Macromolecules **1997,** *30,* 2249−2253 **2249**

Nickel-Mediated Living Radical Polymerization of Methyl Methacrylate[1]

Hiroko Uegaki, Yuzo Kotani, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

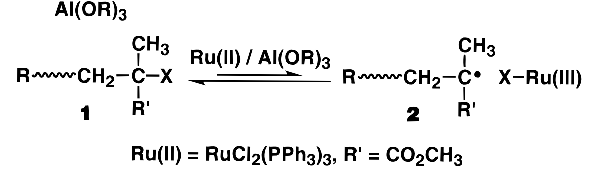
Received September 13, 1996; Revised Manuscript Received February 6, 1997[⊗]

ABSTRACT: Nickel(II) bis(triphenylphosphine)halides [$NiX_2(PPh_3)_2$; X = Cl, Br] were employed for possible living radical polymerization of methyl methacrylate (MMA) in conjunction with an organic halide as an initiator [R−X: CCl_4, CCl_3Br, and $(CH_3)_2CBrCO_2C_2H_5$] in the presence of Al(O*i*Pr)$_3$ in benzene at 80 °C. The bromide-based initiating system [$CCl_3Br/NiBr_2(PPh_3)_2$] gave living polymers with narrow molecular weight distributions, whereas the chloride-based system [$CCl_4/NiCl_2(PPh_3)_2$] led to bimodal molecular weight distributions. The systems involving chloride and bromide [$CCl_4/NiBr_2(PPh_3)_2$ and $CCl_3Br/NiCl_2(PPh_3)_2$] failed to induce living polymerizations. The polymers obtained with $(CH_3)_2CBrCO_2C_2H_5/NiBr_2(PPh_3)_2$ were also living and possessed one initiator moiety at the α-end per polymer chain, which indicates the polymerization proceeds via the activation of the C−Br terminal by the nickel(II) bromide complex.

Introduction

The achievement of living radical polymerization has been one of the ultimate goals in precision polymerizations because of the versatility and applicability of radical polymerizations.[2] The difficulty in its control stems from inherent side reactions such as recombination and disproportionation between the neutral radical growing species. However, recent progress in this area has opened the way for living or controlled processes, where the reactive radical species is in fast equilibrium with a dormant species that possesses a stable but potentially active covalent bond.[3] Therein, the covalent bond is activated thermally, photochemically, or chemically to generate a radical intermediate at an extremely low concentration so as to suppress its bimolecular termination reactions. One of the most extensively studied systems is the nitroxide-mediated living radical polymerization of styrenes, where the growing radical species is temporally end-capped by the stable nitroxyl radical into the dormant C−ON species.[3]

Another methodology is to utilize transition-metal complexes, which have been playing important roles in control of organic reactions as well as polymerizations. Recently, we have reported the living radical polymerization of methyl methacrylate (MMA) mediated by a ruthenium complex, $RuCl_2(PPh_3)_3$, in conjunction with an organic halide (R−X; initiator) such as CCl_4 and an aluminum compound such as Al(O*i*Pr)$_3$.[4−8] According to our proposed mechanism (eq 1),[4,5] the ruthenium complex is crucial for the living polymerization, where the terminal carbon−halogen bond (**1**) that originates from R−X is reversibly and homolytically activated into a radical (**2**) via the single-electron redox reaction of the ruthenium center and the resulting radical species adds to monomer. This process thus involves homolytic cleavage of the carbon−halogen bond of an alkyl halide, the subsequent addition of the resultant radical species to the double bond of an olefin, and the formation of a new carbon−halogen bond in the adduct. Such transition metal-assisted radical addition reactions are well known in organic chemistry,[9] but their use for living radical polymerization has just begun recently.[4−8,10−16] For those organic reactions, several transition metal complexes promote the radical addition reactions, where the central metals include Ru(II), Cu(I), Fe(II), Ni(II), Mo(0), etc. Specifically for living radical polymerization of methacrylates and styrenes, not only Ru(II) complexes[4−8] but also CuCl complexed with bipyridine have been employed.[10−15] More recently, we have also found that $FeCl_2(PPh_3)_2$ is similarly effective for living MMA polymerization.[16] One of the features of such transition metal-catalyzed systems may lie in possible modulation of catalytic activity by the central metals as well as the ligands so as to be suited for control of radical polymerization. An important but unattained subject is, therefore, to define the scope of (transition) metal complexes and their ligands for living radical polymerization.



