New fluorine-containing titanium bis(salicylideneimino) complexes in olefin polymerization

S. Ch. Gagieva,[a] T. A. Sukhova,[b] D. V. Savinov,[c] V. A. Optov,[c] N. M. Bravaya,[b] Yu. N. Belokon´,[d] and B. M. Bulychev[a]★

[a]*M. V. Lomonosov Moscow State University, Department of Chemistry,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: b.bulychev@highp.chem.msu.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
18 Institutskii prosp., 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 5420. E-mail: nbravaya@cat.icp.ac.ru
[c]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 119991 Moscow, Russian Federation.
E-mail: dmsav@yandex.ru
[d]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yubel@ ineos.ac.ru

The titanium salicylideneimino complex $TiCl_2\{\eta^2\text{-}1\text{-}[NR{=}C(H)]\text{-}2\text{-}O\text{-}3,5\text{-}Bu^t_2\text{-}C_6H_2\}_2$ (R = 2,3,5,6-F_4C_6H) was synthesized. In the presence of polymethylaluminoxane, the complex efficiently catalyzes polymerization of ethylene and, to a lesser degree, atactic propylene. The resulting polymers are characterized by high melting points, molecular weights, and polydispersity indices, as well as elastomeric (polypropylene) properties.

Key words: titanium, phenoxyimine complexes, homogeneous catalysis, polymerization, olefins, polyethylene, polypropylene.

Recently[1—4] developed catalysts based on phenoxyimine chelate complexes of titanium and zirconium, $MCl_2\{\eta^2\text{-}1\text{-}[C(H){=}NPh^R]\text{-}2\text{-}O\text{-}Ph^{R'}\}_2$ (FI catalysts (Mitsui Co.)) are comparable in activity with or even superior to the most efficient metallocene catalysts for ethylene polymerization.[5]

In the present work, we synthesized new complexes with phenoxyimine ligands structurally close to the components of FI catalysts and studied their performance in the polymerization of ethylene and propylene under conditions somewhat different from those used previously.[1—4]

Experimental

Complexes were synthesized under argon in anhydrous media. Dichloromethane, toluene, hexane, and ethyl acetate (all reagent grade purity) were additionally purified according to known procedures;[6] $TiCl_4$ and $Ti(OPr^i)_4$ (Fluka) were additionally distilled under argon; $TiCl_2(OPr^i)_4$ was prepared as described earlier.[7] Ligands were synthesized from 2,4-di-*tert*-butylphenol, paraformaldehyde, 4-picoline, salicylaldehyde, 2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoro-4-trifluoromethylaniline, and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (Fluka and Aldrich). ^1H NMR spectra were recorded on Bruker WP-200 and Bruker AMX-400 instruments. IR spectra were recorded on a Magna-IR 750 spectrophotometer.

Synthesis of ligands. *N*-Salicylidene-2,3,5,6-tetrafluoroaniline. 2,3,5,6-Tetrafluoroaniline (0.85 mmol) and *p*-toluenesulfonic acid (0.01 mmol) were added to a solution of salicylaldehyde (0.85 mmol) in toluene. The mixture was refluxed with stirring for 20 h, filtered, concentrated, and purified by column chromatography on silica gel with hexane—ethyl acetate (5 : 1) as eluent to give a yellow oil in 67% yield. Found (%): C, 57.31; H, 2.51; N, 5.28. $C_{13}H_7NOF_4$. Calculated (%): C, 57.99; H, 2.62; N, 5.20. ^1H NMR, δ: 6.40 (m, 1 H, aniline); 6.95 (2 H, H arom.); 7.55 (2 H, H arom.); 9.84 (s, 1 H, CH=N); 11.79 (s, 1 H, OH).

***N*-(3,5-Di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline** was prepared analogously from 3,5-di-*tert*-butylsalicylaldehyde and 2,3,5,6-tetrafluoroaniline. Found (%): C, 66.98; H, 6.58; N, 3.08. $C_{21}H_{23}NOF_4$. Calculated (%): C, 66.14; H, 6.04; N, 3.67. ^1H NMR, δ: 1.50 (s, 18 H, Bu^t); 6.70 (m, 1 H, aniline); 6.82—7.42 (m, 2 H, H arom.); 8.64 (s, 1 H, CH=N); 13.95 (s, 1 H, OH).

