ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 2, pp. 229–234. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © O.I. Kudinova, T.E. Kron, T.A. Ladygina, A.N. Kozhevnikov, E.S. Petrov, L.A. Novokshonova, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 2, pp. 244–249.

Polydentate Phosphine Oxides As External Electron Donors for Titanium–Magnesium Catalysts for Propylene Polymerization

O. I. Kudinova[a], T. E. Kron[b], T. A. Ladygina[a], A. N. Kozhevnikov[b], E. S. Petrov[b], and L. A. Novokshonova[a]

[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia*

[b] *Karpov Institute of Physical Chemistry, Moscow, 103064 Russia*

e-mail: lnov@chph.ras.ru

Received January 27, 2009; in final form, September 18, 2009

Abstract—The possibility of using $R_nP(O)(CH_2OR')_{3-n}$ (R = alkyl, R' = methyl or acyl, $n = 0–2$) polydentate phosphine oxides as external electron donors for the titanium–magnesium catalysts for isotactic polypropylene synthesis is demonstrated for the first time. The kinetics of propylene polymerization in liquid monomer at 70°C and the isotacticity and molecular-weight characteristics of the resulting polypropylene are studied as functions of the nature of the substituents at the phosphorus atoms in the external donor and the molar ratio of the cocatalyst $AlEt_3$ to the external electron donor. Among the compounds examined, isoamyldi(methoxymethyl)phosphine oxide (R = *iso*-Am, R' = Me, $n = 1$) is the most efficient. The isotacticity index of the polypropylene (PP) synthesized on the titanium–magnesium catalyst with this external donor is as high as 94–95%, and the activity of the catalyst (Cat) in the absence of hydrogen is 5.0–6.5 (kg PP) (g Cat)$^{-1}$ h^{-1}. With the optimum combination, the activity of this catalyst is ≈5 (kg PP) (g Cat)$^{-1}$ h^{-1} and the isotacticity index is 94%. These parameters are close to those obtained for propylene polymerization in the absence of hydrogen on the same titanium–magnesium catalyst with phenyltriethoxysilane (external donor used in the industrial synthesis of PP): the activity is 5.6 (kg PP) (g Cat)$^{-1}$ h^{-1}, and the isotacticity index is 95%. The introduction of hydrogen into the reaction zone makes it possible to efficiently control the molecular weight of PP, increases the catalyst activity by a factor of 1.5–2.5, and somewhat decreases the isotacticity index (from 94 to 91–92%).

DOI: 10.1134/S0023158410020102

Supported $TiCl_4/MgCl_2$ catalysts are modified with electron-donor compounds to enhance their stereospecificity in propylene polymerization. The modifier is introduced at the stage of preparation of the $TiCl_4/MgCl_2$ catalyst (internal donor, D_i) and, in combination with the cocatalyst ($AlEt_3$), at the propylene polymerization stage (external donor, D_e). According to the results of numerous studies [1–4], the role of electron donors is to selectively block the active sites of the catalyst on which the atactic polymer forms and to enhance the stereospecificity of the active sites that produce polypropylene with low stereoregularity. To execute these functions, electron-donor compounds should be at least bidentate and should form stable chelate complexes with tetracoordinated magnesium atoms on the $MgCl_2$ surface. The most efficient internal donors known at present are phthalates, diethers, and 2,3-substituted succinates [2]. Diethers can simultaneously serve as external donors.

It is necessary to use external electron-donor modifiers, because, on contact of the $TiCl_4/MgCl_2/D_i$ catalyst with $AlEt_3$, the internal donor sorbed on the catalyst surface passes partially into the solution to form complexes with $AlEt_3$, thus reducing the stereospecificity of the catalyst. This effect is compensated for by the introduction of another bidentate electron-donor compound—external donor—simultaneously with $AlEt_3$. Alkylmethoxysilanes are among the most efficient external donors employed in the industrial synthesis of isotactic polypropylene (PP).

