal vinyl groups indicates the participation of the H_β atom in the growing polymeric chain (Scheme 1) or chain transfer to the metal to form a hydride complex, which is rapidly transformed to the metal-alkyl complex (*a*), or chain transfer to the coordinated monomer (*b*). The third possibility resulting in the formation of terminal vinyl groups is metathesis occurring through the activation of the C—H bond of the coordinated monomer (*c*). In the last case, the terminal vinyl group is formed at the moment of chain nucleation, and the next act of transfer gives polymeric fragments with terminal vinyl groups at the beginning of the chain and saturated groups at the end.

As known, the average degree of polymerization ($\bar{P}_n$) is the indicator of the ratio of the rate of polymeric chain growth to the rate of chain restriction:

$$\bar{P}_n = \frac{k_p[C^*][M]}{\sum_j k_{tr_j}[C^*][A_{tr}]_j}, \qquad (1)$$

where k_p is the effective rate constant of polymerization, $[C^*]$ is the effective concentration of active sites, $[M]$ is the monomer concentration, k_{tr_j} are the rate constants of chain transfer over all possible channels (j), and $[A_{tr}]_j$ are the concentrations of possible agents of chain transfer. It is seen in Table 2 that the tenfold change in the ethylene pressure for complex **1b** (entries *B1—B5*) and fourfold change for complex **2b** (entries *B6—B8*, *A8*) do not result in a considerable change in the average degree of polymerization. This suggests that ethylene is the main agent of chain transfer according to Eq. (1), *i.e.*, $A_{tr} \equiv M$. Chain transfer to the coordinated ethylene molecule can occur *via* two different channels, resulting in the formation of polymeric products with terminal vinyl groups: with the transfer of the H_β atom to the monomer (reaction *b* in Scheme 1) and by the metathesis of the $Zr^+—P$ bond with ethylene (reaction *c* in Scheme 1). The last channel of chain transfer has been described,[22] for example, for ethylene oligomerization by the catalytic system Cp_2ZrMe_2/MAO at low concentration of ethylene and Al/Zr ratio. The results of calculation[23] also show that the activation of the C—H bond of the coordinated monomer followed by metathesis is thermodynamically preferable to β-elimination at the metal for the cationic complex $Cp_2Zr^+—P$ (P is the polymeric chain of PE). Presently, it is difficult to say which channel of chain transfer to the monomer takes place during the formation of low-molecular-weight PE by the three-component catalytic systems presented in this work. However, reaction (*c*) seems less probable. This reaction requires a less hindered coordination

Scheme 1



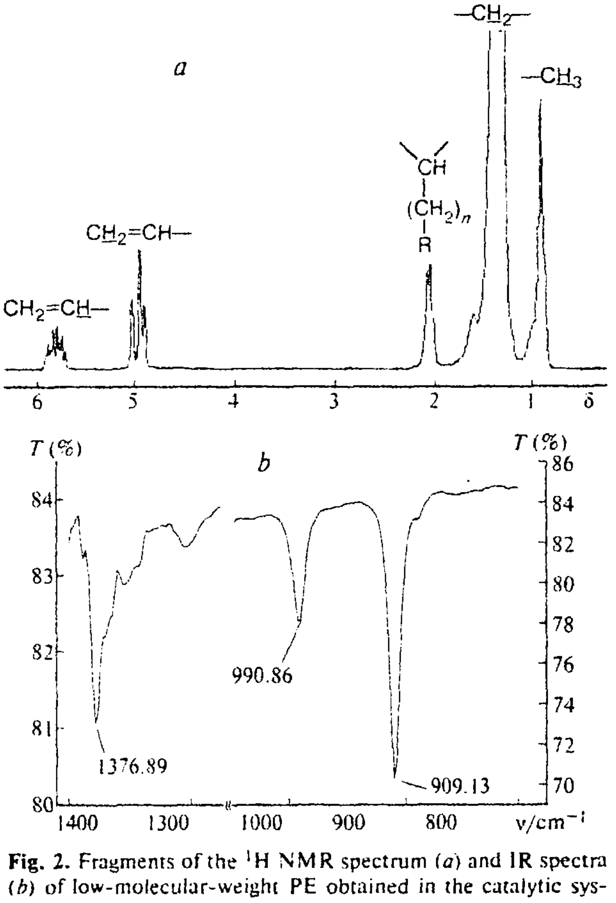


Fig. 2. Fragments of the ¹H NMR spectrum (*a*) and IR spectra (*b*) of low-molecular-weight PE obtained in the catalytic system **1b**/TIBA/3 at an ethylene pressure of 11 atm and temperature of the reaction of 40 °C (entry *A6*).

