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Manganese-Based Controlled/Living Radical Polymerization of Vinyl Acetate, Methyl Acrylate, and Styrene: Highly Active, Versatile, and Photoresponsive Systems

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ABSTRACT: The highly active, versatile, and photoresponsive controlled/living radical polymerizations were developed using $Mn_2(CO)_{10}$ coupled with an alkyl iodide initiator (R−I) under weak visible light. The photoinduced polymerization of vinyl acetate (VAc) proceeded very fast even at 40 °C with a catalytic amount of $Mn_2(CO)_{10}$ (0.025 mol % of VAc or 5.0 mol % of R−I) and completed within a few hours to give the polymers with controlled molecular weights up to 10^5. The controlled polymerization was photoresponsive; that is, the polymerization proceeded only during the lighting period while maintaining the controlled molecular weights for the entire period. This system was also effective in controlled radical polymerizations of conjugated monomers such as styrene and methyl acrylate in conjunction with an appropriate alkyl iodide initiator. The contributions of the metal-catalyzed and the degenerative iodine transfer processes were also examined by analyzing the model reactions.

Introduction

Irrespective of recent remarkable progress in controlled/living radical polymerizations, development of an active and versatile system is still one of the most important subjects from scientific and industrial viewpoints. Among the various living radical polymerization methods, the metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP) is one of the most effective systems for a variety of vinyl monomers and the precision synthesis of well-defined polymers with various complicated structures.[1−15] The polymerization proceeds via the metal-catalyzed reversible activation of the carbon−halogen (C−X) dormant terminals into the growing radical species, in which the metal complex catalytically abstracts the halogen from the C−X bonds via redox processes. The key for controlling the polymerizations is the choice of an appropriate metal catalyst and halogen depending on the monomer structure. Numerous metal complexes such as ruthenium,[1] copper,[2,3,5] iron,[6−8] nickel,[4,9,10] rhodium,[11] palladium,[12] molybdenum,[13] cobalt,[14] and rhenium[15] have been employed in conjunction with alkyl chloride, bromide, and iodide initiators, mostly for conjugated monomers such as methacrylates, acrylates, styrene (St), and acrylamides.

However, these metal catalysts are often necessary at relatively high concentrations, which would be a serious problem especially for industrial applications. In addition, most of these metal catalysts except for a few examples are not suitable for nonconjugated vinyl monomers such as vinyl acetate (VAc) and vinyl chloride due to the "inactivated" C−X terminals derived from these nonconjugated monomers as well as the concomitant formation of the far less reactive primary C−X terminals originating from the head-to-head propagation. Therefore, a highly active metal catalytic system is awaited for a fast and versatile living radical polymerization, though a metal catalyst with a high redox potential is generally unstable and often induces an uncontrolled polymerization due to the instantaneous formation of the highly concentrated radical species in the very early stages of the polymerization. However, quite recent years have witnessed highly effective metal-catalyzed systems with the use of the highly active Cu(0) species[16] or the reducing agents for the accumulated Cu(II) species.[17] These systems enabled a fast controlled/living radical polymerization even with the use of a low concentration of the metal catalysts. Specifically, the Cu(0)-based system proved remarkably active in living radical polymerizations of acrylates, methacrylates, and vinyl chloride even at 25 °C.[16]

In this paper, we focused our attention on a dinuclear manganese carbonyl complex [$Mn_2(CO)_{10}$],[18] which readily undergoes both photochemical and thermal homolysis of the metal−metal bond to form the highly reactive metal-centered radical [$\bullet Mn(CO)_5$]. Although dinuclear complex itself may be stable and inactive in the dark, it can generate a highly active metal species possibly at a controlled concentration under appropriate photoirradiating conditions to be effective for controlled radical polymerizations in the presence of an appropriate organic halide initiator. In organic reactions, it is reported that $Mn_2(CO)_{10}$ can be easily photolyzed via the $\sigma-\sigma^*$ transition to induce the redox-photosensitized reactions with alkyl halides under relatively mild conditions, for example, at ambient temperature with visible light irradiation.[19,20] Its use for radical polymerization can be dated back to the reports by Bamford et al., in which the thermal[21] and photochemical[22] homolysis of $Mn_2(CO)_{10}$ in the presence of CCl_4 led to free radical polymerization of methyl methacrylate.[21−23] The dinuclear Mn complex was further combined with trichlorinated and tribrominated methyl compounds and then utilized for preparing graft and block copolymers of various monomers, though the obtained polymers showed uncontrolled molecular weights and broad MWDs.[24−26]

This paper reports the fast and versatile controlled radical polymerizations of both unconjugated and conjugated monomers such as VAc, methyl acrylate (MA), and St with $Mn_2(CO)_{10}$ in the presence of an alkyl iodide initiator under weak visible light irradiation (Scheme 1). Specifically, the VAc polymerization proceeds in controlled fashion even at 40 °C under fluorescent light conditions with a small amount of the complex ($[M]_0/[Mn_2(CO)_{10}]_0 = 4000/1$ or $[R-I]_0/[Mn_2(CO)_{10}]_0 = 20/1$) to quantitative conversion (>90%) within a few hours to give the polymers with controlled molecular weights up to high molec-

