Organoboron Compounds as Lewis Acid Accelerators for the Aluminum Porphyrin-Mediated Living Anionic Polymerization of Methyl Methacrylate

Hiroshi Sugimoto, Takuzo Aida, and Shohei Inoue*

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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ABSTRACT: The polymerization of methyl methacrylate (MMA) initiated with methylaluminum tetraphenylporphyrin (1, X = Me) was accelerated at room temperature upon addition of the organoboron Lewis acids triphenylboron and tris(pentafluorophenyl)boron, affording polymers of narrow MWD with M_ns close to the expected values. The living character of the polymerization was demonstrated by the two-stage polymerization of MMA. The trialkylboron tri-*n*-butylboron neither accelerated nor terminated the polymerization. Use of other boron-containing Lewis acids such as $BF_3{\cdot}OEt_2$, BCl_3, triphenyl borate, and trimethylboroxin (trimethylcyclotriboroxane) for the polymerization of MMA resulted in rapid termination under similar conditions.

Introduction

Recently, we have discovered that the polymerization of methacrylic esters via enolatealuminum porphyrins (2) as the growing species (Scheme I)[1] is dramatically accelerated upon addition of bulky organoaluminum compounds such as methylaluminum bis(2,4-di-*tert*-butylphenolate) at room temperature (Scheme II: high-speed living polymerization).[2,3] This is understood in terms of the "Lewis acid-assisted coordinate anionic polymerization", where the accelerated attack of the growing species (2) occurs cleanly at the activated monomer upon coordination to the Lewis acidic organoaluminum compound. On the contrary, when simple trialkylaluminum are used as Lewis acids under similar conditions, the polymerization is terminated as a consequence of an undesired transmetalation reaction between the growing species (nucleophiles) and the organoaluminum compounds (electrophiles) (Scheme III).[3,4] Thus, the steric suppression of this undesired reaction is a prerequisite for the high-speed living polymerization assisted by organoaluminum-based Lewis acids.

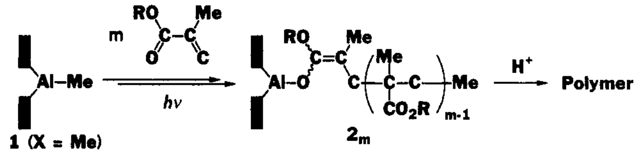
To extend the scope of this Lewis acid–assisted high-speed living polymerization, we chose as second candidates boron compounds. As for organoboron compounds, in particular, boron–carbon bonds are generally of π-bonding character[5] and therefore claimed to be much less subject to nucleophilic substitution reaction than organoaluminum compounds. In the present study, the polymerization of MMA mediated by 2 was investigated by using various boron-containing Lewis acids carrying boron–carbon, –halogen, and –oxygen bonds as accelerating agents, and the results were compared with those using organoaluminum compounds.

Experimental Section

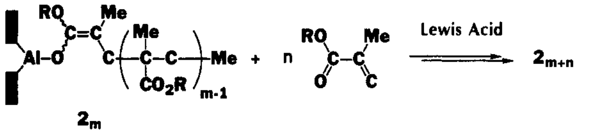
Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole (0.8 mol) and benzaldehyde (0.8 mol) in propionic acid (2.5 L) under reflux for 0.5 h, and the crude product, which precipitated when the reaction mixture was allowed to stand overnight at room temperature, was recrystallized from $CHCl_3$/MeOH (1/2 v/v) to give $TPPH_2$ in 20% yield.[6]

Dichloromethane (CH_2Cl_2) was washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled over CaH_2 in a nitrogen atmosphere. Deuterated dichloromethane (CD_2Cl_2), stirred with triethylaluminum (Et_3Al) at room temperature, was collected in a trap cooled in a liquid nitrogen bath after several freeze–thaw cycles in a nitrogen atmosphere. Benzene (C_6H_6) and deuterated benzene (C_6D_6) were distilled over sodium benzophenone ketyl in a nitrogen atmosphere. Methyl methacrylate (MMA) was fractionally distilled over CaH_2 under reduced pressure in a nitrogen atmosphere.

