ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 2, pp. 168–173. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © N.N. Sigaeva, R.Kh. Yumagulova, R.N. Nasretdinova, A.K. Frizen, S.V. Kolesov, 2009, published in Kinetika i Kataliz, 2009, Vol. 50, No. 2, pp. 182–187.

Kinetics of the Complex-Radical Polymerization of Methyl Methacrylate in the Presence of Initiating Metallocene Systems

N. N. Sigaeva, R. Kh. Yumagulova, R. N. Nasretdinova, A. K. Frizen, and S. V. Kolesov
Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia
e-mail: gip@anrb.ru

Received July 13, 2007

Abstract—The kinetics of methyl methacrylate polymerization in the presence of benzoyl peroxide + metallocene (ferrocene, titanocene dichloride, and zirconocene dichloride) initiating systems is considered, and the effects of the nature and amount of metallocene in the system are reported. The polymerization is assumed to be a complex-radical process. The structure of the complex-radical sites of chain propagation and a scheme of their formation are deduced from quantum-chemical calculations.

DOI: 10.1134/S0023158409020049

INTRODUCTION

Metallocenes are of great interest to macromolecular chemistry [1–5]. Most of the studies in this area have dealt with metallocene-containing catalytic systems involved in ion-coordination polymerization. The great majority of relevant publications have been devoted to the mechanism of catalytic and stereospecific actions and to the nature of the active sites of olefin polymerization in the presence of metallocene ion-coordination systems.

In recent years, highly efficient initiating systems containing metallocenes have been suggested for polymer chain propagation control under radical polymerization conditions [6–10]. The presence of metallocenes in the initiating system provides a higher polymerization rate and a high yield of the stereoregular polymer. However, the polymerization kinetics, including the kinetics of vinyl monomer polymerization in the presence of initiating metallocene systems, has some specific features. Revealing these features would elucidate the mechanism of the process.

Here, we report the kinetics of methyl methacrylate polymerization in the presence of benzoyl peroxide + metallocene (ferrocene, titanocene dichloride, and zirconocene dichloride) initiating systems and the effect of the nature of the metallocene and its amount in the polymerization system at the chain initiation and propagation stages.

EXPERIMENTAL

The bulk polymerization of methyl methacrylate (MMA) was carried out at 60 ± 0.05°C and a benzoyl peroxide (BP) concentration of 1.0×10^{-3} mol/l. To remove the stabilizer, the monomer was shaken with a 10% KOH solution, washed with water until neutral pH, dried over $CaCl_2$, and distilled two times in vacuo. The fraction with bp = 42°C at 100 Torr was collected.

The polymerization kinetics was studied by the dilatometric method. The reaction mixture in the dilatometer was pumped to a residual pressure below 1.33 Pa.

To estimate the effect of the metallocenes on chain initiation, the inhibition time was determined upon the introduction of the stable nitroxyl radical 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxyl into the polymerization system.

The molecular characteristics of poly(methyl methacrylate) were determined by gel permeation chromatography on a Waters GPC 2000 liquid chromatograph at 25°C using chloroform as the eluent. A system of three columns packed with Styragel was calibrated against polystyrene standards with a narrow molecular mass distribution ($M_w/M_n \le 1.2$). Benoit's universal relationship and the equation relating the molecular mass of the polymer to its characteristic viscosity were used in the calibration.

Quantum-chemical calculations were performed by the PBE/3z method [11] using the Priroda program. All geometric parameters were optimized without symmetry constraints. The types of stationary points were determined by estimating analytically calculated second derivatives with respect to energy.