***N*-(3,5-Di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoro-4-trifluoromethylaniline** was prepared analogously from 3,5-di-*tert*-butylsalicylaldehyde and 2,3,5,6-tetrafluoro-4-trifluoromethylaniline. Found (%): C, 58.64; H, 4.58; N, 3.15. $C_{22}H_{22}NOF_7$. Calculated (%): C, 58.80; H, 4.68; N, 3.12. ^1H NMR, δ:

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1605—1609, August, 2003.

1.31—1.45 (s, 18 H, Bu^t); 7.52—7.72 (m, 2 H, H arom.); 9.84 (s, 1 H, CH=N); 11.61 (s, 1 H, OH).

Synthesis of complexes 1—3 (general procedure). Bis(*N*-salicylidene-2,3,5,6-tetrafluoroaniline)titanium(IV) dichloride (1). A solution of *N*-salicylidene-2,3,5,6-tetrafluoroaniline (0.10 mmol) in methylene chloride was stirred in a two-necked flask filled with argon, and TiCi$_2$(OPr^i)$_2$ (0.05 mmol) was added. Twenty hours later, the red precipitate that formed was filtered off and washed with methylene chloride and toluene. The yield of complex **1** was 85%. Found (%): C, 43.20; H, 1.92; N, 3.53. $TiC_{26}H_{12}N_2O_2F_8Cl_2 \cdot CH_2Cl_2$. Calculated (%): C, 43.82; H, 1.91; N, 3.79. IR, ν/cm^{-1}: 1610 (C=N); 520 (Ti—O); 450 (Ti—N).

Complexes **2** and **3** were obtained analogously.

Bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroaniline]titanium(IV) dichloride (2). Found (%): C, 57.87; H, 4.92; N, 2.96. $TiC_{42}H_{44}N_2O_2F_8Cl_2$. Calculated (%): C, 57.34; H, 5.04; N, 3.18. IR, ν/cm^{-1}: 1618 (C=N); 570 (Ti—O); 440 (Ti—N). ^{1}H NMR, δ: 1.54 (s, 36 H, Bu^t); 6.30 (m, 2 H, aniline); 6.90—7.53 (m, 4 H, H arom.); 9.89 (s, 2 H, CH=N).

Bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoro-4-trifluoromethylaniline]titanium(IV) dichloride (3). Found (%): C, 52.90; H, 4.20; N, 4.41. $TiC_{44}H_{42}N_2O_2F_{14}Cl_2$. Calculated (%): C, 52.02; H, 4.14; N, 4.72. IR, ν/cm^{-1}: 1610 (C=N); 560 (Ti—O); 470 (Ti—N). ^{1}H NMR, δ: 1.54 (s, 36 H, Bu^t); 6.90—7.53 (m, 4 H, H arom.); 9.89 (s, 2 H, CH=N).

Ethylene polymerization. Toluene and heptane were special-purity chemicals. Solvents were purified according to a standard procedure.[8] Polymethylaluminoxane (MAO, "Witco Co.") was used as a 10% solution in toluene. Argon and ethylene (special purity grade) were dried by passing through a column packed with a molecular sieve (5Å).

All procedures for preparation of equipment, addition of the test complexes and gaseous ethylene to a reactor, and measurement of polymerization kinetics were described previously.[9] After a solution of a test complex in toluene or heptane was saturated with ethylene, polymerization was initiated by adding a solution of the catalyst to the reactor and terminated by acidifying the mixture with 10% HCl in ethanol. The resulting polymer was filtered off, washed with ethanol and water, and dried *in vacuo* at 50—60 °C to a constant weight.

Propylene polymerization. A reactor was completely filled with polymerization-grade (99.7 vol %) liquefied propylene ($p_{C_3H_6} \approx 40$ atm). A general polymerization procedure was described earlier.[10] In the present work, two ways of adding a catalyst were used. According to one way, ~3/4 of the required amount of 10% MAO in toluene was mixed with liquefied propylene in the reactor; the mixture was stirred, and then the test complex dissolved in the rest of MAO was added. According to the other way, all the required amount of MAO was placed in the reactor, and then a test complex was added as solid. In both cases, the total molar Al : Ti ratio was ~2000.