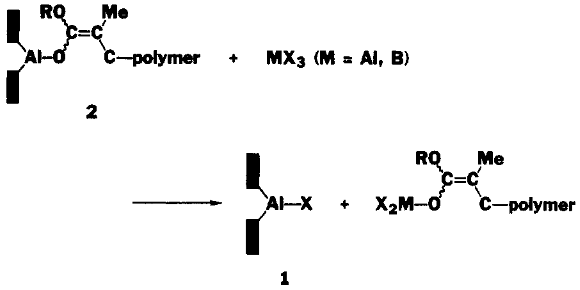
Scheme I



Scheme II



Scheme III



$BF_3{\cdot}OEt_2$, tri-*n*-butylboron (Bu_3B), and Me_3Al were fractionally distilled under reduced pressure in a nitrogen atmosphere. Trimethylboroxin (trimethylcyclotriboroxane) was fractionally distilled in a nitrogen atmosphere. BCl_3 (1.0 M hexane solution, Aldrich) was used as received. Triphenyl borate and triphenylboron ($(C_6H_5)_3B$) were recrystallized from dry C_6H_6 under nitrogen.

Tris(pentafluorophenyl)boron ($(C_6F_5)_3B$) was prepared as follows:[7] To a hexane solution (300 mL) of bromopentafluorobenzene (35 mmol, 4.4 g) was added BuLi (33 mmol, 22 mL of a 1.6 M hexane solution) at −78 °C by a hypodermic syringe in a nitrogen stream. The (pentafluorophenyl)lithium that formed separated from the reaction mixture as white precipitates. After 1 h of stirring at −78 °C, a hexane solution (10 mL) of BCl_3 (10 mmol) was added by a syringe to the reaction mixture. The mixture was stirred at −78 °C for 10 min, allowed to warm to

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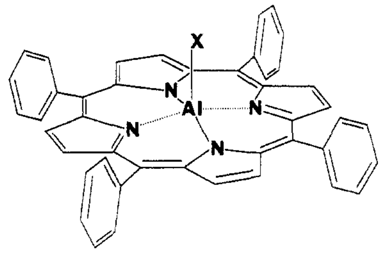
room temperature, and stirred for an additional 10 min at room temperature. After insoluble LiCl settled, the supernatant solution was transferred by a syringe in a nitrogen stream to a separate flask purged with dry nitrogen and evaporated to dryness under reduced pressure. The white powdery residue was subjected to sublimation in vacuo, followed by recrystallization from C_6H_6 in a nitrogen atmosphere, affording $(C_6F_5)_3B$ as white crystals (2.6 g, 50% yield based on BCl_3).

Preparation of Aluminum Porphyrins. Methylaluminum 5,10,15,20-Tetraphenylporphine (1, X = Me). To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing $TPPH_2$ (0.15 g, 0.25 mmol) under dry nitrogen were successively added CH_2Cl_2 (10 mL) and Me_3Al (1.2 equiv, 0.03 mL) by means of hypodermic syringes in a nitrogen stream, and the mixture was stirred for 1 h in a nitrogen atmosphere. Volatile fractions were removed from the reaction mixture under reduced pressure to leave 1 (X=Me) as a purple powder.[8]



(TPP)AlX (1)

Phenylaluminum 5,10,15,20-Tetraphenylporphine (1, X = Ph). To a 10-mL round-bottomed flask connected to a three-way stopcock containing a CH_2Cl_2 solution (1 mL) of $TPPH_2$ (6.1 mg, 0.01 mmol) was added a CH_2Cl_2 solution (0.1 mL) of Et_2AlCl (0.01 mmol) by a syringe in a nitrogen stream, and the mixture was stirred at room temperature under nitrogen. After 1 h, the reaction mixture was evaporated to dryness under reduced pressure to leave chloroaluminum 5,10,15,20-tetraphenylporphine (1, X = Cl) as a purple powder.[9] To this flask containing 1 (X=Cl) were successively added C_6H_6 (1 mL) and an ether solution (0.4 mL) of PhLi (0.03 mmol) by syringes in a nitrogen stream, and the mixture was stirred at room temperature under nitrogen. After 30 min, the reaction mixture was evaporated to dryness under reduced pressure to leave phenylaluminum 5,10,15,20-tetraphenylporphine (1, X = Ph) as a reddish orange powder.[10]

Polymerization. Polymerizations of Methyl Methacrylate (MMA) Initiated with Methylaluminum Porphyrin (1, X = Me) in the Presence of Organoboron Compounds. A typical example is given below by the polymerization of methyl methacrylate (MMA) with (TPP)AlMe (1, X = Me) as initiator: To a 50-mL round-bottom flask attached to a three-way stopcock containing a C_6H_6 solution (10 mL) of 1 (0.25 mmol) was added MMA (50 mmol, 5.4 mL) by a syringe in a nitrogen stream, and the mixture was illuminated at 35 °C by a xenon arc light (300 W) through a filter to cut out light of wavelengths shorter than 420 nm. After 2.5 h, the irradiation was stopped, and a C_6H_6 solution (0.8 mL) of triphenylboron ($(C_6H_5)_3B$, 1 equiv with respect to **2** (R=Me)) was added at room temperature. After the mixture was stirred for a definite time under diffuse light, an aliquot of the reaction mixture was taken out by a syringe in a nitrogen stream and subjected to ^1H NMR and gel permeation chromatography (GPC) analyses to determine the monomer conversion and to estimate the average molecular weights (M_w, M_n) of the polymer, respectively.

