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Evolution of Iron Catalysts for Effective Living Radical Polymerization: Design of Phosphine/Halogen Ligands in $FeX_2(PR_3)_2$[1]

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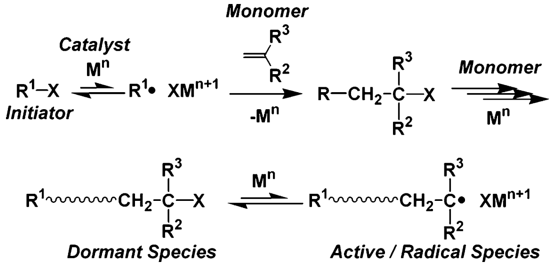
ABSTRACT: In this article, we report the evolved system of iron-complex-catalyzed living radical polymerization of methyl methacrylate (MMA), through design of the ligand, combination of the halogen in the initiator/catalyst, and optimization of the polymerization conditions, toward improvement of the activity and the polymerization-controllability with the applicable catalysts. Introduction of the more basic ligands such as $PMe(Ph)_2$ and P-*n*-Bu_3 in place of PPh_3 in the conventional iron catalyst [$FeX_2(PPh_3)_2$; X = Cl, Br] improved the catalytic performances such as the activity/controllability. In particular, the butylphosphine bromide derivative [$FeBr_2$(P-*n*-$Bu_3)_2$] in conjunction with a bromide initiator [$(MMA)_2Br$] allowed a faster and more precise polymerization, where the conversion reached over 90% without serious deactivation and the molecular weights and their distributions of the obtained PMMAs were fairly controlled ($M_w/M_n = 1.2-1.3$). The high efficiency of the system was demonstrated by the successful monomer-addition experiment and block copolymerization with buthyl methacrylate (BMA).

Introduction

Transition metal-catalyzed living radical polymerization has come in most feasible and useful method for synthesis of well-defined polymers.[2] The pivotal mechanism is reversible and homolytic activation of carbon−halogen bond (C−X) by a transition metal complex (M^n) as a catalyst (Scheme 1). Here, the catalyst in low oxidated state extracts a halogen (leaving group) from a carbon−halogen bond in initiator or polymer chain end through undergoing oxidation (one electron release from catalyst) to give an "activated" carbon radical. During this activation, the radical species repeat an attack to double bonds of a few monomers to propagate a polymer chain. Then, the oxidized complex returns a halogen to the terminal to give a "dormant" carbon−halogen bond, where it is reduced to be an original complex. Now it is well recognized that the living radical polymerization proceeds by repeating this catalytic cycle. Importantly, for living-fashion, fast equilibrium between dormant and activated species is required to reduce the concentration of radical species leading to prevent from side reaction such as coupling/disproportionation. The catalyst should be a most important player and hence a variety of complexes with various central metals such as ruthenium,[3] copper,[4] iron,[5] nickel,[6] etc. have been developed through ligand design according to the metal for more effective living radical polymerization system.

Recently, attempts have been also made to develop workable catalysts because of growing interests in practical application. For example, high activity/efficiency, easy removability from products, and economic features have been desirable as well as high controllability of polymerization. In these views, an iron-based complex should be a potential candidate because the metal is more harmless for humans and richer in natural resources on earth than others. The catalysis of an iron complex in living radical polymerization was first observed with $FeCl_2(PPh_3)_2$.[5a] Since this finding, some iron complexes have been reported with various ligands: nitorogen-based multidentate ligands,[5b,c] cyclopentadiene (Cp)[5d] pentamethyl cylopentadiene (Cp*),[5e] imidazolidene,[5f] isophthalic acid,[5g] diimine,[5h] diiminopyridine,[5i] salicyaldiminato,[5j] and pyridylphosphine.[5k] Indeed, some of them demonstrated acceptable activity or controllability; however they might be less appropriate with respect to controllability, versatility of monomers, and tolerance to functional groups, especially compared to ruthenium or copper complexes. As seen in the early work on the topic,[3,4] an introduction of appropriate ligands should lead to more efficient/functional catalytic system with an iron-based complex.