Table 2. Catalytic properties of the three-component catalytic systems **1b**(**2b**)/TIBA/$CPh_3B(C_6F_5)_4$ and molecular-weight parameters of PE as functions of the ethylene pressure (P)[a]

Entry	Catalyst	$[Zr] \cdot 10^6$ /mol mol^{-1}	P/atm	A[b]	M_w[c]	M_w/M_n
B1	**1b**/TIBA/3	5.0	2	2786	1480	3.0
B2	**1b**/TIBA/3	5.4	5	4460	2020 [d]	4.4
B3	**1b**/TIBA/3	5.9	11	2495	1800 [d]	3.5
B4	**1b**/TIBA/3	6.1	15	1392	1430 [d]	3.8
B5	**1b**/TIBA/3	6.1	20	1734	1780 [d]	3.5
B6	**2b**/TIBA/3	5.5	5	190	36380 [d,e]	2.8
A8	**2b**/TIBA/3	5.7	11	1320	20210 [d]	3.3
B7	**2b**/TIBA/3	5.9	15	1241	27000 [d,e]	3.9
B8	**2b**/TIBA/3	5.4	20	993	31000 [d,e]	2.6

[a] Al/Zr = 500, T = 30 °C.
[b] Activity/(kg PE) ((mol Zr) h atm)$^{-1}$.
[c] GPC data.
[d] Without high-molecular weight "tail."
[e] Without low-molecular weight "tail."

of the monomer than that for the formation of a π-complex with olefin, an intermediate of reaction (*b*). The fact that higher-molecular PE forms on more hindered complex **2b** may indicate the significance of steric factors for the chain transfer to the monomer.

Thus, the three-component catalytic systems under discussion are characterized by the formation of active sites that combine a high rate of chain growth and an unusually high rate of chain transfer to the monomer ($k_p/k_{tr} \approx \bar{P}_n \approx 30-500$). This results in very low molecular weights of polyethylene and the formation of α-olefin, which is especially pronounced for less hindered complex **1b**. According to this, the estimation showed a high content of terminal vinyl groups per 1000 carbon atoms of the polymeric chain (Table 3). The number of branchings per 1000 carbon atoms is also high due to the affinity of the "constrained geometry" complexes to the secondary insertion of the polymeric fragments with the terminal vinyl groups. The increase in the ethylene pressure from 2 to 10 atm results in some decrease in the content of both terminal vinyl groups and branchings in the polymeric chain. However, further pressure increase has no substantial effect on these parameters.

Table 3. Molecular-weight parameters and the content of terminal vinyl groups and branchings in the PE samples obtained in the catalytic system **1b**/TIBA/3

Entry	M_w	M_w/M_n	N_1[a,b]		N_2[b,c]	
			IR[d]	^{1}H NMR[e]	IR[d]	^{1}H NMR[e]
B1	1480	3.0	21 (0.7)[c]	—[f]	22	—[f]
B2	2020	4.4	14 (0.5)	10 (0.3)	17 (0.5)	21 (0.7)
B3	1800	3.5	12 (0.4)	12 (0.4)	14 (0.5)	87 (3.1)
B4	1430	3.8	14 (0.4)	15 (0.4)	15 (0.4)	31 (0.8)
B5	1780	3.5	15 (0.5)	13 (0.5)	15 (0.5)	46 (1.5)

[a] The number of double bonds per 1000 C atoms.
[b] The average values calculated per PE macromolecule is given in parentheses.
[c] Number of branchings per 1000 C atoms.
[d] Determined from the IR spectral data.
[e] Determined from the ^{1}H NMR spectral data.
[f] No data.

The molecular-weight distribution (MWD) curves of low-molecular weight PE obtained in the catalytic system **1b**/TIBA/3 at Al/Zr = 260 are characterized by low polydispersity coefficients (see Table 1, entries *A5*—*A7*), indicating that active sites of the same type carry out the polymerization. The increase in the Al/Zr ratio from 260 to 500 results in a considerable broadening of the MWD curves (entries *A5* and *B3*) and the appearance of high-molecular-weight "tails" (Figs. 3, *b* and 4, *b*), which indicates the appearance, under these conditions, of several types of active sites. However, the fraction of polymers with higher molecular weights is low. An increase in the reaction temperature (entries *A5*—*A7*) and ethylene pressure (entries *B1*—*B5*) does not result in a considerable change in the MWD curves. Thus, the Al/Zr ratio is the most important factor that not only affects the formation of active sites leading to the formation of low-molecular-weight PE, but also can result in the formation of other active sites responsible for the creation of the high-molecular-weight fraction. To examine the molecular-weight parameters of the main low-molecular-weight fraction of PE obtained at a high Al/Zr ratio, we subtracted the contribution of the high-molecular-weight component that broadens the total M_w/M_n value (*cf.* the parameters of PE in entries *A8* and *B8* in Tables 1 and 2). This approach makes it possible to compare the catalytic effects of the active sites responsible for the formation of the low-molecular-weight fraction of PE under different reaction conditions.