Two-Stage Polymerization of Methyl Methacrylate (MMA) in the Presence of Triphenylboron. To a 100-mL round-bottomed flask attached to a three-way stopcock containing a C_6H_6 solution (10 mL) of (TPP)AlMe (1, X = Me: 0.25 mmol) was added MMA (75 mmol, 2.0 mL) by a syringe in a nitrogen stream, and the mixture was irradiated with a xenon arc light (λ > 420 nm) at 35 °C. After 3 h of irradiation, a C_6H_6 solution (0.8 mL) of triphenylboron ($(C_6H_5)_3B$, 1 equiv with respect to **2** (R=Me)) was added, and the reaction mixture was stirred at room temperature under diffuse light. After 3 h, an aliquot of the reaction mixture was taken out by a syringe in a nitrogen stream. This sample was subjected to ^1H NMR analysis to confirm the complete consumption of MMA and analyzed by GPC to estimate the molecular weights of the polymer. The polymerization mixture remaining in the flask was allowed to stand at 25 °C for an additional 48 h, and then a second portion of MMA (150 mmol) was added. After 6 h, MeOH (5 mL) was added to the flask, and the reaction mixture was again subjected to ^1H NMR and GPC analyses.

Measurements. Gel permeation chromatography (GPC) measurements were performed at 40 °C on a TOSOH Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector and a variable-wavelength UV–visible detector, using tetrahydrofuran as eluent with a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes (TOSOH; M_n = 2 890 000, (M_w/M_n = 1.09), 422 000 (1.04), 107 000 (1.07), 43 900 (1.01), 16 700 (1.02), 9000 (1.06), 6200 (1.04), 4000 (1.10), and 2800 (1.05). ^1H and ^{13}C NMR measurements were performed in C_6D_6, $CDCl_3$, or CD_2Cl_2 using a JEOL GSX-270 spectrometer, where the chemical shifts were determined with respect to C_6H_6 (δ 7.40) or $CHCl_3$ (δ 7.28) for ^1H and CD_2Cl_2 (δ 54.0) for ^{13}C as internal standards.

Results and Discussion

Polymerization of Methyl Methacrylate (MMA) via an Enolatealuminum Porphyrin (2, R = Me) in the Presence of Boron Compounds. Various boron compounds were tested as Lewis acid accelerators for the polymerization of MMA initiated with methylaluminum porphyrin (1, X = Me). First examined were $BF_3{\cdot}OEt_2$ and BCl_3, which are highly acidic and commonly used for organic synthesis. For example, a C_6H_6 solution (10 mL) of a mixture of MMA and 1 (X=Me) with the mole ratio of 200 was irradiated at 35 °C with a xenon arc light (λ > 420 nm) to initiate the polymerization. During 3-h irradiation, all the molecules of the initiator (1, X = Me) were transformed into the growing enolate species (**2**, R = Me), and the conversion of MMA reached 6.2%, as determined by ^1H NMR.[11] At this stage, the irradiation was stopped and an equimolar amount of $BF_3{\cdot}OEt_2$ with respect to **2** (R=Me) was added to the system at room temperature, where the color of the solution immediately turned from dark reddish brown characteristic of **2** (R=Me) to dark green.[12] After 10 min under diffuse light, the monomer conversion was again measured, but it was virtually unchanged from the beginning (6.9%) and no longer increased upon prolonged reaction for 20 h under the same conditions. Use of BCl_3 ($[BCl_3]_0/[\mathbf{2}\ (R{=}Me)]_0$ = 1.0) in place of $BF_3{\cdot}OEt_2$ gave a similar result, where the color of the solution changed to dark reddish purple, characteristic of 1 (X=Cl), as soon as BCl_3 was added. When triphenyl borate or trimethylboroxin was used as the Lewis acid under similar conditions, the polymerization was again terminated, where the color of the system immediately turned to bright reddish purple as typically observed for 1 (X=OR,OAr).