Scheme 1. Transition-Metal-Catalyzed Living Radical Polymerization



From these backgrounds, we attempted an evolution of $FeX_2(PR_3)_2$-based complex through design of phosphine (PR_3) and halogen (X), to develop effective iron catalysts for living radical polymerization (Chart1). As mentioned above, some groups have already studied effects of the ligands, containing phosphine-derivatives,[5a,b,k] however, there were few reports on really practicable iron catalysts that would afford advanced control for methacrylates. Here, we targeted methyl methacrylate (MMA) as a monomer to examine the ligand effects on

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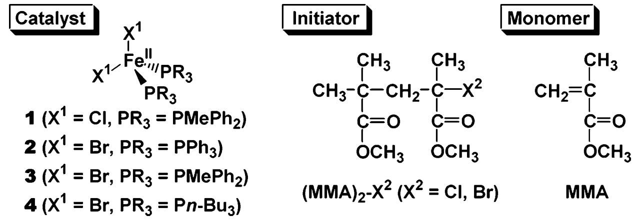
Chart 1. Structures of Catalyst, Initiator, and Monomer in This Work



polymerization behavior. The catalytic performance apparently depended on the ligands and other polymerization conditions; a bromide complex with butyphosphine [$FeBr_2(P$-*n*-$Bu_3)_2$] exhibited higher activity, where the conversion reached 90% in only 5 h even without additives. The butyphosphine catalyst also permitted successful monomer addition for further chain-extension and quantitative block copolymerization with *n*-butyl methacrylate (BMA), which indicates the high controllability of this catalyst.

Experimental Section

Materials. MMA (Tokyo Kasei; >99%) and BMA (Tokyo Kasei; >99%) were purified by reduced distillation with calcium hydride after drying overnight over calcium chloride. Iron halides ($FeCl_2$, $FeBr_2$, Aldrich; >98%) and phosphines [Aldrich; PPh_3 > 99%, $P(MePh_2)_3$ > 99%, $P(n\text{-}Bu)_3$ > 97%] were used as received. The initiators [$(MMA)_2Cl$,[7] $(MMA)_2Br$[8]] were prepared according to literature. Toluene (Kishida Kagaku; >99.5%) was purified by passage through purification column ("Seca Solvent System" manufactured by Glass Contour Co.) before use. An internal standard for gas chromatography, *n*-octane (Wako, >99%), was dried overnight over calcium chloride, distilled twice over calcium hydride, and handled with dry nitrogen for more than 15 min before use. Catalysts were handled in a groove box (M. Braun Labmaster 130) under a moisture-free and oxygen-free atmosphere (H_2O < 1 ppm; O_2 < 1 ppm).

Preparation of Fe Complexes. $FeX_2(PR_3)_2$ was prepared by stirring a mixture of FeX_2 and the corresponding PR_3 in reflux benzene or THF under dry nitrogen for 3−4 h according to the literature.[9] $FeX_2P(MePh_2)_2$ [X = Cl (**1**), Br (**3**)] and $FeBr_2(PPh_3)_2$ (**2**) were recrystallized from the reaction mixture and washed by *n*-hexane three times. Only for $FeBr_2(P$-*n*-$Bu_3)_2$ (**4**) was recrystallization difficult because of the sticky shape. All the complexes were characterized by elemental analysis.

$FeCl_2(PMePh_2)_2$ (**1**). Anal. Calcd for $C_{26}H_{26}Cl_2FeP_2$: C, 59.24; H, 4.97; Cl, 13.45. Found: C, 58.28; H, 4.79; Cl, 13.39.

$FeBr_2(PPh_3)_2$ (**2**). Anal. Calcd for $C_{36}H_{30}Br_2FeP_2$: C, 58.41; H, 4.09; Br, 21.59. Found: C, 58.34; H, 4.11; Br, 21.68.

$FeBr_2(PMePh_2)_2$ (**3**). Anal. Calcd for $C_{26}H_{26}Br_2FeP_2$: C, 50.69; H, 4.25; Br, 25.94. Found: C, 50.60; H, 4.27; Br, 25.80.