^{13}C NMR spectra of 7.5 wt % polypropylene in 1,1,2,3-tetrachloroethane-d$_2$ were recorded on a Bruker AC-200 instrument at 110 °C.

X-ray powder diffraction analysis of polypropylene samples was performed on a DRON-2 diffractometer.

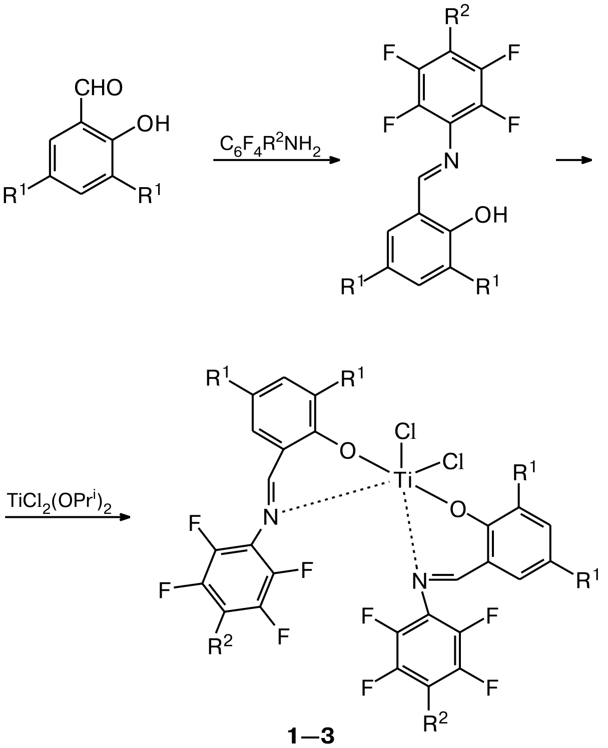
Mechanical tests were carried out with an Instron-1122 machine as described earlier.[11]

The molecular weight characteristics (M_w, M_n, MWD) of polyethylene and polypropylene were measured for their solutions in 1,2-dichlorobenzene at 135 °C by gel permeation chromatography on a Waters 150-C instrument equipped with a linear HT-μ-styragel column.

Results and Discussion

The general route to phenoxyimine complexes **1—3** is shown in Scheme 1. The red products were obtained in 85—88% yields.

Scheme 1



1—3

	1	2	3
R^1	H	Bu^t	Bu^t
R^2	H	H	CF$_3$

According to previous data,[1—3,12—15] as well as the NMR and IR spectra of such titanium complexes, their octahedral structure includes two bidentate [O,N]-chelating ligands with *trans*-arrangement of the oxygen atoms and two chlorine atoms, which are *cis* to each other.

When a solution of MAO is added to a suspension of complex **1** in toluene, the complex dissolves only partly and undergoes reduction even at the step of catalyst formation. Apparently, this is the main reason for the low activity in the catalyzed reaction giving only traces of polyethylene over several hours.

Having a *tert*-butyl group in the *ortho*-position of the Ph ring, complex **2** is well soluble in toluene and resistant to reduction of Ti^{IV} to Ti^{III}.

Table 1. Ethylene polymerization with the **2**—MAO catalytic system (ethylene pressure 0.97 atm)

Entry	Ti 10^6 /mol	[Ti] 10^5 /mol L^{-1}	Al_{MAO} : Ti /mol mol^{-1}	T_p /°C	t/min	Y^a/g	A^b	M_w 10^4	M_w/M_n
1	3.80	18.8	1600	30	5	0.71	22.2	147.60	4.4
2	3.80	18.8	400	30	5	0.81	23.3	165.22	4.8
3	0.63	3.10	600	30	9	0.47	45.2	1114.85	7.1
4	0.13	0.63	600	30	17	0.32	79.0	1853.88	7.3
5 [c]	0.82	4.10	460	30	12	0.55	31.8	747.40	11.2
6 [c]	0.82	4.10	460	70	14	0.30	27.2	583.00	11.1
7 [d]	0.20	1.00	600	30	15	0.49	89.1	—	—
8 [e]	0.20	1.00	600	30	37	0.10	7.4	942.88	21.1

[a] Hereafter, Y is the yield of the polymer.