In marked contrast with the above cases, an organoboron compound such as triphenylboron ($(C_6H_5)_3B$) did accelerate the polymerization without termination. Also in contrast, the polymerization system retained the original color characteristic of **2** (R=Me) throughout the polymerization. For example, when $(C_6H_5)_3B$ was added at room temperature to the polymerization mixture of MMA with **2** (R=Me) ($[MMA]_0/[1\ (X{=}Me)]_0$ = 200, 3-h irradiation, 9.3% conversion) with the mole ratio of $(C_6H_5)_3B$ to **2** of 1.0, a modest heat evolution was initially observed, and the polymerization proceeded up to 74.9% conversion in 2 h (Figure 1 (●)). This corresponds to the acceleration of polymerization by a factor of 12. This value is lower than that with, *e.g.*, methylaluminum bis(2,4-di-*tert*-

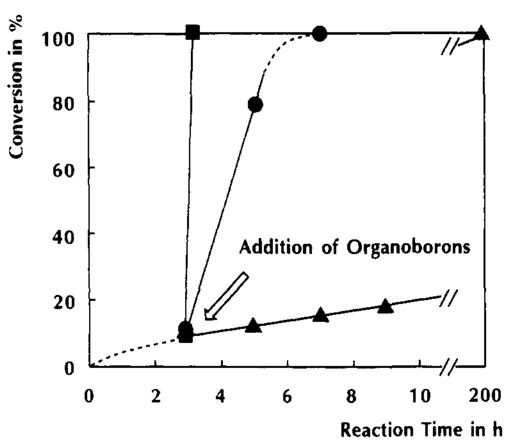


Figure 1. Polymerization of methyl methacrylate (MMA) initiated with (TPP)AlMe (1, X = Me); $[MMA]_0/[1 (X{=}Me)]_0 = 200$, $[1, (X{=}Me)]_0 = 16.2$ mM, C_6H_6 as solvent, room temperature. Effects of triphenylboron (●), tris(pentafluorophenyl)boron (■), and tri-*n*-butylboron (▲) on the rate of polymerization; $[organoboron]_0/[2 (R{=}Me)]_0 = 1.0$.

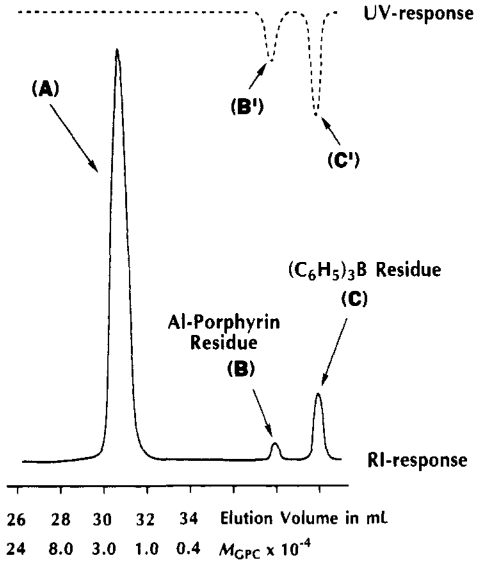


Figure 2. Polymerization of methyl methacrylate (MMA) with the enolatealuminum porphyrin (2, R = Me)–triphenylboron ($(C_6H_5)_3B$) system; (TPP)AlMe (1, X = Me) as initiator ($[MMA]_0/[1 (X{=}Me)]_0 = 200$, $[1, (X{=}Me)]_0 = 16.2$ mM), C_6H_6 as solvent, room temperature, $(C_6H_5)_3B$ added ($[(C_6H_5)_3B]_0/[2 (R{=}Me)]_0 = 1.0$) after irradiation for 3 h (9.3% conversion). GPC profiles (THF as eluent) of the polymerization mixture at 100% conversion (4 h), monitored with differential refractometer and UV (269 nm) detectors.

butylphenolate) as Lewis acid,[1] but almost comparable to that with $(C_6H_5)_3Al$, the organoaluminum analogue of $(C_6H_5)_3B$.[3] When the mole ratio of $(C_6H_5)_3B$ to the growing species (2) was doubled under similar conditions ($[MMA]_0/[1 (X{=}Me)]_0 = 300$), the polymerization was more explicitly accelerated, where the conversion of MMA (4.2% in the beginning) increased to 19.7, 42.2, and 66.0%, respectively, in 20, 44, and 67 min. This corresponds to an approximately 40-fold acceleration.