$FeBr_2(P$-*n*-$Bu_3)_2$ (**4**). Anal. Calcd for $C_{24}H_{54}Br_2FeP_2$: C, 46.47; H, 8.77; Br, 25.76. Found: C, 44.52; H, 8.46; Br, 24.85.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry argon in baked and sealed glass vials. A typical example for polymerization of MMA with $(MMA)_2Br/FeBr_2(P$-*n*-$Bu_3)_2$ is given. In a 50 mL round-bottomed flask was placed $FeBr_2(P$-*n*-$Bu_3)_2$ (19.4 mg, 0.031 mmol), toluene (3.52 mL), *n*-octane (0.39 mL), MMA (3.34 mL, 31.2 mmol), and a solution of $(MMA)_2Br$ (0.53 mL of 590.4 mM in toluene) at room temperature, where the total volume was 7.8 mL. Immediately after mixing, five aliquots (0.5 mL−1.0 mL each) of the solutions were injected into baked glass tubes. The reaction vaials were sealed and placed in an oil bath kept at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the residual monomer measured by gas chromatography with *n*-octane as an internal standard. The quenched reaction solutions were diluted with toluene and rigorously shaken with a solid, porous absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] to remove the metal-containing residues. After the absorbent was separated by filtation (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

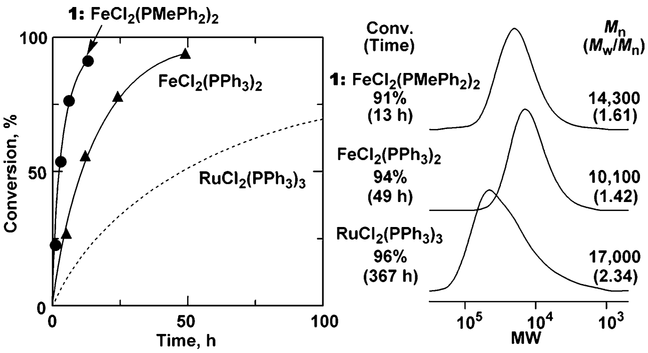


Figure 1. Polymerization of MMA with $(MMA)_2Cl$/catalyst in toluene at 80 °C: $[MMA]_0$ = 2.0 M; $[(MMA)_2Cl]_0$ = 20 mM; $[Catalyst]_0$ = 10 mM.

Measurements. The MWD, M_w, and M_w/M_n ratios of the polymers were measured by SEC in chloroform at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L; pore size = 20−1000 Å, 8.0 mm i.d. × 30 cm, flow rate = 1.0 mL/min) connected to a Jasco PU-980 precision pump and a Jasco930-RI refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; M_w = 630−220 000; M_w/M_n = 1.06−1.22). ^1H NMR spectra of the obtained polymers were recorded in $CDCl_3$ at 25 °C on JEOL JNM-LA500 spectrometer operating at 500.16 MHz. Polymer samples for ^1H NMR were fractionated by preparative SEC (column: Shodex K-2002).

Results and Discussion

More Active Iron Catalyst: $FeCl_2(PMePh_2)_2$. One of the effective strategies to enhance catalytic activity in living radical polymerization should be an elevation of an electron density of central metal through the attached ligands, since the catalyst gives one electron to the dormant polymer chain to activate the terminal bond. Actually, some ruthenium-based catalysts have been evolved to active catalysts according to this strategy.[3e,3f] From this finding, we first attempted a new iron catalyst [$FeCl_2(PMePh_2)_2$], where a more basic phosphine ($PMePh_2$)[10] was installed in place of PPh_3 of a conventional catalyst [$FeCl_2(PPh_3)_2$].

The methyl diphenyl phosphine catalyst was employed for polymerization of MMA in conjunction with $(MMA)_2Cl$ as an initiator without an additive in toluene at 80 °C ($[MMA]_0/[(MMA)_2Cl]_0/[FeCl_2PMePh_2]_0$ = 2000/20/10 mM). As shown in Figure 1, this catalyst led to smooth MMA polymerization and the conversion reached 91% in only 13 h. Importantly, the rate is clearly larger than the conventional iron catalyst [$FeCl_2(PPh_3)_2$][5a] as well as ruthenium derivative [$RuCl_2(PPh_3)_3$] under the none-additive condition, which would indicate that enhanced ligand-basicity allows higher activity, and iron complexes are potentially active catalysts. However, under the condition with the chlorine initiator, the prepared polymers were not so controlled with broader molecular weight distributions (M_w/M_n = 1.7−2.0).

