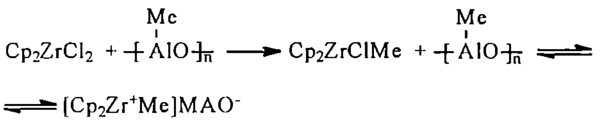
N. M. BRAVAYA, A. N. PANIN, O. N. BABKINA,
N. D. KARPOVA
Laboratory of Catalysis of Polymerization Processes
Department of Polymer and Composite Materials
the Institute of Problems of Chemical Physics
Russian Academy of Sciences
142432 Chernogolovka, Moscow Region, Russia

From the nature of zirconocene/activator catalysts to polymerization performance and polyethylene properties*)

Summary — The influence of the activation procedure applied to a metallocene on its catalytic behavior in ethylene polymerization is discussed and the effect of the zirconocene/activator nature on the properties of PE is demonstrated. MAO and TIBA/$CPh_3B(C_6F_5)_4$ are intercompared as cocatalysts. The catalytic behavior and the kinetics of ethylene polymerization catalyzed by TIBA/$CPh_3B(C_6F_5)_4$-activated metallocene complexes allowed to infer that, in ternary catalytic systems with dichloride precatalysts, TIBA acts not only as an impurity scavenger or simply an alkylating agent, but also as a cocatalyst giving rise to heteronuclear cationic species providing lower chain propagation and chain transfer rates than those generated upon MAO action. When activated with TIBA/$CPh_3B(C_6F_5)_4$ dichloride zirconocenes were moderately active as compared with MAO and yielded PEs of considerably higher *M*. A halide or alkyl ligand present in the outer coordination sphere of active sites affects considerably both the catalytic performance of active species and the properties of the resulting PE. The Cl-keeping Al—Zr heteronuclear active sites give rise to high-*M* linear PE; alkyl holders are highly capable of chain propagation and chain transfer to monomer. The high reactivity of the Zr—Cl bond in the latter active sites manifests itself also in the high ability to incorporate alfa-olefins to yield PE chains containing branches with 4—10 incorporated ethylene units.

Key words: activation of metallocenes, TIBA in active cationic species, catalytic properties in ethylene polymerization, effect of zirconocene/activator nature on polyethylene properties.

The cationic catalysts derived from metallocene (and recently post-metallocene) precatalysts involving polymethylaluminoxane (MAO) as activator have been extensively investigated and used in numerous processes for making polyolefins. Several other activators have also been used for producing highly effective catalytic systems. The idealized routes for generating active species by means of most widely used cocatalysts may be generalized as follows:



$$Cp_2ZrCl_2 + \left[\overset{Me}{\overset{|}{Al}}O\right]_n \longrightarrow Cp_2ZrClMe + \left[\overset{Me}{\overset{|}{Al}}O\right]_n \rightleftharpoons [Cp_2Zr^{+}Me]MAO^{-} \qquad (1)$$

$$Cp_2ZrMe_2 + B(C_6F_5)_3 \longrightarrow Cp_2Zr^{+}Me.....MeB^{-}(C_6F_5)_3 \qquad (2)$$

$$Cp_2ZrMe_2 + (CPh_3)[B(C_6F_5)_4] \xrightarrow{-\,CPh_3Me} Cp_2Zr^{+}Me...B^{-}(C_6F_5)_4 \qquad (3a)$$

$$Cp_2ZrMe_2 + (NHMe_2Ph)[B(C_6F_5)_4] \longrightarrow$$
$$\xrightarrow{-\,CH_4,\ -\,NMe_2Ph} Cp_2Zr^{+}Me.....B^{-}(C_6F_5)_4 \qquad (3b)$$

$$L_2MCl_2 + AlR_2 \longrightarrow L_2MR_2 + (CPh_3)[B(C_6F_5)_4] \longrightarrow$$
$$\longrightarrow L_2M^{+}R.....B^{-}(C_6F_5)_4 + CPh_3R \qquad (4)$$

Homogeneous catalysts obtained by interaction of metallocene dichloride or metallocene dialkylated complexes with MAO according to route (1) have been well known and widely investigated. Binary catalytic systems derived from dialkylated metallocene complexes and strong Lewis acids, mainly perfluorophenyl borates

---

*) Presented at the 7th Seminar on "Organometallic Complexes as Catalysts of Vinyl Compounds Polymerization", Turawa n/Opole, 12—17 September 1999.