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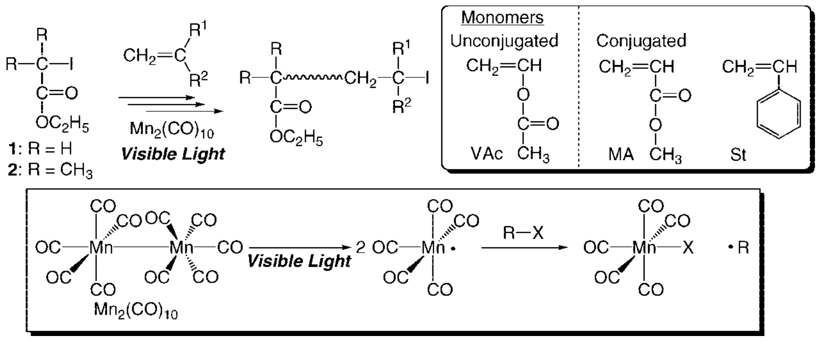
Scheme 1. Controlled Radical Polymerization of Various Monomers with R−I/$Mn_2(CO)_{10}$



ular weights ($M_n \geq 10^5$). The polymerization can be photoresponsive while maintaining the molecular weights controlled; that is, the reaction proceeded only with light irradiation to lead to a molecular weight increase, while it ceased with light-shielding but maintained the same molecular weight. The reaction mechanism was also evaluated by examining the photolysis of the Mn complex in the presence of the initiator.

Experimental Section

Materials. VAc (Wako, >98%), MA (Tokyo Kasei, >99%), and St (Wako, >99%) were distilled under reduced pressure to remove the inhibitors. Ethyl acetate (Kishida, >99%) as a solvent, n-Bu_3N (Wako, >98%) as an additive, and n-octane (Wako, >98%) as an internal standard for gas chromatography and ^1H NMR spectroscopy were distilled from calcium hydride and bubbled with dry nitrogen for 15 min just before use. Ethyl iodoacetate (**1**; Aldrich, >98%) was distilled under reduced pressure before use. Ethyl 2-iodoisobutyrate (**2**) was prepared according to the literature.[27] $Mn_2(CO)_{10}$ (Aldrich, 98%) and $Fe_2Cp_2(CO)_4$ (Aldrich, 99%) were used as received. I−$Mn(CO)_5$ was prepared according to the literature.[28] These complexes were handled in glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere (O_2 < 1 ppm). 2,2′-Azobisisobutyronitrile (AIBN) (Kishida, >99%) was purified by recrystallization from methanol.

Polymerization. Polymerization was carried out by the syringe technique under dry nitrogen in oven-dried and shield glass tubes. A typical example for VAc polymerization with **1**/$Mn_2(CO)_{10}$/n-Bu_3N is given subsequently. $Mn_2(CO)_{10}$ (48.7 mg, 0.125 mmol) was mixed with VAc (4.29 g, 49.8 mmol), n-Bu_3N (0.31 mL of 400 mM solution in n-octane, 0.12 mmol), and **1** (0.25 mL of 1.0 M solution in n-octane, 0.25 mmol) sequentially in this order under light shielding condition. The total volume of the reaction mixture was thus 5.16 mL. Immediately after mixing, aliquots (0.7 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic water bath at 40 °C under the 27 W fluorescent light with diffuser [3 M Filter Light (λ > 400 nm), the detail data about the light source are shown in Supporting Information]. In predetermined intervals, the polymerization was terminated by cooling the reaction mixture 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 mixture was diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (~5 g) to remove the metal-containing residues. After the absorbent was separated by filtration, the filtrate was washed with aqueous citric acid solution and water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers.

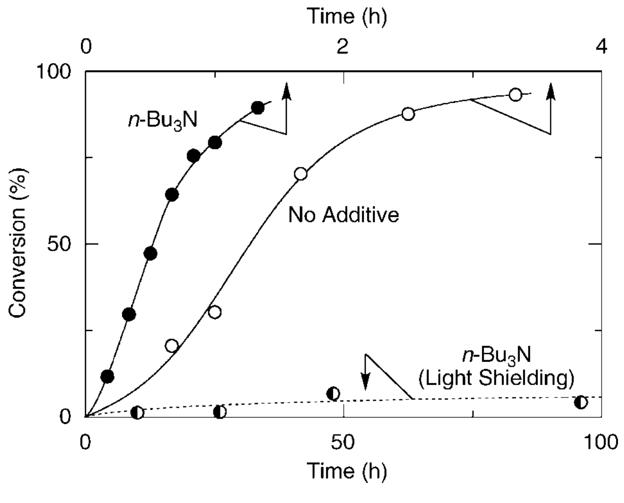


Figure 1. Time-conversion curves for the polymerization of vinyl acetate with **1**/$Mn_2(CO)_{10}$ in the presence (●) or the absence (○) of n-Bu_3N under visible light or in the presence of n-Bu_3N under light shielding condition (◐) in bulk at 40 °C; [vinyl acetate]$_0$ = 9.6 M; [**1**]$_0$ = 48 mM; [$Mn_2(CO)_{10}$]$_0$ = 24 mM; [n-Bu_3N]$_0$ = 0 or 24 mM.