RESULTS AND DISCUSSION

The initial rate of MMA polymerization in the presence of BP and titanocene dichloride (0.1×10^{-3} mol/l; Fig. 1, curve *2*) is considerably higher than that in the presence of BP alone (curve *1*). The bulk radical polymerization of many monomers, including the commercially important monomer MMA, shows autoacceleration (gel effect). This effect manifests itself as a simul-

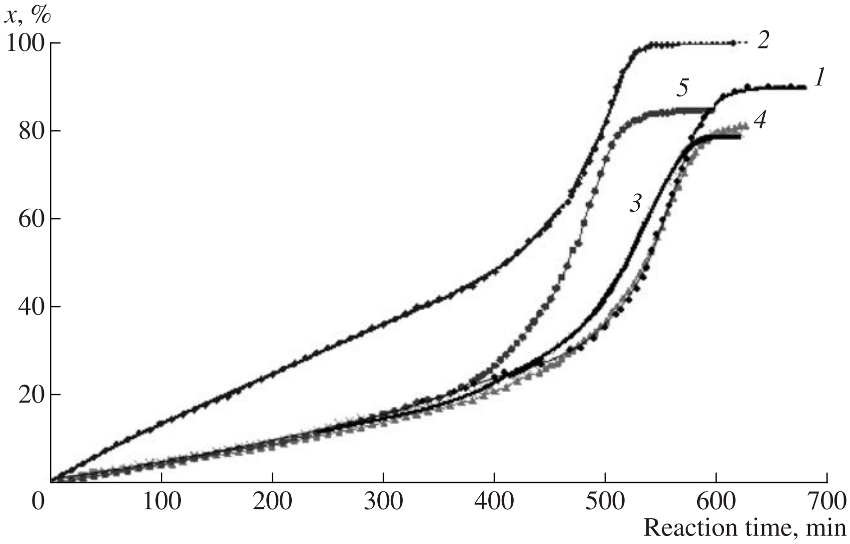


Fig. 1. Polymerization of MMA at 60°C in the presence of BP (1.0×10^{-3} mol/l) and Cp_2TiCl_2 at concentrations of (*1*) 0, (*2*) 0.1×10^{-3}, (*3*) 0.5×10^{-3}, (*4*) 1.0×10^{-3}, and (*5*) 1.5×10^{-3} mol/l.

taneous sharp increase in the polymerization rate and in the molecular mass of the resulting polymer after a certain monomer conversion is reached. Figure 1 indicates a well-defined gel effect. In the presence of titanocene dichloride (0.1×10^{-3} mol/l), this effect comes into play later and at higher MMA conversions than the same effect in the absence of a metallocene.

At metallocene concentrations of 0.5×10^{-3} and 1.0×10^{-3} mol/l in the polymerization system, the polymerization curves in the presence of both BP and Cp_2TiCl_2 and in the absence of the latter almost coincide (Fig. 1, curves *1*, *3*, *4*). As the Cp_2TiCl_2 concentration is raised to 1.5×10^{-3} mol/l (curve *5*), the onset point of the gel effect shifts to shorter reaction times and to lower monomer conversions. The initial polymerization rates in the presence of BP alone and in the presence of BP + Cp_2TiCl_2 ($(0.5–1.5) \times 10^{-3}$ mol/l) are equal. A similar situation is observed for MMA polymerization in the presence of the BP + Cp_2ZrCl_2 system.

The introduction of any concentration of ferrocene into the polymerization system increases the initial polymerization rate (Fig. 2). At $[Cp_2Fe] = 0.1 \times 10^{-3}$ and 0.2×10^{-3} mol/l, the kinetic curves indicate a pronounced gel effect. However, at $[Cp_2Fe] = 1.0 \times 10^{-3}$ mol/l (Fig. 2, curve *4*), almost no gel effect is observed, and this is among the findings indicating that the polymerization proceeds as a controlled complex-radical reaction. The weakening of the gel effect (i.e., a more uniform course of the reaction) was also observed for the polymerization of MMA and styrene [9, 10] when dicyclopentadienyltitanium dichloride, bis(isopropylcyclopentadienyl)tungsten dichloride, or bis(ethylcyclopentadienyl)niobium dichloride was introduced into the initiating system.

Thus, the metallocenes affect the kinetics of MMA polymerization. The character of their influence depends on the nature of the metallocene. In addition, the effect of a given metallocene on the process may depend substantially on its amount in the polymerization system.