(route 2) and ionic borate salts (routes 3a, 3b), are also known to be highly effective catalysts. However, their use is still far from the application to a large-scale production of polymers, mainly owing to the high thermal and chemical instability of these cationic complexes. Another approach to catalyst formation involves *in situ* alkylation of dichloride complexes by organoaluminum compounds with the following generation of cationic species under the action of Lewis acids (route 4). Organoaluminum compounds have also been mentioned to act as impurity scavengers in binary catalytic systems. However, non-MAO activated catalysts, especially those operating in the presence of organoaluminum compounds, have numerous obscure aspects both as regards the chemistry, active site nature and catalytic action.

This paper sets out to reveal some specific features of the catalytic systems derived from zirconocene with MAO or trisisobutylaluminum/perfluorophenyl borate as activators in terms of both catalytic performance in the homogeneous ethylene polymerization and in the properties of the resulting polyethylenes. Special attention is paid to the catalytic systems involving TIBA, to understand the outlook for these catalytic systems.

RESULTS AND DISCUSSION

Table 1 presents results of a comparative analysis of the catalytic performance of the series of substituted bis-Cp zirconocenes upon activation with MAO and with a combined activator TIBA/$CPh_3B(C_6F_5)_4$. Since so far the catalytic systems showed considerably different kinetics of ethylene polymerization, we used the initial polymerization rate as a measure of catalyst activity. The molecular weights of the resulting PEs formed are also presented for comparison. The ternary catalytic systems are seen to exhibit a considerably lower activity than do the MAO-activated systems. At the same time, the molecular weights of the PEs formed over ternary catalytic systems are considerably higher. An interesting relationship has been observed to occur between the molecular weight of PE and activity of ternary catalytic systems. In particular, the catalysts showing a lower polymerization activity (low propagation rate) generated PE of higher molecular weights (low chain transfer rate). Evidently, the polar factor of the substituents is more pronounced in the active centers formed in ternary catalytic systems. So far no such relationship has been found to occur for MAO-activated zirconocenes [1]. The more detailed analysis of the effect of substituents on the catalytic properties of biscyclopentadienyl zirconocenes activated with TIBA/$CPh_3B(C_6F_5)_4$ has been reported elsewhere [2—4]. The differences in molecular weight of PEs formed with the same pre-catalyst and various activators, as well as the distinctive response of both catalytic activity and PE molecular weight to the combined action of the inductive and sterical effects of the substituents made us believe in the differentiated nature of the cationic species formed in the catalytic systems compared. An additional argument for this conclusion is provided by the analysis of the structure of the PEs formed. Comparison of IR spectra showed each PE obtained with MAO as cocatalyst to demonstrate a higher branching degree than the PE prepared in the ternary catalytic systems (Fig. 1). The absorption band of 1378 cm^{-1} (symmetric deformation of branching methyl groups) is more pronounced for the MAO-derived PEs.

Table 1. Ethylene polymerization*) over catalytic systems derived from zirconocene dichloride and MAO or Al-*i*-Bu_3/$CPh_3B(C_6F_5)_4$ as activator

Catalytic system	R_{p0}	M_w
$(MeCp)_2ZrCl_2$/MAO	3030	345500
$(MeCp)_2ZrCl_2$/TIBA/$CPh_3B(C_6F_5)_4$	780	397000
(*i*-PrCp)$_2ZrCl_2$/MAO	2600	291200
(*i*-PrCp)$_2ZrCl_2$/TIBA/$CPh_3B(C_6F_5)_4$	663	519000
(*n*-BuCp)$_2ZrCl_2$/MAO	830	323300
(*n*-BuCp)$_2ZrCl_2$/TIBA/$CPh_3B(C_6F_5)_4$	651	665000
$(Me_3SiCp)_2ZrCl_2$/MAO	1290	654700
$(Me_3SiCp)_2ZrCl_2$/TIBA/$CPh_3B(C_6F_5)_4$	107	828000