In this work, we studied the possibility of using polydentate phosphine oxides as external donors for the titanium–magnesium catalysts (TMC) in the synthesis of isotactic PP. The electron-donor (coordinating) centers of the phosphine oxides are the phosphoryl group (P=O) and oxygen atoms in the substituents at the phosphorus atom [5]. Organophosphorus compounds of this type were suggested earlier for use only as solvating additives [6] or polar solvents [7].

EXPERIMENTAL

Materials

The commercial TMC (Moscow Petroleum Refinery) containing 2.06 wt % Ti and dibutyl phthalate as the internal donor was used as the catalyst. The cocatalyst was $AlEt_3$ (Aldrich). Propylene was polymerization-purity grade (Moscow Petroleum Refinery). Phenyltriethoxysilane was purchased from Aldrich. *n*-Heptane (Aldrich) used in the preparation of the

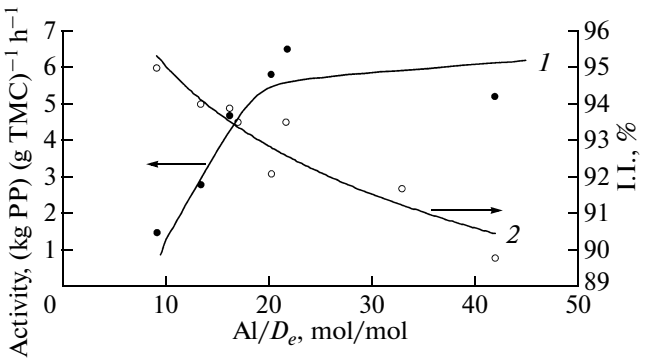

Fig. 1. (*1*) Activity of the TMC with the external donor *iso*-$AmP(O)(CH_2OCH_3)_2$ in propylene polymerization in liquid monomer and (*2*) the isotacticity index of polypropylene as a function of the Al/D_e molar ratio (polymerization temperature of 70°C).

TMC suspension and solutions of catalyst components was dried by distillation from sodium. Hydrogen was passed through columns with molecular sieve 4A and the Ni–Cr catalyst to remove the water and oxygen traces. Phosphine oxides were used as solutions in *n*-heptane.

Synthesis of Substituted Phosphine Oxides

Samples of the following polydentate phosphine oxides were used in tests as external donors for the TMC: $Me_2P(O)CH_2OMe$ (**I**), $MeP(O)(CH_2OMe)_2$ (**II**), $Bu_2P(O)CH_2OMe$ (**III**), $BuP(O)(CH_2OMe)_2$ (**IV**), $(MeOCH_2)_3P(O)$ (**V**), *iso*-$AmP(O)(CH_2OMe)_2$ (**VI**), $Me_2P(O)CH_2OAc$ (**VII**), $Bu_2P(O)CH_2CH_2OMe$ (**VIII**), $[Bu_2P(O)CH_2]_2O$ (**IX**). Tetrakis(hydroxymethyl)phosphonium chloride was used in the synthesis of compounds **I**, **II**, and **IV**–**VII** [8–11]. Compounds **III** and **VIII** were prepared from dibutylphosphonous acid [5]. Diphosphine dioxide (**IX**) was synthesized by the reaction of 1,2-dichlorodimethyl ether with the potassium salt of dibutylphosphonous acid in anhydrous tetrahydrofuran (T_b = 212–214°C/1 Torr). Commercial tributylphosphine oxide (**X**) was purified by distillation. The structures of all compounds were confirmed by recording ^{1}H NMR spectra ($CDCl_3$) on a Bruker WM-250 spectrometer. The purity of the compounds was at least 98%.