The GPC curve of the polymer formed at 100% conversion in Figure 1 (●) ($[(C_6H_5)_3B]_0/[2]_0 = 1.0$) was unimodal and very sharp (Figure 2), where the M_w/M_n value, as estimated based on polystyrene standards, was 1.04 and the degree of polymerization of the polymer (220) was very close to the initial monomer-to-initiator mole ratio of 200. This was also the case for the polymerization ($[MMA]_0/[1 (X{=}Me)]_0 = 300$) when the molar quantity of $(C_6H_5)_3B$ was twice that of 2. As shown in Figure 3, M_w/M_n of the polymer was almost constant in the range 1.05–1.06, and the M_n–conversion plots provided a linear line (solid line), which is close to the theoretical line (broken line) from the assumption that every molecule of 2 generated before the addition of $(C_6H_5)_3B$ participates in the subsequent rapid polymerization. Accordingly, as exemplified by the results shown in Figure 4 ($[(C_6H_5)_3B]_0/[2]_0 = 1.0$), the M_n value of the polymer was nicely controlled, retaining the narrow MWD ($M_w/M_n = 1.05$–1.06), by changing the initial monomer-to-initiator mole ratio ($[MMA]_0/[1 (X{=}Me)]_0$).

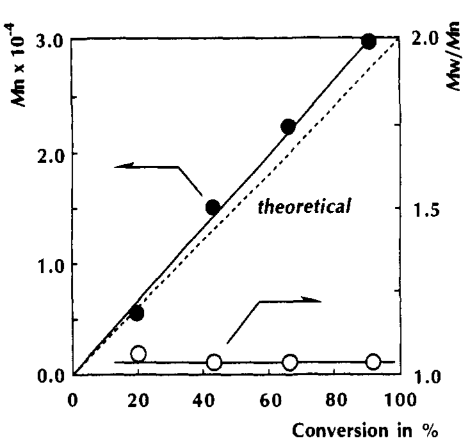


Figure 3. Polymerization of methyl methacrylate (MMA) with the enolatealuminum porphyrin (2, R = Me)–triphenylboron ($(C_6H_5)_3B$) system; (TPP)AlMe (1, X = Me) as initiator ($[MMA]_0/[1 (X{=}Me)]_0 = 300$, $[1 (X{=}Me)]_0 = 13.9$ mM), CH_2Cl_2 as solvent, room temperature, $[(C_6H_5)_3B]_0$ added ($[(C_6H_5)_3B]_0/[2 (R{=}Me)]_0 = 2$) after irradiation for 3 h (4.2% conversion). Relationship between M_n (●) (M_w/M_n (○)) of the polymer and conversion.

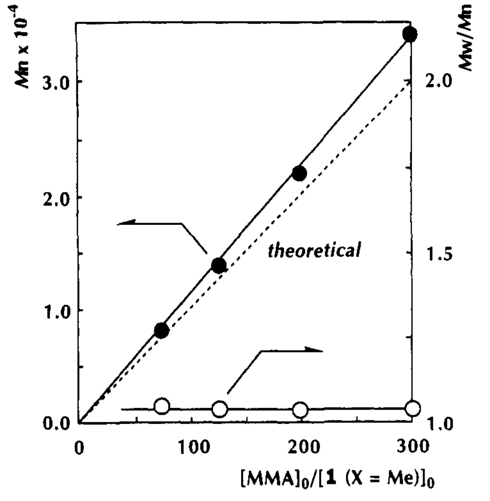


Figure 4. Polymerization of methyl methacrylate (MMA) with the enolatealuminum porphyrin (2, R = Me)–triphenylboron ($(C_6H_5)_3B$) system; (TPP)AlMe (1, X = Me) as initiator, CH_2Cl_2 as solvent, room temperature, $(C_6H_5)_3B$ added $[(C_6H_5)_3B]_0/[2 (R{=}Me)]_0 = 1.0$) after irradiation for 3 h (7–9% conversion). Relationship between M_n (●) (M_w/M_n (○)) of the polymer and the initial monomer-to-initiator mole ratio ($[MMA]_0/[1 (X{=}Me)]_0$) at 100% conversion.

