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$NiBr_2(Pn\text{-}Bu_3)_2$-Mediated Living Radical Polymerization of Methacrylates and Acrylates and Their Block or Random Copolymerizations[1]

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ABSTRACT: Nickel(II) bromide bis(tri-*n*-butylphosphine) [$NiBr_2(Pn\text{-}Bu_3)_2$] induced living radical polymerization of methyl methacrylate (MMA), methyl acrylate (MA), and *n*-butyl acrylate (BA) in conjunction with an organic bromide initiator [R−Br: CCl_3Br, $(CH_3)_2CBrCO_2C_2H_5$, and $(CH_3)_2CBrCOPh$] in the presence of $Al(Oi\text{-}Pr)_3$ additive. In addition, the initiating system with an MMA "dimer" model of the bromine-capped dormant polymer [$(CH_3)_2C(CO_2CH_3)CH_2(CH_3)CBrCO_2CH_3$] gave living polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.1$). Similar living polymerizations were possible in the absence of $Al(Oi\text{-}Pr)_3$. $NiBr_2(Pn\text{-}Bu_3)_2$ led to faster living polymerizations at a high temperature (120 °C; ~90% conversion in 2.5 h) or at its high concentration, because it is more thermally stable and more soluble in organic solvents than $NiBr_2(PPh_3)_2$. This feature permitted the synthesis of living PMMA of higher molecular weight ($\bar{M}_n \sim 4 \times 10^5$) with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.2{-}1.4$). The $NiBr_2(Pn\text{-}Bu_3)_2$-based system was also applicable to living block polymerizations as well as living random copolymerizations of MMA with MA and BA.

Introduction

Recent progress in controlled radical polymerization has permitted the synthesis of polymers with controlled molecular weights, narrow molecular weight distributions (MWDs), and uniform terminal structure, in contrast to the long-standing view that free radical polymerization would be inherently difficult to precisely control or that bimolecular termination inherent to radical intermediates would be difficult to avoid.[2] The living or controlled radical systems that have been developed extensively in these few years can be mostly categorized into two series: one based on the capping of the polymer terminal with a stable nitroxide radical and the other based on the activation (radical cleavage) of a stable carbon−halogen (C−X) bond with a transition metal complex. In the latter, a carbon radical is generated from the C−X bond of an organic halide (R−X) via the single-electron redox reaction of the metal complex, and it adds to monomer to generate the adduct of R−X and a monomer. The resulting carbon−halogen bond is reversibly and homolytically cleaved into a radical species to induce living radical polymerization via the metal-complex-mediated repetitive formation of growing radicals from the terminal C−X bond. A key to such living radical polymerization is therefore to employ metal complexes that can activate the dormant carbon−halogen terminal reversibly and homolytically into radicals. Up to now, not only the initially employed $RuCl_2(PPh_3)_3$[3−8] but also other triphenylphosphine-based complexes such as $FeCl_2(PPh_3)_2$,[9] $NiBr_2(PPh_3)_2$,[10,11] and $RhCl(PPh_3)_3$[12,13] have been found effective in living radical polymerizations of methyl methacrylate (MMA). Similar controlled polymerizations catalyzed by metal complexes but with nitrogen-based ligands such as Ni{$C_6H_3(CH_2NMe_2)_2$-*o,o′*}Br[14] and CuCl/2,2′-bipyridyl[15−17] were also reported.

Recently, for example, we have reported that $NiBr_2(PPh_3)_2$ provides living polymers of MMA in the presence of an organic bromide such as CCl_3Br as an initiator and $Al(Oi\text{-}Pr)_3$ additive, where the Ni(II) catalyst homolytically cleaves the terminal carbon−bromine bond via redox reaction between Ni(II) and Ni(III) species.[10] Though effective it might be, however, this triphenylphosphine complex appears not to be stable and soluble enough in organic solvents, and some decomposition has been noted in prolonged use at relatively high temperatures, thus considerably retarding the polymerization.

To overcome these disadvantages, we employed in this study a more thermally stable and soluble nickel(II) compound, $NiBr_2(Pn\text{-}Bu_3)_2$, where the ligand tri-*n*-butylphosphine is more basic and is of a smaller cone angle than triphenylphosphine. These electronic and steric features affect the shape of the complexes; $NiBr_2(Pn\text{-}Bu_3)_2$ has a square planar structure different from the pseudotetrahedral structure of $NiBr_2(PPh_3)_2$.[18] Such differences may in turn affect the metal-catalyzed radical addition reactions via activation of a carbon−halogen bond. For example, $NiCl_2(Pn\text{-}Bu_3)_2$ induces radical addition of CH_2Cl_2 to 1-hexene in which the yield was lower than that with $NiCl_2(PPh_3)_2$,[19] but there were no reports on $NiBr_2(Pn\text{-}Bu_3)_2$-induced radical reactions.