The metallocene present in the initiating system changes both the polymerization rate and the molecular mass characteristics of the resulting polymer. Figure 3 plots M_w (curve *1*) and M_n (curve *2*) versus the MMA conversion (x) for poly(methyl methacrylate) obtained in the presence of the BP + Cp_2TiCl_2 initiating system. Both molecular masses increase with an increase in the monomer conversion. The polydispersity of the polymer (M_w/M_n) also increases. The molecular mass distri-

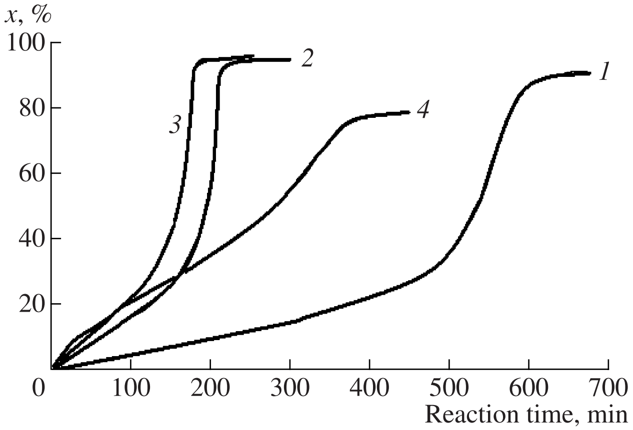


Fig. 2. Polymerization of MMA at 60°C in the presence of BP (1.0×10^{-3} mol/l) and Cp_2Fe at concentrations of (*1*) 0, (*2*) 0.1×10^{-3}, (*3*) 0.2×10^{-3}, and (*4*) 1.0×10^{-3} mol/l.

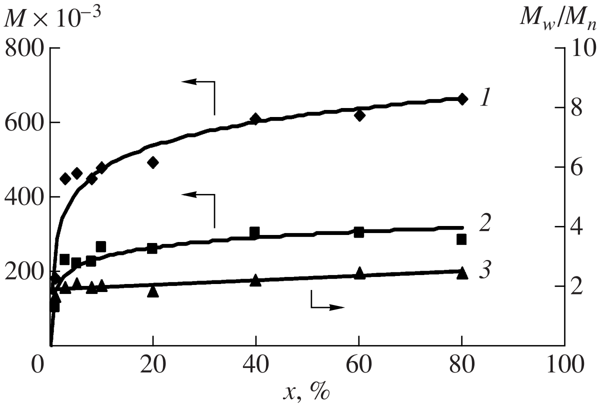


Fig. 3. (*1*) M_w, (*2*) M_n, and (*3*) M_w/M_n as a function of the monomer conversion for poly(methyl methacrylate) samples obtained in the presence of the BP + Cp_2TiCl_2 system. The reaction temperature is 60°C, and [BP] = [Cp_2TiCl_2] = 1.0×10^{-3} mol/l.

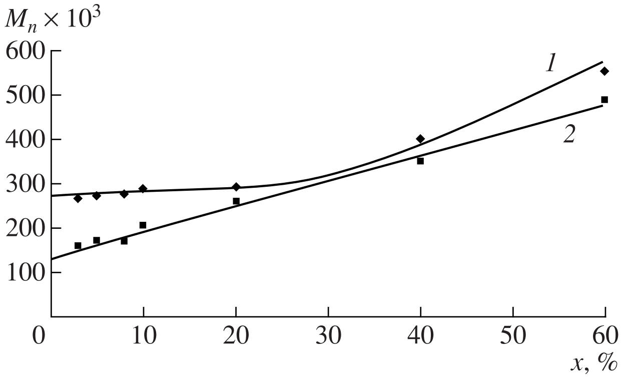


Fig. 4. M_n as a function of the monomer conversion for poly(methyl methacrylate) samples obtained in the presence of the BP + Cp_2Fe system with [Cp_2Fe] = (*1*) 0.1×10^{-3} and (*2*) 1.0×10^{-3} mol/l. The reaction temperature is 60°C, and [BP] = 1.0×10^{-3} mol/l.

bution curves are unimodal and the distribution shifts to larger molecular masses. For the polymers obtained under classical radical polymerization conditions, this increase in M_w and M_n with an increase in x is unnatural. If the kinetics of the process undergoes no sharp changes, the molecular mass values usually remain invariable and the M_w/M_n ratio is close to 2.