Photolysis of $Mn_2(CO)_{10}$ and 1. Photolysis was carried out with the use of a syringe under a dry nitrogen atmosphere in a sealed NMR tube or in a 10 mm × 10 mm quartz cell tube equipped with a three-way stopcock. For a typical example: $Mn_2(CO)_{10}$ (31.2 mg, 80 μmol) was mixed with benzene-d_6 (1.84 mL) and **1** (0.16 mL of 500 mM solution in benzene-d_6, 80 μmol) sequentially in this order under light shielding condition. The total volume of the reaction mixture was thus 2.00 mL. Immediately after mixing, the solution was charged into a NMR tube (0.7 mL), and the tube was sealed by flame under a nitrogen atmosphere. In addition, aliquot (0.1 mL, 4.0 μmol) of the residual solution was diluted with 7.9 mL of benzene, the diluted solution was distributed (0.30 mL, 0.15 μmol) via a syringe into the quartz cell tube and was further diluted with 2.70 mL of benzene. The tubes were immersed in thermostatic water bath at 40 °C under the 27 W fluorescent light with diffuser. The predetermined intervals, consumption rate of **1** and $Mn_2(CO)_{10}$ were measured by ^1H NMR and UV−vis spectrophotometer, respectively.

Measurements. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography [Shimadzu GC-8A equipped with a thermal conductivity detector and a 3.0 mm i.d. × 2 m stainless steel column packed with SBS-200 (Shinwa Chemical Industries Ltd.) supported on Shimalite W (for VAc) or PEG 20 M (Shinwa Chemical Industries Ltd.) supported on Chromosorb W (for St); injection and detector temperature = 150 °C, column temperature = 120 °C; under He gas flow] or ^1H NMR spectroscopy (for MA) with n-octane as an internal standard. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Gemini 2000 spectrometer, operating at 400 MHz. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex K-805 L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to SIC WP-03 precision pump and a Shodex RI-71S detector. The columns were calibrated against eight standard polystyrene samples [Shodex; M_p

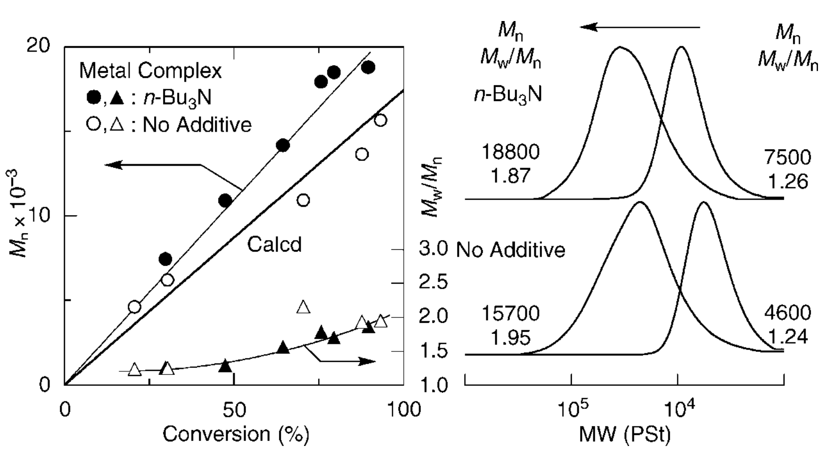


Figure 2. M_n, M_w/M_n and size-exclusion chromatograms of poly(vinyl acetate) obtained with **1**/$Mn_2(CO)_{10}$ in the presence (●,▲) or the absence (○,△) of *n*-Bu$_3$N in bulk at 40 °C under visible light; [vinyl acetate]$_0$ = 9.6 M; [**1**]$_0$ = 48 mM; [$Mn_2(CO)_{10}$]$_0$ = 24 mM; [*n*-Bu$_3$N]$_0$ = 0 or 24 mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per one **1** molecule.

Table 1. Radical Polymerization of Vinyl Acetate with $Mn_2(CO)_{10}$ or $Fe_2Cp_2(CO)_4$ under Various Conditions[a]

entry	metal complex	[metal]$_0$, mM	[*n*-Bu$_3$N]$_0$, mM	time, h	conv, %[b]	M_n(calcd)[c]	M_n[d]	M_w/M_n[d]
1	$Mn_2(CO)_{10}$	24	24	1.3	90	15600	18800	1.87
2	$Mn_2(CO)_{10}$	12	12	1.7	92	16100	16500	1.75
3	$Mn_2(CO)_{10}$	2.4	2.4	2.5	95	16500	18000	1.75
4	$Mn_2(CO)_{10}$	24	0	3.3	93	16300	15700	1.95
5	$Mn_2(CO)_{10}$	12	0	6	96	16700	18100	1.81
6	$Mn_2(CO)_{10}$	2.4	0	24	28	5000	6200	1.40
7	$Fe_2Cp_2(CO)_4$	24	24	47	81	14100	17800	1.95
8	$Fe_2Cp_2(CO)_4$	2.4	2.4	345	25	4600	5700	1.68

[a] Polymerization conditions: [vinyl acetate]$_0$/[**1**]$_0$ = 200, [vinyl acetate]$_0$ = 9.6 M in bulk at 40 °C under visible light. [b] The monomer conversion was determined by gas chromatography. [c] M_n (calcd) = MW (vinyl acetate) × [vinyl acetate]$_0$/[**1**]$_0$ × conv + MW(**1**). [d] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography in THF (polystyrene standard).