*) Polymerization conditions for polymerization runs with MAO as cocatalyst: toluene, [Zr] = $2 \cdot 10^{-7}$ mol/L; Al/Zr = 2000, ethylene pressure 0.54 atm, 30°C. Polymerization conditions for catalytic systems with binary activator: toluene, [Zr] = $1 \cdot 10^{-5}$ mol/L, Al/Zr = 500, 1 atm, 20°C.

The formation of a branched PE, even in the absence of an external α-olefin, is the specific feature of the catalytic system derived from "constrained geometry" zirconocene Me_2SiCp^*N-*t*-$BuZrCl_2$ ($Cp^* = (CH_3)_4Cp$) and MAO as cocatalyst [5]. The PE prepared over this catalytic system (Fig. 1, spectrum 2c) really shows the highest 1378 cm^{-1} absorption band. This pre-catalyst activated by a combined cocatalyst TIBA/$CPh_3B(C_6F_5)_4$ generates a linear unbranched PE (Fig. 1, spectrum 1c) of a very high molecular weight (Table 2, entry 4).

The experiments on ethylene polymerization catalyzed by systems (*i*-PrCp)$_2ZrCl_2$/TIBA/$CPh_3B(C_6F_5)_4$ have shown [3] the polymerization to proceed as a first-order with respect to monomer and an effective reaction order of about of 0.4 with respect to TIBA. Contrary to lower AlR_3, TIBA has recently been reported [6—8] not to act as a chain transfer agent in metallocene-derived catalytic systems. Our results and the literature evidence have made us conclude that TIBA does not simply operate as an alkylating agent or as an impurity scavenger, but that it is incorporated into the active center as a heteronuclear alkyl or halide bridged Zr-Al cationic complex. Equilibrium formation of similar cationic complexes has been repeatedly reported [9, 10] to occur in the course of interactions of cationic complexes $L_2M^+(CH_3)...B^-(C_6F_5)_4$ (L — η-bound ligand; M = Zr, Hf) with AlR_3 (R = Me, Et).

Experiments with a ternary catalytic system composed of "constrained geometry" dichloride or dimethylated zirconocenes and a combinated activator TIBA/$CPh_3B(C_6F_5)_4$ allowed us to conclude about the crucial role of σ-bound ligand in both the calatyst per-

