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New efficient boron-containing initiators of methyl methacrylate radical polymerization

S. Yu. Erdyakov,[a] O. A. Mel´nik,[b] M. E. Gurskii,[a]★ A. V. Ignatenko,[a] and Ya. S. Vygodskii[b]

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: bor@ioc.ac.ru
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

An efficient method for methyl methacrylate radical polymerization by tri-*n*-propyl-, triisopropyl-, and triisobutylborane ammonia complexes, including the addition of a boron-containing initiating agent into the monomer in air, was developed. An advantage of this method is that the reaction occurs at room temperature, requires no peroxide components, and leads to polymers with enhanced thermal stability.

Key words: radical polymerization, methyl methacrylate, trialkylborane ammonia adducts, nuclear magnetic resonance.

The use of organoboron compounds to initiate radical (co)polymerization of acrylic monomers makes it possible to obtain polymeric materials with improved physico-mechanical properties.[1,2] Of all polymerization initiators based on organoboranes, the first of which were proposed[3] as early as in 1942, the systems containing trialkylborane and stable organoelement peroxides as cocatalysts have been studied in most detail.[4]

One of the routes of further using organoboron compounds for radical polymerization initiation is related to transition of very air-sensitive alkylboron derivatives to their stable complexes with organic amines.[5,6] This compels, however, to introduce an additional component for amine binding into an already complicated system.

The purpose of this work is to study the radical polymerization of methyl methacrylate (MMA) by trialkylborane ammonia complexes, determine the influence of the trialkylborane ammonia structure on their initiating ability, and study the properties of polymers formed.

Results and Discussion

Ammonia complexes of tri-*n*-propyl- (**1**), triisopropyl- (**2**), and triisobutylborane (**3**) were taken for the study. This choice was due, first of all, to the difference in structures of hydrocarbon radicals formed by the oxidation of these substances with air oxygen.

The trialkylborane ammonia complexes were prepared using a standard scheme for the syntheses of amine adducts of organoboron compounds[7] (Scheme 1).

Scheme 1

$$R_3B \xrightarrow{NH_3} \underset{\mathbf{1-3}}{R_3B \cdot NH_3}$$

R = Pr^n (**1**), Pr^i (**2**), Bu^i (**3**)

Compounds **1—3** are colorless and much less pyrophoric liquids than the starting trialkylboranes; they can store in air for some time without self-ignition. Purity of the synthesized complexes was confirmed by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy. We also proposed a new method for synthesizing the tri-*n*-propylborane ammonia complex in an aqueous solution. This approach can be applied to compounds **2** and **3** as well (monitoring by the ^{11}B NMR spectrum of the organic phase). However, these complexes, unlike compound **1**, are distilled with partial (for **2**) or complete decomposition (for **3**) to the starting trialkylborane.

Taking into account that the synthesized ammonia complexes, unlike the complexes with amines, dissociate rather readily, we believed that they could be used as initiators of radical polymerization even without ligand removal by an acidic agent.

In the absence of peroxides, trialkylboranes do not initiate polymerization,[8] and the key step of initiation is the decomposition of a borane—peroxide—monomer complex (Scheme 2).

Since peroxyalkylboranes formed by the oxidation of trialkylboranes with air oxygen (Scheme 3) can act as peroxide, the addition of an organoboron compound to a

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Scheme 2

$$R_3B\cdot R'OOR'\cdot M \longrightarrow RM^{\cdot} + R'O^{\cdot} + R_2BOR'$$

M is monomer molecule

monomer in a non-inert atmosphere would allow one to avoid the use of peroxide components and maximally simplify the initiating composition. For another possible variant used for the initiation by alkylboranes of the radical addition of alkylmercaptanes at multiple carbon—carbon bonds,[9] an organoboron initiator can be introduced into a monomer under argon, thus excluding the stage of deaerating of the reaction mixture. It was not ruled out that, as for the use of an alkylborane—oxygen system, the process with conversion higher than 30% cannot be achieved.[10]

Scheme 3

$$R_3B + O_2 \longrightarrow R_2BOO^{\cdot} + R^{\cdot} \quad (1)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \quad (2)$$

$$ROO^{\cdot} + R_3B \longrightarrow (ROO)BR_2 + R^{\cdot} \quad (3)$$

Polymerization was carried out by the addition in air of 0.2—2.0 wt.% organoboron ammonia adduct into a monomer followed by the deaeration of the reaction mixture. As a result, solid transparent poly(methyl methacrylate) (PMMA) is formed in high yield.