Analysis of the structure of the PE samples and polymerization kinetics suggested the nature of the ac-

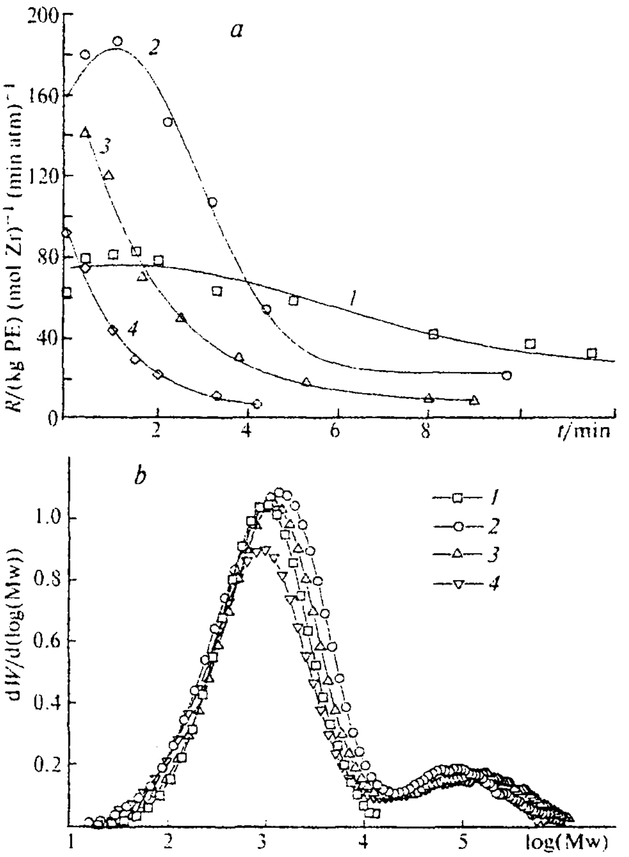


Fig. 3. Change in the rate of ethylene absorption (*R*) by the catalytic system **1b**/TIBA/**3** with time (*a*) and differential GPC curves of PE samples (*b*) obtained at different ethylene pressures: 2 (*1*), 5 (*2*), 10 (*3*), and 20 atm (see Table 2, entries *B1*, *B2*, *B3*, and *B5*). d*W*/d(log(Mw)) is the weight fraction for a specific molecular weight (Mw).

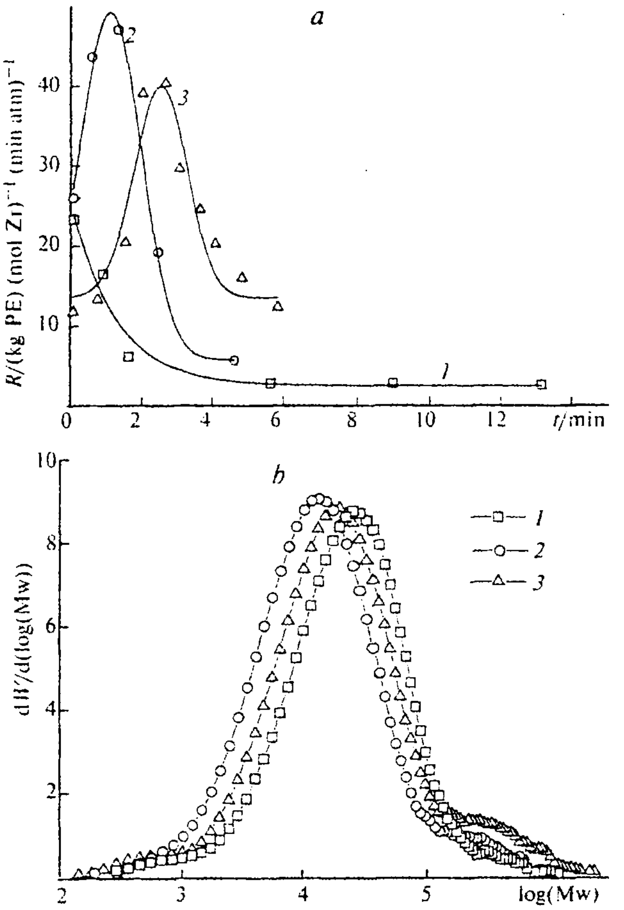
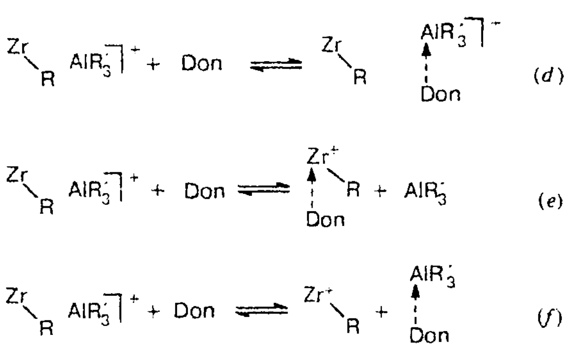


