ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 4, pp. 531–536. © MAIK "Nauka/Interperiodica" (Russia), 2008.
Original Russian Text © I.S. Il'ichev, N.B. Valetova, M.V. Moskalev, D.F. Grishin, 2008, published in Kinetika i Kataliz, 2008, Vol. 49, No. 4, pp. 556–561.

III INTERNATIONAL CONFERENCE "CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

Polymerization of Methyl Methacrylate Using the $NiX_2(PPh_3)_2$/Zn Catalytic System

I. S. Il'ichev, N. B. Valetova, M. V. Moskalev, and D. F. Grishin

Research Institute for Chemistry, Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, 630600 Russia
e-mail: ilis@uic.nnov.ru

Received November 19, 2007

Abstract—The $NiBr_2(PPh_3)_2$/Zn catalytic system in combination with the PhI initiator ensures methyl methacrylate polymerization in a wide temperature range. The polymer yield is determined by the ligand environment of the nickel atom, the reaction temperature, and the ratio of the components of the catalytic system. An analysis of the macrokinetic relationships and of the molecular-weight characteristics of the products indicates that polymerization occurs in a controlled regime.

DOI: 10.1134/S0023158408040125

INTRODUCTION

In recent years, transition metal complexes, including nickel complexes, have found wide use in controlled free-radical polymerization [1, 2]. For example, in 1996 the nickel(II) complex NiBr[*o*,*o*'-$(Me_2NCH_2)_2C_6H_3$] was used for the first time in the polymerization of methyl methacrylate (MMA) via the atom transfer radical polymerization (ATRP) mechanism [3]. Nickel complexes containing phosphine ligands [4–6] also efficiently accelerate the living radical polymerization of MMA via the ATRP mechanism, including that the process in the presence of Lewis acids acting as activators [1]. Alkyl halides, such as CCl_3Br, were suggested as polymerization initiators. Drawbacks of the $NiBr_2(PPh_3)_2$ complex are its low thermal stability above 80°C and its weak solubility in organic solvents (mainly toluene) under the MMA polymerization conditions. As a consequence, the process is slowed down.

The NiX_2L_2/Zn system, which is known rather well from the literature, is mainly used in combination with aryl halides to carry out the homo- and cross-coupling reactions of these aryl halides [7–11]. This is one of the most active systems generating nickel(0), which can perform homogeneous catalysis. The fact that Ni(II) is reducible to Ni(0) in situ under mild conditions makes it possible to carry out the reaction without an induction period and at lower temperatures than are required for organic systems involving Ni(0).

The NiX_2L_2/Zn system was not applied earlier to the polymerization of (meth)acrylates (except for the above-mentioned cases of using NiX_2L_2 complexes alone). Studies of the low-valence nickel complexes are few and deal with the use of nickel(0) complexes in combination with benzyl halides in styrene polymerization [12].

Using styrene, we showed earlier that it is possible to carry out the polymerization of vinyl monomers catalyzed by the $NiBr_2(PPh_3)_2$ nickel complex (5 mol % of the amount of monomer) in combination with zinc powder and PhI as the initiator [13].

Here, we report the initiator, solvent, temperature, and catalyst concentration effects on MMA polymerization in the presence of $NiX_2(PPh_3)$/Zn/PhX and on the properties of the resulting polymers.

EXPERIMENTAL

Chemicals

Acetonitrile, iodobenzene, bromobenzene, chlorobenzene, hexane, chloroform, acetone, and ethyl acetate were dried over calcined calcium chloride. Pyridine was dried over sodium hydroxide. All reagents were distilled under atmospheric pressure. Halogenated derivatives were stored in a dark vessel [14]. The boiling points of all solvents were in agreement with reference data [15].

Commercial products (alumina and $NiCl_2(PPh_3)_2$) were used without further purification.

Methyl methacrylate was washed to remove the inhibitor with a 10% aqueous solution of sodium hydroxide and then with water until neutral pH, dried over calcined sodium chloride, and purified by vacuum distillation [16].