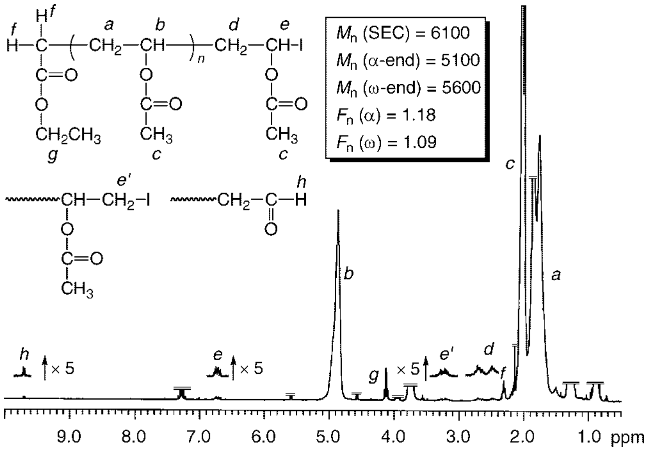


Figure 3. ^1H NMR spectrum ($CDCl_3$, 25 °C) of poly(vinyl acetate) obtained with **1**/$Mn_2(CO)_{10}$ in bulk at 40 °C under visible light; [vinyl acetate]$_0$ = 9.6 M;[**1**]$_0$ = 48 mM; [$Mn_2(CO)_{10}$]$_0$ = 12 mM.

= 520−900000; M_w/M_n = 1.01−1.14; for poly(vinyl acetate) and polystyrene] or seven standard poly(methyl methacrylate) samples [Shodex; M_p = 1990−1950000; M_w/M_n = 1.02−1.09; for poly(methyl acrylate)]. Absorption spectra were recorded in ethyl acetate or benzene at 20 °C by Jasco V-550 spectrophotometer.

Results and Discussion

1. Controlled Radical Polymerization of VAc with R−I/$Mn_2(CO)_{10}$ under Visible Light.

a. Polymerization Conditions. The bulk polymerization of VAc was carried out with the dinuclear manganese complex [$Mn_2(CO)_{10}$] in conjunction with ethyl iodoacetate (**1**) as an initiator at 40 °C ([M]$_0$/[**1**]$_0$/[$Mn_2(CO)_{10}$]$_0$ = 9600/48/24 mM). As shown in Figure 1, under light-shielding conditions, no polymerization occurred. On the other hand, upon weak visible light irradiation, the Mn complex induced a fast polymerization and the conversion reached ~90% in 3 h. Furthermore, addition of *n*-Bu$_3$N, an effective additive for the VAc polymerization with R−I/$Fe_2Cp_2(CO)_4$,[29] accelerated the polymerization, and the reaction was almost completed within 2 h. The Mn complex thus proved highly active for the VAc polymerization even at 40 °C.

Figure 2 shows the M_n, M_w/M_n, and SEC curves of the poly(VAc) obtained with **1**/$Mn_2(CO)_{10}$ in the presence and absence of *n*-Bu$_3$N under visible light. The M_n increased in direct proportion to the monomer conversion and agreed with the calculated values assuming that one initiator (**1**) molecule generates one polymer chain. The MWDs were unimodal and relatively narrow (M_w/M_n ~ 1.2) in the early stages of the reactions. As the polymerization proceeded, the SEC curves shifted to high molecular weights though the MWDs became broader. One of the main reasons for the broadening of the MWDs in the later stages of the polymerization would be the accumulation of the less reactive primary C−I terminal originating from the head-to-head addition, which is inherent in VAc radical polymerization,[29−32] as discussed later. These results indicate that $Mn_2(CO)_{10}$ is effective for the fast and controlled radical polymerization of VAc under weak light irradiation, which induces slow and continuous generation of the highly active manganese pentacarbonyl radical species [•$Mn(CO)_5$]. To the best of our knowledge, this is the first example of photoinduced controlled radical polymerization of VAc using a photosensitive transition metal complex.

The VAc polymerizations with **1**/$Mn_2(CO)_{10}$ were further investigated at varying concentrations of $Mn_2(CO)_{10}$ (0.025−0.25 mol% relative to the monomer) in the presence or absence of *n*-Bu$_3$N (Table 1). Under all the conditions, the polymerization proceeded to give the polymers, the M_n of which were controlled by the VAc/**1** ratio and the monomer conversion. The concentration of $Mn_2(CO)_{10}$ had almost no effects on the polymer

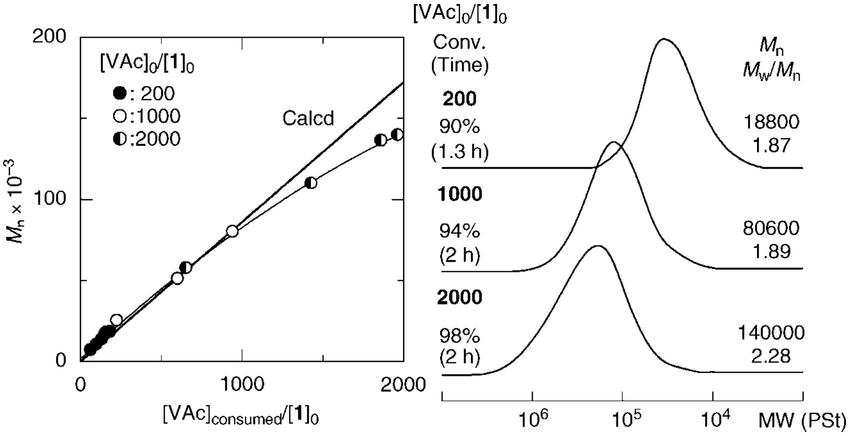


Figure 4. M_n curves of poly(vinyl acetate) obtained with varying the [vinyl acetate]$_0$/[**1**]$_0$ ratio in the presence of *n*-Bu$_3$N in bulk at 40 °C under visible light; [vinyl acetate]$_0$ = 9.6 M, [vinyl acetate]$_0$/[**1**]$_0$ = 200 (●), 1000 (○), 2000 (◐), [**1**]$_0$/[Mn$_2$(CO)$_{10}$]$_0$/[*n*-Bu$_3$N]$_0$ = 2/1/1. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per one **1** molecule.