Herein we report that $NiBr_2(Pn\text{-}Bu_3)_2$ leads to living radical polymerization of MMA even at 120 °C to give polymers of precisely controlled molecular weights (Scheme 1). The high solubility of $NiBr_2(Pn\text{-}Bu_3)_2$ also permits living polymerization in the absence of $Al(Oi\text{-}Pr)_3$, which is needed for living polymerization with $NiBr_2(PPh_3)_2$. Another aspect of this study is the block and random copolymerizations of MMA and acrylates where precise reaction control is also achieved with the butylphosphine complex.

Results and Discussion

1. Living Polymerization of Methyl Methacrylate with $NiBr_2(Pn\text{-}Bu_3)_2$. (a) Comparison with

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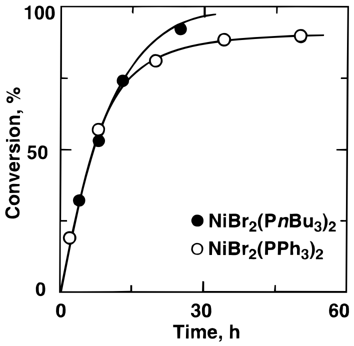
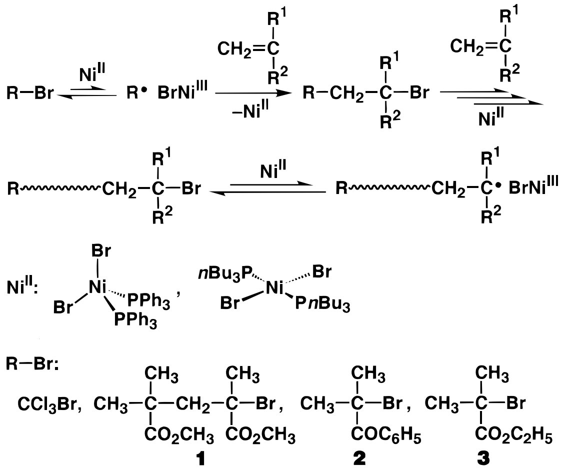


Figure 1. Polymerization of MMA with $CCl_3Br/NiBr_2(PR_3)_2$ (R = *n*-Bu, Ph)/$Al(O\textit{i}\text{-}Pr)_3$ in benzene at 80 °C. $[M]_0 = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(P\textit{n}\text{-}Bu_3)_2]_0 = 80$ mM; $[NiBr_2(PPh_3)_2]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. Key: (●) $NiBr_2(P\textit{n}\text{-}Bu_3)_2$; (○) $NiBr_2(PPh_3)_2$.

Scheme 1



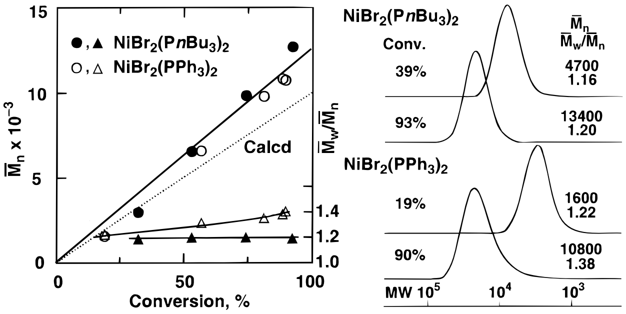


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $CCl_3Br/NiBr_2(PR_3)_2$ (R = *n*-Bu, Ph)/$Al(O\textit{i}\text{-}Pr)_3$ in benzene at 80 °C. $[M]_0 = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(P\textit{n}\text{-}Bu_3)_2]_0 = 80$ mM; $[NiBr_2(PPh_3)_2]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. Key: (●, ▲) $NiBr_2(P\textit{n}\text{-}Bu_3)_2$; (○, △) $NiBr_2(PPh_3)_2$.

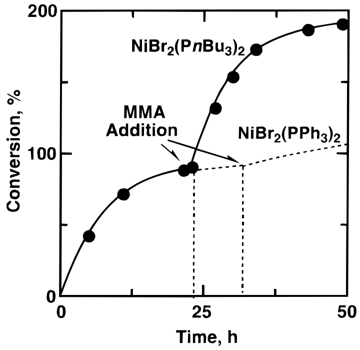


Figure 3. Monomer-addition experiment for polymerization of MMA with $CCl_3Br/NiBr_2(P\textit{n}\text{-}Bu_3)_2/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C. $[M]_0 = [M]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(P\textit{n}\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM.

$NiBr_2(PPh_3)_2$. $NiBr_2(P\textit{n}\text{-}Bu_3)_2$ was employed for polymerization of MMA in conjunction with CCl_3Br (initiator R−X) and $Al(O\textit{i}\text{-}Pr)_3$ in benzene at 80 °C. The high solubility of $NiBr_2(P\textit{n}\text{-}Bu_3)_2$ in the solvent enabled its use at a high concentration (80 mM), in contrast to less soluble $NiBr_2(PPh_3)_2$ for which the highest concentration is about 10 mM. As shown in Figure 1, the butylphosphine complex induced a smooth polymerization of MMA without an induction phase. Conversion reached 90% in 30 h; under similar conditions, the polymerization with $NiBr_2(PPh_3)_2$ apparently slowed in 20 h due to its thermal decomposition. As shown later, $NiBr_2(P\textit{n}\text{-}Bu_3)_2$ also induced smooth MMA polymerization even with its use at a lower concentration (10 mM) (see Figure 8).