Effects of Halogens in Initiator/Catalyst. In metal-catalyzed living radical polymerization, choice of halogen species as a leaving group derived from an initiator or a catalyst is a dominant factor to achieve controlled polymerization according to monomer and catalyst. Then, to improve the controllability, effects of leaving groups (−Cl vs −Br) were examined with

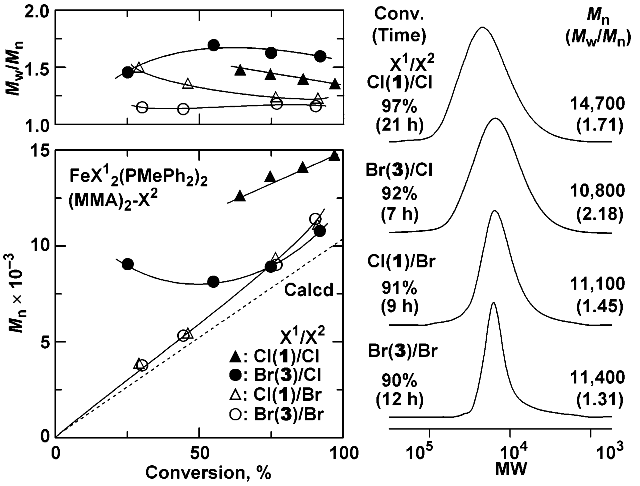


Figure 2. Effects of halogen-combination in catalyst [$FeX^1_2(PMePh_2)_2$: X^1 = Cl, Br] and initiator [$(MMA)_2X^2$: X^2 = Cl, Br] for polymerization of MMA in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[(MMA)_2X^2]_0 = 40$ mM; $[FeX^1_2(PMePh_2)_2]_0 = 10$ mM.

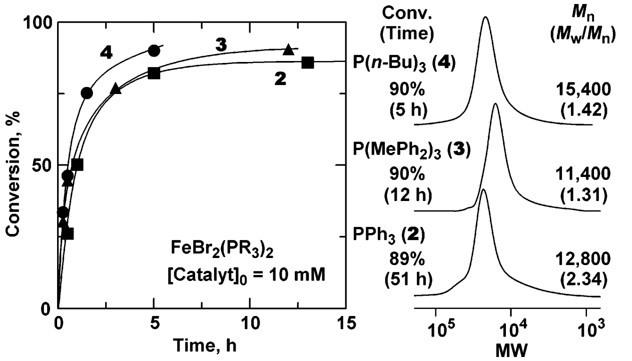


Figure 3. Polymerization of MMA with $(MMA)_2Br/FeBr_2(PR_3)_2$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M, $[(MMA)_2Br]_0 = 40$ mM; $[FeBr_2(PR_3)_2]_0 = 10$ mM. (●) $FeBr_2(P\text{-}n\text{-}Bu_3)_2$ (**4**); (▲) $FeBr_2(PMePh_2)_2$ (**3**); (■) $FeBr_2(PPh_3)_2$ (**2**).

four combinations of two initiators [$(MMA)_2X$: X = Cl, Br] and two catalysts [$FeX_2(PMePh_2)_2$: X = Cl (**1**), Br (**3**)]. Figure 2 shows the plots of the number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) against the MMA-conversion and SEC curves of the prepared PMMAs. As shown in Figure 2, the bromine initiator (●, ○) is superior to the chlorine counterpart (▲, △) in conjunction with either catalysts, in terms of narrowness of the MWDs and correspondence to the theoretical molecular weight calculated from the assumption that one polymer is generated from one initiator. Additionally, matched combination of the halogen (▲, ○) induced better control than mismatched (△, ●), which would due to the effects of halogen exchange between leaving group and catalyst; the mismatched combinations would lead to two kinds of polymer terminal. The bromide combination [initiator: $(MMA)_2Br$, catalyst: $FeBr_2(PMePh_2)_2$] led to relatively well-controlled polymerization (MWD = 1.2−1.3) with a reasonable polymerization rate (conversion 90%, 12 h).