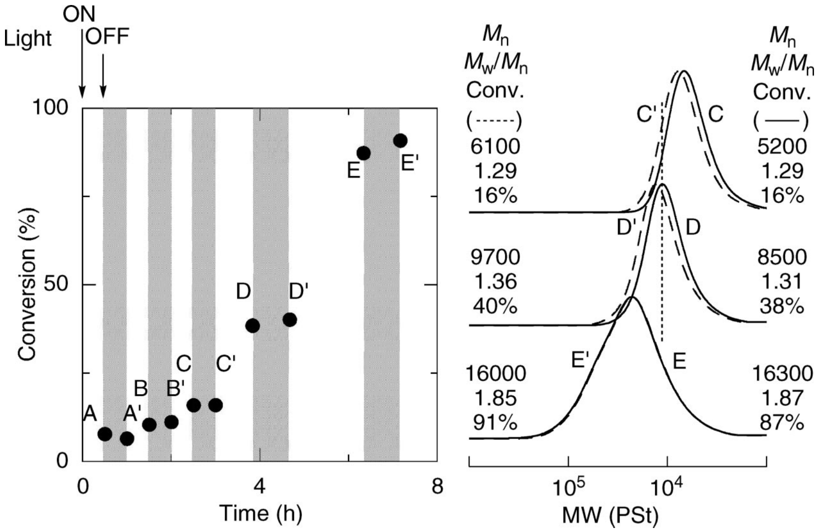


Figure 5. Effect of visible light during the polymerization of vinyl acetate with **1**/Mn$_2$(CO)$_{10}$ in bulk at 40 °C; [vinyl acetate]$_0$ = 9.6 M; [**1**]$_0$ = 48 mM; [Mn$_2$(CO)$_{10}$]$_0$ = 24 mM. The shaded regions indicate the period of that lights were out.

molecular weights. Even at a low concentration of Mn$_2$(CO)$_{10}$ ([VAc]$_0$/[Mn$_2$(CO)$_{10}$]$_0$ = 4000; 0.025 mol% relative to VAc) with the amine additive, the polymerization reached quantitative conversion within a few hours to give the polymers, where the obtained M_n agreed well with the calculated values assuming that one molecule of R−I generates one polymer chain (entry 3). The MWDs of the obtained polymers became narrower with the decreasing Mn concentration. However, the polymerization with 0.025 mol% of Mn$_2$(CO)$_{10}$ without the amine additive was very slow and stopped around 30% conversion (entry 6), though the obtained polymers had controlled molecular weights and narrow MWDs.

The polymerization was also investigated at a higher temperature (60 °C). As shown in Figure S4 in Supporting Information, it was faster than that at 40 °C but became slower in the later stages. The molecular weight distributions of the obtained polymers at 60 °C were slightly broader than those at 40 °C, and the molecular weights became lower. These results suggest termination and chain transfer reactions occur at a higher temperature. Thus, a suitable polymerization temperature would be around 40 °C in terms of the rate and the control of the polymerization.

Table 1 also compares the polymerizations with **1**/Mn$_2$(CO)$_{10}$ to those with **1**/Fe$_2$Cp$_2$(CO)$_4$ and shows that the Mn complex induced a faster polymerization than the Fe complex under the same conditions to give the controlled polymers with narrow MWDs.[29] Thus, Mn$_2$(CO)$_{10}$ proved to be a more effective metal complex in terms of the activity and controllability in the controlled radical polymerizations of VAc.

b. Polymer Analysis. The terminal structure of the polymers obtained with **1**/Mn$_2$(CO)$_{10}$ under visible light was analyzed by ^{1}H NMR spectroscopy (Figure 3). In addition to the large absorptions attributed to the repeat units of VAc at 1.5−2.2 (*a* and *c*) and 4.8−5.2 (*b*) ppm, there are several characteristic signals originating from **1**; that is, the methylene terminal (*f*) and the ethyl ester protons (*g*) at the α-end were observed at 2.3 and 4.1 ppm, respectively. In addition, the methine (*e*) and methylene (*d*) protons at the iodide ω-terminal VAc unit, which was formed via the head-to-tail addition, were observed at 6.8 and 2.6 ppm, respectively.[30−32] The highly downfield-shifted peak (*h*) at 9.7 ppm is attributed to the aldehyde chain ends caused by the decomposition of the secondary (head-to-tail) C−I terminal by the moisture during the polymerization and/or the recovery process. On the other hand, the methylene (*e′*) proton, which was formed via the head-to-head addition, was also observed at 3.2 ppm. The M_n originating from the α- (*g*/2) and ω-end signals (*e*+*h*+*e′*/2) to the main-chain VAc units (*b*) was 5100 and 5600, respectively, which are in good agreement with the calculated value [M_n (calcd) = 5100] and that by SEC [M_n (SEC) = 6100] though based on the polystyrene calibration for