$$R{-}X \xrightarrow[\text{Al(OR)}_3]{\text{Ru(II)}} \xrightarrow{\text{MMA}}$$

$$\underset{\mathbf{1}}{R\!\sim\!CH_2{-}\overset{CH_3}{\underset{R'}{C}}{-}X} \xrightleftharpoons{\text{Ru(II) / Al(OR)}_3} \underset{\mathbf{2}}{R\!\sim\!CH_2{-}\overset{CH_3}{\underset{R'}{C}}\bullet}\;\; X{-}\text{Ru(III)} \qquad (1)$$

$$\text{Ru(II)} = RuCl_2(PPh_3)_3,\; R' = CO_2CH_3$$

Given this concept, this study was to develop an Ni(II)-mediated living radical polymerization of MMA based on the homolytic and reversible activation of the terminal carbon−halogen bond. The wide variety of possible oxidation states of nickel (0−IV) and types of its complexes permits their wide use not only in organic synthesis but also in polymerization reactions. The application of nickel compounds to polymerization dates back to the discovery of the Ziegler catalysts, and several complexes have recently been employed for living polymerizations of isocyanides, dienes, allenes, and α-olefins.[17] Polymerizations with reduced nickel [Ni(0)] in conjunction with benzyl halides were also reported, where the molecular weights increased with conversion while the MWDs were bimodal.[18] As for radical addition reactions of small organic compounds, reported examples include nickel(II) complexes such as Ni{$C_6H_3(CH_2NMe_2)_2$-*o,o′*}Br[19] and $NiCl_2(PPh_3)_2$.[20] The former is one of the most effective catalysts in radical addition reactions and, in fact, an attempt of its use has been reported for polymerization of styrene.[15] More

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S0024-9297(96)01367-8 CCC: $14.00

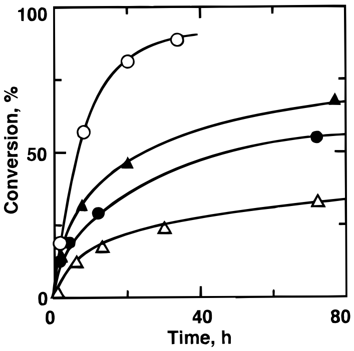
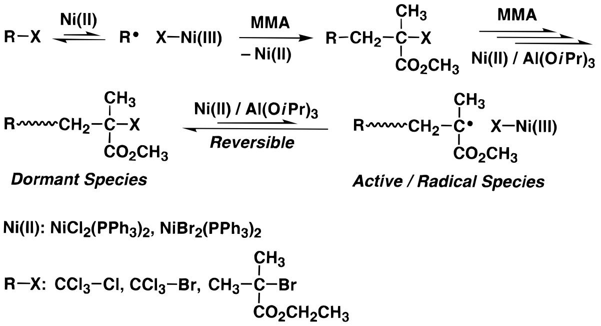


Figure 1. Polymerization of MMA with $CCl_3X/NiX_2(PPh_3)_2$ (X = Cl, Br)/$Al(OiPr)_3$ in benzene at 80 °C: $[M]_0 = 2.0$ M; $[CCl_3X]_0 = 20$ mM; $[NiX_2(PPh_3)_2]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM. (○) $CCl_3Br/NiBr_2(PPh_3)_2$; (▲) $CCl_4/NiBr_2(PPh_3)_2$; (●) $CCl_3Br/NiCl_2(PPh_3)_2$; (△) $CCl_4/NiCl_2(PPh_3)_2$.

recently, Teyssié and his group found that the same bromide induces a well-controlled radical polymerization of MMA in the presence of carbon tetrachloride.[21]

Independently of these, we selected bis(triphenylphosphine)nickel halides [$NiX_2(PPh_3)_2$; X = Cl, Br], Ni(II) complexes that carry the same ligand as does $RuX_2(PPh_3)_3$. They differ from Ni{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}Br in that they are complexed with phosphines rather than the bidentate amine in the latter. For MMA, $NiX_2(PPh_3)_2$ complexes were employed in conjunction with organic halides as an initiator [R−X: CCl_4, CCl_3Br, and $(CH_3)_2CBrCO_2C_2H_5$] in the presence of $Al(OiPr)_3$ (eq 2).[1] Herein we report that the alkyl bromide [CCl_3Br or $(CH_3)_2CBrCO_2C_2H_5$]/$NiBr_2(PPh_3)_2$ systems induced living radical polymerization of MMA.