Effects of Phosphines with $FeBr_2(PR_3)_2$. To investigate the effects of ligand basicity and develop more ideal catalysts, three bromide-derivatives with different phosphines [$FeBr_2(PR_3)_2$; PR_3 = PPh_3 (**2**), $PMePh_2$ (**3**), P-*n*-Bu_3 (**4**)] were compared in conjunction with $(MMA)_2Br$ for MMA polymerization (Figure 3; ($[MMA]_0/[(MMA)_2Br]_0/[FeBr_2(PR_3)_2]_0$ = 2000/20/10 mM)). Predictably, the polymerization rate increased as phosphine basicity [basicity: P-*n*-Bu_3 (**4**) > $PMePh_2$ (**3**) > PPh_3 (**2**)[10]]. The butylphosphine based (**4**) exhibited highest activity among these, where the conversion reached 90% in only 5 h. However, the controllability with every catalyst was worse to give broader MWD.

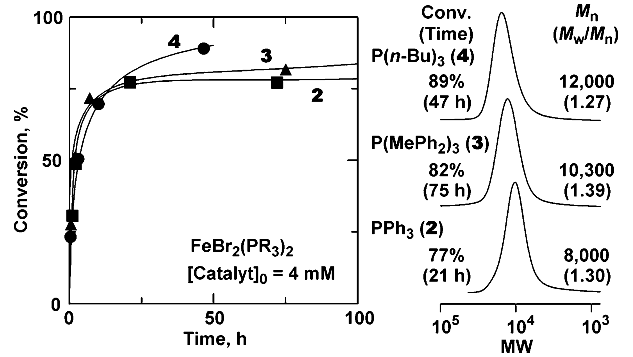


Figure 4. Polymerization of MMA with $(MMA)_2Br/FeBr_2(PR_3)_2$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M, $[(MMA)_2Br]_0 = 40$ mM; $[FeBr_2(PR_3)_2]_0 = 4.0$ mM. (●) $FeBr_2(P\text{-}n\text{-}Bu_3)_2$ (**4**); (▲) $FeBr_2(PMePh_2)_2$ (**3**); (■) $FeBr_2(PPh_3)_2$ (**2**).

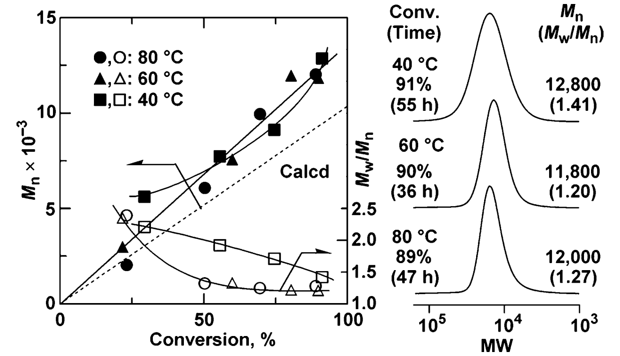


Figure 5. Effects of temperature on polymerization of MMA with $(MMA)_2Br$/**4** in toluene: $[MMA]_0 = 4.0$ M, $[(MMA)_2Br]_0 = 40$ mM; $[\mathbf{4}]_0 = 4.0$ mM. (●, ○) 80 °C; (▲, △) 60 °C; (■, □) 40 °C.

Then, we attempted to improve the controllability by decreasing the catalyst concentration from 10 to 4 mM (Figure 4). Triphenyl phosphine (**2**) and methyl diphenyl phosphine (**3**) derivatives obviously resulted in stagnation of the conversions at around 80%. In contrast, the butylphosphine based (**4**) allowed to keep the activity even at later stage and to reach higher conversion (∼ 90%), although the total rate was decreased. Importantly, the MWDs of the obtained polymers became narrower (M_w/M_n = 1.27, conversion 89%) than those under 10 mM condition. Such difference in activity/controllability between the ligands might be caused by the thermal stabilities of the catalysts or their three-valence complexes (oxidized); **4** would be more stable than **2** and **3**, possibly due to the more basic ligand.