Propylene Polymerization

Propylene was polymerized in liquid monomer in a 0.25-l stainless steel reactor fitted with a temperature-controlled jacket; a stirrer (up to 3000 rpm); and a system for introduction of catalyst components, monomer, and admixtures. Polymerization was carried out in under complete filling conditions, which made it possible to measure the polymerization kinetics in liquid propylene. The reactor was prepumped at 70–90°C for 1 h and was purged several times with gaseous propylene. Next, the preset amount of hydrogen from a calibrated volume (if necessary) was introduced into the reactor filled with liquid propylene. Solutions of $AlEt_3$ and an external donor (separately or together) and a suspension of the Ti–Mg catalyst in *n*-heptane were added. Fore polymerization was carried out at 30°C for 2 min. Subsequent polymerization was carried out at 70°C. The polymerization time was usually 1 h. The amount of TMC per run was 0.0035–0.0050 g, which corresponded to a TMC concentration of 0.014–0.020 g/l. The Al/Ti molar ratio was 400–600. The molar ratio of $AlEt_3$ to the external donor ($AlEt_3/D_e$) was varied between 9 and 50. At the polymerization temperature of 70°C, the propylene concentration was 11 mol/l.

Characteristics of Polypropylene

The isotacticity index (I.I.) of polypropylene was determined as the amount of the polymer fraction insoluble in boiling *n*-heptane. Molecular-weight characteristics were measured with a Waters 150 gel permeation chromatograph at 135°C in *o*-dichlorobenzene. The macrotacticity parameter of the isotactic fraction of polypropylene was determined by IR spectroscopy from the ratio of band intensities at 998 and 973 cm^{-1} (D_{998}/D_{973}).

RESULTS AND DISCUSSION

The activity of the TMC in propylene polymerization, kinetics of propylene polymerization in liquid monomer, and the stereoregularity and molecular-weight characteristics of the resulting polymer were studied with different types of synthesized phosphine oxides, which were used as external donors, and at different $AlEt_3/D_e$ molar ratios. The electron-donor (coordinating) centers of the organophosphorus compounds $R_nP(O)(CH_2OR')_{3-n}$ include the phosphoryl group (P=O) and oxygen atoms in the substituents at the phosphorus atom. The properties of the synthesized compounds as external donors were compared with those of phenyltriethoxysilane, which is among the efficient external donors employed in the synthesis of isotactic polypropylene. The results of these studies are presented in Table 1 and in Figs. 1 and 2.

As is clear from these data, the maximum isotacticity index of polypropylene obtained on the TMC in the presence of substituted phosphine oxides is 93–95% at Al/D_e ~ 9–20 mol/mol, which is nearly equal to the I.I. value achieved on the TMC used with the external donor phenyltriethoxysilane, 95% (Table 1, entry 1). The degree of isotacticity of the polymer decreases for all phosphine oxides as the Al/D_e ratio increases, i.e., as the D_e concentration decreases at a constant $AlEt_3$ concentration, as is demonstrated in Fig. 1 (curve *2*) and Fig. 2 (curve *2*) for the donors *iso*-$AmP(O)(CH_2OMe)_2$ and $(MeOCH_2)_3P(O)$, respectively.

Table 1. Properties of the TMC in the presence of polydentate phosphine oxides and phenyltriethoxysilane as external donors in propylene polymerization in liquid monomer at 70°C

Entry	TMC, g	Al/Ti, mol/mol	Al/D_e, mol/mol	Activity, (kg PP) (g Cat)$^{-1}$ h^{-1}	I.I., %	$M_w \times 10^{-3}$	M_w/M_n
			$PhSi(OEt)_3$				
1	0.0034	417	20.0	5.6	95.0	1000	8.6
			$Me_2P(O)CH_2OMe$ **(I)**				
2	0.0037	448	8.3	1.4	93.0	600	7.5
3	0.0037	415	20.0	2.6	89.0	1000	5.0
			$MeP(O)(CH_2OMe)_2$ **(II)**				
4	0.0048	496	12.0	1.8	93.9	830	7.0
5	0.0039	524	23.2	1.5	90.2	960	9.6
			$Bu_2P(O)CH_2OMe$ **(III)**				
6	0.0048	508	13.0	2.1	90.6	–	–
7	0.0048	473	26.0	5.0	87.5	–	–
			$BuP(O)(CH_2OMe)_2$ **(IV)**				
8	0.0039	509	10.0	2.2	93.0	650	8.0
9	0.0048	491	37.5	6.8	90.8	–	–
			$(MeOCH_2)_3P(O)$ **(V)**				
10	0.0052	481	21.7	3.6	93.5	–	–
11	0.0048	497	45.3	4.6	92.2	900	11.0
			iso-$AmP(O)(CH_2OMe)_2$ **(VI)**				
12	0.0052	503	13.5	2.8	94.0	–	–
13	0.0046	532	16.3	4.7	93.9	–	–
14	0.0050	502	20.3	5.8	92.1	–	–
			$Me_2P(O)CH_2OAc$ **(VII)**				
15	0.0049	504	10.0	1.7	99.0	–	–
16	0.0055	625	20.0	2.7	96.0	–	–
			$Bu_2P(O)CH_2CH_2OMe$ **(VIII)**				
17	0.0049	536	20.2	3.8	92.3	–	–
18	0.0049	517	31.5	5.3	89.3	–	–
			$[Bu_2P(O)CH_2]_2O$ **(IX)**				
19	0.0056	565	20.0	3.3	87.8	–	–
			$Bu_3P(O)$ **(X)**				
20	0.0048	459	22.5	14.4	71.4	–	–