[b] Reduced activity, kg of polyethylene (mmol of Ti h $[C_2H_4])^{-1}$.

[c] Polymerization in heptane.

[d] Polymerization in toluene in the presence of hex-1-ene; the molar ratio of hex-1-ene to ethylene was 1.1.

[e] Polymerization in toluene in the presence of hex-1-ene; the molar ratio of hex-1-ene to ethylene was 2.2.

A catalyst formed in the **2**—MAO system exhibited a high activity in ethylene polymerization (Table 1). Polymerization was carried out and the kinetics and properties of polymers were studied as described earlier.[9—11] The catalyst activity is comparable with the most efficient metallocene catalytic systems and highly efficient FI titanium chelate complexes.[1,12,13] It can be seen from Table 1 that at a relatively high concentration of the complex and a high molar Al_{MAO} : Ti ratio (1600), the specific activity of the catalyst reaches 22.2 kg of polyethylene (mmol of Ti h $[C_2H_4])^{-1}$ (entry *1*). The activity of the catalytic system changes insignificantly when the concentration of the cocatalyst decreases four times (entry *2*). At the same time, the activity of metallocene systems usually increases with an increase in the molar MAO : catalyst ratio up to 10^3 to 10^4 mol mol^{-1}.[16,17]

When the concentration of complex **2** was decreased six and thirteen times at a molar Al_{MAO} : Ti ratio of 600, the specific activity of the catalyst increased by factors 2 and 3.4, respectively (entries *3*, *4*). A possible reason for this is that mass transfer is hindered by rapid formation of large amounts of the polymer in concentrated solutions of the catalyst.

Complex **2** is well soluble in heptane. The reduced activity in ethylene polymerization in this medium is approximately half as high as in toluene (see Table 1; *cf.* entries *4*, *5*). This difference can be associated both with the lower polarity of the medium and with partially heterogeneous polymerization because MAO is insoluble in heptane.

Close kinetic profiles of polymerization in toluene and heptane (Fig. 1; *cf.* curve *4* and curves *5*, *6*) are probably due to similar deactivation reactions in both solvents.

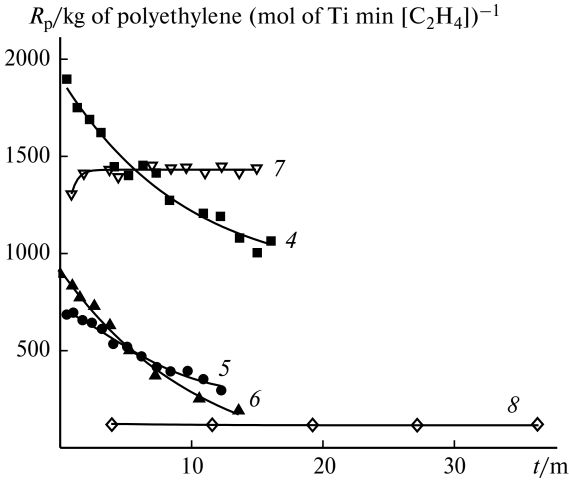


Fig. 1. Plots of the reduced polymerization rate (R_p) vs. the reaction time for ethylene polymerization in (*4*) toluene, (*5*, *6*) heptane, (*7*, *8*) toluene in the presence of hex-1-ene at (*4*, *5*, *7*, *8*) 30 and (*6*) 70 °C with the **2**—MAO catalytic system. The curve numbering is the same as the entry numbering in Table 1.

The melting points (DSC data) of polyethylene samples prepared both in toluene and heptane (see Table 1, entries *3*, *5*, *6*) are very high (142 °C), which indicates their high molecular weights. Indeed, even at relatively high concentrations of the complex, the polyethylene obtained has $M_w \sim 1\ 500\ 000$ g mol^{-1} (entries *1*, *2*). An increase in the molar Al_{MAO} : Ti ratio from 400 to 1600 mol mol^{-1} does not change the molecular weight characteristics of the resulting polyethylene. Therefore, MAO is not a chain transfer agent. However, longer polymerization times under a decreased catalyst concentration, all other factors being the same (entries *3*—*5*), result in significant growth of the molecular weight of the polyethylene. The molecular weight of the polyethylene obtained even at 70 °C in heptane (entry *6*) cannot be reliably determined by gel permeation chromatography ($M_w > (3—4) \cdot 10^6$ g mol^{-1}). Unlike FI catalysts,[1—4,12—15]