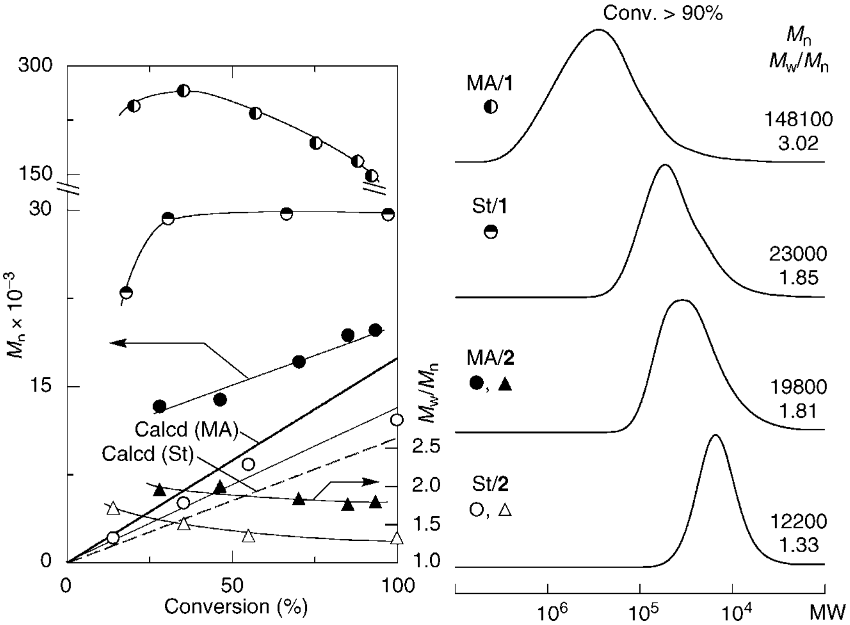


Figure 6. Polymerization of methyl acrylate in ethyl acetate with **1**/$Mn_2(CO)_{10}$ (◐) or **2**/$Mn_2(CO)_{10}$ (●,▲) and styrene in bulk with **1**/$Mn_2(CO)_{10}$ (◓) or **2**/$Mn_2(CO)_{10}$ (○,△) at 40 °C; [methyl acrylate]$_0$ = 4.0 M; [methyl acrylate]$_0$/[initiator]$_0$/[$Mn_2(CO)_{10}$]$_0$ = 400/2/1; [styrene]$_0$ = 8.0 M; [styrene]$_0$/[initiator]$_0$/[$Mn_2(CO)_{10}$]$_0$ = 400/4/1.

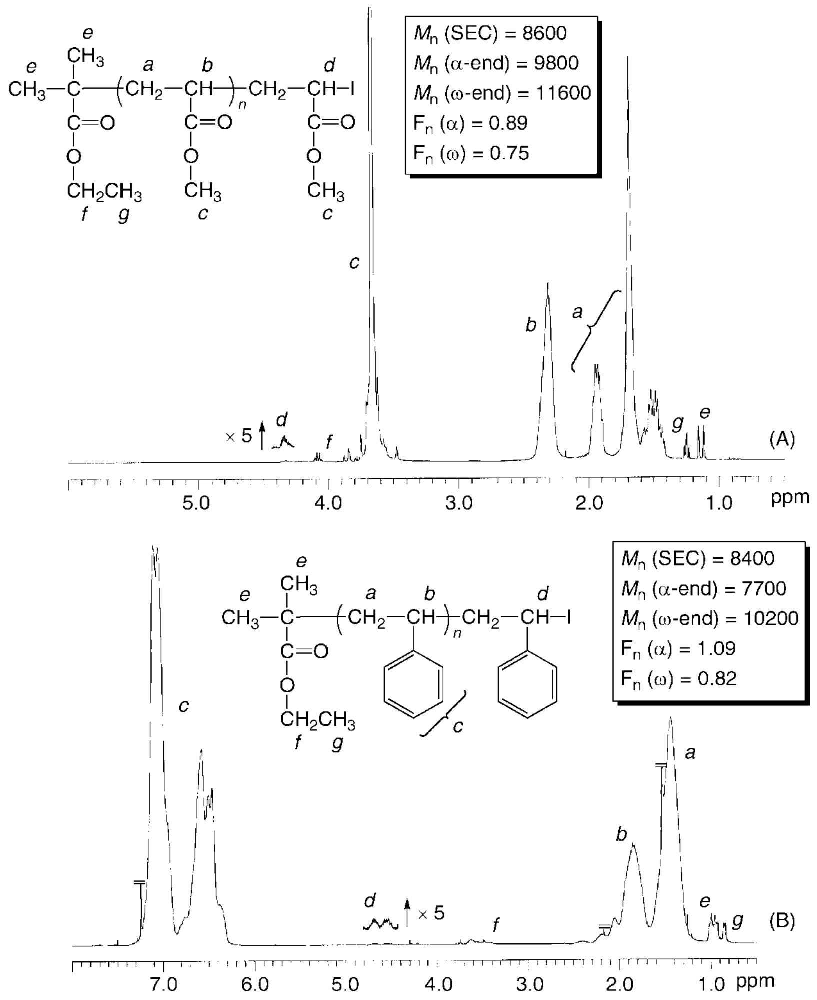
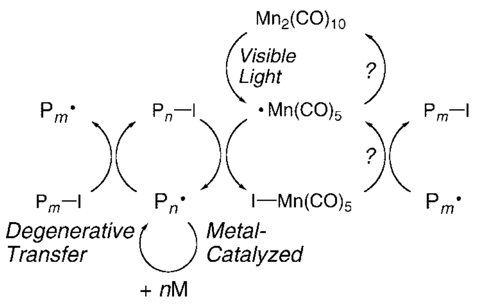


Figure 7. ^1H NMR spectra ($CDCl_3$, 25 °C) of (A) poly(methyl acrylate) and (B) poly(styrene) obtained with **2**/$Mn_2(CO)_{10}$ in ethyl acetate (methyl acrylate) or bulk (styrene) at 40 °C under visible light.

the latter. The number-average end functionality (F_n) was close to unity for both the α- and ω-terminals: $F_n(\alpha) = 1.18$ and $F_n(\omega) = 1.09$, where $F_n = M_n$ (SEC)/M_n (α- or ω-end). These results indicate that **1** served as the initiator to form one polymer chain

Scheme 2. Assumption Mechanism of Photoinduced Controlled Radical Polymerization with R−I/$Mn_2(CO)_{10}$



per molecule and that the polymerization proceeds via the activation of the C−I bond by the Mn complex and/or by the degenerative iodine transfer.