The results obtained indicate that compounds **1—3** are efficient initiators of methyl methacrylate radical polymerization at 20 °C (Fig. 1). The highest conversion of the monomer is achieved in the presence of 1.0% initiator for almost all organoboron compounds proposed by us. In the case of compounds **1** and **3**, in concentration intervals of 0.2—1.5 and 0.5—1.5%, the molecular weight of PMMA decreases with an increase in the conversion expressed in units of intrinsic viscosity ($\eta_{\log}$) (Fig. 2). When using complex **2**, the conversion decreases with both the decrease and increase in the amount of the initiator over 1.0%. Primary trialkylboranes are more active initiating agents than secondary trialkylboranes,[6] which is related to a decrease in the complexation ability with respect to peroxide due to an increase in steric hindrances on going to compounds containing a Me group in the α-position to the boron atom.[11] Therefore, a similar dependence could be expected on going from complexes **1** and **3** to compound **2**, which, however, was not observed. It turned out that complex **3** is more active than **1**, which is explained by a higher constant of chain transfer to Bu^i_3B than to Pr^i_3B.[12] It is also remarkable that for using complex **3** the initiator concentration has a comparatively low effect on the MMA conversion. At the same time, for complex **1**, the yield increases substantially with an increase in the complex concentration to 2.0%, and for complex **2** more than twofold conversion decrease is observed with a change in the initiator concentration beyond 0.5—1.5%.

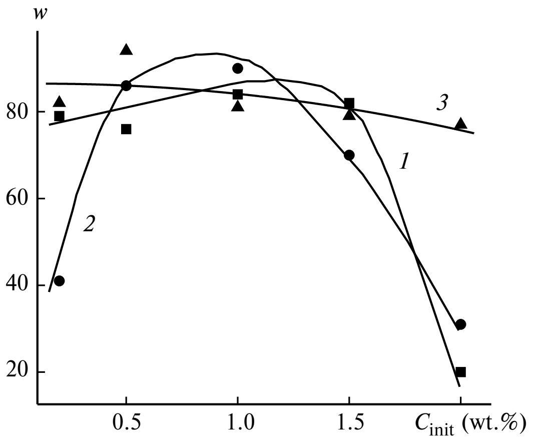

Fig. 1. Conversion of MMA (*w*) as a function of the initiator concentration (C_{init}) (polymerization at 20 °C, 48 h): $Pr^n_3B\cdot NH_3$ (*1*), $Pr^i_3B\cdot NH_3$ (*2*), and $Bu^i_3B\cdot NH_3$ (*3*).

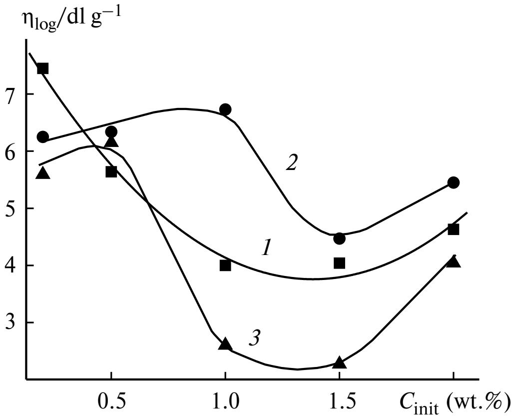

Fig. 2. Intrinsic viscosity of PMMA ($\eta_{\log}$) as a function of the initiator concentration (C_{init}) (polymerization at 20 °C, 48 h): $Bu^i_3B\cdot NH_3$ (*1*), $Pr^i_3B\cdot NH_3$ (*2*), and $Pr^n_3B\cdot NH_3$ (*3*).

Glass transition point and temperature of decomposition beginning are among the main characteristics of polymers, determining the region of their operating capacity. The thermomechanical and thermogravimetric studies showed that the PMMA obtained by us has enhanced glass transition point (130 °C) and temperature of decomposition beginning (320 °C) compared to the polymers synthesized in the presence of other radical initiators.[13] When the polymerization time decreases to 24 and 6 h (Fig. 3), a higher activity of complexes **3** and **1** compared to that of **2** becomes pronounced. In the first two cases, the polymer is formed already within 24 h in a yield close to that observed for 48 h, although with somewhat lower intrinsic viscosity.