Fig. 4. Change in the rate of ethylene absorption (*R*) by the catalytic system **2b**/TIBA/**3** with time (*a*) and differential GPC curves of PE samples (*b*) obtained at different ethylene pressures: 5 (*1*), 11 (*2*), and 20 atm (*3*) (see Table 2, entries *B6*, *A8*, and *B8*). Designations are presented in Fig. 3.

tive sites in these three-component systems and specific features of their catalytic effect. The published data[24—26] indicate that minor additives of α-olefin increase the rate of ethylene absorption by the metallocene catalytic systems. To reveal a possible influence of α-olefin formed by the polymerization on the state of the active site and the rate of ethylene absorption, we examined the polymerization kinetics and MWD of the PE samples obtained under different pressures of the monomer. Analysis showed that both catalytic systems exhibited a complex dependence of the specific rate of ethylene absorption on the reaction time at different ethylene pressures (see Figs. 3, *a* and 4, *a*). For example, the **1b**/TIBA/**3** system exhibits a rather stable catalytic effect at a pressure of 2 atm (see Fig. 3, *a*, curve *1*). An increase in the ethylene pressure to 5 atm is accompanied by a considerable increase in the rate at the beginning of the reaction, but when the highest rate of ethylene absorption is achieved, a fast exponential decrease is observed (curve *2*). Further increase in the pressure results in some decrease in the initial rate and a similar fast exponential decrease in the curves of ethylene absorption (curves *3* and *4*). In the **2b**/TIBA/**3** catalytic system, the profiles of the curves of ethylene absorption rates pass through a maximum, and the time of achievement of the latter increases with pressure increase (see Fig. 4, *a*). As a whole, the polymerization rates in the presence of catalytic system **2b** are much lower than those in the presence of system **1b**. However, despite these significant differences in the kinetics of ethylene absorption at different monomer pressures, the polymeric products formed in each system are characterized by approximately similar MWD (see Figs. 3, *b* and 4, *b*). Therefore, the observed change in the reaction rate is related to the change in the concentration of the active sites responsible for the formation of low-molecular-weight polyethylene. Thus, the presented data show that the catalytic properties of the zirconium complexes are primarily determined by the structure of the precatalyst that is a component of the active site. The specific features of the precatalyst appear in both the activity of the catalytic system and the molecular-weight parameters of PE. It is seen that a higher-molecular polymeric product is formed on the more hindered complex **2b** with a lower activity.

We supposed that the labilization of the active sites that form low-molecular-weight PE occurs due to the coordination of the basic substrates, donors (Don), with the initial heteronuclear Zr—Al-cationic complex. This interaction can proceed, *e.g.*, *via* a route presented in Scheme 2.

Scheme 2



Substrate coordination with the heteronuclear active site by route (*d*) weakens the electron-withdrawing capability of aluminum in the Zr—Alk—Al bridge, thus activating the Zr—C bond. Aluminum alkyl can also be displaced from the active site by the base (*e*, *f*). Ethylene can act as a weak base, and α-olefin formed due to intense chain transfer can serve as a stronger base. The equilibrium is shifted to the right by α-olefin, whose concentration increases in the reaction course, and results in an increase in the concentration of the active sites that form low-molecular-weight PE.

To verify the possible effect of the base on an increase in the concentration of the active sites, which are characterized by simultaneously high rates of olefin insertion and chain transfer, we performed experiments on the introduction of amine (Ph_2NH) and the replacement of cation-generating borate **3** with **4**. The experiments with borate **4** were of interest because the reaction of this borate with dialkyl derivatives of metallocenes affords alkane, and the liberating dimethylaniline fragment is capable of coordinating with the heteronuclear cationic complex.