Effects of Temperature with $FeBr_2(P\text{-}n\text{-}Bu_3)_2$. We examined the $FeBr_2(P\text{-}n\text{-}Bu_3)_2$-catalyzed polymerization at lower temperature (40 and 60 °C) to further improve the polymerization control (Figure 5). The activity of this catalyst seems to be high enough to catalyze the polymerization even at 40 °C, however MWDs of the polymres obtained at 40 °C became broader (M_w/M_n > 1.4), which might be due to the slower exchange reaction between dormant and active. On the other hand, for the polymerization at 60 °C, better controlled-polymerization was achieved to give 1.20 of M_w/M_n at 90% conversion. Interestingly, the time required for 90% conversion was 36 h, rather shorter than that for the polymerization at 80 °C (>47 h), which would indicate that the thermal stability of the catalyst or the oxidized form is not so high. Thus, we found that 60 °C is appropriate temperature for control of polymerization with $FeBr_2(P\text{-}n\text{-}Bu_3)_2$.

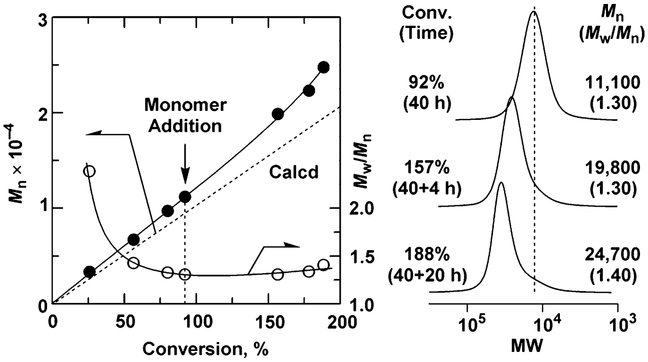


Figure 6. M_n, M_w/M_n, and MWD curves of poly(MMA) obtained in a monomer-addition experiment with $(MMA)_2Br$/**4** in toluene at 60 °C: $[MMA]_0 = [MMA]_{add} = 4.0$ M, $[(MMA)_2Br]_0 = 40$ mM; $[\mathbf{4}]_0 = [\mathbf{4}]_{add}$ 4.0 mM.

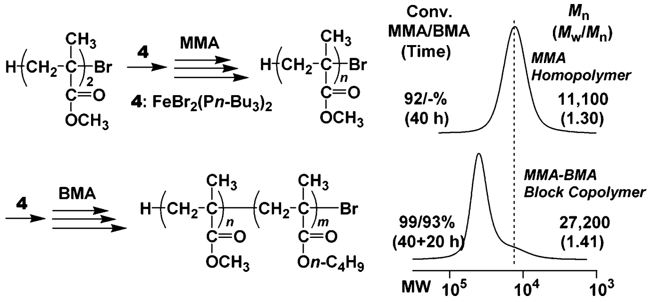


Figure 7. SEC curves of poly(MMA) and MMA−BMA block copolymer obtained with $(MMA)_2Br$/**4** in toluene at 60 °C: $[MMA]_0 = [BMA]_{add} = 4.0$ M, $[(MMA)_2Br]_0 = 40$ mM; $[\mathbf{4}]_0 = [\mathbf{4}]_{add}$ 4.0 mM.

Nature of Living Polymerization. (a) Monomer Addition Experiment. To examine the living nature of the polymerization with $FeBr_2(P\text{-}n\text{-}Bu_3)_2$, a fresh feed of MMA was directly added to the polymerization solution when the polymerization was almost finished (conversion ∼ 90%). After the addition, the rate of the MMA-consumption was obviously reduced and finally the polymerization stopped. Possibly, a part of the loaded $FeBr_2(P\text{-}n\text{-}Bu_3)_2$ was decomposed at the later stage, and thus the catalyst was also added simultaneously with the monomer-addition, as seen in $NiBr_2(PPh_3)_2$-mediated polymerization.[6b] Consequently, the addition of $FeBr_2(P\text{-}n\text{-}Bu_3)_2$ in MMA solution ($[FeBr_2(P\text{-}n\text{-}Bu_3)_2]_{add} = 4.0$ mM, $[MMA]_{add} = 2.0$ M) induced further monomer consumption, and the conversion reached 188% in the additional 20 h (Figure 6). The M_n increased in direct proportion to monomer-conversion even at the second-phase, and it agreed closely with the calculated values assuming that one molecule of the initiator generates on polymer chain. The MWD curves of the polymers shifted to higher molecular weight keeping the narrow distributions (M_w/M_n ∼ 1.3−1.4).