The nature of substituents in $R_nP(O)(CH_2OR')_{3-n}$ affects the properties of the catalysts. An increase in the number of methoxymethyl groups ($-CH_2OMe$) in the donor molecule from 1 to 3 and the corresponding decrease in the number of alkyl substituents (R = Me, *n*-Bu) afford a more isospecific catalyst (Table 1, entries 2–11). For example, for $Bu_2P(O)(CH_2OMe)$ (Table 1, entries 6, 7), the I.I. value of polypropylene is 90.6–87.5% at Al/D_e = 13–26. For $BuP(O)(CH_2OMe)_2$ (Table 1, entries 8, 9), I.I. = 93.0–90.8% at Al/D_e = 10–37.5. For $(MeOCH_2)_3P(O)$ (Table 1, entries 10, 11; Fig. 2, curve *2*), I.I. = 93.5–92.2% at Al/D_e = 21.7–45.3. When the phosphine oxide molecule contains no methoxymethyl groups, the isospecificity of the catalyst is much lower, as is demonstrated by the data obtained for $Bu_3P(O)$ (Table 1, entry 20).

The volume of the alkyl substituent in the $R_nP(O)(CH_2OR')_{3-n}$ (R = Me, *n*-Bu, *iso*-Am) molecule also affects the stereospecificity of the forming catalyst. The bulkiest substituent isoamyl, which causes some steric hindrance to monomer coordina-

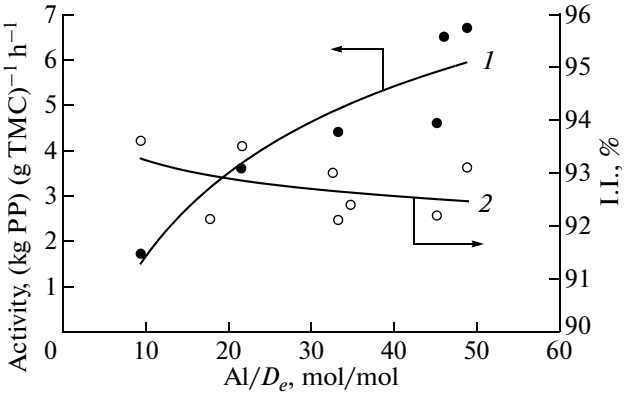

Fig. 2. (*1*) Activity of the TMC with the external donor $(CH_3OCH_2)_3P(O)$ in propylene polymerization in liquid monomer and (*2*) the isotacticity index of polypropylene as a function of the Al/D_e molar ratio (polymerization temperature of 70°C).