The results of these experiments are presented in Table 4 and Figs. 5 and 6. It can be seen that the introduction of a stoichiometric amount of Ph_2NH (molar ratio Ph_2NH/Zr = 1 : 1) into the catalytic systems **1b**(**2b**)/TIBA/**3** results in a ~2—3-fold increase in the specific activity of the system (see Table 4, entries *B3*, *C4* and *A8*, *C8*; Figs. 5, *a* and 6, *a*, curves *1* and *3*). At the same time, the presence of amine has no effect on the molecular-weight parameters of the main fraction of the polymeric product (see Figs. 5, *b* and 6, *b*, curves *1* and *3*). However, the introduction of Ph_2NH into both catalytic systems prevents the formation of the active sites responsible for the formation of the high-molecular-weight fraction of PE. The integral catalytic activity of both complexes decreases when borate **3** is replaced by **4** (entries *B3*, *C3* and *A8*, *C7*). This results in a small shift of the MWD curves towards lower molecular weights (see Figs. 5, *b* and 6, *b*, curves *2*). The similar values of the molecular-weight parameters of PE formed in each system in the presence of both the π-donor olefin substrates (ethylene and formed α-olefin) and σ-donor basic reactants indicate that the active sites carrying out polymerization are identical. Their concentration is determined by the efficiency of the effect of a base, whose measure is the distribution coefficient $\log P$ ($P = pK_{oc}/pK_w$, pK_{oc} is the dissociation constant of the base in octanol, and pK_w is the dissociation constant of the base in water). For ethylene, $\log P$ = 1.13[27]; for α-olefins,[28] the distribution coefficient increases in the order hex-1-ene ($\log P$ = 3.4) < hept-1-

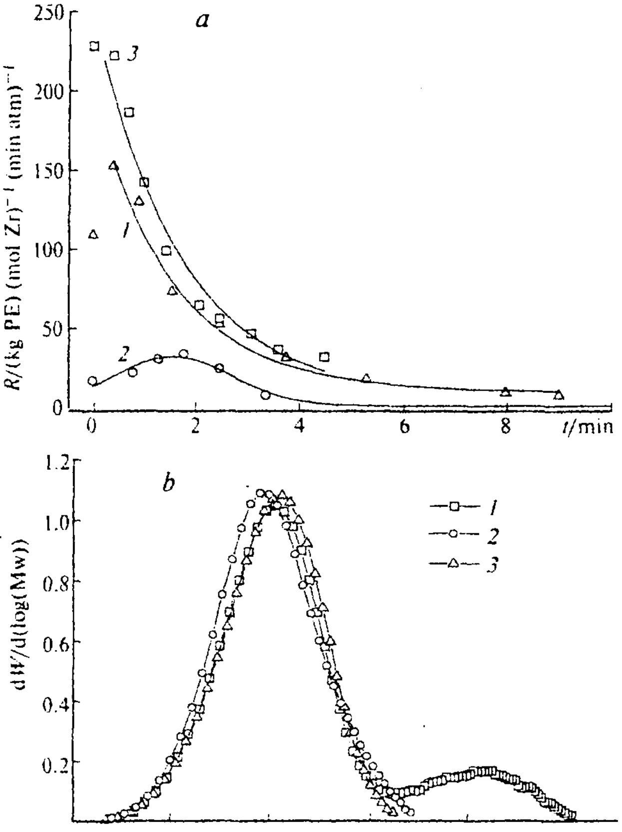


Fig. 5. Change in the rate of ethylene absorption (*R*) with time (*a*) and differential GPC curves of PE samples (*b*) obtained in the presence of the catalytic systems **1b**/TIBA/**3** (*1*), **1b**/TIBA/**4** (*2*), and **1b**/TIBA/**3**/A (*3*) (see Table 4, entries *B3*, *C3*, and *C4*). Designations are presented in Fig. 3.

Table 4. Dependences of the catalytic properties of the three-component catalytic systems **1a,b(2a,b)**/TIBA/**3**(**4**) and molecular-weight parameters of PE on the type of borate and presence of the modifier (**A** = Ph_2NH)[a]

Entry	Catalyst	[Zr] · 10^6 /mol mol^{-1}	Al/Zr	A[b]	M_w[c]	M_w/M_n
A1	**1a**/TIBA/**3**	2.7	260	275	>2000000	—
C1	**1a**/TIBA/**4**	10.1	250	86	1940 [d]	3.9
C2	**1a**/TIBA/**3**/**A**	5.6	500	126	2462	—
B3	**1b**/TIBA/**3**	5.9	500	2495	1800 [e]	3.5
C3	**1b**/TIBA/**4**	4.1	500	473	2070	4.5
C4	**1b**/TIBA/**3**/**A**	5.0	500	5744	1870	3.6
A4	**2a**/TIBA/**3**	6.0	500	75	>2000000	—
C5	**2a**/TIBA/**4**	13.0	250	642	27760 [d]	2.4
C6	**2a**/TIBA/**3**/**A**	4.3	500	115	135000	6.0
A8	**2b**/TIBA/**3**	5.7	500	1320	20210 [e]	3.3
C7	**2b**/TIBA/**4**	14.6	250	652	13400	4.3
C8	**2b**/TIBA/**3**/**A**	5.2	500	2949	21900	4.9

[a] Ethylene pressure 11 atm, T = 30 °C.
[b] Activity/(kg PE) ((mol Zr) h atm)$^{-1}$.
[c] GPC data.
[d] Without the low-molecular-weight "tail."
[e] Without the high-molecular-weight "tail."