In the accelerated polymerization of MMA using $(C_6H_5)_3B$ as Lewis acid, the *living* character of polymerization was clearly demonstrated by a sequential two-stage polymerization (Figure 5). At the first stage, $(C_6H_5)_3B$ was added to the polymerization system ($[MMA]_0/[1 (X{=}Me)]_0 = 75$) initiated by irradiation ($[(C_6H_5)_3B]_0/[2 (R{=}Me)]_0 = 1.0$), and the polymerization was allowed to proceed up to 100% conversion (3 h). Then after a 48 h at 25 °C, 200 equiv of MMA was again charged to the system, whereupon a rapid polymerization of MMA ensued and was completed within 6 h. The GPC profile of this two-stage polymerization showed a clear increase in M_n of

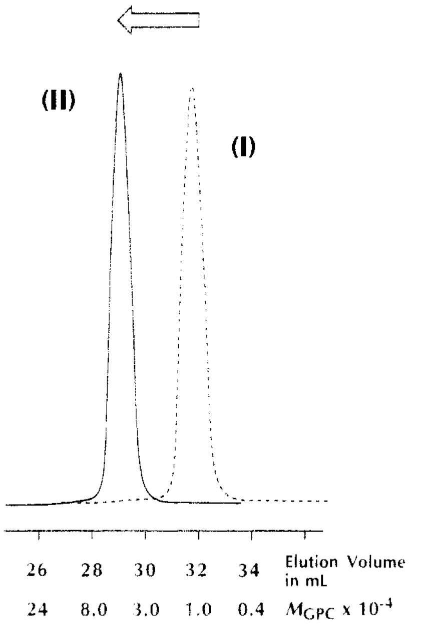


Figure 5. Two-stage polymerization of methyl methacrylate (MMA) in C_6H_6 at room temperature by the enolatealuminum porphyrin (**2**, R = Me)–triphenylboron ($(C_6H_5)_3B$) system; (TPP)AlMe (**1**, X = Me) as initiator, C_6H_6 as solvent, room temperature, $(C_6H_5)_3B$ added [$[(C_6H_5)_3B]_0/[\mathbf{2}\ (R{=}Me)]_0 = 1.0$) after irradiation for 3 h (7.1% conversion). GPC profiles of the polymers formed at the first stage (I; $[MMA]_0/[\mathbf{1}\ (X{=}Me)]_0 = 75$, 100% conversion, $M_n = 8400$, $M_w/M_n = 1.06$) and the second stage (II; $[MMA]_0/[\mathbf{2}]_0 = 200$, 100% conversion, $M_n = 29\,000$, $M_w/M_n = 1.07$).

the polymer from 8400 (curve (I)) to 29 000 (curve (II)) from the first to the second stages, respectively, retaining the narrow MWD (M_w/M_n from 1.06 to 1.07). Such a perfect livingness succession is surprising, considering the long interval between the first and second stages in the absence of the monomer.

$(C_6H_5)_3B$ by itself did not bring about the polymerization of MMA under similar conditions.[13] In connection with this observation, the reaction mixture, formed at 100% conversion from the accelerated polymerization of MMA ($[MMA]_0/[\mathbf{1}\ (X{=}Me)]_0 = 100$) with the **2** (R=Me)–$(C_6H_5)_3B$ (1.0/1.0) system, was treated with MeOH[14] and subjected to GPC analysis (Figure 2). Although the initiator (aluminum porphyrin) (B′) and $(C_6H_5)_3B$ (C′) residues, observed near the end of the chromatogram, showed clear UV responses when monitored at 269 nm,[15] the polymer fraction (peak (A) in the solid line, M_n (M_w/M_n) = 22 000 (1.04)) was totally silent (broken line). Thus, the polymer carries no aromatic groups originating from $(C_6H_5)_3B$.

Tris(pentafluorophenyl)boron ($(C_6F_5)_3B$), a triarylboron bearing electron-withdrawing perfluorinated phenyl rings, was found to be much more powerful than $(C_6H_5)_3B$ as a Lewis acid accelerator for the present polymerization. Upon addition of $(C_6F_5)_3B$ at room temperature to the polymerization system ($[MMA]_0/[\mathbf{1}\ (X{=}Me)]_0 = 200$, 3-h irradiation, 8.8% conversion) with the mole ratio of $(C_6F_5)_3B$ to the growing species (**2**, R = Me) of unity, the polymerization took place rapidly with a considerable heat evolution and was completed within only 13 min (Figure 1 (■)). The polymerization is estimated to be 150 times faster than that in the absence of $(C_6F_5)_3B$ and 12.5 times faster than that with $(C_6H_5)_3B$ as a Lewis acid under similar conditions. The M_n of the polymer (20 400) was close to the expected value of 20 000, and the MWD was narrow ($M_w/M_n = 1.16$). Again, in this case no change in color of the system was observed throughout the polymerization.