(b) Block Copolymerization of MMA/BMA. The success in monomer addition experiment promoted us to perform a block copolymerization of MMA with *n*-buthyl methacrylate (BMA) with $FeBr_2(P\text{-}n\text{-}Bu_3)_2$. As the MMA-addition experiment, additional catalyst (4.0 mM) was injected along with BMA. The second-phase polymerization also proceeded without retardation and the conversion of BMA reached 93% in additional 20 h (Figure 7). The size-exclusion chromatography (SEC) curves of the prepared polymers remained unimodal and shifted to higher molecular weight with consumption of BMA, although a very small shoulder, which would be originated from the remaining pre-PMMA, was observed. The product was analyzed by ^1H NMR spectroscopy (Figure 8). The spectrum showed the absorptions derived from the BMA repeat units (e−i) in addition to those of the MMA units (a−c). The unit ratio calculated from the relative peak intensities of MMA pendant methoxy group ($-COOCH_3$, c) to BMA pendant methylene next to oxygen atom ($-COOCH_2CH_2CH_2CH_3$, f) was 99/90 (MMA/BMA), in good agreement with the calculated ratio (99/93) from the consumption of the both monomers measured by GC. Additionally, the terminal methoxy proton (c′) observed in pre-PMMA disappeared in the spectrum of the block copolymer. These results suggest that the BMA was quantitatively polymerized from PMMA terminal to give a block copolymer (PMMA-*block*-PBMA).

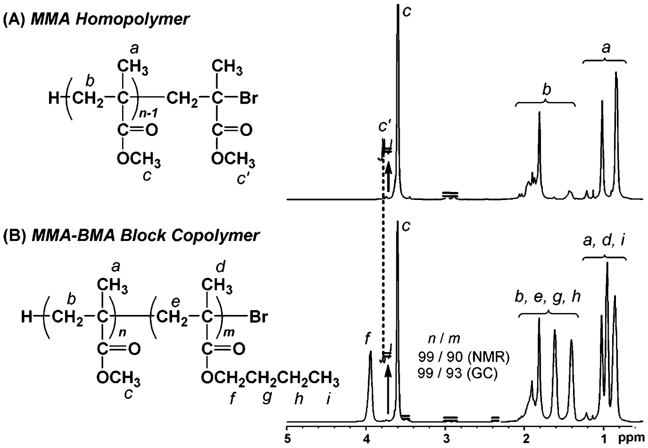


Figure 8. ^1H NMR spectra of MMA homopolymer (A) and MMA−BMA block copolymer (B) obtained with $(MMA)_2Br$/**4** in toluene at 60 °C: See the polymerization condition in Figure 7.

Along with these catalytic performances, the $FeBr_2(P\text{-}n\text{-}Bu_3)_2$ appeared to excel in removability as other similar iron complexes,[11] which was supported by that the red-brown color of polymerization solution, originated from catalyst, turned into colorless via water-washing. The efficient removability would be helpful for actual application.

In conclusion, evolution of $FeX_2(PR_3)_2$ for living radical polymerization of MMA was achieved through the ligand design (phosphine/halogen), the halogen matching in initiator/catalyst, and the optimization of polymerization conditions. The butylphosphine derivative $[FeBr_2(P\text{-}n\text{-}Bu_3)_2]$ exhibited predominant performance about the activity/controllability to achieve the monomer addition experiment and the block copolymerization with BMA.

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(1) This work was presented in part at the following meetings: (a) The 52th Annual Meeting on the Society of Polymer Science, Nagoya, Japan, May 2003: paper IPf006: Uchiike, C.; Wakioka, M.; Terashima, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **2003**, *52* (2), 152. (b) Presented at the 52th Symposium on Macromolecules, the Society of Polymer Science, Yamaguchi, Japan, Sept 2003: paper IPf008. Uchiike, C.; Terashima, T.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2003**, *52*, 1263. (c) Presented at the 53th Annual Meeting on the Society of Polymer Science, Kobe, Japan, May 2004: paper IIC09. Uchiike, C.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2004**, *53*, 162.

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