2106 *Russian Chemical Bulletin, International Edition, Vol. 55, No. 11, pp. 2106—2108, November, 2006*

Novel initiating systems based on nickel phosphine complexes

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Binary composites based on dibromobis(triphenylphosphine)nickel and iodobenzene in the presence of zinc dust were shown to efficiently initiate polymerization of vinyl monomers in a wide temperature range (from –5 to +70 °C), which was shown for the synthesis of poly(methyl methacrylate) and polystyrene. The initiation scheme including reversible redox transformations of the nickel atom during polymerization was proposed.

Key words: initiating systems, radical polymerization, styrene, methyl methacrylate, dibromobis(triphenylphosphine)nickel.

The use of initiating systems based on organometallic compounds for radical polymerization is of unambiguous interest from the viewpoint of developing efficient methods for controlling polymeric chain growth[1,2] to purposefully govern the kinetic parameters of polymerization, molecular-weight characteristics of macromolecules, and, in some cases, the composition and structure of prepared polymers.[3] From practical point of view it seems urgent to search for novel low-temperature initiators controlling chain growth that allow polymerization of vinyl monomers without gel effect to be performed up to high conversion. Therefore, it is especially interesting to study transition metal complexes, whose ability to change reversibly the oxidation state in chemical reactions[4] can be used for purposeful synthesis of macromolecules in the regime of "living" chains.[5,6]

In the present work, we proposed novel binary initiators based on dibromobis(triphenylphosphine)nickel and iodobenzene for polymerization of vinyl monomers.

Experimental

Organic reagents (bromobenzene, iodobenzene, chloroform, ethyl acetate, and hexane) were dried over calcium chloride and distilled under atmospheric pressure.[7] Freshly distilled monomers were used for polymerization.[8]

The $NiBr_2(PPh_3)_2$ catalyst was synthesized from triphenylphosphine and nickel bromide trihydrate $NiBr_2 \cdot 3H_2O$ using an earlier described procedure[9]; commercial PPh_3, $NiBr_2 \cdot 3H_2O$, and $NiBr_2$ (anhydrous) were used.

Zinc dust was activated according to Clemmensen[10] by treatment with a 2% solution of hydrochloric acid followed by washing with water, ethanol, and acetone and drying to a constant weight under reduced pressure.

To conduct polymerization, precise weighed samples of zinc dust (0.0282 g) and $NiBr_2(PPh_3)_2$ (0.2 g) were placed in an ampule, and a calculated amount of monomer (0.62 mL of styrene or 0.57 mL of methyl methacrylate) and iodobenzene as coinitiator (0.06 mL) were added. The ampule was attached to a vacuum setup and deaerated three times cooling with liquid nitrogen, and then the ampules were sealed and placed in a thermostat. The prepared polymers were purified by reprecipitation with hexane from an ethyl acetate solution.

Results and Discussion

The initiating systems based on iodobenzene and bis(triphenylphosphine)nickel tribromide were found to be able in the presence of zinc dust to efficiently initiate polymerization of styrene (ST) and methyl methacrylate (MMA) in a wide temperature range from –5 to +70 °C (Table 1). It is known[11] that for the synthesis of poly(methyl methacrylate) using standard radical initiators self-acceleration resulting in a spontaneous increase in the polymerization rate and, correspondingly, uncontrolled growth of the molecular weight is observed already at 30% conversion (Fig. 1, curve *1*). A distinctive feature of the studied processes is the uniform (without gel effect) occurrence of polymerization up to high conversion (Fig. 1, curves *2* and *3*). This fact and a possibility to synthesize macromolecules with high conversion in a wide temperature range are of unambiguous interest for practical use.

The study of the effect of each component of the initiating system (PhI, Zn, and $(Ph_3P)_2NiBr_2$) showed

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2027—2029, November, 2006.

Table 1. Synthesis of polystyrene using the PhI—Ni(PPh_3)$_2$Br$_2$—Zn system[a]

Entry	Coinitiator	T/°C	τ/h	Conversion of monomer (%)
1	PhI	–5	27	11
2	PhI	25	27	45
3	PhI	70	1	31
4	PhI	70	3	37
5	PhI	70	7	61
6	PhI	70	27	93
7[b]	PhI	70	8.5	0
8[c]	PhI	70	12	8
9[d]	PhI	25	27	11
10[d]	PhI	–5	27	2
11[e]	PhI	70	1	2
12[f]	PhI	70	1	7
13	PhBr	70	1	4
14	$CHCl_3$	70	3	13

[a] The concentrations of $(Ph_3P)_2NiBr_2$, coinitiator, and zinc dust are 0.05, 0.1, and 0.08 mol mol^{-1} of monomer, respectively.

[b] No zinc additives.

[c] The concentration of $(Ph_3P)_2NiBr_2$ is 0.001 mol mol^{-1} of monomer, and the concentration of zinc dust is 0.001 mol mol^{-1} of monomer.

[d] Copolymerization of ST in the presence of MMA (50 : 50).

[e] $NiBr_2$ was used as initiator instead of $(Ph_3P)_2NiBr_2$.