The $NiBr_2(PPh_3)_2$ complex was synthesized according to a described procedure [17] from $NiBr_2 \cdot 3H_2O$ and triphenylphosphine in butanol. The trihydrate $NiBr_2 \cdot 3H_2O$ was used as received. Triphenylphosphine was recrystallized from ethanol.

Zinc powder was activated according to a known procedure [18] using a hydrochloric acid solution.

Table 1. Effect of the nature of the coinitiator and catalyst on the poly(methyl methacrylate) yield*

Entry	PhHal	$NiHal_2(PPh_3)_2$	PMMA yield, %
1	PhI	$NiCl_2(PPh_3)_2$	12.5
2		$NiBr_2(PPh_3)_2$	17
3	PhBr	$NiCl_2(PPh_3)_2$	4
4		$NiBr_2(PPh_3)_2$	7
5	PhCl	$NiCl_2(PPh_3)_2$	2
6		$NiBr_2(PPh_3)_2$	3

* Reaction conditions: $T = 65°C$, reaction time of 5 h, and acetonitrile/pyridine = 1 : 1 (vol/vol) medium, PhHal : MMA : $NiHal_2(PPh_3)_2$: Zn = 1 : 4 : 0.05 : 1 mol/mol.

Polymerization at 65°C

Accurately weighed samples of zinc powder (0.1228 g) and $NiBr_2(PPh_3)_2$ (0.0698 g) were placed in a reaction vessel, which was a tube with a magnetic stirrer, and then appropriate amounts of methyl methacrylate (0.8 ml), iodobenzene (0.2 ml), acetonitrile (0.32 ml), and pyridine (0.32 ml) were added. The tube was connected to a vacuum system and outgassed three times using liquid nitrogen for cooling. Next, the tube was sealed off and placed for a precisely prescribed time in a thermostat maintained at 65°C. After that, the tube was taken out of the thermostat and unsealed. The solution was decanted from the precipitate on the bottom of the tube, the precipitate was washed two times with small amounts of acetonitrile, and the liquid obtained was combined with the earlier decanted solution. The mixture was washed with chloroform and filtered using a folded filter. The filtrate was poured into stirred hexane. No polymer precipitated. To remove the residual monomer and initiator from poly(methyl methacrylate) (PMMA), the polymer was reprecipitated from chloroform. To separate the inorganic impurities, a solution of PMMA in chloroform was passed through a 5-mm-thick Al_2O_3 bed on a Schott filter and was washed with pure chloroform. Polymer samples were dried to constant weight in vacuo.

Polymerization at 85°C

Accurately weighed samples of zinc powder (0.02510 g) and $NiBr_2(PPh_3)_2$ (0.01430 g) were placed in a tube with a magnetic stirrer, and appropriate amounts of methyl methacrylate (1.61 ml), iodobenzene (0.043 ml), and the solvent (0.39 ml) were added. The subsequent procedures were carried out as described above.

Analysis of Products

The molecular weight (MW) and molecular weight distribution (MWD) of PMMA samples were determined by gel permeation chromatography on a Knauer (Germany) liquid chromatograph with a Linear-2 linear column (Phenomenex, United States). An RI Detector K-2301 differential refractometer and a UV detector with a working wavelength of 254 nm were used for measurements. The flow rate of the eluent (chloroform) was 1 ml/min at 25°C. Standard narrow-MWD polystyrene samples were used in calibration. The average MW values for the polymers under study were calculated using the results of calibration against polystyrene samples and standard formulas for PMMA [19].

NMR spectra were recorded on a Specord DPX 200 NMR Fourier spectrometer. Samples for NMR were dissolved in chloroform-d_1 ($CDCl_3$) and placed in special-purpose tubes.

RESULTS AND DISCUSSION

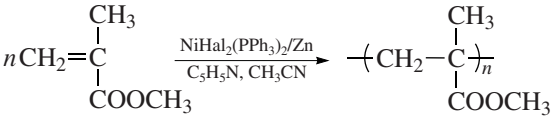
The catalyst based on zero-valence nickel was prepared in situ by the reduction of the $NiX_2(PPh_3)_2$ complex with zinc powder in the presence of CH_3CN as the solvent and pyridine:

$$NiX_2(PPh_3)_2 + Zn \longrightarrow Ni(PPh_3)_2 + ZnX_2,$$

where X = Cl or Br.