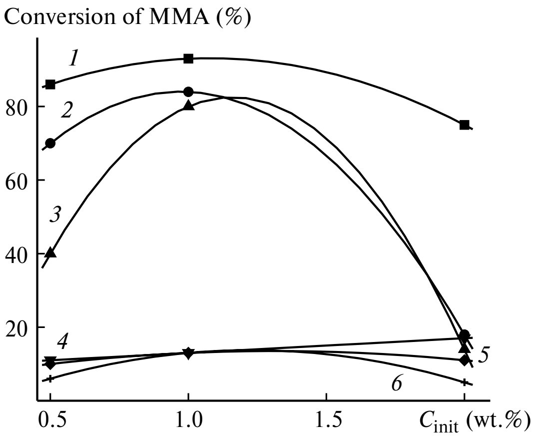

Fig. 3. Conversion of the monomer as a function of the concentration of initiators: $Bu^i_3B \cdot NH_3$ (*1*, *2*), $Pr^n_3B \cdot NH_3$ (*3*, *4*), and $Pr^i_3B \cdot NH_3$ (*5*, *6*) for reaction times of 24 (*1*, *3*, *5*) and 6 h (*2*, *4*, *6*).

The complicated plot of the molecular weight of PMMA (η_{log}) *vs.* initiator concentration (see Fig. 2) can be explained by a considerable influence of the $R_3B : O_2$ ratio on the polymerization rate.[10] When 1.0—1.5% concentrations of the initiator are used, the whole amount of unoxidized trialkylborane binds with monoperoxyborane, increasing the content of the "initiating source" in the system and, hence, the polymerization rate and polymer yield. In this case, however, the degree of polymerization decreases. At the same time, when the initiator concentration decreases, the amount of the initiating complex decreases, because the content of the oxidized species exceeds the content of free trialkylboranes.

When using the non-deaerated monomers, the reaction mixture solidifies completely only after 120 h (**1**, 1.0 wt.%), and the polymer is characterized by fairly high yield (61%) and intrinsic viscosity (3.47 dl g^{-1}). The decreased reaction rate can be due to considerable exceeding of the trialkylborane concentration over the oxygen concentration. It is of interest that this monomer does not virtually polymerize in the absence of oxygen (using thoroughly deaerated MMA). The reaction in air is inefficient either: the yield of PMMA after 240-h polymerization in the presence of 1.0% **1** was at most 5%.

Determination of thermodynamic parameters of dissociation of ammonia trialkylboranes. To reveal a relationship between the stability of the ammonia complexes of trialkylboranes, their structure, and initiating ability, we determined the thermodynamic parameters of dissociation of compounds **1—3** using ^{11}B NMR spectroscopy.

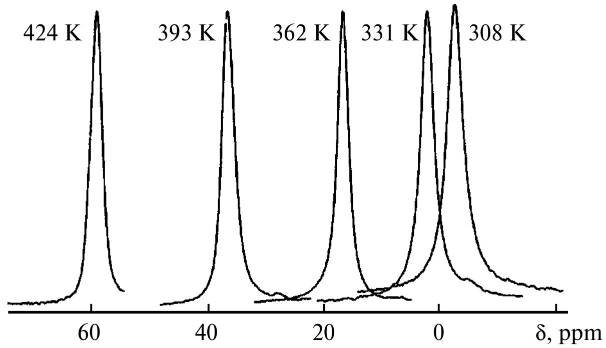

Fig. 4. Temperature plot of the ^{11}B NMR spectrum of complex **3**.

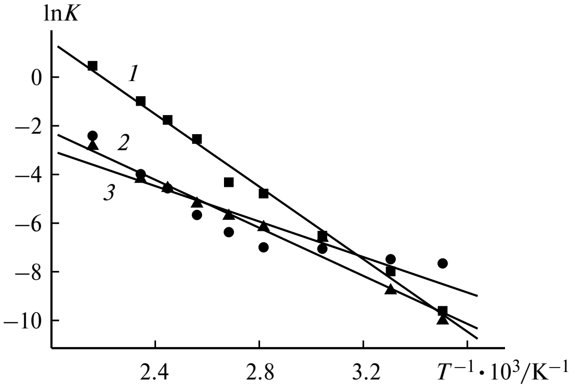

Fig. 5. Logarithm of the dissociation constant of the trialkylborane ammonia adducts as a function of the inverse temperature: $Bu^i_3B \cdot NH_3$ (*1*), $Pr^i_3B \cdot NH_3$ (*2*), and $Pr^n_3B \cdot NH_3$ (*3*).