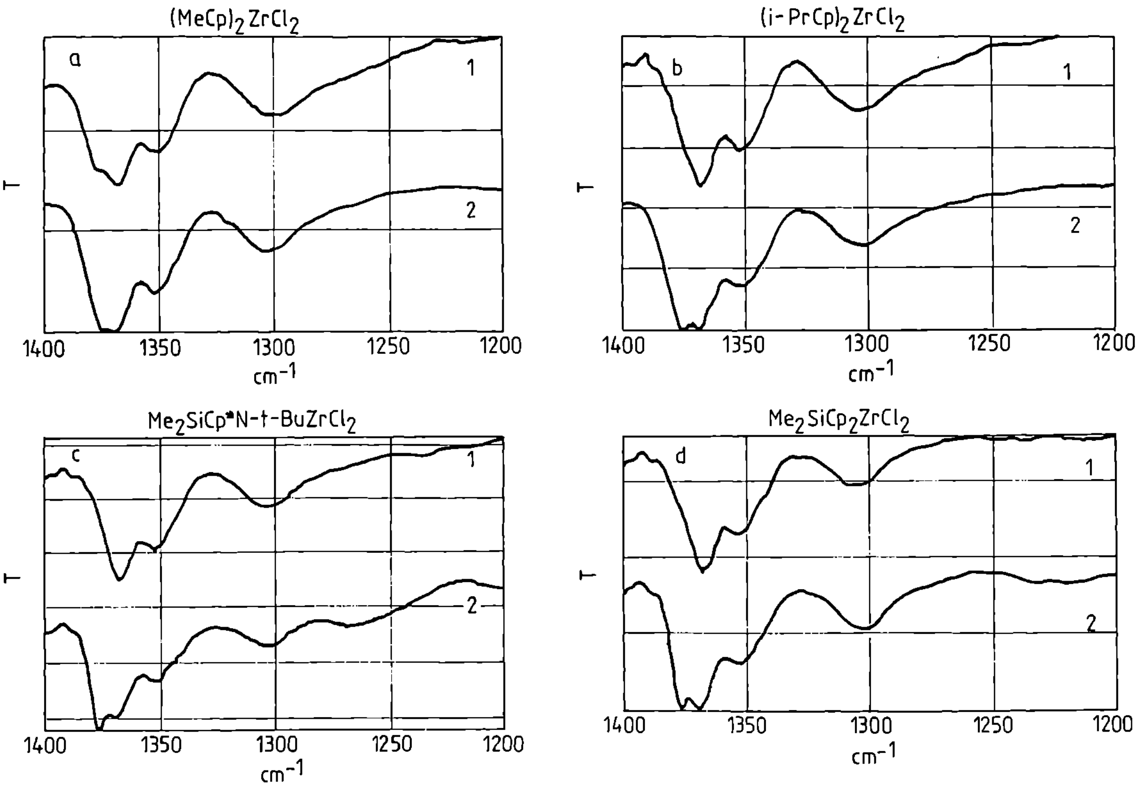


Fig. 1. IR spectra of PE prepared over dichloride zirconocenes (marked at the top) with $TIBA/CPh_3B(C_6F_5)_4$ (curve 1) and MAO (curve 2) as cocatalysts. Polymerization conditions: (a, b) low ethylene pressure, (c, d) high ethylene pressure (for detailed polymerization conditions (a, b, c) see Tables 1, 2, (d) $T = 30^oC$, $p = 11{,}5$ atm, (curve 1) $[Zr] = 6 \cdot 10^{-6}$ mol, $Al/Zr = 500$, (curve 2) $[Zr] = 6{,}9 \cdot 10^{-6}$ mol, $Al/Zr = 1000$)

Table 2. Some characteristics of ethylene polymerization over Me_2SiCp^*N-*t*-$BuZrX_2$ [$Cp^* = (CH_3)_4Cp$; X = Cl (1Cl); X = Me (1Me)] pre-catalysts under action of $TIBA/CPh_3B(C_6F_5)_4$ and properties of polyethylene formed

Entry	Catalyst	$[Zr] \cdot 10^6$, mol	Al/Zr	T_p, °C	*P*, atm	t_p, min	Y_{PE}, g	*A*, kg/(mmol Zr · h · $[C_2H_4]$) mol/L	$M^{*)}_w$	M_w/M_n
T1	1Cl	2.7	260	30	11.5	60	7.9	2.6	>2000000**)	
T2	1Cl	2.9	260	70	11.5	60	5.9	2.8	1830000**)	
T3	1Cl	4.9	260	90	11.5	10	7.6	18.4	127000**)	
T4	1Me	3.5	260	20	11.5	11	29.0	30.8	2050	2.3
T5	1Me	3.6	260	40	11.5	9	43.4	72.0	2500	2.6
T6	1Me	3.5	260	60	11.5	6	35.0	123.2	2430	2.6
T7	1Me	5.0	500	30	2.0	15	7.0	25.4	1480	3.0
T8	1Me	5.4	500	30	5.0	10	19.4	40.6	2020***)	4.4
T9	1Me	5.9	500	30	10.0	9	22.2	20.6	1800***)	3.5
T10	1Me	6.1	500	30	15.0	9	19.4	12.7	1430***)	3.8
T11	1Me	6.1	500	30	20.0	4	14.7	15.8	1780***)	3.5

*) GPC data. **) Viscosimetric measurements. ***) GPC curves of marked samples demonstrate the presence of high-*M* or low-*M* "tails".