The number-average content of the $-CH_2-I$ terminal in one polymer chain ($-CH_2-I$ fraction, %), calculated from the peak intensity ratio of the primary iodide ω-end ($e'/2$) to the α-end ($g/2$),[32] increased as the polymerization proceeded [$-CH_2-I$ fraction: 14% (21% monomer conversion) and 73% (96% monomer conversion); see Figure S5 in Supporting Information]. Thus, the less reactive primary C−I terminal accumulated during the Mn-induced polymerization as in the other iodide-based polymerization of VAc[29−32] and led to broadening of the MWDs in the later stages of the polymerization. In contrast, in the recently developed Co-mediated polymerizations,[33−35] more precise control of the molecular weights is achievable most probably due to the difference in the dormant species (C−I vs C−Co).

c. Synthesis of High Molecular Weight Poly(VAc) with Controlled Molecular Weight. We then investigated the synthesis of high molecular weight poly(VAc) with the **1**/$Mn_2(CO)_{10}$/*n*-Bu_3N-system under visible light at 40 °C by varying the $[VAc]_0/[\mathbf{1}]_0$ ratio from 200 to 2000, while the $[\mathbf{1}]_0/[Mn_2(CO)_{10}]_0/[n\text{-}Bu_3N]_0$ ratio remained constant ($[\mathbf{1}]_0/[Mn_2(CO)_{10}]_0/[n\text{-}Bu_3N]_0 = 2/1/1$). Even at a low concentration of the initiator and the complex in comparison to VAc ($[VAc]_0/[\mathbf{1}]_0/[Mn_2(CO)_{10}]_0 = 9600/4.8/2.4$ mM), a quantitative polymerization occurred relatively fast (98% conversion in 2 h). Figure 4 shows the M_n values and SEC curves of the polymers obtained with **1**/$Mn_2(CO)_{10}$ at different $[VAc]_0/[\mathbf{1}]_0$ ratios with varying the conversions, in which $[VAc]_{consumed}/[\mathbf{1}]_0$ corresponds to the theoretical degree of polymerization and can be calculated by ($[VAc]_0/[\mathbf{1}]_0$) × conversion. The M_n increased inversely proportional to $[\mathbf{1}]_0$ and agreed well with the calculated value. Although the MWDs became broader with the decreasing concentration of the initiator, a relatively high molecular weight poly(VAc) was obtained ($M_n \sim 140000$) at a high $[VAc]_0/[\mathbf{1}]_0$ ratio. This again indicates the effectiveness of the manganese-based system for controlled radical polymerization of VAc in terms of the activity and controllability.

d. Effects of Visible Light: Photoresponsive Polymerization. To study the effects of visible light on the polymerization with the **1**/$Mn_2(CO)_{10}$ system, the light irradiation was turned off intermittently during the VAc polymerization. As shown in Figure 5, the polymerization ceased immediately upon switching off and the conversion remained unchanged during the dark period, while the reaction proceeded again when the light was turned on to finally result in almost quantitative monomer consumption. All the SEC curves were unimodal and narrow similar to those obtained under continuous light irradiation. Furthermore, no substantial SEC curve shifts and no significant molecular weight increase were observed during the dark period. The M_n's of the obtained polymers also increased in direct proportion to the monomer conversion and were almost the same values as those with the continuous light irradiation as shown above. The Mn-based controlled radical polymerization is thus photoswitchable, where the reaction stops in the dark but can restart under light while keeping the controlled molecular weights. This is due to the fact that, upon the light irradiation, $Mn_2(CO)_{10}$ generates •$Mn(CO)_5$, which can activate the C−I terminal into the growing radical species and induces the radical propagation, while the dinuclear manganese complex is intact under dark conditions, and the C−I bond is completely dormant without the formation of the manganese radical species.

2. Polymerization of Methyl Acrylate and Styrene. *a. Effects of Initiator.* $Mn_2(CO)_{10}$ was also employed for the controlled radical polymerizations of conjugated monomers, MA and St, under visible light in conjunction with **1** or ethyl 2-iodoisobutyrate (**2**) as an initiator at 40 °C. Figure 6 shows the M_n, M_w/M_n, and SEC curves of poly(MA) and polystyrene obtained with **1**/$Mn_2(CO)_{10}$ or **2**/$Mn_2(CO)_{10}$ under visible light.

The poly(MA) obtained with **1** had an uncontrollable M_n, much higher than the calculated values, and broad MWDs. However, the M_n's of poly(MA) with **2** increased with monomer conversion though they were slightly higher than the calculated values during the early stages of the polymerizations. Thus, **2** with a tertiary and more reactive C−I bond is a better initiator for the controlled radical polymerization of acrylates than **1**, which possesses a primary and less reactive C−I, due to the fact that the acrylate dormant terminal C−I bond is secondary and also reactive.[36] However, slightly higher M_n and broader MWDs indicate a still slower initiation even with **2** in the acrylate polymerization.