The molecular weight distributions (MWDs) of the polymers obtained with the $CCl_3Br/NiBr_2(P\textit{n}\text{-}Bu_3)_2/Al(O\textit{i}\text{-}Pr)_3$ system were narrow throughout the reaction ($\bar{M}_w/\bar{M}_n \sim 1.2$) (Figure 2), and were narrower than those with the PPh_3-based nickel complex. The number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion, although they were slightly higher than the calculated values assuming that one molecule of CCl_3Br generates one living polymer chain. These results suggest that $NiBr_2(P\textit{n}\text{-}Bu_3)_2$ induced living polymerization of MMA in conjunction with CCl_3Br and $Al(O\textit{i}\text{-}Pr)_3$.

We also investigated the polymerizations with nickel(II) chloride with butylphosphine, $NiCl_2(P\textit{n}\text{-}Bu_3)_2$, coupled with CCl_3Br and $Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C. The obtained polymers had higher molecular weights ($\bar{M}_n$ = 25 900) and broader MWDs ($\bar{M}_w/\bar{M}_n = 1.65$). Another $NiCl_2(P\textit{n}\text{-}Bu_3)_2$-based system, with CCl_4 in place of CCl_3Br, also gave uncontrolled polymers with much higher $\bar{M}_n$ (397 000) and much broader MWDs ($\bar{M}_w/\bar{M}_n = 6.91$). These results were similar to those for PPh_3-based nickel halides, where controlled polymerizations were only possible with the bromide complex and the bromide initiator.[10]

(b) Living Polymerization and Narrow MWD Polymers. To investigate the living nature of the polymerization with $CCl_3Br/NiBr_2(P\textit{n}\text{-}Bu_3)_2/Al(O\textit{i}\text{-}Pr)_3$, a fresh feed of MMA was added to the reaction mixture at 80 °C in toluene when most of the initial charge of MMA was consumed (> 90% conversion in 23 h). After the addition, a smooth second-phase polymerization took place, and conversion reached 190% (90% consumption of the added MMA) in an additional 26 h (Figure 3). This is in contrast to the polymerization with $NiBr_2(PPh_3)_2$, where the second-phase polymerization was considerably slower than the first due to the loss of the complex by thermal decomposition (dashed line in Figure 3).

Figure 4 shows $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWDs of the polymers obtained with $NiBr_2(P\textit{n}\text{-}Bu_3)_2$. The MWDs remained unimodal and narrow even after the monomer addition and shifted to higher molecular weight, practically free from the remaining prepolymer. The $\bar{M}_n$ increased in direct proportion to monomer conversion throughout the two-phase polymerization. These results showed that $NiBr_2(P\textit{n}\text{-}Bu_3)_2$ is more suitable for living polymerization of MMA than $NiBr_2(PPh_3)_2$.

Recently we have found that a bromoester, **1**, an authentic "dimer" model of the dormant end with two MMA units and a terminal bromide, acts as an excellent

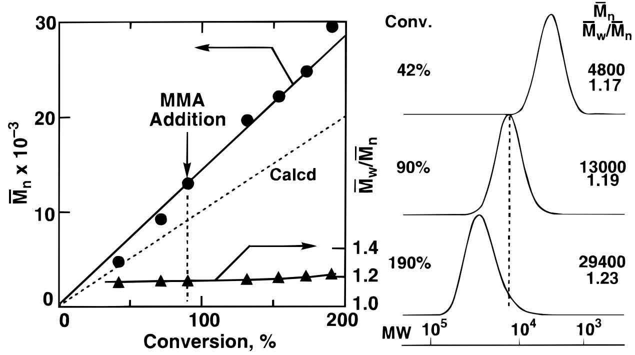


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in a monomer-addition experiment with CCl_3Br/$NiBr_2(Pn\text{-}Bu_3)_2$/$Al(Oi\text{-}Pr)_3$ in toluene at 80 °C. $[M]_0 = [M]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

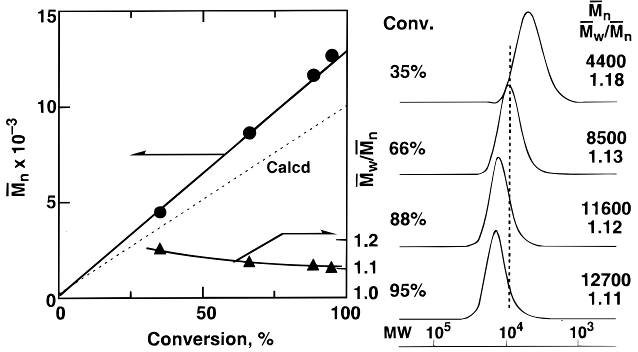
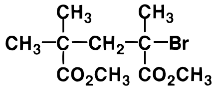