Complexes of organoboron compounds with nitrogen-containing ligands at room temperature are characterized, as a rule, by a fast exchange,[14] *i.e.*, the ^{11}B NMR spectrum contains only one averaged peak, whose position corresponds to a specified content of the non-dissociated complex and free trialkylborane in a given equilibrium mixture (Fig. 4).

The thermodynamic parameters of dissociation of compounds **1—3** (Table 1) were calculated from the plot of the logarithm of dissociation constants of the complexes *vs.* inverse temperature. The data obtained indicate that at 298 K all three complexes differ slightly in stability, whereas at higher temperatures complex **3** exhibits a substantially higher affinity to dissociation.

According to the accepted mechanism of R_3B oxidation,[15] the formation of the second necessary component of the initiating system (alkylperoxyborane) is preceded

Table 1. Thermodynamic parameters of dissociation of the trialkylborane ammonia complexes

Complex	ΔG_{298}	ΔH	ΔS_{298} /J mol^{-1} K^{-1}
	kJ mol^{-1}		
$Pr^n_3B \cdot NH_3$	19.7±0.2	41.0±2.3	72±7
$Pr^i_3B \cdot NH_3$	17.9±0.5	30.3±5.3	42±10
$Bu^i_3B \cdot NH_3$	17.7±0.2	61.9±2.1	148±7

Table 2. Microstructures of the synthesized samples of PMMA

Initiator	rr	mr	mm	Pm/r	Pr/m	P_Σ	n_m	n_r	n
		%							
$Pr^n_3B \cdot NH_3$	0.68	0.25	0.07	0.64	0.16	0.80	1.56	6.44	4.0
$Pr^i_3B \cdot NH_3$	0.60	0.28	0.12	0.54	0.19	0.73	1.86	5.29	3.6
$Bu^i_3B \cdot NH_3$	0.63	0.25	0.12	0.51	0.17	0.68	1.96	6.04	4.0

Note. rr is a syndiotactic dyad (sequence of two syndiotactic units); mr is a heterotactic dyad (sequence of syndiotactic and isotactic units); mm is an isotactic dyad; Pm/r and Pr/m are the probabilities of iso- and syndioaddition to syndio- and isotactic dyads, respectively; P_Σ = Pm/r + Pr/m; n_m, n_r, and n are average lengths of iso-, syndio-, and all units, respectively.

by the radical oxidation of the starting complex including the initiation step (see Scheme 3, reaction (1)). This requires, however, a preliminary dissociation of the complex, because an adduct of the donor-acceptor type $Alk_3B \cdot O_2$ is irreversibly formed[16] in the initial step of trialkylborane oxidation with molecular oxygen. In this case, the dissociation energy of ammonia trialkylboranes should affect substantially the number of oxidized species that formed and, correspondingly, the initiating ability.

Therefore, it seemed important to elucidate the true composition of an initiator after it was added to methyl methacrylate. According to the ^{11}B NMR spectroscopic data, the content of the oxidized species decreases on going from complex **3** (38% BOOR) to compounds **1** and **2** (17 and 15% BOOR, respectively), which contradicts their stability. Thus, in this case, the determining factor is the structure of the alkyl radical at the boron atom rather than the affinity of the $R_3B \cdot NH_3$ complexes to dissociation.

Study of microstructures of synthesized polymers. The ^1H NMR study of PMMA synthesized using complexes **1**—**3** shows (Table 2) that the microstructures of the samples obtained somewhat differ, although they correspond, as a whole, to predominantly syndiotactic PMMA (high-resolution ^1H NMR spectra of PMMA are well studied, and the signals were assigned using the published data[17,18]).

In a series of the organoboron initiators, the number of syndiotactic (r) units decreases on going from the tri-*n*-propylborane complex to the triisobutyl- and triisopropylborane complexes. The statistics of the units also shows some decrease in the average length of syndiotactic units (n_r) in the series of initiators **1** < **3** < **2**. As can be seen from the presented results, in all cases, the chain growth does not obey the Bernulli statistics (in this case, $P_\Sigma = 1$). Polymerization in the presence of organoboron compounds has a complex-radical character,[19,20] and the propagation occurs when the monomer adds to the growing radical, whose coordination involves the low-lying p_z-orbital of the boron atom. This suggests an increase in steric hindrance for the corresponding r-orientation of the monomer to the growing radical in the series of complexes **1** < **3** < **2**.