Table 2. Bulk propylene polymerization with the **2**—MAO catalytic system (reaction temperature 50 °C, reaction time 1.5 h)

Entry	Ti 10^6 /mol	[Ti] 10^5 /mol L^{-1}	Al_{MAO} : Ti /mol mol^{-1}	Y/g	A[a]	M_w 10^4	M_w/M_n
1 [b]	4.47	2.23	2300[c]	5.0	0.07	87.22	8.8
2 [d]	4.72	2.36	2000	6.9	0.09	95.23	10.1

[a] Reduced activity, kg of polypropylene (mmol of Ti h $[C_2H_4])^{-1}$.

[b] The catalyst was added as a solution in 10% MAO in toluene.

[c] Total ratio.

[d] The catalyst was added in the solid state.

the polyethylene in a **2**—MAO system is characterized by the high polydispersity M_w/M_n = 4—5. All these features suggest that chain propagation in this system is possibly limited by a bimolecular reaction of active centers bearing a growing polymer chain.

As shown previously,[1,2] the FI titanium complex catalysts with the phenoxyimine fragment bearing electron-withdrawing F and CF_3 substituents in the *para-* and *meta*-positions exhibit enhanced activity. However, an ambiguous role of such substituents can be illustrated by changes in catalytic properties when passing from complex **2** to complex **3**, which contains the CF_3 group in the *para*-position of the phenyl ring. The **3**—MAO catalytic system is ~70 times less active than the **2**—MAO system, all other factors being equal, although the Taft functions for F and CF_3 are rather close.[18]

Data on the catalytic properties of the **2**—MAO system in polymerization of liquid propylene are given in Table 2. It can be seen that the reduced activity of the system is approximately 1000 times lower than in ethylene polymerization, which was noted earlier.[3] Unlike the ethylene polymerization process discussed above, the propylene polymerization rate gradually increases to a constant value as the reaction proceeds (Fig. 2).

The X-ray diffraction and ^{13}C NMR data suggest that the polypropylene obtained is an atactic polymer with a considerable number of 2,1-added units (~5 mol %). The distribution of the methyl pentads in the ^{13}C NMR spectrum of this polymer is close to that for an ideal atactic polypropylene. Like polyethylene, polypropylene has a high molecular weight (~1 000 000), while its polydispersity is even higher (M_w/M_n = 8—11). Moreover, the polypropylene obtained exhibits high elastomeric properties: in a tensile test up to 300% of the original length (ε_{300}), the residual deformation of its samples was at most 21%. In this respect, this polymer is close to elastomeric stereoblock polypropylene composed of short isotactic or syndiotactic blocks separated by atactic units.[19]

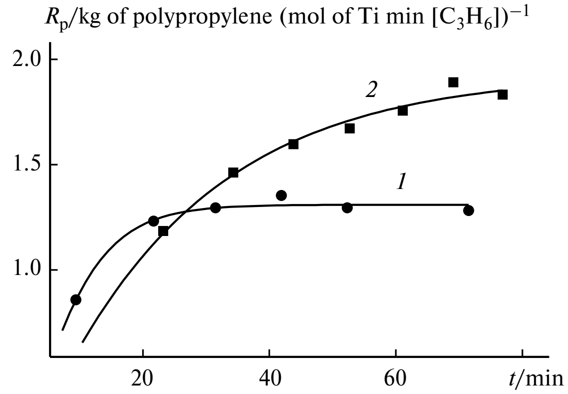


Fig. 2. Plots of the reduced rate of propylene bulk polymerization (R_p) vs. the reaction time. The catalyst was added (*1*) as a solution in 10% MAO in toluene or (*2*) as solid. The curve numbers and the polymerization conditions correspond to the entry numbers in Table 2.