formance and properties of the resulting polyethylenes. Over these catalytic systems ethylene polymerizations have been conducted at an ethylene pressure of 11.5 atm. The dichloride complex was examined in ethylene polymerization carried out at temperatures of 30, 70 and 90°C (Table 2: entries 1—3). At both 30 and 70°C, ethylene was consumed at a low and stable rate. As the polymerization temperature was raised from 70 to 90°C, the starting ethylene consumption rate rose sharply by a factor of 14, followed by an exponential decrease of the rate in the course of the reaction. The most interesting was the simultaneous sharp decrease in molecular weight from above $2 \cdot 10^6$ to 127,000 (entry 3). Such an increase in the polymerization rate is hardly due to an increase in the efficiency of active sites formation. The sharp, rather than progressive, decrease in the molecular weight points to the formation of a quite different type of active centers under these conditions. If rather than two different types of active species (formed either from less alkylated (monoalkyl monochloride) and from dialkylated complexes or as a result of Cl-alkyl exchange) TIBA is assumed to be involved in the active site formed in the reaction medium, then

$$\mathrm{Me_2SiCp^*N\text{-}}t\mathrm{\text{-}BuZrR...(ClAl\text{-}}i\mathrm{\text{-}Bu_3)]^+ ...B^-(C_6F_5)_4} \quad k_{p1}, k_{tr1} \quad \text{(I)}$$

$$\mathrm{Me_2SiCp^*N\text{-}}t\mathrm{\text{-}BuZrR...(RAl\text{-}}i\mathrm{\text{-}Bu_3)]^+ ...B^-(C_6F_5)_4} \quad k_{p2}, k_{tr2} \quad \text{(II)}$$

and consequently, these active sites may give rise to quite different effective constant rates of chain propagation, chain transfer and, presumably, deactivation reactions. One may expect the activity of the complex (I) to be lower due to the presence of the chloride ligand in the outer coordination sphere of an active center. A somewhat similar effect of the σ-bound ligand as a "bridged" ligand between a cationic center and an anionic MAO counter-ion has been reported [11] for mono-Cp trihalide complexes of titanium in the synthesis of syndiotactic polystyrene. When activated with MAO, trifluorine complexes showed a considerably higher activity than did trichloride complexes under comparable conditions.

To elucidate the effect of σ-bound ligand, we carried out a series of ethylene polymerizations with dimethylated derivative of a "constrained geometry" complex. With both chloride ligands replaced for methyl ligands, the catalyst performance and the properties of polyethylene products underwent dramatic changes (Table 2: entries 4—11), *viz.*, the activity rose abruptly and the molecular weight fell to the value of a wax-like PE. At 60°C, the activity of the dimethylated complex exceeded about 50 times that of the dichloride complex operated at 70°C with a simultaneous decrease in PE molecular weight by a factor of 10^3. The effective activation energy for polymerization of ethylene over the ternary catalytic system derived from the dimethylated complex is about 4 kcal/mol — a value very low even for the cationic metallocene-catalyzed ethylene polymerization. To our knowledge, this is an unprecedented example of behavior in a cationic metallocene-catalyzed olefin polymerization: the combination of extremely high-propagation and chain-transfer reactions.

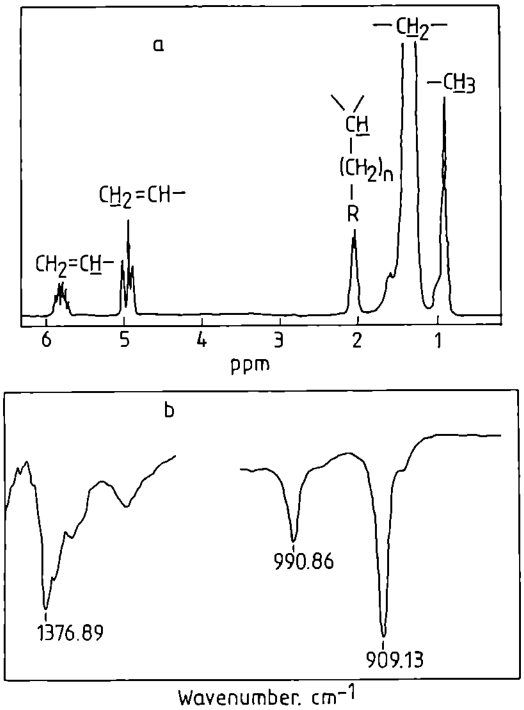


Fig. 2. (a) ^1H NMR and (b) IR spectra of low-M PE formed over catalytic system Me_2SiCp^*N-t-$BuZrMe_2$/TIBA/ /$CPh_3B(C_6F_5)_4$ at ethylene pressure of 11.5 atm and reaction temperature of 40°C (Table 2, entry 5)