When Cp_2Fe at a concentration of 0.1×10^{-3} mol/l is introduced into the polymerization system (Fig. 4, curve *1*), the molecular mass at the early stages of the reaction remains almost unchanged. Both M_w and M_n increase dramatically in the monomer conversion at which the gel effect sets in. Thus, the above ferrocene concentration only accelerates the polymerization process without exerting any effect on the molecular mass characteristics of the product. In the presence of 1.0×10^{-3} mol/l of ferrocene, the molecular mass of poly(methyl methacrylate) increases from the very beginning of the process. The dependence of M_n on x is linear, which can be due to the reaction taking place via the "quasi-living" polymerization mechanism. However, the polydispersity increases during polymerization, and the M_w/M_n ratios are larger than the values characteristic of the "living" polymerization processes. Similar results were published earlier [9, 10].

The above data show that the influence of the metallocene is not limited to its catalytic effect on BP decomposition, contrary to what was assumed previously [6]. The specific features of the effect of ferrocene on MMA polymerization and on the molecular mass characteristics of the resulting polymer can be attributed to the complex-radical character of the reaction considered. We believe (by analogy with an earlier study [8]) that metallocene–BP complexes form in this case. The chain grows on both free and complex-bound radical sites. The possibility and mechanism of the formation of the complex radical sites depend on the nature of the metallocene and on the polymerization conditions.

Since metallocenes affect the chain propagation step, they should also influence the initiation step. Indeed, when the polymerization occurs in the presence of the stable nitroxyl radical 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxyl, the duration of the induction period depends on the metallocene. For example, at [Cp_2TiCl_2] = 0.5×10^{-3} mol/l and an inhibitor concentration of 0.375×10^{-4} mol/l, the induction period is 40 min, whereas it is 90 min in the presence of Cp_2ZrCl_2 under the same conditions. Almost no induction period is observed when the nitroxyl radical is introduced into the polymerization system containing Cp_2Fe (the induction period is 4.5 min at an inhibitor concentration of 1.25×10^{-4} mol/l). In the last case, the induction period remains unchanged at higher inhibitor concentrations.

The nature of the metallocene has an effect on the initiation rate (see the table), which was calculated using the familiar equation

$$w_i = \mu Z/\tau,$$

where τ is the induction period, Z is the inhibitor concentration, and μ is the stoichiometric coefficient for the reaction between the inhibitor and the propagating radical. It is assumed that each stable radical terminates one reaction chain; that is, $\mu = 1$.

The data listed in the table demonstrate that the initiation rates in the systems containing Cp_2TiCl_2 and Cp_2ZrCl_2 differ by a factor of ~3. The initiation rate increases slightly with an increasing metallocene concentration. The initiation rate in the presence of the ferrocene-containing system is considerably higher than the initiation rate in the presence of Cp_2TiCl_2 or Cp_2ZrCl_2.

Rates of polymerization initiation and MMA polymerization in the presence of the BP + metallocene systems at 60°C and $[BP] = 1.0 \times 10^{-3}$ mol/l

Metallocene (MC)	$[MC] \times 10^3$, mol/l	$w_i \times 10^6$, mol l^{-1} min^{-1}	$w_p \times 10^3$, mol l^{-1} min^{-1}	$k_{prop}/k_{term}^{1/2}$, $mol^{1/2}$ $(l\ min)^{-1/2}$
Cp_2TiCl_2	0.2	0.6	6.3	0.9
	0.5	1.1	5.6	0.6
	1.0	1.2	4.7	0.5
Cp_2ZrCl_2	1.0	0.4	4.1	0.7
Cp_2Fe	0.2	21.9	18.5	0.4
	0.5	27.1	25.3	0.5
	1.0	30.0	28.2	0.6