ene (log$P$ = 3.99) < oct-1-ene (log$P$ = 4.57); for Me_2NPh, log$P$ = 2.31 [28,29]; and for Ph_2NH, log$P$ = 3.5.[27,28] It follows from the presented data that the active sites are most efficiently formed in the presence of Ph_2NH and α-olefin. Presently, we have no data by which to choose one of the above proposed schemes of the formation of active sites that actively form low-molecular-weight PE by the action of a base. However, it cannot be ruled out that the formation of these active sites occurs *via* channel (*e*) because the coordination of the donor substrate with the cationic active site can result in a "trigger" mechanism of olefin insertion[30] or a decrease in the energy barrier of monomer insertion during the coordination of the second olefin molecule.[31]

Since a base can be coordinated by the heteronuclear active site, it was of interest to compare the catalytic behavior of the dichloride complexes in the three-component catalytic systems in the presence of bases. As mentioned above, complexes **1a** and **2a** affected by the combined activator TIBA/**3** exhibit a rather low, but stable activity in ethylene polymerization and form high-molecular-weight PE. The replacement of borate **3** by borate **4** in these systems (see Table 4, entries *A1*, *C1* and *A4*, *C5*) results in the formation of active sites that form low-molecular-weight, branched PE with a high content of terminal vinyl groups (Figs. 7 and 8). The effects of borate **4** on the catalytic activity of the dichloride precatalysts differ: for the **1a**-based system, this replacement decreases the activity, and that for **2a** increases the activity. For both dichloride catalytic systems containing borate **3**, the introduction of Ph_2NH into the reaction medium results in an insignificant increase in the activity of the catalytic system and a decrease in the molecular weight of the products (see

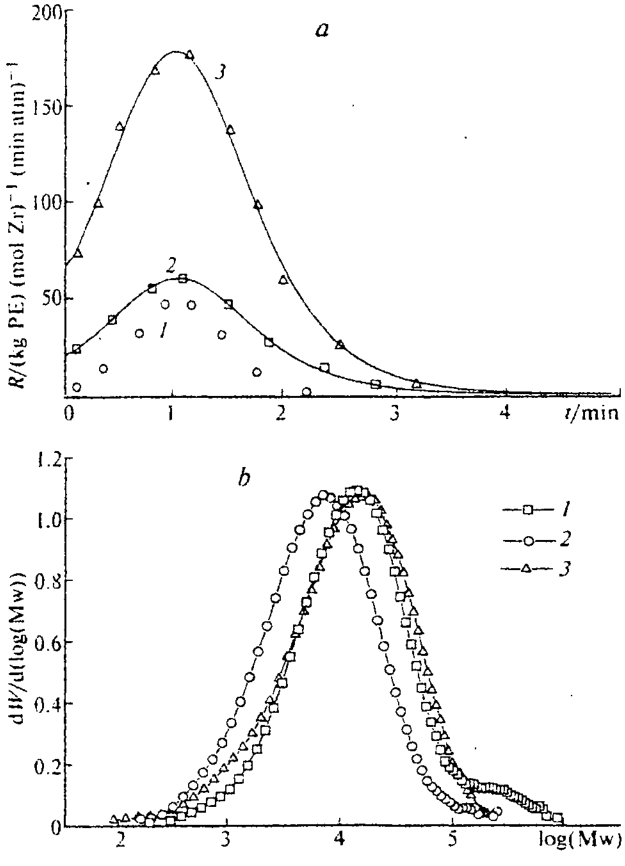


Fig. 6. Change in the rate of ethylene absorption (R) with time (t) (*a*) and differential GPC curves of PE samples (*b*) obtained in the presence of the catalytic systems **2b**/TIBA/**3** (*1*), **2b**/TIBA/**4** (*2*), and **2b**/TIBA/**3**/**A** (*3*) (see Table 4, entries *A8*, *C7*, and *C8*). Designations are presented in Fig. 3.