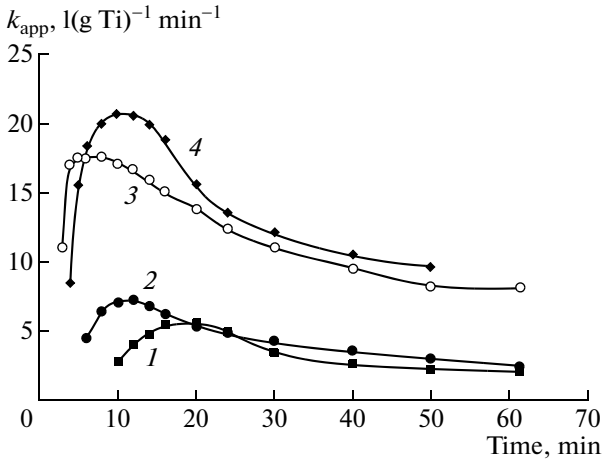

Fig. 3. Kinetics of propylene polymerization in liquid monomer on the TMC with the external donor *iso*-$AmP(O)(CH_2OCH_3)_2$ at Al/D_e molar ratios of (*1*) 9.3, (*2*) 13.5, (*3*) 16.5, and (*4*) 20.3 (polymerization temperature of 70°C).

tion on the active site, leads to the highest isospecificity of the catalyst at all Al/D_e ratios examined. The maximum I.I. value for *iso*-$AmP(O)(CH_2OMe)_2$ is 95–94% at Al/D_e = 9.3–16.3 (Fig. 1, curve *2*). As was shown above, a similar result was obtained for $(MeOCH_2)_3P(O)$ (Fig. 2, curve *2*).

The macrotacticity parameters of the isotactic fractions of polypropylene determined from the D_{998}/D_{973} ratio in the IR spectra in the case of the donors *iso*-$AmP(O)(CH_2OMe)_2$ and $(MeOCH_2)_3P(O)$ were 96–98%. This parameter for the isotactic fraction of the polymer synthesized on the same TMC with phenyltriethoxysilane as D_e was also 97%.

The catalyst activity in propylene polymerization, like stereospecificity, depends on the nature of substituents in phosphine oxide and the $AlEt_3/D_e$ molar ratio, all other polymerization conditions being equal.

The data presented in Table 1 and in Figs. 1 and 2 show that the highest activity of the TMC is achieved with phosphine oxides containing one *iso*-Am or *n*-Bu group, two $MeOCH_2$ groups, and three $MeOCH_2$ groups. The optimum combination of the activity and isotacticity index for the donor *iso*-$AmP(O)(CH_2OMe)_2$ (**VI**) in polymerization without hydrogen is about 5 (kg PP) (g Cat)$^{-1}$ h^{-1} and 94%, respectively, which is similar to the results obtained on the same TMC with the standard donor phenyltriethoxysilane as D_e without hydrogen: activity of 5.6 (kg PP) (g Cat)$^{-1}$ h^{-1} and I.I. = 95%.

The dependences of the catalyst activity in propylene polymerization in the presence of the donors *iso*-$AmP(O)(CH_2OMe)_2$ (**VI**) and $(MeOCH_2)_3P(O)$ (**V**) on the $AlEt_3/D_e$ ratio are plotted in Figs. 1 and 2 (curves *1*), respectively. As can be seen from Fig. 1, in the case of donor **VI**, the activity increases to 5.0–6.5 (kg PP) (g Cat)$^{-1}$ h^{-1} with an increase in Al/D_e to 16–22. As Al/D_e is further increased to ~42, implying a decrease in the external donor concentration, the catalytic activity changes insignificantly. When donor **VI** is used, a catalytic activity of about 6.5 (kg PP) (g Cat)$^{-1}$ h^{-1} is achieved at Al/D_e ~ 20 (Fig. 1). With donor **V**, the same activity is attained at much larger Al/D_e ratios of 45–49.

The nature of R' in the substituent ($-CH_2OR'$) in phosphine oxide also exerts an effect on the catalytic properties of the TMC. At similar Al/D_e ratios, the replacement of methyl in this group with acyl ($-CH_2OAc$) increases the isotacticity index without affecting the catalytic activity, as is evident from a comparison of the results obtained for D_e = $Me_2P(O)(CH_2OAc)$ (Table 1, entries 15, 16) and $Me_2P(O)(CH_2OMe)$ (Table 1, entries 2, 3).