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with **1**/$NiBr_2(Pn\text{-}Bu_3)_2$/$Al(Oi\text{-}Pr)_3$ in toluene at 80 °C. $[M]_0 = 2.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

initiator for living radical polymerization of MMA with $RuCl_2(PPh_3)_3$:[8]



$CH_3-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-Br$

1

The dimeric initiator **1** was then employed for MMA polymerization with $NiBr_2(Pn\text{-}Bu_3)_2$ in the presence of $Al(Oi\text{-}Pr)_3$. The polymerization proceeded at almost the same rate as with CCl_3Br. As shown in Figure 5, the MWDs of the obtained polymers were very narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$), and the $\bar{M}_n$ increased in direct proportion to monomer conversion. Thus, the dimeric initiator **1** is particularly suited for living polymerization of MMA with $NiBr_2(Pn\text{-}Bu_3)_2$ to form polymers with very narrow MWDs.

A series of experiments was carried out, where the mole ratio of monomer to **1** was varied (100, 500, and 1000), while the concentrations of $NiBr_2(Pn\text{-}Bu_3)_2$ and $Al(Oi\text{-}Pr)_3$ were kept constant. Figure 6 plots the $\bar{M}_n$ of the polymers against the ratio of the consumed concentration of MMA to the initial concentration of **1**. The $\bar{M}_n$ were inversely proportional to the initial concentration of **1** up to 120 000 and were in almost agreement with the calculated values. The MWDs were narrow throughout the reaction ($\bar{M}_w/\bar{M}_n < 1.2$). This indicates that the molecular weights and MWDs can be well controlled with use of the dimeric bromide initiator **1**, and that it serves as an efficient initiator for $NiBr_2(Pn\text{-}Bu_3)_2$-mediated living polymerization of MMA.

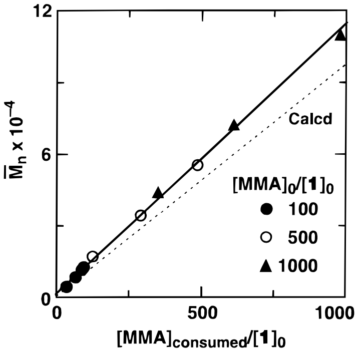


Figure 6. $\bar{M}_n$ as a function of $[\mathbf{1}]_0$ in the polymerization of MMA with **1**/$NiBr_2(Pn\text{-}Bu_3)_2$/$Al(Oi\text{-}Pr)_3$ in toluene at 80 °C: $[M]_0/[\mathbf{1}]_0 = 2000/20$ (●), 5000/10 (○), 5000/5.0 (△) mM. $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

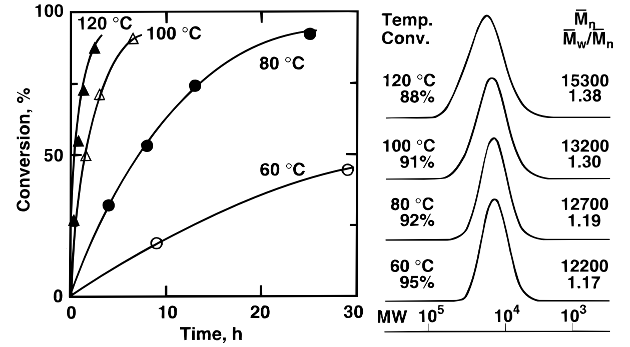


Figure 7. Effects of temperature on polymerization of MMA with CCl_3Br/$NiBr_2(Pn\text{-}Bu_3)_2$/$Al(Oi\text{-}Pr)_3$ in toluene. $[M]_0 = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. Key: (▲) 120 °C; (△) 100 °C; (●) 80 °C; (○) 60 °C.

To confirm the radical mechanism, a radical scavenger (TEMPO, 200 equiv to CCl_3Br) and anion scavengers (MeOH or H_2O, 20 vol %) were added to the polymerization mixture at a conversion of 52%. In the presence of TEMPO, the polymerization clearly ceased in an additional 18 h, while the systems with the anion scavengers reached over 80% conversion. The molecular weights were unchanged after the TEMPO addition, whereas those with the anion scavengers increased even after the addition. These results indicate that the polymerization can be completely terminated by TEMPO but not by the protonic scavengers, and thus it proceeds via a radical mechanism, as do those with $RuCl_2(PPh_3)_3$[7] and $NiBr_2(PPh_3)_2$.[10]

2. Fast Living Polymerization with $NiBr_2(Pn\text{-}Bu_3)_2$. (a) Effect of Temperature. The thermal stability of $NiBr_2(Pn\text{-}Bu_3)_2$ prompted us to examine a series of polymerizations at higher temperatures (Figure 7). The polymerizations proceeded smoothly irrespective of the temperatures. The rate of polymerization increased with temperature, and specifically at 120 °C the conversion reached ~90% in 2.5 h whereas those at 80 °C needed 24 h to reach a similar conversion. The MWDs of the polymers were unimodal and narrow in all the polymerizations, although they became slightly broader at higher temperatures. The broadening of MWDs is probably due to that thermal acceleration is greater for propagation than for interconversion rate between the dormant and the activated species with temperature. The $\bar{M}_n$ increased in direct proportion to monomer conversion. Thus, a thermally stable nickel complex, $NiBr_2(Pn\text{-}Bu_3)_2$, induced a faster living polymerization of MMA at 120 °C.