The resulting catalyst remains in the solution probably due to the coordination of its triphenylphosphine with acetonitrile, pyridine, or monomer molecules.

In the presence of the initiator (iodobenzene), the synthesized active nickel complexes induce MMA polymerization:



The aryl halides were iodobenzene, bromobenzene, and chlorobenzene. It turned out that MMA polymerization depends on the nature of the phenyl halide initiator. In particular, bromobenzene and chlorobenzene diminish the activity of the initiating system and decrease the polymer yield (Table 1, entries 4, 6). In addition, the coupling of MMA and these aryl halides favors, to a considerable extent, the formation of the homocoupling product, namely, biphenyl.

Under the same conditions, but with iodobenzene, the polymer yield is increased to 17% (Table 1, entry 2) and the biphenyl yield is reduced to trace amounts. The yield of the coupling product also depends on the aryl halide nature: it is highest for iodobenzene, whereas this product does not form at all when chlorobenzene is involved in the reaction.

On the whole, the catalytic system $(PPh_3)_2NiBr_2/Zn$ is less selective in reactions involving aryl chlorides and aryl bromides than in reactions using aryl iodides.

The nickel dichloride triphenylphosphine complexes were also used as precursors of the polymerization catalyst (Table 1). The highest efficiency of the formation of the zero-valence nickel complex was achieved with $NiBr_2(PPh_3)_2$. In this case, the polymer yield was higher (Table 1, entries 2, 4, 6). The yield of the coupling product of MMA and the corresponding aryl halide was also higher. Probably, unlike $NiBr_2(PPh_3)_2$, $NiCl_2(PPh_3)_2$ catalyzes both the polymerization and side processes of aryl halide homocoupling.

The experiments showed that the molecular weight characteristics of PMMA depend on the nature of the nickel phosphine complex. It follows from Fig. 1 that the shape of the MMD curves of the polymers synthesized in the presence of $NiCl_2(PPh_3)_2$ and $NiBr_2(PPh_3)_2$ depends substantially on the nature of the initiator. For iodobenzene as the initiator, the curve is unimodal, regardless of the nature of the nickel complex, whereas bimodal distributions are observed for bromobenzene and chlorobenzene.

Thus, the specific features of the polymerization process catalyzed by $NiX_2(PPh_3)_2$ depend markedly on the nature of the initiating component, as well as on the kind of halogen in the nickel phosphine complex.

The $NiBr_2(PPh_3)_2$/Zn/PhI catalytic system in the CH_3CN solvent and in CH_3CN in the presence of a base (pyridine) was used earlier in the cross-coupling of styrene with bromobenzene [20]. In our experiments, we varied the concentrations of MMA, $NiBr_2(PPh_3)_2$, and iodobenzene, as well as the reaction time and reaction medium.

As was expected, use of bulk polymerization increases the PMMA yield. In this case, as distinct from the synthesis of the polymer in solution, the higher the ratio between the amounts of the catalyst and MMA, the higher the PMMA yield, and vice versa. In addition, the final mixture contains no iodobenzene homocoupling product, i.e., biphenyl. This enhances the efficiency of this system as a polymerization catalyst.

We also carried out MMA polymerization at a higher temperature (85°C) and lower concentrations of the catalyst and initiator, i.e., under conditions similar to those used in an earlier study [21]. When the reaction was carried out in benzene using a catalyst ($NiBr_2(PPh_3)_2$ complex) and an initiator (iodobenzene), the PMMA yield was 7%. The addition of zinc powder to this system, favoring the in situ synthesis of the homogeneous nickel complex, increases the polymer yield to 44% (Table 4, entry 1).