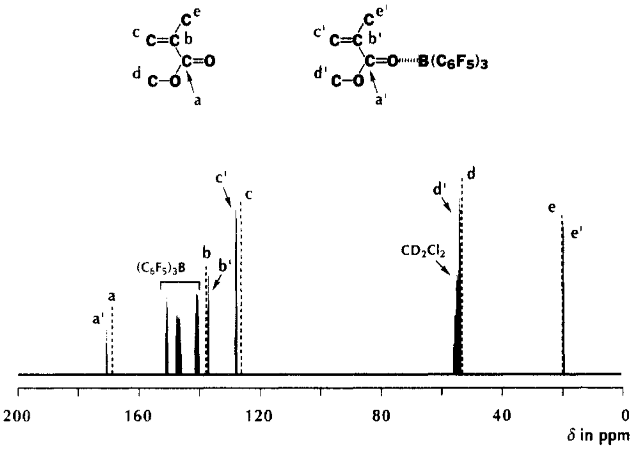


Figure 6. ^{13}C NMR profile in CD_2Cl_2 at 25 °C of an equimolar mixture of methyl methacrylate (MMA) and tris(pentafluorophenyl)boron ($(C_6F_5)_3B$). Broken lines represent the signals due to MMA in the absence of $(C_6H_5)_3B$.

Unlike triarylborons, a trialkylboron such as tri-*n*-butylboron (Bu_3B) neither accelerated nor terminated the polymerization under similar conditions ($[Bu_3B]_0/[\mathbf{2}\ (R{=}Me)]_0 = 1.0$) (Figure 1 (▲)). Even when the mole ratio of Bu_3B to the growing species (**2**) was increased to 20.0, the polymerization still required 183 h for completion. The polymer formed here had M_n(GPC) = 21 300 (M_n(theory) = 20 000) and $M_w/M_n = 1.08$. As we have already reported, use of trialkylaluminums such as trimethyl- and triethylaluminums as Lewis acids under similar conditions for the polymerization of MMA via **2** results in termination, due to the undesired transmetalation between **2** and these Lewis acids (Scheme III).[3] Thus, no termination of polymerization in the presence of Bu_3B indicates the essential difference between organoboron and organoaluminum compounds in the reaction with the enolatealuminum porphyrin growing species (**2**).

NMR Studies. To investigate the interaction of MMA with organoboron compounds, ^{13}C NMR studies were made. In the ^{13}C NMR spectrum (CD_2Cl_2, 25 °C) of an equimolar mixture of MMA and $(C_6F_5)_3B$ (Figure 6) clear downfield shifts were observed for the signals of MMA due to $C{=}O$ (168.3 (a) → 170.1 (a′)), $CH_2{=}$ (125.6 (c) → 127.2 (c′)), and CH_3O (52.2 (d) → 53.1 (d′)). When the mole ratio of $(C_6F_5)_3B$ to MMA was increased from 1.0 to 5.0, the downfield shifts became more remarkable, particularly for the signal due to $C{=}O$ ($\Delta\delta = 3.4$ ppm) (Figure 7 (■)). Thus, a coordination interaction exists between the carbonyl group of MMA and the boron atom of $(C_6F_5)_3B$. When $(C_6H_5)_3B$ was present in place of $(C_6F_5)_3B$ under similar conditions, the downfield shifts of the MMA signals were again observed (●), but they were less explicit than those observed for the MMA–$(C_6F_5)_3B$ system (■). For example, the magnitude of the downfield shift for the MMA $C{=}O$ signal was only 0.1 ppm even at the mole ratio $[(C_6H_5)_3B]/[MMA]$ of 5. On the other hand, in the MMA–Bu_3B system, the change in the chemical shifts of the MMA signals versus the mole ratio of Bu_3B to MMA was much smaller than in the above two triarylboron cases, where the MMA $C{=}O$ signal, for example, shifted only by 0.1 ppm when the mole ratio of Bu_3B to MMA was increased to 10 (▲). When these results are compared with those for two representative MMA–organoaluminum ($MeAl(OC_6H_2(2,4,6\text{-tri-}t\text{-Bu}))_2$, $(C_6H_5)_3Al$) systems, the extents of the downfield shifts for the MMA $C{=}O$ signal increase in the order Bu_3B (▲) < $(C_6H_5)_3Al$ (○) ~ $(C_6H_5)_3B$ (●) < $(C_6F_5)_3B$ (■) < $MeAl(OC_6H_2(2,4,6\text{-tri-}t\text{-Bu}))_2$ (□) (Figure 7). This order roughly corresponds to the order