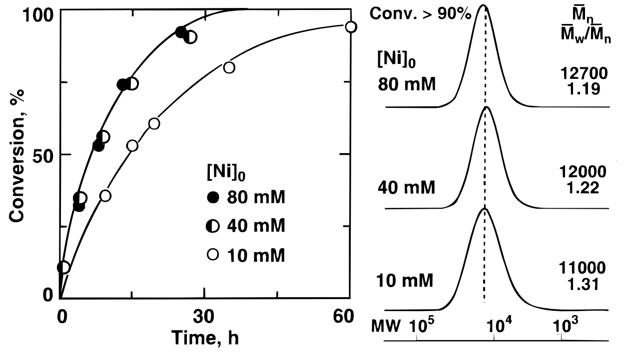


Figure 8. Effects of nickel complex concentration on polymerization of MMA with CCl$_3$Br/NiBr$_2$(Pn-Bu$_3$)$_2$/Al(Oi-Pr)$_3$ in toluene at 80 °C: [M]$_0$ = 2.0 M; [CCl$_3$Br]$_0$ = 20 mM. [NiBr$_2$(Pn-Bu$_3$)$_2$]$_0$ = 10 (○), 40 (◐), and 80 (●) mM. [Al(Oi-Pr)$_3$]$_0$ = 40 mM.

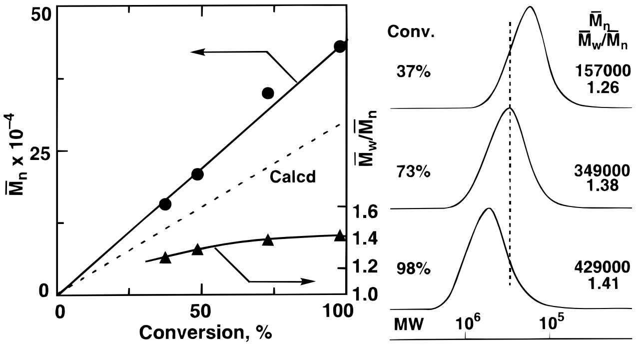


Figure 9. Synthesis of higher molecular weight PMMA with CCl$_3$Br/NiBr$_2$(Pn-Bu$_3$)$_2$/Al(Oi-Pr)$_3$ in toluene at 80 °C. [M]$_0$ = 6.0 M; [CCl$_3$Br]$_0$ = 2.0 mM; [NiBr$_2$(Pn-Bu$_3$)$_2$]$_0$ = 80 mM; [Al(Oi-Pr)$_3$]$_0$ = 40 mM.

(b) Effect of NiBr$_2$(Pn-Bu$_3$)$_2$ Concentration. Figure 8 compares a series of polymerizations at different concentrations of the complex (10−80 mM). The polymerization proceeded faster as the nickel concentration increased from 10 mM to 40 mM, while almost no significant acceleration was observed beyond that level. There are some effects on MWDs, where they became narrower with higher concentration of the nickel complex. This is most probably because large amount of NiBr$_2$(Pn-Bu$_3$)$_2$ effectively fastens the interconversion between the dormant and activated species.

The faster polymerization and the narrower MWDs prompted us to prepare higher molecular weight PMMA with the NiBr$_2$(Pn-Bu$_3$)$_2$ system at a high concentration of NiBr$_2$(Pn-Bu$_3$)$_2$ (80 mM) and at a high monomer-to-initiator ratio ([M]$_0$/[CCl$_3$Br]$_0$ = 6000/2.0 mM) (Figure 9). Under these conditions, the polymerization occurred smoothly, and monomer conversion reached 98% in 23 h. The $\bar{M}_n$ increased in direct proportion to monomer conversion up to 4×10^5 (DP$_n$ ≥ 4×10^3) with relatively narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.2−1.4), although they were slightly higher than the calculated values based on the ratio of monomer to initiator.

3. Effects of Al(OiPr)$_3$ and Other Additives. All the polymerizations with NiBr$_2$(Pn-Bu$_3$)$_2$ discussed thus far were carried out in the presence of Al(Oi-Pr)$_3$, which was similarly needed for RuCl$_2$(PPh$_3$)$_3$[4] or NiBr$_2$(PPh$_3$)$_2$[10] to accelerate the polymerizations and to make polymer MWD narrower. However, with CCl$_3$Br/NiBr$_2$(PPh$_3$)$_2$ it turned out that smooth polymerizations occurred even in the absence of Al(Oi-Pr)$_3$, and there were almost no effects of Al(Oi-Pr)$_3$ on the rate of the polymerizations.