These results clearly show that, regardless of the nature of the solvent used in MMA polymerization, the addition of zinc powder leads to a substantial increase in the PMMA yield even at low concentrations of the catalyst and initiator with respect to MMA. This is convincing evidence of the formation of a new catalyst, namely, a zero-valence nickel complex, and suggests that, as compared to the Ni(II) compounds, this catalyst is more active both in the homo- and cross-coupling

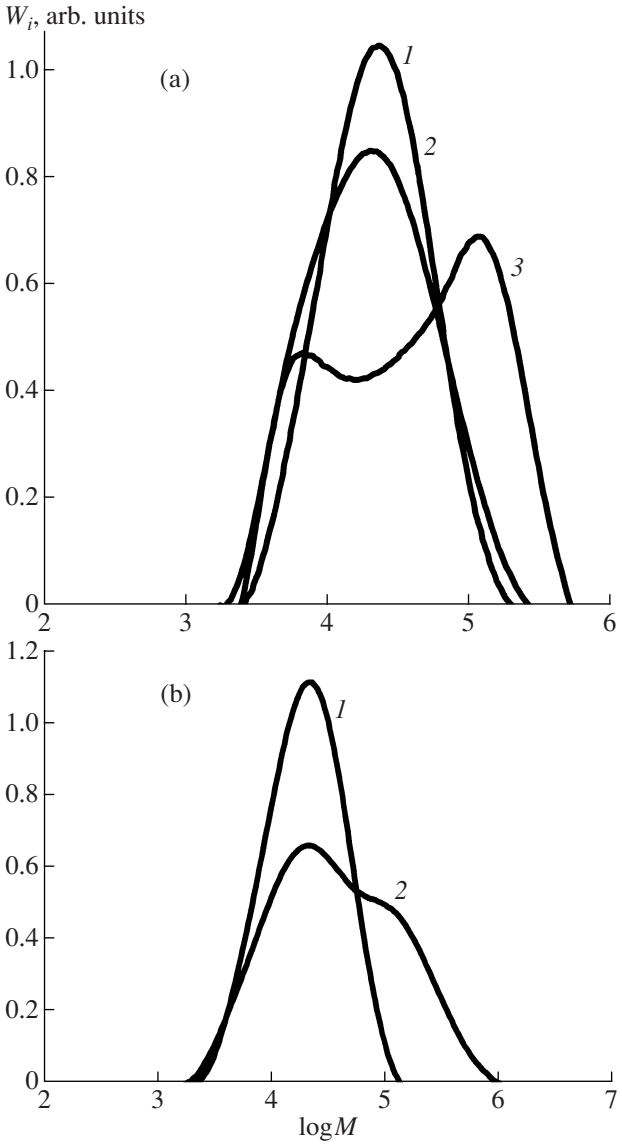


Fig. 1. Molecular-weight distribution curves for the PMMA samples obtained by MMA polymerization in the presence of the (a) $NiCl_2(PPh_3)_2$/Zn and (b) $NiBr_2(PPh_3)_2$/Zn systems and the initiators (*1*) iodobenzene, (*2*) bromobenzene, and (*3*) chlorobenzene. Reaction conditions: $T = 65$°C, reaction time of 5 h, and acetonitrile/pyridine = 1 : 1 (vol/vol) medium.

reactions described in the literature and in MMA polymerization. Furthermore, the addition of zinc powder to the catalytic system based on the nickel(II) phosphine complex decreases the molecular weight of the polymer. At the same time, the polydispersity index remains virtually unchanged.

The nature of the solvent is a factor affecting the MMA polymerization rate. It follows from the results presented (see Table 2) that the PMMA yield increases in the following order of solvents: benzene < dioxane < acetonitrile < pyridine. The dipole moment of these organic solvents increases in a different order, namely,

Table 2. Effect of the nature of the catalyst and solvent on the yield of poly(methyl methacrylate) and its molecular-weight characteristics*

Entry	Medium	Catalyst							
		$NiBr_2(PPh_3)_2$/Zn				$NiBr_2(PPh_3)_2$			
		PMMA yield, %	$M_n \times 10^{-3}$	TOF, h^{-1}	M_w/M_n	PMMA yield, %	$M_n \times 10^{-3}$	TOF, h^{-1}	M_w/M_n
1	Benzene	44	62	35	2.3	7	56	5.6	2.1
2	Dioxane	52	128.3	42	2.2	20	198	16	2.4
3	CH_3CN	57	23.5	46	2.2	12	20	9.5	2.1
4	Py	68	131	54	2.3	13	251	10	3.1
5	Bulk MMA	71	69	57	2.1	32	256	26	1.9
6**	Toluene	–	–	–	–	29	28	23	1.3