(2)

Results and Discussion

1. Polymerization with $CCl_3X/NiX_2(PPh_3)_2$ (X = Cl, Br).

The two nickel complexes [$NiX_2(PPh_3)_2$; X = Cl, Br] were employed for polymerization of MMA coupled with CCl_4 or CCl_3Br in the presence of $Al(OiPr)_3$ in benzene at 80 °C (Figure 1). A combination of bromides, CCl_3Br and $NiBr_2(PPh_3)_2$, induced smooth polymerizations without an induction phase, and conversion reached 90% in 50 h (open circles). In contrast, the polymerization with the chloride counterpart, $CCl_4/NiCl_2(PPh_3)_2$, was very slow (open triangles). Mixed-halide systems such as $CCl_4/NiBr_2(PPh_3)_2$ and $CCl_3Br/NiCl_2(PPh_3)_2$ gave results (filled triangles and circles, respectively) similar to those with the chlorides.

As shown in Figure 2A, the molecular weight distributions (MWDs) of the polymers obtained with $CCl_3Br/NiBr_2(PPh_3)_2$ were unimodal and shifted to higher molecular weight with conversion. The polymers with $CCl_4/NiCl_2(PPh_3)_2$ showed unimodal MWDs at the initial stage of the polymerizations (Figure 2D), whereas the molecular weight was higher than that with the bromide. In addition, as the polymerization proceeded, polymers with much higher molecular weights formed, which led to bimodal MWDs. The mixed-halide systems, $CCl_4/NiBr_2(PPh_3)_2$ and $CCl_3Br/NiCl_2(PPh_3)_2$, also gave bimodal distributions at high MMA conversion (Figures 2B and 2C, respectively).

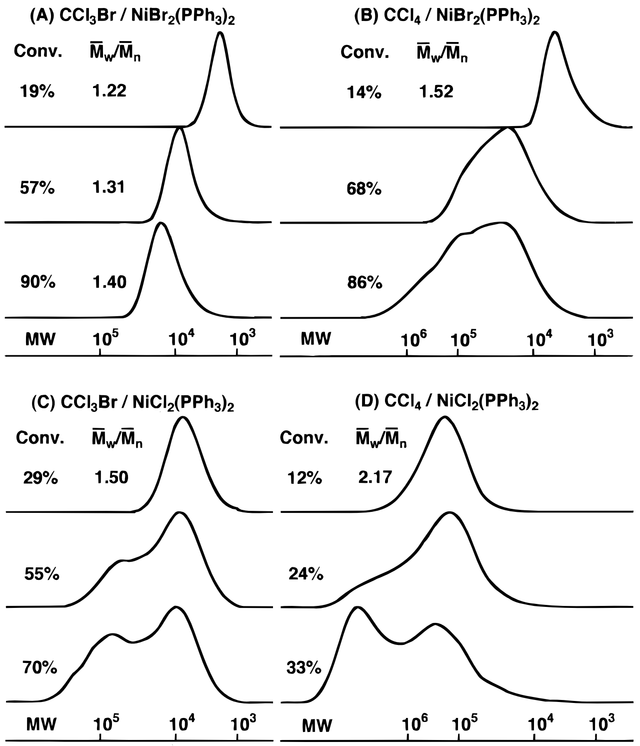


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $CCl_3X/NiX_2(PPh_3)_2$ (X = Cl, Br)/$Al(OiPr)_3$ in benzene at 80 °C: $[M]_0 = 2.0$ M; $[CCl_3X]_0 = 20$ mM; $[NiX_2(PPh_3)_2]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM. (A) $CCl_3Br/NiBr_2(PPh_3)_2$; (B) $CCl_4/NiBr_2(PPh_3)_2$; (C) $CCl_3Br/NiCl_2(PPh_3)_2$; (D) $CCl_4/NiCl_2(PPh_3)_2$.