It can be seen in Fig. 1 that the reduced initial rate of ethylene polymerization without mass transfer control is maximum. Therefore, catalytically active centers appear quite rapidly in this case, but their subsequent deactivation is also rapid. In contrast, the gradual acceleration of propylene polymerization (see Fig. 2) indicates the low rates of formation of active centers, while a constant polymerization rate over a prolonged time suggests some stabilization of these centers. The nature of this phenomenon remains unclear, but it was also found in runs on the copolymerization of ethylene with hex-1-ene (see Fig. 1, curves *7*, *8*). In this case, selective polymerization of only ethylene by the catalyst was found (see Table 1, entries *7*, *8*). The IR spectrum of the polyethylene obtained (entry *7*) shows no absorption band for the bending vibrations of the Me groups in branches (1378 cm^{-1}). At the same time, the low melting point of this sample (133 °C) suggests that its macromolecules are branched, although with a very low frequency; *i.e.*, hex-1-ene is vastly inferior to ethylene in the insertion ability. However, even in this case, hex-1-ene does probably affect some characteristics of the active centers and change their properties (in an equimolar mixture of hex-1-ene with ethylene, the catalyst remains active, while the lifetime of active centers is significantly extended). These data can be useful for stabilization of the **2**—MAO catalytic system in ethylene polymerization, even at elevated temperatures.

This work was financially supported by the DOW-Chemical Co. and the Russian Foundation for Basic Research (Project Nos. 02-03-32580, 01-03-9700, and 03-03-06378).

References

1. H. Makio, N. Kashiwa, and T. Fujita, *Adv. Syth. Catal.*, 2002, **344**, 1.
2. M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327.
3. M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 7888.
4. S. Ishii, J. Saito, M. Mitani, J. Mohri, N. Natsukawa, Y. Tohi, S. Matsui, N. Kashiwa, and T. Fujita, *J. Mol. Catal. A: Chem.*, 2002, **179**, 11.
5. W. Kaminsky and M. Arndt, *Adv. Polym. Sci.*, 1997, **127**, 143.
6. *Organikum*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1978, **2**.
7. C. Dijkgraff and J. Rousseau, *J. Am. Chem Soc.*, 1990, **112**, 3952.
8. A. N. Panin, T. A. Sukhova, and N. M. Bravaya, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 1901.
9. T. A. Sukhjva, A. N. Panin, O. N. Babkina, and N. M. Bravaya, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1083.
10. P. M. Nedorezova, V. I. Tsvetkova, A. M. Aladyshev, D. V. Savinov, A. N. Klyamkina, V. A. Optov, and D. A. Lemenovskii, *Vysokomol. Soedin., Ser. A*, 2001, **43**, 605 [*Polym. Sci., Ser. A*, 2001, **43** (Engl. Transl.)].
11. V. I. Tsvetkova, P. M. Nedorezova, N. M. Bravaya, D. V. Savinov, I. L. Dubnikova, and V. A. Optov, *Vysokomol. Soedin., Ser. A*, 1997, **39**, 389 [*Polym. Sci., Ser. A*, 1997, **39** (Engl. Transl.)].
12. Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, *Organometallics*, 2001, **20**, 4793.
13. T. Matsugi, S. Matsui, S. Kojoh, Y. Takagi, I. Inoue, T. Nakano, T. Fujita, and N. Kashiwa, *Macromolecules*, 2002, **35**, 4880.
14. S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847.
15. N. Matsukawa, S. Matsui, M. Mitani, J. Saito, K. Tsuru, N. Kashiwa, and T. Fujita, *J. Mol. Catal. A: Chem.*, 2001, **169**, 99.
16. R. Kleinschmidt, Y. Van der Leek, M. Reffke, and G. Fink, *J. Mol. Catal. A: Chem.*, 1999, **148**, 29.
17. E. Y.-X. Chen and T. Marks, J. *Chem. Rev.*, 2000, **100**, 1391.
18. E. T. Denisov, *Kinetika gomogennykh khimicheskikh reaktsii* [*Kinetics of Homogeneous Reactions*], Vysshaya Shkola, Moscow, 1988, 184 pp. (in Russian).
19. N. M. Bravaya, P. M. Nedorezova, and V. I. Tsvetkova, *Usp. Khim.*, 2002, **71**, 57 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].

Received April 21, 2003;
in revised form May 3, 2003