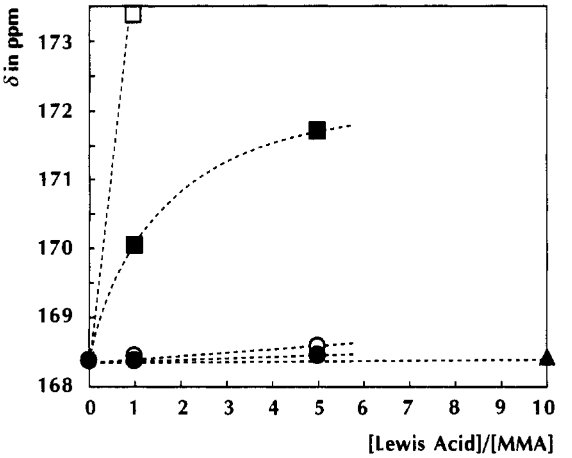


Figure 7. ^{13}C NMR profiles in CD_2Cl_2 at 25 °C of methyl methacrylate (MMA)–Lewis acid mixtures. Relationships between the chemical shift of the C=O signal of MMA and the mole ratio of Lewis acid to MMA. Lewis acids: triphenylboron (●), tris(pentafluorophenyl)boron (■), tri-*n*-butylboron (▲), triphenylaluminum (○), and methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (□) (○ and □; data from ref 3).

of the observed acceleration effects of these Lewis acids for the **2**-mediated polymerization.[3]

In relation to the living character of polymerization with the **2** (R=Me)–organoboron systems, a C_6D_6 solution of $(C_6H_5)_3B$ was added to an equimolar amount of the living polymer of MMA carrying an enolate reactive terminal (**2**, R = Me), prepared with $[\mathrm{MMA}]_0/[\mathbf{1}\ (\mathrm{X{=}Me})]_0$ of 10 at 100% conversion, and the mixture was studied by ^1H NMR at 30 °C. The living polymer (**2**) alone in C_6D_6 shows a characteristic signal at δ 0.53–0.62 due to the MeO group in the terminal enolate unit attached to the aluminum porphyrin moiety,[2a] while $(C_6H_5)_3B$ in C_6D_6 provides a set of signals at δ 7.88–7.36. If the transmetalation takes place between **2** (R=Me) and $(C_6H_5)_3B$, these signals should disappear, while new sets of signals due to **1** (X=Ph) (Al*Ph*: δ 2.73 (*o*-H, d), 5.83 (*m*-H, m), 6.08 (*p*-H, t))[10] and the corresponding boron enolate species should appear. However, throughout the observation over a period of 24 h at 25 °C, the signals due to the starting aluminum enolate species (**2**, R = Me) and $(C_6H_5)_3B$ remained unchanged in their relative intensities to the pyrrole β protons of the aluminum porphyrin moiety (δ 9.37, 8H, s), and no new signals characteristic of **1** (X=Ph) appeared.[10] This observation is in conformity with the result of the two-stage polymerization of MMA with the **2** (R=Me)–$(C_6H_5)_3B$ system (Figure 5), where the livingness of polymerization proceeded perfectly from the first to the second stage even when a long interval (48 h) was placed before the second monomer feed. More surprisingly, no ligand exchange reaction took place when the mixture of **2** and $(C_6H_5)_3B$ was heated at 60 °C for 3 h.

Conclusion

The living polymerization of methyl methacrylate via an enolatealuminum porphyrin (**2**) as the growing species was found to be cleanly accelerated by triarylborons as Lewis acidic monomer activators. Unlike organoaluminum compounds, organoborons were very reluctant, even at a temperature as high as 60 °C, to undergo transmetalation with the enolatealuminum porphyrin species (**2**) (Scheme III) and could be used as accelerators for the living polymerization without steric protection of their Lewis acidic centers from the nucleophilic attack of the growing species. On the other hand, the results were unsuccessful with the more acidic boron compounds such as $BF_3{\cdot}OEt_2$, BCl_3, and boric acid esters, due to the susceptibility of their boron–halogen and boron–oxygen bonds toward nucleophilic substitution reaction. From a practical viewpoint, the acceleration effects of organoboron compounds are not so large as those of the organoaluminum diphenolate family, but $(C_6H_5)_3B$, for example, has the advantages that it is commercially available, easy to handle, and needs no special precautions with respect to air and moisture.

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(11) From the relative intensity of the OCH_3 signals of MMA (δ 3.75) to the polymer (δ 3.65).
(12) The green color is typically observed for the axial ligand exchange reaction of (TPP)AlCl with KF (unpublished result).
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(14) In the reaction with MeOH, the aluminum enolate species at the growing terminal of the polymer (**2**, R = Me) is decomposed by protonation to release **1** (X=OMe).
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