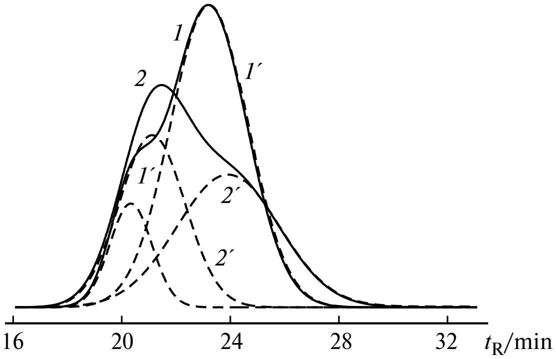

Fig. 6. Change in the shape of the GPC curve of PMMA (*1*, *2*) and its computer expansion (*1*′, *2*′) *vs.* time of polymerization: *1*, M_n = 75400, M_w = 165900, M_z = 377500, M_w/M_n = 2.20; *2*, M_n = 173 400, M_w = 575 000, M_z = 1068200, M_w/M_n = 3.32; $Bu^i_3B \cdot NH_3$ (1.5%), 48 (*1*) and 6 h (*2*). M_n is number-average molecular weight, M_w — weight-average molecular weight, M_z — *Z*-average molecular weight.

Superposition of two parallel mechanisms of polymerization (normal radical and complex-radical mechanisms) in the presence of the systems proposed is also indicated by the molecular weight characteristics of the synthesized polymers: the GPC curves of PMMA are evidence for a bimodal molecular weight distribution (Fig. 6).

Thus, radical MMA polymerization under the action of initiating systems based on the trialkylborane ammonia complexes $R_3B \cdot NH_3$ (R = Pr^n, Pr^i, Bu^i) and air oxygen occurs at room temperature, requires no additional peroxide components, and produces polymers with enhanced thermal stability. The triisobutylborane complex manifests the highest activity. The studies of the resulting polymers by GPC and NMR indicate that the propagation *via* two mechanisms: radical and complex-radical.

Experimental

All procedures on the synthesis of organoboron compounds were carried out under dry argon. Solvents were thoroughly dehydrated according to standard procedures.[21]

The starting tri-*n*-propyl-, triisopropyl-, and triisobutylboranes were synthesized from the corresponding alkyl halides using standard procedures.[22,23] Before polymerization, methyl methacrylate (Aldrich) was purified by distillation (b.p. 59 °C (10 Torr), $n_D^{20} = 1.4140$).

^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AC-200P instrument (working frequency 200.13 (^{1}H), 50.32 (^{13}C), and 64.21 MHz (^{11}B)). ^{1}H NMR spectra of PMMA were recorded on a Bruker DRX-500 instrument (500.13 MHz) at 298 K for 5% solutions of PMMA in $CDCl_3$.

The intrinsic viscosity was determined in an Ostwald viscometer at 25.0 °C for solutions of the polymer (20 mg) in chloroform (10 mL).

Thermomechanical curves were obtained at a constant load of 100 g and a punch diameter of 4 mm. The heating rate was 2.5 °C min^{-1}.

The thermal stability of polymers was determined by dynamic thermogravimetric analysis in air at a heating rate of 5 °C min^{-1} on a Q-1500 derivatograph.

Molecular weight characteristics of polymers were determined by GPC on a GPC-2 Waters chromatograph with a refractometric detector and three columns packed with ultrastirogel with a pore size of 10^4, 10^5, and 10^6 Å in THF at 30 °C. The number-average molecular weights (M_n) obtained by polystyrene standards were recalculated to true values by the universal calibration method using the following parameters of the Mark—Kuhn—Houwink—Sakurada equation: $k_1 = 1.6 \cdot 10^{-4}$, $a_1 = 0.706$ (polystyrene)[24]; $k_2 = 7.3 \cdot 10^{-5}$, $a_2 = 0.746$ (poly(methyl methacrylate)[13]).

Tri-*n*-propylborane ammonia complex (1). Tri-*n*-propylborane (15.13 g, 0.108 mol) was slowly added to a 25% aqueous solution of ammonia (8 mL, 0.120 mol), and the temperature of the system was maintained at a level not higher than 25 °C. The contents of the flask was stored for 1 h, transfered to a separating funnel, and the lower layer was poured out. The upper layer was purified by fractional distillation *in vacuo*. The yield of $Pr^n_3B \cdot NH_3$ was 6.8 g (70%), b.p. 50—51 °C (2 Torr) (*cf.* Ref. 25). ^{11}B NMR (*m*-xylene, 233 K), δ: –5.6. ^{1}H NMR ($CDCl_3$), δ: 0.25 (t, 6 H, CH_2B, J = 10.2 Hz); 0.92 (t, 9 H, CH_3, J = 6.2 Hz); 1.15 (m, 6 H, $C\underline{H_2}CH_3$); 3.73 (br.s, 3 H, NH). ^{13}C NMR ($CDCl_3$), δ: 18.6 (CH_3); 19.4 (CH_2); 27.8 (br, BC).