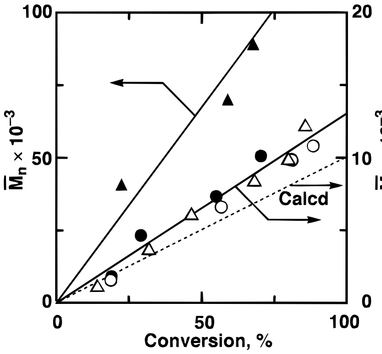


Figure 3. $\bar{M}_n$ of poly(MMA) obtained with $CCl_3X/NiX_2(PPh_3)_2$ (X = Cl, Br)/$Al(OiPr)_3$ in benzene at 80 °C: $[M]_0 = 2.0$ M; $[CCl_3X]_0 = 20$ mM; $[NiX_2(PPh_3)_2]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM. (○) $CCl_3Br/NiBr_2(PPh_3)_2$; (△) $CCl_4/NiBr_2(PPh_3)_2$; (●) $CCl_3Br/NiCl_2(PPh_3)_2$; (▲) $CCl_4/NiCl_2(PPh_3)_2$.

Figure 3 plots the number-average molecular weights ($\bar{M}_n$) of the polymers against conversion. The $\bar{M}_n$ increased in direct proportion to conversion in all the polymerizations. Except for those with $CCl_4/NiCl_2(PPh_3)_2$ (filled triangles), the observed molecular weights almost agreed with the calculated values assuming that one molecule of the organic halide (CCl_3Br or CCl_4) generates one living polymer chain. With $CCl_4/NiCl_2(PPh_3)_2$, however, the molecular weights were much higher than the calculated values. The results on the molecular weights and their distributions (Figures 2 and 3) indicate that the $CCl_3Br/NiBr_2(PPh_3)_2$ system in fact induced living polymerization of MMA in the presence

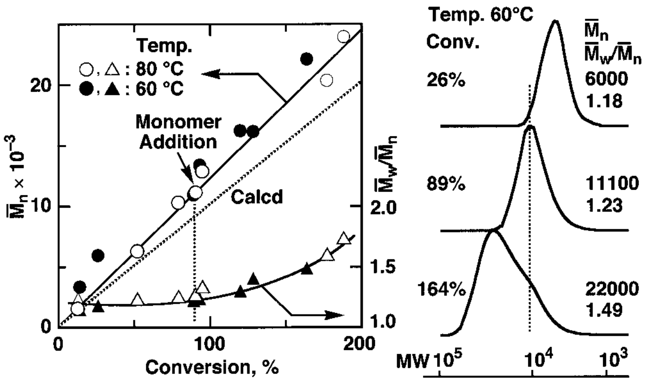


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in monomer-addition experiments with $CCl_3Br/NiBr_2(PPh_3)_2/Al(O\mathit{i}Pr)_3$ in benzene at 80 and 60 °C: $[M]_0 = [M]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(PPh_3)_2]_0 = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM. (○, △) 80 °C; (●, ▲) 60 °C.

of $Al(O\mathit{i}Pr)_3$; see also the following section. The failure in controlled polymerizations with the systems except for this bromide pair is probably due to the lower reactivity of the C−Cl terminal toward the nickel complexes and possible halogen exchange reactions between the C−X terminal and the complexes. This is in contrast to the $RuCl_2(PPh_3)_3$-based system, where living polymers can be obtained irrespective of the halogens in alkyl halides.[4,5]

The $CCl_3Br/NiBr_2(PPh_3)_2$ system without $Al(O\mathit{i}Pr)_3$ led to a slower polymerization that reached 42% conversion in 12 h with polymers of a narrow MWD ($\bar{M}_w/\bar{M}_n = 1.21$; $\bar{M}_n = 5200$) but needed 125 h to give 68% yield and a much broader MWD ($\bar{M}_w/\bar{M}_n = 1.60$; $\bar{M}_n = 8300$).