In this sense it was of interest to reveal the main route for such a pronounced chain transfer reaction. Potential reactions include chain transfer to organoaluminum compound, β-H transfer to zirconium and β-H elimination to monomer. As mentioned above, in these catalytic systems TIBA does not act as a chain transfer agent. Analysis of IR spectra of low-*M* PEs formed in these experiments showed the macromolecules of PEs to be mainly vinyl-group ended polymers (Fig. 2). Such a structure of the resulting macromolecules testifies that the chain transfer reaction proceeds with the participation of β-H atom of the growing polymer chain either by the transfer to zirconium with the formation of a hydride-like species fast regenerating to the metal-alkyl cationic upon addition of the ethylene molecule or by transfer to the coordinated monomer. So far as the number-average polymerization degree is the ratio of chain propagation to chain transfer rates:

$$\overline{P}_n = \frac{k_p[C^*][M]}{\sum_j k_{tr_j}[C^*][A_{tr}]_j} \quad (5)$$

where k_p is the effective chain propagation rate constant, [C*] is the effective concentration of active species, [M] is the concentration of monomer (ethylene), k_{tr} are the effective chain transfer rate constants on all possible routes j, and $[A_{tr}]_j$ are the effective concentrations of possible chain transfer agents, the response of the P_n-value to the monomer concentration will testify to the most probable mechanism of chain transfer. If the main route of chain transfer is β-H transfer to Zr, the molecular weight will rise as the monomer concentration is increased. In the case of the bimolecular reaction of β-H elimination to monomer, the molecular weight will remain unaffected by monomer concentration. Table 2 (entries 7—11) shows that, as the ethylene pressure was raised from 2 to 20 atm, the molecular weight of the resulting wax-like PEs did not change, whereby in these catalytic systems the bimolecular reaction of β-H transfer to coordinated monomer is seen to be the main route of chain transfer. In the polymerizations conducted at Al/Zr = 260 (entries 4—6), the polydispersity indices of PEs samples were rather low (2.3—2.6). As the Al/Zr ratio was raised to 500, the M_w/M_n indices considerably rose (Table 2: entries 7—11) and the GPC curves showed low-*M* and high-*M* "tails", suggestive of formation of several types of active sites under these conditions.

The main bands in the ^{1}H NMR spectra (Fig. 2a) of low-*M* PE generated by the dimethyl-derived ternary catalytic system are presented by the end methyl groups (0.8—1.1 ppm), methylene groups of oligomeric chain (1.3 ppm), hydrogen atoms at ternary carbon atoms of branches (1.9—2.2 ppm), and vinyl-ended fragments (5.69—5.96 ppm; 4.85—5.09 ppm). The presence of branches and vinyl-ended polymer chains is also confirmed by the IR spectra of polymer samples (Fig. 2b): absorption bands at 1378 cm^{-1} (symmetric deformation of methyl groups) and 909, 991 cm^{-1} (deformations of =CH-, and =CH$_2$ groups, resp.). As mentioned above, the main route for chain transfer in the ternary catalytic systems derived from the dimethylated complex is the chain transfer to monomer. The low values of k_p/k_{tr} ~ 30—500 predetermine a high concentration of vinyl-ended polymer chains (products of chain transfer to monomer). Accordingly, the estimated number of vinyl groups per 1000 carbon atoms of polymer chain is very high (Table 3). The degree of branching resulting from reinsertion of vinyl-ended groups is also very high for these PE samples (Table 3). This fact also demonstrates the high reactivity of the Zr-C bond in the cationic species formed in the ternary catalytic systems derived from a dimethylated pre-catalyst.