Trisiopropylborane ammonia complex (2). Ammonia (1.31 g, 0.077 mol) was added to triisopropylborane (12.5 mL, 9.78 g, 0.070 mol) with vigorous stirring and cooling. The reaction mixture was stirred for 3 h to remove excess NH_3. The yield of compound **2** was 100% (*cf.* Ref. 26). ^{11}B NMR (*m*-xylene, 233 K), δ: –6.1. ^{1}H NMR ($CDCl_3$), δ: 0.73 (m, 3 H, CH); 0.80 (d, 18 H, CH_3, J = 5.2 Hz); 2.15 (s, 3 H, NH). ^{13}C NMR ($CDCl_3$), δ: 17.97 (br, BC); 20.67 (CH_3).

Triisobutylborane ammonia complex (3). Ammonia (0.94 g, 0.055 mol) was added to triisobutylborane (13.8 mL, 9.218 g, 0.050 mol) with vigorous stirring and cooling. The reaction mixture was stirred for 3 h to remove excess NH_3. The yield of compound **3** was 100%. ^{11}B NMR (*m*-xylene, 233 K), δ: –5.6. ^{1}H NMR ($CDCl_3$), δ: 0.21 (d, 6 H, CH_2, J = 6.4 Hz); 0.85 (d, 18 H, CH_3, J = 6.6 Hz); 1.60 (m, 3 H, CH); 2.17 (s, 3 H, NH). ^{13}C NMR ($CDCl_3$), δ: 25.9 (CH_3); 27.1 (CH); 36.1 (br, BC).

Determination of constants and thermodynamic parameters of dissociation of ammonia complexes of trialkylboranes. ^{11}B NMR spectra were recorded for 20% solutions of compounds **1—3** in *m*-xylene sealed under argon. A temperature sensor of an NMR spectrometer (Variable temperature unit B-VT 1000/ER 4111 VT) was calibrated relatively to the ^{1}H NMR spectrum of a 80% solution of ethylene glycol in $CDCl_3$ for positive temperatures and of a 4% solution of methanol in DMSO-d_6 for negative temperatures (solutions available from Bruker served as standards). The influence of the temperature factor on a change in the chemical shift of a standard was compensated by the detection at each temperature of the ^{11}B NMR spectrum of $BF_3 \cdot Et_2O$, whose signal at this temperature was accepted as zero of the chemical shift scale. Each temperature of an ampule containing a sample was maintained constant in a resonator of a spectrometer. The position of the signal that remained unchanged with the further temperature decrease was taken as a true chemical shift, and the average value of three measurements was taken for calculation. Dissociation parameters were determined by a standard procedure.[14]

Polymerization of methyl methacrylate *in vacuo*. An initiator was added in air to a preliminarily weighed sample of the monomer. The reaction mixture was filtered in air into a glass ampule and deaerated. The temperature of the ampule was maintained at a needed level, and the ampule was opened in a specified time. The product was isolated by precipitation from a chloroform solution with methanol, multiply washed with methanol, and dried *in vacuo* at 60 °C.

Polymerization of methyl methacrylate in argon. ***A.*** Methyl methacrylate was placed in a glass ampule calcined *in vacuo* ($2 \cdot 10^{-2}$ Torr). After deaeration, complex **1** (1.0 wt.%) was added to the monomer under argon. The temperature of the ampule was maintained at 20 °C for 48 h, and the resulting PMMA was isolated and purified according to the above procedure.

B. The non-deaerated monomer and **1** (1.0 wt.%) were placed in a glass ampule under argon. The temperature of the ampule was maintained at 20 °C for 120 h, and PMMA was isolated according to the above procedure.

Polymerization of methyl methacrylate in air. A reaction mixture containing 1.0 wt.% complex **1** was filtered in air into a glass ampule, and the ampule was then stored for 240 h at 20 °C, after which the polymer was isolated by the above-presented procedure.

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