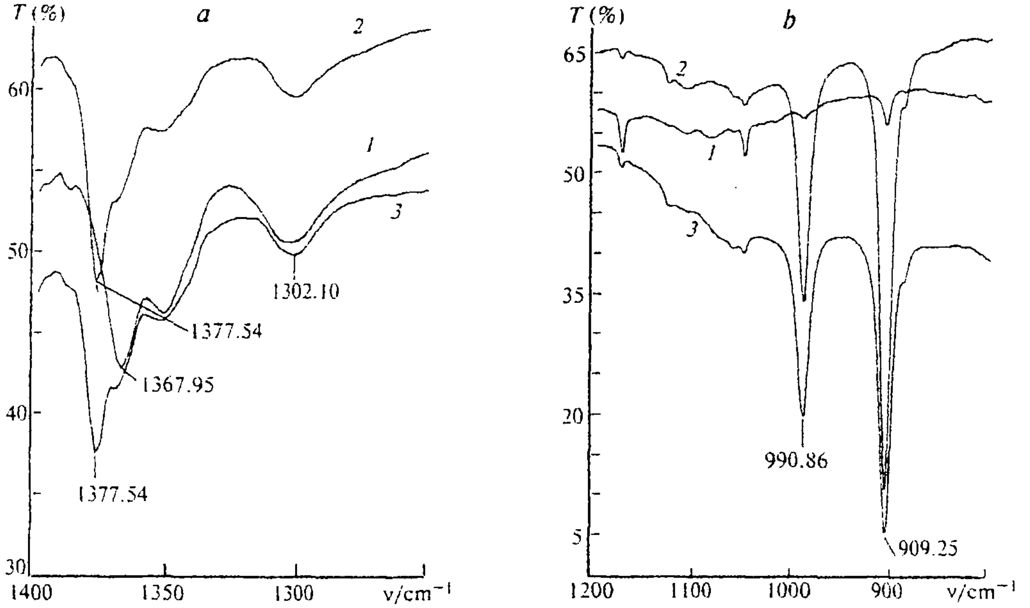


Fig. 7. Fragments of the IR spectra in the regions of 1400—1250 cm^{-1} (*a*) and 1200—800 cm^{-1} (*b*) of PE samples obtained in the catalytic systems **1a/TIBA/3** (*1*), **1a/TIBA/4** (*2*), and **1a/TIBA/3/A** (*3*) (see Table 4, entries *A1*, *C1*, and *C2*).

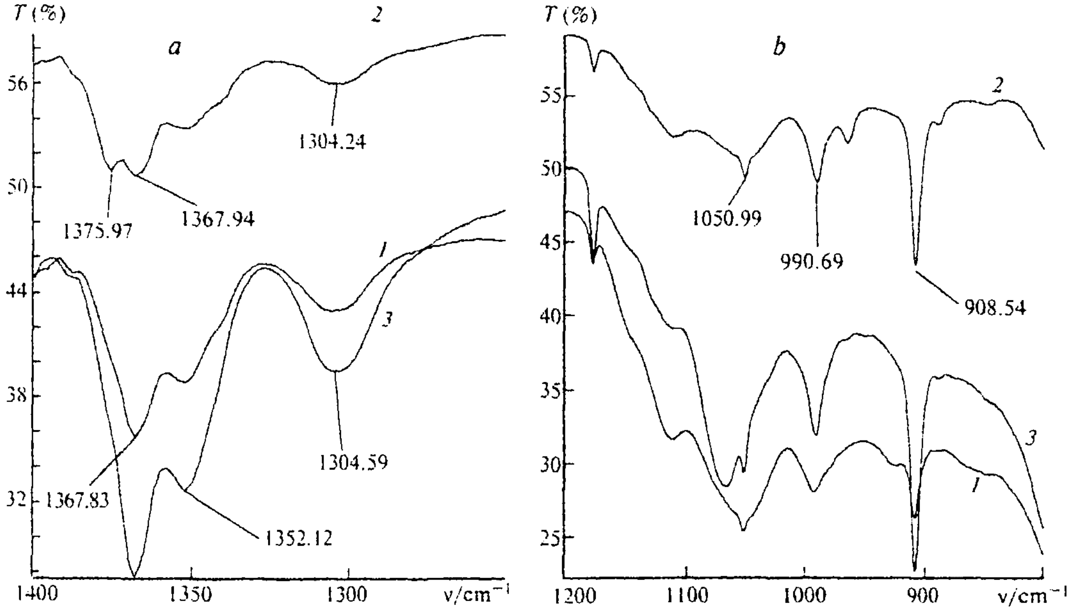


Fig. 8. Fragments of the IR spectra of PE samples obtained in the catalytic systems **2a/TIBA/3** (*1*), **2a/TIBA/4** (*2*), and **2a/TIBA/3/A** (*3*) (see Table 4, entries *A4*, *C5*, and *C6*).

Table 4, entries *A1*, *C2* and *A4*, *C6*). However, it follows from the IR spectral data that when Ph_2NH is used in the **1a/TIBA/3** and **2a/TIBA/3** systems, the polymer structures strongly differ (see Figs. 7 and 8). For example, the first system with Ph_2NH is characterized by the formation of strongly branched PE, whereas in the second system the presence of Ph_2NH in the reaction medium does not lead to the appearance of branchings in the polymer. It can be seen that the presence of the chloride ligand in the coordination sphere of the active site substantially changes the influence of the coordinating base on the reactivity of the metal—carbon bond and chain transfer.

The performed study of the properties of three-component catalytic systems based on the dichloride and dimethyl derivatives of zirconocenes, TIBA, and perfluorophenyl borates in ethylene polymerization suggests that TIBA in these systems acts not only as an alkylating agent or a reactant, but also as the component participating in the formation of the active heteronuclear Zr—Al-cationic complex.