The steady-state radical polymerization rate is

$$w_p = \frac{k_{prop}}{(k_{term})^{0.5}}[M]\sqrt{w_i},$$

where [M] is the monomer concentration; k_{prop} and k_{term} are the rate constants of chain propagation and termination, respectively; w_p and w_i are the experimentally determined polymerization and initiation rates, respectively. The $k_{prop}/k_{term}^{1/2}$ values determined from this equation for the reactions that occur in the presence of the metallocenes are larger than those for polymerization in the presence of BP alone. $k_{prop}/k_{term}^{1/2}$ values of the same order of magnitude were observed for MMA polymerization in the presence of the classical Lewis acids $AlBr_3$ and $ZnCl_3$ (0.14 and 0.47, respectively) [12]. However, the acid/monomer molar ratio was 0.15 and 0.5, respectively. In the presence of the metallocenes, $k_{prop}/k_{term}^{1/2}$ changes considerably already at a metallocene-to-MMA ratio on the order of 10^{-4}. This means that the effect of the metallocene differs from the effect of the classical Lewis acids.

The increase in the $k_{prop}/k_{term}^{1/2}$ ratio can be due to an increase in the effective constant k_{prop} and a decrease in k_{term}. It was shown that k_{term} is smaller by four orders of magnitude in the presence of the metallocenes [13]. As follows from our data, active propagation sites uninvolved in chain termination appear in the system under certain conditions. Therefore, the small k_{term} value is a consequence of the decrease in the fraction of free radicals involved in quadratic-law termination.

Thus, the influence of the metallocene nature is due to the fact that the polymerization proceeds via a complex-radical mechanism involving both free and complex-bound radical active sites in the elementary events of chain propagation and termination. On the one hand, the metallocene coordinated to the growing radical participates directly in the chain propagation step. The metallocene nature affects the number of both the forming free radicals and complex-bound radicals. This is likely the way in which the process in the presence of titanocene or zirconocene dichloride in the initiating system takes place. On the other hand, it can be assumed that the direct formation of a ferrocene–BP complex occurs in the presence of ferrocene. This complex can decompose to yield a complex radical and a free radical. The complex radicals lead the polymerization, but they cannot be deactivated under the action of an inhibitor or via a disproportionation or recombination reaction.

It was reported that ferrocene forms a charge-transfer complex with BP [14]. The structure of this complex was determined by quantum-chemical calculations. The calculated ΔE value for the reaction

$$Cp_2Fe + (PhCOO)_2 \longrightarrow \underset{\mathbf{1}}{Cp_2Fe(PhCOO^{\bullet})_2} \qquad (I)$$

is –91.5 kJ/mol; i.e., the formation of this complex is energetically very favorable and, hence, the complex is very stable. According to the calculations, complex **1** is a ferrocene molecule bonded to two benzoyloxyl radicals (Fig. 5). The calculated charge on the ferrocene molecule is +1.2, and, accordingly, the charge on each $PhCOO^{\bullet}$ radical is –0.6. The decomposition of complex **1** via the reaction

$$Cp_2Fe(PhCOO^{\bullet})_2 \longrightarrow Cp_2Fe(PhCOO^{\bullet}) + PhCOO^{\bullet}, \qquad (II)$$

which yields one free $PhCOO^{\bullet}$ radical and one $Cp_2Fe(PhCOO^{\bullet})$ radical coordinated to ferrocene, is unlikely because the calculated ΔE value for this reaction is 131 kJ/mol. The generation of radicals by complex **1** via the reaction

$$Cp_2Fe(PhCOO^{\bullet})_2 \longrightarrow Cp_2Fe + 2PhCOO^{\bullet} \qquad (III)$$

is still less probable because ΔE of this reaction is 189.1 kJ/mol. Thus, the ferrocene–BP complex alone cannot generate propagating radicals at a high rate. However, it can be assumed that monomer molecules participate in the formation of radicals from this complex. Quantum-chemical simulation of the interaction of complex **1** with an MMA molecule showed that this