2. Living Polymerization with $CCl_3Br/NiBr_2(PPh_3)_2$. To investigate the living nature of the polymerization with $CCl_3Br/NiBr_2(PPh_3)_2/Al(O\mathit{i}Pr)_3$ in benzene at 80 °C, a fresh feed of monomer was added to the reaction mixture when the initial charge of the monomer was almost consumed (90% conversion in 32 h). After the addition, the polymerizations were retarded, and it took an additional 180 h to reach 88% conversion of the added MMA. The $\bar{M}_n$ of the obtained polymers increased in direct proportion to monomer conversion after the addition (open symbols in Figure 4), and the peak top of the MWD curves shifted to higher molecular weights. However, the MWDs became broader with small fractions of the unreacted prepolymers. This suggests that part of the living ends were dead during the second-phase polymerization. The decrease of polymerization rate is most probably due to the decomposition of $NiBr_2(PPh_3)_2$ at such a high temperature as 80 °C.[22]

The monomer-addition experiments were also examined at 60 °C. The rate of the first-phase polymerization was smaller than at 80 °C; conversion reached 89% in 92 h. However, the products had narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$) and molecular weights that almost agreed with the calculated values. On addition of a fresh feed of MMA, the added feed was consumed at a lower rate than the first phase. Along with this, the MWDs broadened as in the monomer-addition experiment at 80 °C. The decomposition of the complex was thus observed at 60 °C also.[21] The loss of living ends after the monomer addition is apparently related to the partial decomposition of the complex, which requires more time for consumption of the monomer and facilitates termination reaction(s) relative to propagation.

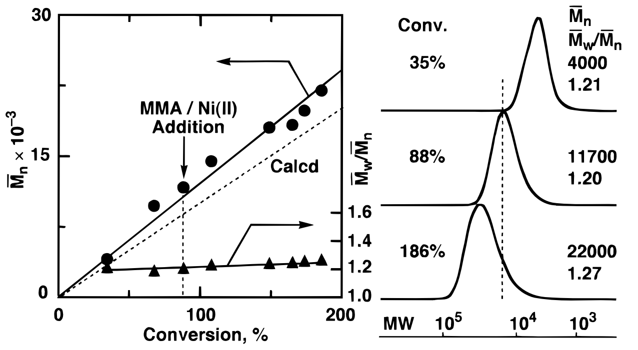


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in a monomer and Ni(II)-addition experiment with $CCl_3Br/NiBr_2(PPh_3)_2/Al(O\mathit{i}Pr)_3$ in benzene at 60 °C: $[M]_0 = [M]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[NiBr_2(PPh_3)_2]_0 = [NiBr_2(PPh_3)_2]_{add} = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM.

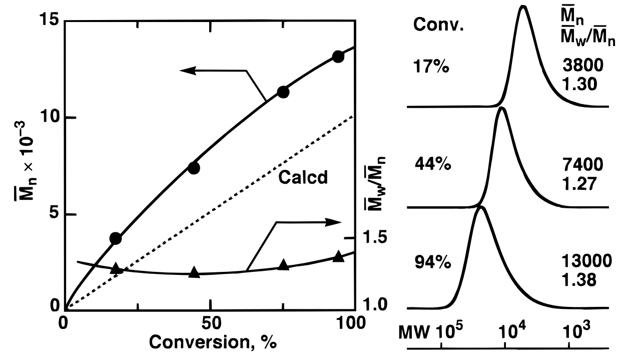


Figure 6. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $(CH_3)_2CBrCO_2C_2H_5/NiBr_2(PPh_3)_2/Al(O\mathit{i}Pr)_3$ in benzene at 80 °C: $[M]_0 = 2.0$ M; $[(CH_3)_2CBrCO_2C_2H_5]_0 = 20$ mM; $[NiBr_2(PPh_3)_2]_0 = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM.

To compensate the loss of $NiBr_2(PPh_3)_2$ with time, the complex was then added along with the addition of a fresh feed of MMA. Upon addition of a mixture of $NiBr_2(PPh_3)_2$ with MMA at 60 °C, the rate of the second-phase polymerization did not decrease, and conversion reached 186% in additional 150 h. As shown in Figure 5, the MWDs of the products remained unimodal and narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) after the addition. The $\bar{M}_n$ increased in direct proportion to monomer conversion and, more importantly, it agreed closely with the calculated values assuming that one molecule of CCl_3Br generates one living polymer chain. Thus, living polymerization of MMA indeed occurred with $CCl_3Br/NiBr_2(PPh_3)_2/Al(O\mathit{i}Pr)_3$ under selected conditions. Polymerizations with more thermally stable nickel(II) complexes such as $NiBr_2(P\mathit{n}Bu_3)_2$ are now under investigation.