The presence of the chloride ligand in the heteronuclear active site results in the reactions of polymerization and chain transfer with low rates to form high-molecular-weight PE.

The replacement of the chloride ligands by alkyl ligands substantially changes the catalytic properties of the active sites formed in the three-component systems. Chain transfer in the course of polymerization occurs predominantly to the monomer, resulting in the formation of low-molecular-weight PE with terminal vinyl groups and a high branching degree. The latter appears due to the coordination and insertion into the growing chain of transfer products with terminal unsaturated groups. Their presence allows these polymeric products to be subsequently functionalized.

The properties of the zirconium complexes in the active site are determined by their structure. For example, PE with a high molecular weight and a lower branching degree forms on the more hindered complex **2b**. The "constrained geometry" complex **1b** forms low-molecular-weight PE with terminal vinyl groups and a high branching degree.

New active sites characterized by the combination of high rates of chain growth and transfer to ethylene are probably formed due to the coordination of the bases by the heteronuclear Zr—Al-active site. The efficiency of formation of these active centers depends on the nature of the basic substrates, metallocene, and σ-bound ligand and, to an insignificant extent, on the polymerization conditions in the studied interval of temperatures and ethylene pressures.

References

1. C. Sishta, R. M. Hathorn, and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 1112.
2. G. G. Hlatky, H. W. Turner, and R. R. Eckman, *J. Am. Chem. Soc.*, 1989, **111**, 2728.
3. X. Yang, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 3623.
4. Y.-X. Chen, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, 1997, **119**, 2582.
5. J. C. W. Chien, W. Song, and M. D. Rausch, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 2387.
6. W.-M. Tsai and J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 149.
7. Y.-X. Chen, M. D. Rausch, and J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 2093.
8. N. Naga and K. Mizunuma, *Polymer*, 1998, **39**, 5059.
9. G. Luft, R. A. Dyroff, C. Götz, S. Schmitz, T. Wieczorek, R. Klimesch, and A. Gonioukh, *Metalorganic Catalysts for Synthesis and Polymerization*, Ed. W. Kaminsky, Springer, Berlin,1999, p. 651.
10. S. Liu, G. Yu, and B. Huang, *J. Appl. Polym. Sci.*, 1997, **66**, 1715.
11. I. Kim and C. S. Choi, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1523.
12. I. Kim, *J. Appl. Polym. Sci.*, 1999, **71**, 875.
13. A. N. Panin, O. N. Babkina, and N. M. Bravaya, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 301 [*Russ. Chem. Bull.*, 2000, **49**, (Engl. Transl.)].
14. K. Teranishi and K. Sugahara, *Kobunshi Kagaku*, 1966, **23**, 512.
15. R. Blom, A. Follestad, and O. Noel, *J. Mol. Catal.*, 1994, **91**, 237.
16. J. C. Randall, *JMC-Rev. Macromol. Chem. Phys.*, 1989, **C29**, 201.
17. N. M. Bravaya, V. V. Strelets, Z. M. Dzhabieva, O. N. Babkina, and V. P. Mar'in, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1535 [*Russ. Chem. Bull.*, 1998, **47**, 1491 (Engl. Transl.)].
18. M. Bochmann and S. J. Lancaster, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1634.
19. M. Bochmann, *Topics in Catalysis*, 1999, **7**, 9.
20. J. C. Stevens, *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1996, **101**, 11.
21. W. Kaminsky and S. Lenk, *Macromol. Symp.*, 1997, **118**, 45.
22. A. R. Siedle, W. M. Lamanna, R. A. Newmark, and J. N. Schroepfer, *J. Mol. Catal., A: Chem.*, 1998, **128**, 257.
23. T. K. Woo, L. Fan, and T. Ziegler, *Organometallics*, 1994, **13**, 2252.
24. J. Koivumaki and J. V. Seppala, *Polymer*, 1993, **34**, 1958.
25. K. J. Chu and T. H. Park, 1997, **31**, 11.
26. P. Peitikainen and J. V. Seppala, *Macromolecules*, 1994, **27**, 1325.
27. C. Hansch and A. J. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York, 1979.
28. J. Sangster, *J. Phys. Chem. Ref.*, 1989, **18**, 1111.
29. T. Fujita, J. Iwasa, and C. Hansch, *J. Am. Chem. Soc.*, 1964, **86**, 5175.
30. M. Ystenes, *Makromol. Chem. Makromol. Symp.*, 1993, **66**, 71.
31. M. H. Prosenc, F. Schaper, and H. H. Brintzinger, *Metalorganic Catalysts for Synthesis and Polymerization*, Ed. W. Kaminsky, Springer, Berlin, 1999, p. 223.

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