* M_w is the weight-average MW, and M_n is the number-average MW. Reaction conditions: $[NiBr_2(PPh_3)_2]$ = 0.125 mol %, [PhI] = 2.5 mol %, [Zn] = 2.5 mol % based on MMA, [MMA] = 7.55 mol/l, 85°C, and reaction time of 10 h.
** Data from [21]. Ethyl 2-bromopropionate at a concentration of 0.25 mol % based on MMA was used instead of PhI and Zn.

benzene < dioxane < pyridine < acetonitrile. However, the maximum polymer yield is achieved in the presence of pyridine (Table 2, entry 4). Probably, in this case, pyridine, which is a stronger coordinating agent [22] than acetonitrile, can better keep the zero-valence nickel complex in the system. Nevertheless, the solvent polarity plays an important role in MMA polymerization in the presence of the initiating composition considered.

The highest polymer yield is observed in bulk polymerization, i.e., in the absence of a solvent (Table 2, entry 5).

Our results made it possible to calculate one of the most important quantities characterizing the efficiency of the catalyst, namely, the turnover number (TON), as well as the turnover frequency (TOF) [23]. As can be seen from the data in Table 2, zinc powder increases the TOF of the catalyst (nickel(II) complex), i.e., the number of complete catalytic cycles performed by this catalyst in a unit time. The higher polymer yield on the zero-valence nickel complex can be considered only a relative estimate of its efficiency, whereas the calculated TOF values serve as a quantitative measure of the higher catalytic activity of Ni(0) as compared to $NiBr_2(PPh_3)_2$ under identical conditions of the polymerization process.

The reaction temperature also affects the TOF and TON of the catalyst. For instance, at 65°C, for the MMA polymerization catalyzed by the $NiBr_2(PPh_3)_2$/Zn/PhI system, TOF is 12 h^{-1}, while at 85°C TOF = 57 h^{-1}.

The turnover number is the absolute number of catalytic cycles performed by a catalyst until it is completely deactivated. In the present work, the TON of the catalyst at 65°C was 5700 and that at 85°C was 57000. A large TON value is a feature of a stable, long-living catalyst. In our case, TON takes intermediate values and increases with increasing temperature.

Table 3. Changes in the yield and molecular-weight characteristics of PMMA during MMA polymerization in the presence of the $[NiBr_2(PPh_3)_2]$/Zn/PhI system

Entry	Reaction time, h	PMMA yield, %	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1	1	31	5.8	9.4	1.64
2	2	43	15	27.8	1.85
3	3	54	17.1	32.8	1.92
4	5	69	20.7	40.5	1.95
5	7	83	22.2	46.3	2.08

Note: Reaction conditions: $[NiBr_2(PPh_3)_2]$ = 1.25 mol %, [PhI] = 25 mol %, [Zn] = 25 mol % (based on MMA), [MMA] = 7.52 mol/l, and reaction temperature of 65°C.

The results presented in Table 3 show that the yield and molecular weight of PMMA increase gradually with an increase in the reaction time. This means that polymerization proceeds uniformly (without a gel effect) up to high conversions (Fig. 2).

As follows from the data in Fig. 2, the logarithmic plot of the ratio of the initial monomer concentration $[M]_0$ to its current concentration $[M]_t$ vs. reaction time is linear. This indicates the absence of chain termination processes and is characteristic of "living" polymerization (Fig. 3).