The substitution of the methoxyethyl group (donor **VIII**) for methoxymethyl group in $Bu_2P(O)(CH_2OMe)$ leads to some increase in the catalyst isospecificity at the same Al/D_e (Table 1, entries 17, 18). This is possibly due to the formation of a more optimal chelate. However, this substitution reduces the catalytic activity.

The diphosphine dioxide $[Bu_2P(O)CH_2]_2O$ (**IX**) is a less efficient D_e than the polydentate phosphine monoxides (Table 1, entry 19).

The kinetic curve of propylene polymerization in liquid monomer at 70°C at different Al/D_e molar ratios for *iso*-$AmP(O)(CH_2OMe)_2$ are shown in Fig. 3. In all cases, the maximum polymerization rate is achieved rapidly and then decreases with time. These kinetic data reflect the above-discussed effect of the Al/D_e ratio on the catalytic activity. Note that Al/D_e has some effect on the rate of decrease of the catalytic activity with time at a constant $AlEt_3$ concentration.

Hydrogen, which is used in olefin polymerization as a chain termination agent for molecular weight con-

Table 2. Influence of hydrogen on propylene polymerization on the TMC in the presence of polydentate phosphine oxides and phenyltriethoxysilane as external donors (polymerization in liquid monomer at 70°C)

Entry	TMC, g	Al/Ti, mol/mol	Al/D_e, mol/mol	$H_2 \times 10^{-2}$, mol/l	Activity, (kg PP) (g Cat)$^{-1}$ h^{-1}	I.I., %	$M_w \times 10^{-3}$	M_w/M_n
$PhSi(OEt)_3$								
1	0.0034	417	20.0	0	5.6	95.0	1000	8.6
2	0.0039	724	24.0	0.8	11.4	94.8	375	6.0
$Me_2P(O)CH_2OMe$ **(I)**								
3	0.0037	415	20.0	0	2.6	89.0	1000	5.0
4	0.0039	458	18.0	0.8	3.1	87.7	230	6.0
$MeP(O)(CH_2OMe)_2$ **(II)**								
5	0.0055	519	39.5	0	1.9	88.7	800	9.0
6	0.0039	515	35.5	0.8	3.0	81.3	180	5.6
$(MeOCH_2)_3P(O)$ **(V)**								
7	0.0048	497	45.3	0	4.6	92.2	900	11
8	0.0048	475	43.5	0.8	6.7	89.3	190	5.3
iso-$AmP(O)(CH_2OMe)_2$ **(VI)**								
9	0.0052	503	13.5	0	2.8	94.0	–	–
10	0.0052	515	13.2	0.8	5.8	92.1	–	–
11	0.0046	532	16.3	0	4.7	93.9	–	–
12	0.0046	611	16.7	0.8	8.9	91.1	–	–

trol, usually exerts an activating effect on the polymerization process [2]. In the case of phenyltriethoxysilane as the external donor, the activity of the TMC increases by a factor of 2–2.5 upon the introduction of 0.8×10^{-2} mol/l of H_2 (Table 2, entries 1, 2). When polydentate phosphine oxides are used as D_e for the TMC, the introduction of hydrogen into the polymerization zone also allows one to efficiently control the molecular weight of polypropylene and increases the polymerization rate. The corresponding data for the donors examined here are listed in Table 2 (entries 3–12). As can be seen, in the presence of hydrogen (0.8×10^{-2} mol/l), the catalytic activity increases by a factor of 1.5–2.5, depending on the nature of substituents in the phosphine oxide. The kinetic curves of propylene polymerization in liquid monomer in the presence and absence of hydrogen for isoamyl donor **VI** at two Al/D_e ratios (Fig. 4) also demonstrate the catalyst activation effect. The rate of propylene polymerization, which begins to decrease with time after reaching its maximum, falls more rapidly in the presence of hydrogen than without it. Note that, for the phosphine oxides examined, as distinct from silane, the introduction of hydrogen decreases the isotacticity index of polypropylene. For isoamyl donor **VI**, the I.I. value decreases from 94.0 to 91.1–92.1 (Table 2, entries 9–12).