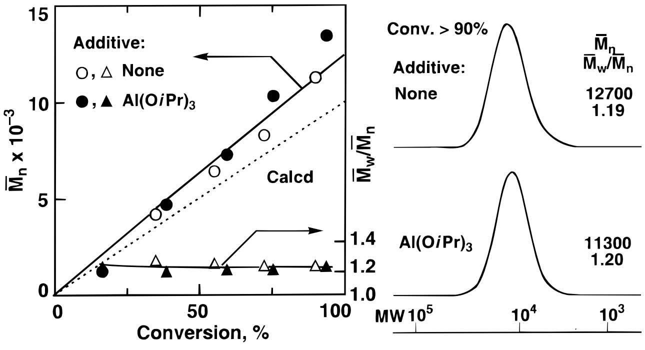


Figure 10. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with CCl$_3$Br/NiBr$_2$(Pn-Bu$_3$)$_2$ in the presence and absence of Al(Oi-Pr)$_3$ in toluene at 80 °C. [M]$_0$ = 2.0 M; [CCl$_3$Br]$_0$ = 20 mM; [NiBr$_2$(Pn-Bu$_3$)$_2$]$_0$ = 80 mM. [Al(Oi-Pr)$_3$]$_0$ = 40 (●, ▲), 0 (○, △) mM.

The MWDs of the polymers obtained without Al(Oi-Pr)$_3$ were as narrow as those in its presence ($\bar{M}_w/\bar{M}_n$ ∼ 1.2) (Figure 10). The $\bar{M}_n$ values were directly proportional to monomer conversion and were close to the calculated values. No effects of Al(Oi-Pr)$_3$ were also observed on molecular weights and their distributions, either. This is in contrast to the other metal-complex-catalyzed systems with RuCl$_2$(PPh$_3$)$_3$[4] and NiBr$_2$(PPh$_3$)$_2$[10] where addition of aluminum alkoxides narrowed the MWDs.

Separate experiments in our groups have shown the effects of other additives such as Al(acac)$_3$ and acetonitrile, where the former narrowed the polymer MWD in the RuCl$_2$(PPh$_3$)$_3$-mediated polymerization of MMA[20] and the latter did the same for styrene polymerization with RuCl$_2$(PPh$_3$)$_3$.[21] However, Ni(acac)$_2$ and acetonitrile did not affect the NiBr$_2$(Pn-Bu$_3$)$_2$-based system.

4. End-Group Analysis. Polymerization of MMA was also carried out with another organic bromide initiator (**2**), (CH$_3$)$_2$CBrCOPh, coupled with NiBr$_2$(Pn-Bu$_3$)$_2$ and Al(Oi-Pr)$_3$ in toluene at 80 °C ([M]$_0$/[**2**]$_0$/[NiBr$_2$(Pn-Bu$_3$)$_2$]$_0$/[Al(Oi-Pr)$_3$]$_0$ = 1000/20/80/40 mM). The polymerization proceeded almost at the same rate as with CCl$_3$Br to give polymers with narrow MWDs (e.g. $\bar{M}_n$ = 10 000; $\bar{M}_w/\bar{M}_n$ = 1.30; conversion = 84%, in 32 h). The $\bar{M}_n$ were nearly proportional to monomer conversion but slightly larger than the calculated values. Thus, (CH$_3$)$_2$CBrCOPh also serves an effective initiator for NiBr$_2$(Pn-Bu$_3$)$_2$-mediated living polymerization of MMA. Similar results were obtained with a bromoester [**3**: (CH$_3$)$_2$CBrCO$_2$C$_2$H$_5$] as an initiator.

The use of (CH$_3$)$_2$CBrCOPh was intended to analyze the terminal structure of the polymers by ^{1}H NMR spectroscopy (Figure 11). In addition to the large absorptions of the main-chain repeat units (e, f, and g), there appeared the characteristic signals of the initiator moiety; e.g., peaks b−d were attributed to the aromatic protons of the phenyl ketone group at the α-end. The $\bar{M}_n$ obtained from the peak intensity ratio 5(g + h)/3(b + c + d) [$\bar{M}_n$(NMR)] was 2030, which was in good agreement with that by size-exclusion chromatography [$\bar{M}_n$(SEC) = 2080] calibrated against standard PMMA samples. The number-average end functionality $\bar{F}_n$ of the initiator unit, calculated as $\bar{M}_n$(SEC)/$\bar{M}_n$(NMR), was 1.02 and close to unity. These results indicate that the living polymerization proceeds via activation of the C−Br bond originated from the initiator by the nickel complex.