[f] The concentrations of $(Ph_3P)_2NiBr_2$, coinitiator, and zinc dust are 0.01, 0.02, and 0.016 mol mol^{-1} of monomer, respectively.

that no polymerization of MMA and ST occurred when one of them was absent. The experimental data indicate that the mole ratio of the monomer and initiator components [ST] : [$(Ph_3P)_2NiBr_2$] : [PhI] : [Zn] = 1 : 0.05 : 0.1 : 0.08 is optimum for the kinetics of the process and conversion. A decrease in the concentration of the components of the initiating system retards the process substantially (see Table 1). The introduction of acetonitrile as a complexing agent decreases dramatically the polymerization rate. In the presence of this compound, the limiting conversion within 12 h was at most 6%.

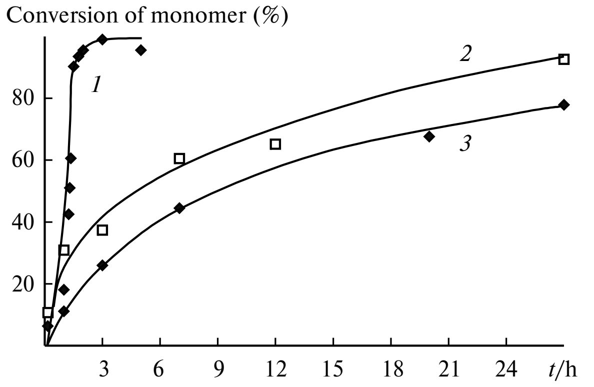
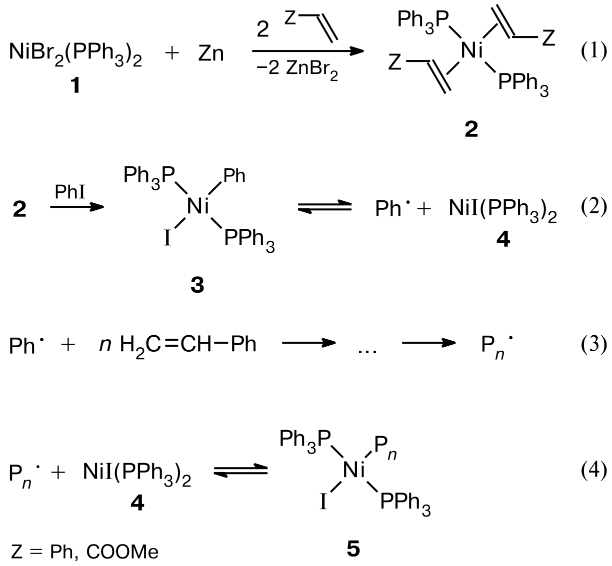


Fig. 1. Kinetic curves of polymerization of MMA (curves *1* and *3*) and ST (*2*) in the presence of azobutyric acid dinitrile (0.001 mol mol^{-1} of monomer) as initiator (*1*) and complex organometallic initiator (*2* and *3*). Conditions: $(Ph_3P)_2NiBr_2$ (0.05 mol mol^{-1} of monomer), PhI (0.1 mol mol^{-1} of monomer), Zn (0.08 mol mol^{-1} of monomer), T = 70 °C.

An interesting feature of vinyl monomer polymerization in the presence of the initiators under study is that the rate of ST polymerization under comparable conditions is somewhat higher than the rate of MMA polymerization (see Fig. 1, curves *2* and *3*). As known,[12] when using traditional radical initiators (azo compounds and peroxides) acryl and methacryl monomers in polymerization processes exhibit higher activity than ST. The results of studying ST polymerization in the presence of MMA and nickel-containing initiators also indicate a decrease in the rate of macromolecule synthesis upon the addition of the methacrylic monomer to the system (see Table 1). It cannot be ruled out that the observed features of MMA and ST polymerization in the presence of the nickel-containing catalysts are related to different coordination abilities of these unsaturated compounds toward the metal transition atom.

The results obtained along with published data on the reactivity of the halogen-containing nickel complexes, in particular, in homo- and cross-coupling reactions,[13—15] suggest the scheme of initiation in the presence of the systems under study (Scheme 1).

Scheme 1



Probably, the reaction of zinc with $(Ph_3P)_2NiBr_2$ affords the complex of zero-valent nickel (**2**) that oxidatively adds iodobenzene to form complex **3**. Similar compounds have been described earlier.[16] This complex is unstable and capable of homolytic dissociation to form phenyl radicals and, hence, is capable of initiation polymerization. Phenyl radicals actively initiate polymerization to form growing macroradicals $P_n^{\bullet}$ that can reversibly add to the nickel atom producing complex **5**. It is reasonable to assume that the reversible interaction of the growth radical with the univalent nickel compound prevents bimolecular termination and spontaneous increase in the molecular weight with high conversion, providing control of the polymeric chain growth under the radical initiation conditions.

A participation of the nickel complexes in the step of chain growth is indirectly confirmed by the fact that the formed polymers are slightly colored, and the initially red-colored polymer turns green at the moment of opening the ampule (probably, due to the oxidation of nickel sites). The direct proof of zinc involvement in the process of initiation of the polymerization is that virtually no polymer formation is observed (see Table 1), because Ni^{II} does not directly react with PhI.

Thus, we developed original catalytic composites based on bis(triphenylphosphine)nickel dibromide and iodobenzene, which in the presence of zinc dust can efficiently initiate polymerization of vinyl monomers in the wide temperature range (from –5 to +70 °C). This temperature interval corresponding to the conditions of industrial synthesis of the macromolecules and no necessity to use aluminum alkoxides as cocatalysts, which are easily hydrolyzed and inconvenient in work, are advantages of the proposed initiators compared to the known nickel-based analogs.[17,18]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32668).

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Received August 25, 2006