Thus, the structure-related regularities revealed in the influence of polydentate phosphine oxides as external donors on the properties of the TMC in propylene polymerization show the way to structurally optimal phosphoryl-containing electron donors combining high activity and stereospecificity parameters. It seems most promising to study phosphine oxides containing methoxymethyl and acetoxymethyl groups

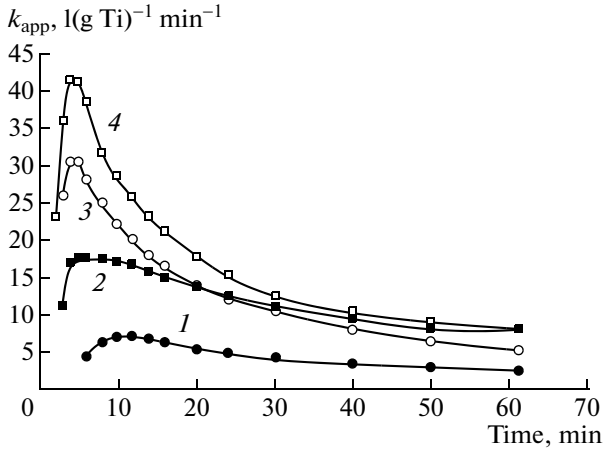

Fig. 4. Activating effect of hydrogen on the kinetics of propylene polymerization in liquid monomer on the TMC with the external donor *iso*-$AmP(O)(CH_2OCH_3)_2$: (*1*, *2*) propylene polymerization without hydrogen and (*3*, *4*) polymerization in the presence of hydrogen at $[H_2] = 0.8 \times 10^{-2}$ mol/l. The polymerization temperature is 70°C. Al/D_e = (*1*, *3*) 13.5 and (*2*, *4*) 16.5.

as substituents at the phosphorus atom in combination with branched alkyls.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-03-32761.

REFERENCES

1. Galli, G.V.J., *J. Polym. Sci., Part A: Polym. Chem.*, 2004, vol. 42, p. 396.
2. Albizatti, E., Giannini, U., Collina, G., Norista, L., and Resconi, L., in *Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications*, Moore, E.P., Jr., Ed., Cincinnati, Ohio: Hanser-Gardner, 1996, p. 11.
3. *Polypropylene Past, Present and Future: The Challenge Continues*, Milan: Montell Polyolefins, 1998.
4. Galli, P, Cecchin, G, Chadwick, J.C, Duca, D, and Veccelio, G, in *Metallorganic Catalysts for Synthesis and Polymerization*, Kaminsky, W., Ed., Berlin: Springer, 1999, p. 14.
5. Osipenko, N.G., Tsvetkov, E.N., Shcherbina, T.M., Ranneva, Yu.I., Petrov, E.S., Shatenshtein, A.I., and Kabachnik, M.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, no. 7, p. 1578.
6. Osipenko, N.G., Petrov, E.S., Ranneva, Yu.I., Tsvetkov, E.N., and Shatenshtein, A.I., *Zh. Obshch. Khim.*, 1977, vol. 47, no. 9, p. 1956.
7. Osipenko, N.G., Petrov, E.S., Ranneva, Yu.I., Tsvetkov, E.N., and Shatenshtein, A.I., *Zh. Obshch. Khim.*, 1977, vol. 47, no. 10, p. 2172.
8. Tsvetkov, E.N., Kron, T.E., Mironova, Z.N., and Kabachnik, M.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, no. 8, p. 1859.
9. Raevskii, O.A., Ignat'eva, T.I., Novikov, V.P., Solotnov, A.F., Kron, T.E., and Tsvetkov, E.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, no. 5, p. 1095.
10. Mironova, Z.N., Tsvetkov, E.N., Nikolaev, A.B., Kabachnik, M.I., and Dyadin, Yu.A., *Zh. Obshch. Khim.*, 1974, vol. 44, no. 6, p. 1217.
11. Mironova, Z.N., Tsvetkov, E.N., Nikolaev, A.B., and Kabachnik, M.I., *Zh. Obshch. Khim.*, 1967, vol. 37, no. 12, p. 2747.