5. Living Radical Polymerization of Acrylates. (a) Homopolymerization. In contrast to the variety

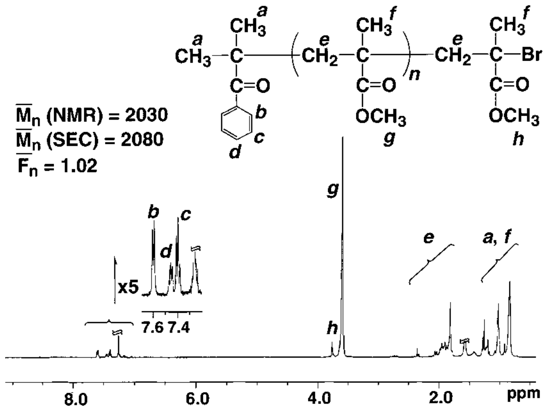


Figure 11. ^{1}H NMR spectrum of poly(MMA) obtained with $(CH_3)_2CBrCOPh/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$ (20/80/40 mM) in toluene at 80 °C. $\bar{M}_n(NMR) = 2030$ (see text); $\bar{M}_n(SEC) = 2080$; $\bar{M}_w/\bar{M}_n(SEC) = 1.16$.

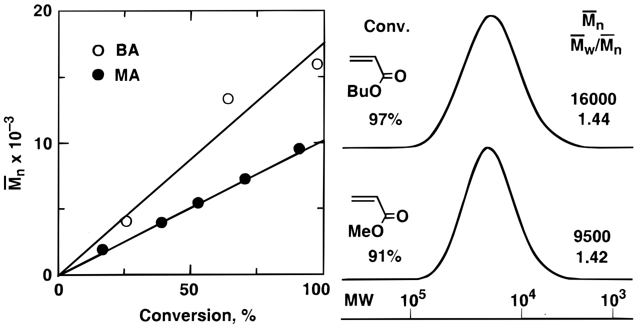


Figure 12. Polymerization of MA (●) and BA (○) with $CCl_3Br/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C. $[M]_0 = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

of transition metal complexes that induced living polymerization of MMA, few examples have been reported for acrylates living polymerizations via activation of carbon−halogen bonds with metal complexes except for the $RuCl_2(PPh_3)_3$-[5] and CuCl/2,2′-bipyridyl-based initiating systems.[22,23] The $NiBr_2(Pn\text{-}Bu_3)_2$-based initiating system with CCl_3Br and $Al(Oi\text{-}Pr)_3$ was then employed for polymerizations of methyl acrylate (MA) and butyl acrylate (BA). Both polymerizations proceeded smoothly, and monomer conversion reached 90% in 30 h. The obtained polymers had relatively narrow MWDs ($\bar{M}_w/\bar{M}_n = 1.3-1.5$), and the $\bar{M}_n$ increased in direct proportion with monomer conversion, which agreed with the calculated values (Figure 12). These results show that $NiBr_2(Pn\text{-}Bu_3)_2$ enables living radical polymerization of acrylates as well as MMA. Similar well-controlled processes for acrylates have been achieved with Cu(I)-based initiating systems.[22,23]

(b) Block Copolymerization of Acrylates with MMA. The success in living radical polymerization of acrylates and MMA with the $NiBr_2(Pn\text{-}Bu_3)_2$-based system urged us to investigate living radical copolymerization of these monomers. For example, sequential block copolymerizations from MMA to BA or MA were examined with $CCl_3Br/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$. A feed of BA or MA, equimolar to the initially added MMA, was added into the living PMMA when the MMA feed was almost consumed (90% conversion in 23 h). After the second monomer addition, polymerizations occurred smoothly. The MWDs of the obtained polymers remained unimodal and shifted to higher molecular weight with consumption of the second monomer,

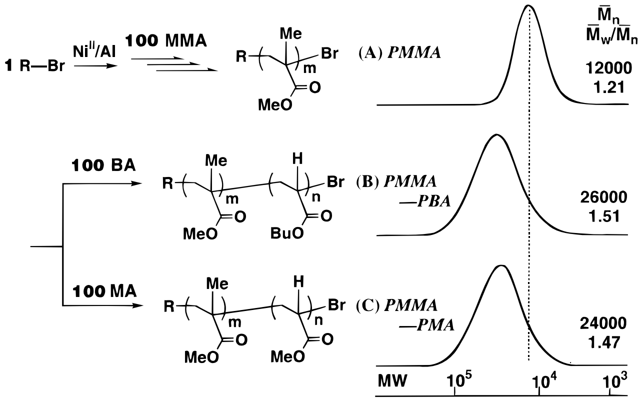


Figure 13. MWD curves of poly(MMA) (A), MMA-BA block (B), and MMA-MA block (C) copolymers obtained with $CCl_3Br/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C. $[MMA]_0 = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. The molar ratio of the monomers to CCl_3Br: MMA = 100 (A); MMA/BA = 100/100 (B); MMA/MA = 100/100 (C).