The MWD curves of all PMMA samples synthesized in the presence of the proposed system are unimodal regardless of the MMA conversion (Fig. 3). An analysis of the MWD of the PMMA samples obtained at 65°C shows that the mode shifts progressively to

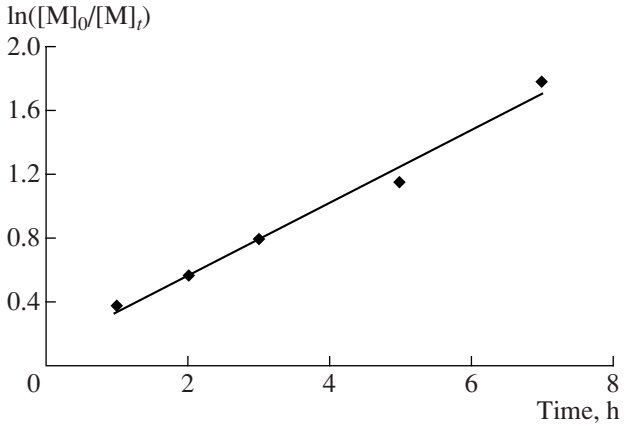


Fig. 2. Plot of $\ln([M]_0/[M]_t)$ vs. the reaction time for polymerization at 65°C in the presence of the $NiBr_2(PPh_3)_2/Zn/C_6H_5I$ catalytic system (the component concentrations are 1.25, 25, and 25 mol %, respectively).

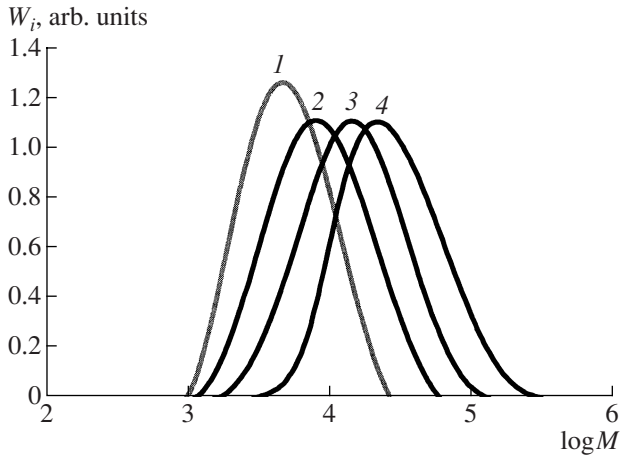


Fig. 3. Molecular-weight distribution curves for the polymer samples obtained at 65°C in the presence of the $NiBr_2(PPh_3)_2/Zn/C_6H_5I$ catalytic system (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 5 h after the beginning of the reaction.

higher molecular weights as the polymer yield increases (Table 3, Fig. 3). This situation is indicative of controlled polymerization.

A ^1H NMR study of the microstructure and stereoregularity of the PMMA samples showed that the polymer is atactic and is enriched with isotactic units. In particular, in the spectrum of PMMA obtained at 75°C in the presence of the classical initiator AIBN, the signals from the protons of the methyl group attached to the main chain are related as 56 : 38 : 6 (syndio-, hetero-, and isotactic signals, respectively) [4]. This ratio is 54 : 34 : 12 in the spectrum of the polymer synthesized at 65°C in the presence of the catalytic system proposed by us. However, the stereoregularity of the polymer obtained in the presence of $NiBr_2(PPh_3)_2$ and the ethyl 2-bromoisobutyrate initiator is similar to that of PMMA synthesized under similar conditions using the classical initiator AIBN (the signal ratios are 60 : 36 : 4 and 56 : 38 : 6, respectively) [4]. A comparison of these data with the results of the present work unambiguously indicates that the polymerization mechanism in our case differs from the ATRP mechanism proposed for the process that occurs in the presence of $NiBr_2(PPh_3)_2$ [4, 24, 25].

Thus, efficient MMA polymerization occurs in the presence of the catalytic system $NiBr_2(PPh_3)_2/Zn/PhI$ and the natures of the solvent, ligands, initiator, and halogen in the nickel complex have considerable effects both on the catalytic activity and on the properties of the resulting polymers.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 07-03-12017) and by the Russian Federation President's Foundation (grant no. MK-4197.2007.3).

The authors are grateful to T.A. Knyazeva for assistance in experiments.