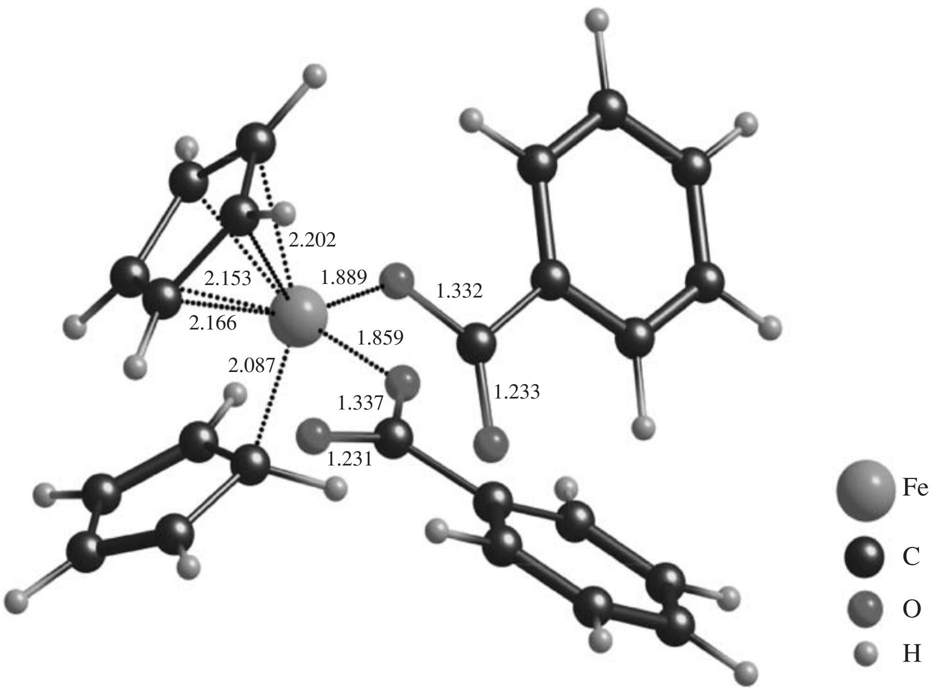


Fig. 5. Structure of charge-transfer complex $Cp_2Fe(PhCOO^{\bullet})_2$ (**1**). The interatomic distances are in Å.

interaction indeed generates free radicals and radicals bound to ferrocene:

$$Cp_2Fe(PhCOO^{\bullet})_2 + CH_2{=}C(CH_3)(COOCH_3) \longrightarrow Cp_2Fe(PhCOO^{\bullet}) + PhCOO{-}CH_2{-}{}^{\bullet}C(CH_3)(COOCH_3). \quad \text{(IV)}$$

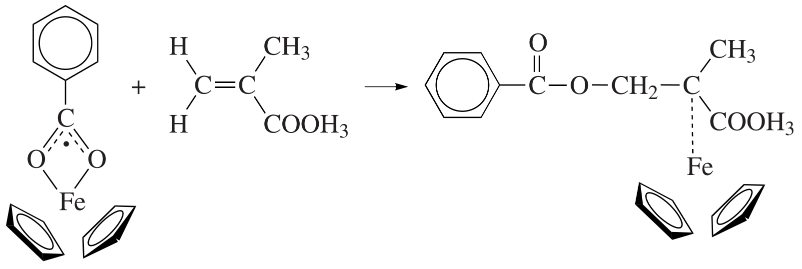
The calculated heat of reaction (IV) is 33.9 kJ/mol, indicating that this reaction can occur. Thus, both free and complex sites of chain propagation are generated in the system at the initiation stage.

It was assumed earlier [8] that the growing radicals ($R^{\bullet}$) turn into complex-bound radicals, for instance, via the reaction

$$Cp_2Fe + R^{\bullet} \longrightarrow Cp_2Fe\cdots R^{\bullet}. \quad \text{(V)}$$

Quantum-chemical calculations [15] demonstrated that an energy of >130 kJ/mol is required for this reaction to occur. Therefore, this route of the formation of growth sites is unlikely.