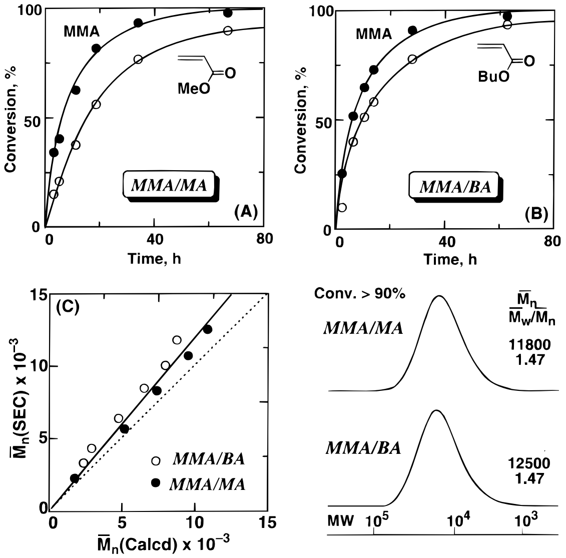


Figure 14. (A, B) Time-conversion curves for the copolymerizations of MMA (●) with MA (○) (A) or BA (○) (B) with $CCl_3Br/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C. $[MMA]_0 = [MA]_0 = [BA]_0 = 1.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(Pn\text{-}Bu_3)_2]_0 = 80$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. (C) $\bar{M}_n(SEC)$ vs calculated $\bar{M}_n$ for the copoly(MMA/MA) (●) and copoly(MMA/BA) (○).

although they became a little broader (Figure 13). Thus, sequential block copolymers (MMA-*b*-MA and MMA-*b*-BA) were synthesized with the initiating system based on $NiBr_2(Pn\text{-}Bu_3)_2$. NMR analysis also supported this conclusion.

(c) Random Living Copolymerization of Acrylates with MMA. Random copolymerizations between MMA and MA or BA were also investigated. Thus, an equimolar mixture of MMA with MA or BA was polymerized with the $CCl_3Br/NiBr_2(Pn\text{-}Bu_3)_2/Al(Oi\text{-}Pr)_3$ initiating system. Both monomers were polymerized almost simultaneously where MMA was consumed slightly faster than the acrylates (Figure 14). The order of reactivity of MMA and MA or BA is the same as in conventional radical copolymerizations with AIBN. The $\bar{M}_n$ of the obtained polymers increased in direct proportion to polymer yield and agreed with the calculated values, assuming that one molecule of initiator generates one living polymer chain. The MWDs were unimodal and relatively narrow ($\bar{M}_w/\bar{M}_n = 1.3-1.5$)

throughout the reaction. These results show that the NiBr$_2$(P*n*-Bu$_3$)$_2$-based system makes it possible to synthesize living random copolymers between acrylates and methacrylates such as MMA-*co*-MA and MMA-*co*-BA.

6. Conclusions. NiBr$_2$(P*n*-Bu$_3$)$_2$, a highly soluble and thermally stable complex, induced living radical polymerization of MMA in conjunction with CCl$_3$Br in toluene at 60−120 °C to give polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.1−1.2) and molecular weights controlled by feed ratio of monomer to initiator. These features of the complex enabled faster living polymerizations at higher temperature or with higher concentration of the complex. Further, aluminum additives such as Al(O*i*-Pr)$_3$ were unnecessary for the living radical polymerization. The initiating system was appeared to effective for living polymerization of acrylates, and also can be applied to the synthesis of block copolymers and random copolymers of MMA and acrylates. The polymerization proceeds via radical mechanism, where the terminal carbon−bromine bond is reversibly and homolytically activated into a radical species via the single electron redox reaction between Ni(II) and Ni(III).

Experimental Section

Materials. MMA (Tokyo Kasei; purity > 99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. NiBr$_2$(P*n*-Bu$_3$)$_2$ (Aldrich; purity > 97%), NiBr$_2$(PPh$_3$)$_2$ (Aldrich; purity > 99%), and Al(O*i*-Pr)$_3$ (Aldrich; purity > 99.99%) were used as received. CCl$_3$Br, (CH$_3$)$_2$CBrCO$_2$C$_2$H$_5$ (both Wako Chemicals; purity > 99%), and (CH$_3$)$_2$CBrCOPh (Aldrich; purity > 98%) were doubly distilled over calcium hydride under atmospheric and reduced pressure, respectively, before use. Dimethyl 2-bromo-2,4,4-trimethylglutarate (**1**) was prepared and purified as already reported.[8] Benzene, toluene (solvent), and *n*-hexane (internal standard for gas chromatography) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass tubes.[4] A typical example is given below. The polymerization was initiated by adding solutions of Al(O*i*-Pr)$_3$ (0.90 mL) and NiBr$_2$(P*n*-Bu$_3$)$_2$ (1.10 mL) in toluene, sequentially in this order, into a mixture (0.80 mL) of MMA (0.60 mL), *n*-hexane (0.178 mL), and CCl$_3$Br (0.022 mL) in toluene at room temperature. The total volume of the reaction mixture was thus 2.8 mL. The solution was immediately placed in a water bath kept at 80 °C. The polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-hexane as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL), washed with water, and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco RI-930 refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $\bar{M}_n$ = 630−220 000; $\bar{M}_w/\bar{M}_n$ = 1.06−1.22) as well as the monomer. ^{1}H NMR spectra were recorded in CDCl$_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002) to be freed from low molecular impurities originated from the catalysts.

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