REFERENCES

1. Kamigaito, M., Ando, T., and Sawamoto, M., *Chem. Rev.*, 2001, vol. 101, p. 3689.
2. Braunecker, W.A. and Matyjaszewski, K., *Prog. Polym. Sci.*, 2007, vol. 32, p. 93.
3. Granel, C., Dubois, Ph., Jerome, R., and Teyssie, Ph., *Macromolecules*, 1996, vol. 29, p. 8576.
4. Uegaki, H., Kotani, Y., Kamigaito, M., and Sawamoto, M., *Macromolecules*, 1997, vol. 30, p. 2249.
5. Hawker, C.J., Hedrick, J.L., Malmastrom, E.E., Trollsas, M., Mecerreyes, D., Moineau, G., Dubois, Ph., and Jerome, R., *Macromolecules*, 1998, vol. 31, p. 213.
6. Uegaki, H., Kotani, Y., Kamigaito, M., and Sawamoto, M., *Macromolecules*, 1998, vol. 31, p. 6756.
7. Feng, C.C., Nandi, M., Sambaiah, T., and Cheng, C.-H., *J. Org. Chem.*, 1999, vol. 64, p. 3538.
8. Hassan, J., Sévignon, M., Gozzi, C., Schulz, E., and Lemaire, M., *Chem. Rev.*, 2002, vol. 102, p. 1359.
9. Boldrini, G.P., Savoia, D., Tagliavini, E., Trombini, C., and Ronchi, A.U., *J. Organomet. Chem.*, 1986, vol. 301, p. C62.
10. Lebedev, S.A., Lopatina, V.S., Petrov, E.S., and Beletskaya, I.P., *J. Organomet. Chem.*, 1988, vol. 344, p. 253.
11. Zembayashi, M., Tamao, K., Yoshida, J., and Kumada, M., *Tetrahedron Lett.*, 1977, vol. 47, p. 4089.
12. Otsu, T., Tazaki, T., and Yoshioka, M., *Chem. Express*, 1990, vol. 5, p. 801.
13. Grishin, D.F., Valetova, N.B., Il'ichev, I.S., Prokhorova, M.G., and Beletskaya, I.P., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 11, p. 2027.
14. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Technics of Organic Chemistry*, vol. 7:

Organic Solvents: Physical Properties and Methods of Purification, New York: Wiley, 1955.

15. *Kratkii spravochnik po khimii* (Concise Handbook of Chemistry), Goronovskii, I., Nazarchenko, Yu.P., and Nekrach, E.F., Eds., Kiev: Naukova Dumka, 1974.
16. Rabinovich, V.A. and Khavin, Z.Ya., *Kratkii khimicheskii spravochnik* (Concise Handbook of Chemistry), Leningrad: Khimiya, 1978.
17. Venanzi, L.M., *J. Chem. Soc.*, 1958, vol. 2, p. 719.
18. Fieser, L. and Fieser, M., *Reagents for Organic Synthesis*, New York: Wilry, 1967.
19. Belen'kii, V.G. and Vilenchik, L.Z., *Khromatografiya polimerov* (Chromatography of Polymers), Leningrad: Khimiya, 1978.
20. Lebedev, S.A., Lopatina, V.S., Petrov, E.S., and Beletskaya, I.P., *J. Organomet. Chem.*, 1988, vol. 344, p. 253.
21. Moineau, G., Minet, M., Dubois, Ph., Teyssie, Ph., Senninger, T., and Jerome, R., *Macromolecules*, 1999, vol. 32, p. 27.
22. Sustmann, R., Hopp, P., and Boese, R., *J. Organomet. Chem.*, 1989, vol. 375, p. 259.
23. Diederich, F. and Stang, P.J., *Metal Catalyzed Cross-Coupling Reactions*, New York: Wiley–VCH, 1998.
24. Duquesne, E., Habimana, J., Degee, P., and Dubois, P., *Macromolecules*, 2005, vol. 38, p. 9999.
25. Uegaki, H., Kamigaito, M., and Sawamoto, M., *J. Polym. Sci., Part A: Polym. Chem.*, 1999, vol. 37, p. 3003.