Table 3. Analysis of end double bonds content and branching degree for low molecular weight PE samples obtained over catalytic system $Me_2SiCp^*N\text{-}t\text{-}BuZrMe_2/TIBA/CPh_3B(C_6F_5)_4$

Entry	Catalyst	Double bonds/1000 C		Branch., n/1000 C	
		IR	^{1}H NMR	IR	^{1}H NMR
T7	1Me	21 (0.7)$^{*)}$	—	22	—
T8	1Me	14 (0.5)	10 (0.3)	17 (0.5)	21 (0.7)
T9	1Me	12 (0.4)	12 (0.4)	14 (0.5)	87 (3.1)
T10	1Me	14 (0.4)	15 (0.4)	15 (0.4)	31 (0.8)
T11	1Me	15 (0.5)	13 (0.5)	15 (0.5)	46 (1.5)

$^{*)}$ In parenthesis is estimated number for one polymer chain.

CONCLUSION

The present results may be summed up as follows:

— When activated with TIBA/CPh$_3$B(C$_6$F$_5$)$_4$, dichloride zirconocenes exhibited moderate activities as compared with those activated with MAO and gave rise to polyolefins of considerably higher molecular weight.

— In ternary catalytic systems with dichloride pre-catalysts TIBA acts not only as impurity scavenger or simply an alkylating agent, but also as a cocatalyst giving rise to heteronuclear cationic species providing lower chain propagation and chain transfer constant rates than those generated upon the MAO action. The degree of branching of PEs prepared over ternary catalytic systems is also considerably lower than that in binary catalytic systems with MAO as cocatalyst.

— The presence of a halide or alkyl ligand in the outer coordination sphere of active sites has a considerable effect on both the catalytic performance of active species and on the properties of PEs formed. Chlorine-keeping Al-Zr heteronuclear active sites give rise to high-*M* linear PE with moderate activity, whereas alkyl holders exhibit extremely high abilities of both chain propagation and an unprecedented chain transfer to monomer. The extremely high reactivity of the Zr-C bond in the latter active sites is also manifested in the extremely high ability to incorporate α-olefins giving rise to polyethylene chains containing the branch on average with 4—10 incorporated ethylene units.

Experiments aimed at analyzing the nature of active centers and their catalytic behavior are in progress.

ACKNOWLEDGMENT

This research was supported by the Grant from the Russian Foundation for Basic Research (No. 97-03-32243a).

REFERENCES

1. Bravaya N. M., Strelets V. V., Dzhabieva Z. M., Babkina O. N., Maryin V. P.: *Russ. Chem. Bull.* 1998, **47**, 1491.
2. Panin A. N., Babkina O. N., Bravaya N. M.: *Russ. Chem. Bull.* 2000, **49**, 303.
3. Panin A. N., Babkina O. N., Bravaya N. M.: *Polimery* 2001, **46**, 44.
4. Khukanova O. M., Babkina O. N., Rishina L. A., Nedorezova P. M., Bravaya N. M.: *Polimery* 2000, **45**, 328.
5. Stevens J. C.: "Studies in Surface Science and Catalysis", Elsevier Science Publ. B. V., Amsterdam 1996, 101, p. 11.
6. Naga N., Mizunuma K.: *Polymer* 1998, **39**, 5059.
7. Luft G., Dyroff R. A., Götz C., Schmitz S., Wieczorek T., Klimesch R., Gonioukh A.: "Ternary Metallocene Based Catalysts in High Temperature, High Pressure Polymerization" in "Metallorganic Catalysts for Synthesis and Polymerization" (Ed., Kaminsky W.), Springer, Berlin 1999, p. 651.
8. Liu S., Yu G., Huang B.: *J. Appl. Polym. Sci.* 1997, **66**, 1715.
9. Bochmann M., Lancaster S. J.: *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 1634.
10. Bochmann M.: *Topics in Catalysis* 1999, **7**, 9.
11. Kaminsky W., Lenk S.: *Micromol. Symp.* 1997, **118**, 45.