To confirm the radical mechanism, a radical scavenger, TEMPO (10 equiv to CCl_3Br), was added to the polymerization mixture at a conversion of ~50%. On addition, the polymerization clearly ceased even when it was kept unquenched beyond 55 h, where the system without the additives reached nearly quantitative conversion. The molecular weights did not increase, either, and stayed unchanged after the addition. These indicate that the polymerization was immediately and completely terminated by TEMPO and that the polymerization proceeds via a radical mechanism.

3. End-Group Analysis of the Polymers by ^1H NMR. Polymerization of MMA was also carried out with another organic bromide, $(CH_3)_2CBrCO_2C_2H_5$, as an initiator to be coupled with $NiBr_2(PPh_3)_2$ and $Al(O\mathit{i}Pr)_3$ in benzene at 80 °C. The polymerization proceeded almost at the same rate as with CCl_3Br (cf. Figure 1, open circles). As shown in Figure 6, the polymer MWDs were as narrow as those with CCl_3Br.

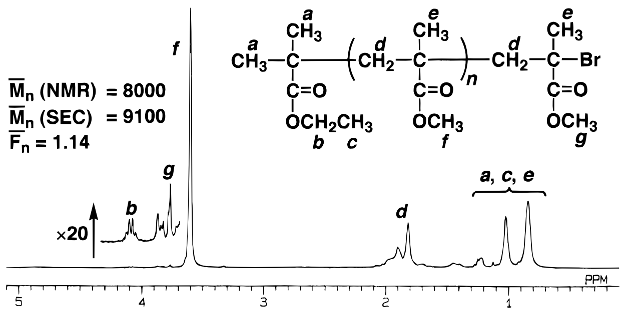


Figure 7. ^{1}H NMR spectrum of poly(MMA) obtained with $(CH_3)_2CBrCO_2C_2H_5/NiBr_2(PPh_3)_2/Al(OiPr)_3$ in benzene at 80 °C. $\bar{M}_n$(NMR) = 8000 (see text); $\bar{M}_n$(SEC) = 9100; $\bar{M}_w/\bar{M}_n$(SEC) = 1.22.

The $\bar{M}_n$ were nearly proportional to monomer conversion but slightly larger than the calculated values. Thus, $(CH_3)_2CBrCO_2C_2H_5$ also induced living polymerization of MMA in conjunction with $NiBr_2(PPh_3)_2$ and $Al(OiPr)_3$.

The bromo ester was used so that the terminal structure of the polymers could be analyzed by ^{1}H NMR spectroscopy (Figure 7). In addition to the large absorptions of the main-chain repeat units (d, e, and f), there appeared the characteristic signals of the initiator moiety; e.g., peak b was attributed to the methylene protons of the ethyl ester group at the α-end. Furthermore, the small signal (g) on the shoulder of the main-chain methyl ester protons (f) was due to the ester methyl protons adjacent to the bromine atom at the ω-end.[23] The $\bar{M}_n$ obtained from the peak intensity ratio f/b was 8000, which was in close agreement with that by size-exclusion chromatography [$\bar{M}_n$(SEC) = 9100] 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 1.14 and close to unity. These results indicate that the living polymerization proceeded via activation of the C−Br bond of the $(CH_3)_2CBrCO_2C_2H_5$ initiator by $NiBr_2(PPh_3)_2$ to attach the ethyl ester at the α-end.

^{13}C NMR analysis of the polymers showed that the polymers were more or less syndiotactic (rr:rm:mm = 60:36:4), similar in steric structure to a sample (e.g., rr:rm:mm = 58:38:6) radically prepared with AIBN in toluene at 80 °C.