We believe that the benzoyloxyl radicals coordinated to ferrocene, $Cp_2Fe(PhCOO^{\bullet})$, which result from reaction (IV), are precursors of the complex-radical sites of chain propagation ($Cp_2Fe\cdots R^{\bullet}$), which cannot participate in chain termination reactions. It can be assumed that these "living" active sites form via the insertion of the first MMA molecule into the Fe–O bond:



In the presence of the cyclopentadienyl derivatives of titanium and zirconium dichlorides, polymerization can proceed as a "living" reaction without chain termination [9, 10] via the atom transfer radical polymerization (ATRP) mechanism. In this mechanism, a halogen atom is transferred to the growing polymer radical, which is impossible for ferrocene.

Thus, the absence of the inhibition effect of the stable nitroxyl radical in the presence of the ferrocene + BP initiating system is likely due to the fact that propagating radicals coordinated to ferrocene, which cannot participate in chain termination reactions, form already at the initiation stage. At low ferrocene concentrations (lower than the BP concentration), the number of the resulting complex-bound sites of chain growth is not large. However, an increase in the amount of ferrocene increases the fraction of these sites, weakening the gel effect.

REFERENCES

1. Kaminsky, W., *J. Chem. Soc., Dalton Trans.*, 1998, no. 9, p. 1413.
2. Soares, J.B.P. and Hamielec, A.E., *Polymer*, 1995, vol. 36, no. 11, p. 2257.
3. Ewen, J.A., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 21, p. 6355.
4. Kaminsky, W., Kulper, K., Brintzinger, H.H., and Wild, F.R.W.P., *Angew. Chem.*, 1985, vol. 97, no. 6, p. 507.
5. Ewen, J.A., Jones, R.L., and Rasavi, A., *J. Am. Chem. Soc.*, 1988, vol. 110, no. 18, p. 6255.
6. Puzin, Yu.I., Yumagulova, R.Kh., Kraikin, V.A., Ionova, I.A., and Prochukhan, Yu.A., *Vysokomol. Soedin., Ser. B*, 2000, vol. 42, no. 4, p. 691 [*Polym. Sci., Ser. B* (Engl. Transl.), vol. 46, nos. 3–4, p. 90].
7. Kraikin, V.A., Ionova, I.A., Puzin, Yu.I., Yumagulova, R.Kh., and Monakov, Yu.B., *Vysokomol. Soedin. Ser. A*, 2000, vol. 42, no. 9, p. 1569 [*Polym. Sci., Ser. A* (Engl. Transl.), vol. 42, no. 9, p. 1042].
8. Sigaeva, N.N., Kolesov, S.V., Abdulgalimova, A.U., Garifullina, R.N., Prokudina, E.M., Spivak, S.I., Budtov, V.P., and Monakov, Yu.B., *Vysokomol. Soedin., Ser. A*, 2004, vol. 46, no. 8, p. 1305 [*Polym. Sci., Ser. A* (Engl. Transl.), vol. 46, no. 8, p. 784].
9. Grishin, D.F., Semenycheva, L.L., Telegina, E.V., Smirnov, A.S., and Nevodchikov, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 2003, no. 2, p. 482.
10. Grishin, D.F., Shchepalov, A.A., Telegina, E.V., Ignatov, S.K., Razuvaev, A.G., and Semenycheva, L.L., *Vysokomol. Soedin., Ser. A*, 2005, vol. 47, no. 6, p. 943 [*Polym. Sci., Ser. A* (Engl. Transl.), vol. 47, no. 6, p. 574].
11. Laikov, D.N. and Ustynyuk, Y.A., *Russ. Chem. Bull., Int. Ed.*, 2004, vol. 54, no. 3, p. 820.
12. Kabanov, V.A., Zubov, V.P., and Semchikov, Yu.D., *Kompleksno-radikal'naya polimerizatsiya* (Complex-Radical Polymerization), Moscow: Khimiya, 1987.
13. Prokudina, E.M., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Ufa: Inst. Org. Chem., 2004.
14. Rixin, L., Xiaohong, Z., and Shikang, W., *Acta Polym. Sci.*, 1994, no. 3, p. 374.
15. Frizen, A.K. and Khursan, S.L., *Bashkir. Khim. Zh.*, 2006, vol. 13, no. 1, p. 111.