In conclusion, a simple Ni(II) complex, $NiBr_2(PPh_3)_2$, induced living radical polymerization of MMA when coupled with an alkyl bromide such as CCl_3Br and $(CH_3)_2CBrCO_2C_2H_5$ in the presence of $Al(OiPr)_3$. The polymerization most likely proceeds via the radical mechanism, where the carbon−bromine bond at the polymer terminal was homolytically activated via the single redox reaction between Ni(II) and Ni(III) (eq 2). This indicates that the transition metal-catalyzed living polymerizations were feasible with a complex of nickel, which is a group 10 element, different from those of ruthenium (group 8) and copper (group 11). Living polymerizations of other Ni(II) complexes and the effects of the central metals are now under investigation in our group.

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. $NiBr_2(PPh_3)_2$ (Aldrich; purity >99%), $NiCl_2(PPh_3)_2$ (Aldrich; purity >98%), and $Al(OiPr)_3$ (Aldrich; purity >99.99%) were used as received. CCl_3Br and $(CH_3)_2CBrCO_2C_2H_5$ (both Wako Chemicals; purity >99%) were doubly distilled over calcium hydride under atmospheric and reduced pressure, respectively, before use. CCl_4 (Wako Chemicals; purity >99%) was dried over calcium chloride, doubly distilled over phosphorus pentoxide, and then dried over calcium hydride before use. Benzene (solvent) and n-octane (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.[5] A typical example is given below. The polymerization was initiated by adding solutions of $Al(OiPr)_3$ (0.90 mL) and $NiBr_2(PPh_3)_2$ (1.10 mL) in benzene, sequentially in this order, to a mixture (0.80 mL) of MMA (0.60 mL), n-octane (0.178 mL), and CCl_3Br (0.022 mL) in benzene 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-octane as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL) and rigorously shaken with a solid, porous absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (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.

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).

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research for Young Scientists (No. 08751027) from the Ministry of Education, Science, Culture, and Sports, Japan, for which M.K. is grateful.

References and Notes

(1) This work was presented in part at the following meetings: (a) International Conference on Recent Advances in Polymer Synthesis, York, U.K., August 1996: Sawamoto, M.; Kamigaito, M. Paper L2. (b) The 45th Symposium on Macromolecules, Society of Polymer Science, Hiroshima, Japan, October 1996; paper 2C04: Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1996**, *45*, 1139.

(2) (a) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science: Oxford, U.K., 1995; p 315. (b) Webster, O. W. *Science* **1991**, *351*, 887.

(3) For recent reviews on living/controlled radical polymerizations, see: (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Sawamoto, M.; Kamigaito, M. *Polymer Synthesis (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; VCH: Weinheim, Germany, in press.

(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(5) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.

(6) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979.

(7) Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3585.

(8) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.

(9) For recent reviews on transition metal-mediated radical addition reactions, see: (a) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M.. Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 4, p 715. (b) Iqbal, J.; Bahita, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519.

(10) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(11) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.

(12) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.

(13) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866

(14) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

(15) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.

(16) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, in press.

(17) (a) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043. (b) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101. (c) Deming, T. J.; Novak, B. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2366. (d) Tomita, I.; Kondo Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413. (e) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(18) Otsu, T.; Tazaki, T.; Yoshioka, M. *Chem. Express* **1990**, *5*, 801.

(19) (a) Grove, D. M.; van Koten, G.; Vershuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169. (b) Grove, D. M.; Vershuuren, A. H. M.; van Koten, G.; van Beak, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1.

(20) Inoue, Y.; Ohno, S.; Hashimoto, H. *Chem. Lett.* **1978**, 367.

(21) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.

(22) The green solution of the polymerization mixture gave a beige precipitate with time on keeping at a temperature higher than 60 °C. The precipitate is probably free $NiBr_2$ generated by the decomposition of the complex, which is also suggested by the light brown color of pure $NiBr_2$. The liberation of PPh_3 with time was also indicated by the ^{1}H NMR analysis of the $NiBr_2(PPh_3)_2$ solution in the absence of CCl_3Br, $Al(O\textit{i}Pr)_3$, and MMA in benzene-d_6 at 80 °C.

(23) The downfield shift of the methyl ester group at the ω-end is confirmed by the ^{1}H NMR spectrum of the model compound $Me_2C(CO_2{}^{\alpha}Me)CH_2CMe(CO_2{}^{\omega}Me)Br$, where $^{\omega}$Me protons absorb at 3.8 ppm and $^{\alpha}$Me protons at 3.7 ppm. See: Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron*, submitted.

MA961367K