Similar results were also obtained in the polymerization of St. The M_n values of the polystyrene obtained with **2** increased in direct proportion to monomer conversion and were close to the calculated values with relatively narrow MWDs ($M_w/M_n \sim 1.3$). In contrast, the polymer molecular weights obtained with **1** were higher than the calculated values and were uncontrollable. These results are also due to a slow initiation from **1** for these conjugated monomers because of the high activation energy of the primary C−I bond compared with that of the secondary and conjugated dormant C−I terminal derived from MA and styrene. Although the design or the choice of the initiator is necessary for fine control, the $Mn_2(CO)_{10}$-based system is quite versatile not only for conjugated but also for unconjugated monomers.

b. Polymer Analysis. The obtained poly(MA) and polystyrene were also analyzed by ^1H NMR spectroscopy. Figure 7 shows the ^1H NMR spectra of poly(MA) (A) and polystyrene (B) obtained with the **2**/$Mn_2(CO)_{10}$ system. In addition to the large absorptions (*a*,*b*, and *c*) attributed to the repeat units of each monomer of MA and St, the dimethyl terminal (*e*) and ethyl ester protons (*f* and *g*) at the α-end and the methine protons (*d*) at the iodine ω-terminal were observed in both spectra. The M_n values of poly(MA) and polystyrene calculated from the main chain to the α-terminal signals were 9800 [$9c/3(g+e)$] and 7700 [$9c/5(g+e)$], respectively, in agreement with those by SEC [M_n (SEC) = 8600 and 8400, respectively]. The F_n values of the α-end [$F_n(\alpha) = 0.89$ and 1.09], which are close to unity, show that **2** served as the initiator to form one polymer chain per molecule in each polymerization. These results also indicate that the manganese complex is effective for the activation of the C−I bond under photo irradiation to generate the polymer chains with controlled molecular weights even for the conjugated monomers such as acrylates and styrene using appropriate initiators.

3. Polymerization Mechanism. The proposed mechanism for the Mn-based photoinduced controlled radical polymerization is outlined in Scheme 2. The polymerization is triggered by the active manganese radical species formation [•$Mn(CO)_5$], where

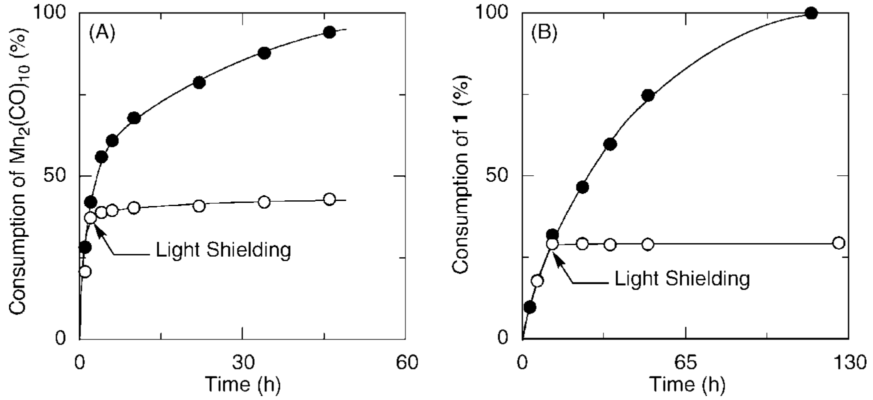


Figure 8. Consumption of (A) $Mn_2(CO)_{10}$ measured by UV−vis in benzene at 40 °C ($[Mn_2(CO)_{10}]_0 = [\mathbf{1}]_0 = 0.05$ mM) and (B) **1** measured by ^{1}H NMR in benzene-d_6 at 40 °C ($[\mathbf{1}]_0 = [Mn_2(CO)_{10}]_0 = 40$ mM).

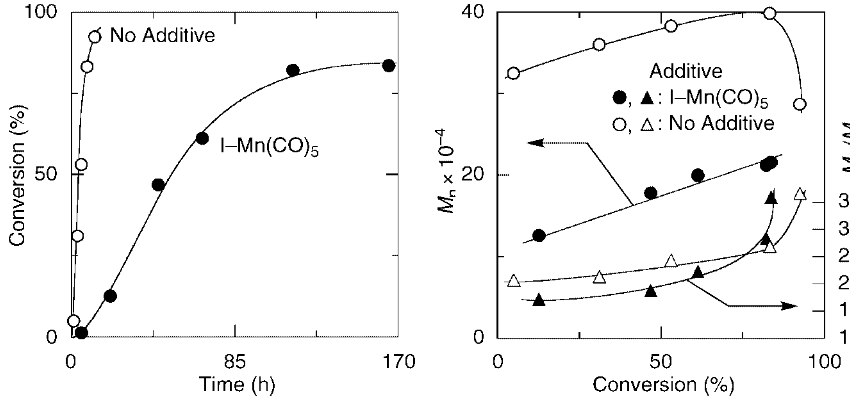


Figure 9. Free radical polymerization of vinyl acetate in bulk with or without $I{-}Mn(CO)_5$ at 40 °C under visible light; [vinyl acetate]$_0$ = 9.9 M, [2,2′-azobisisobutyronitrile]$_0$ = 11 mM, $[I{-}Mn(CO)_5]_0$ = 0 or 22 mM.

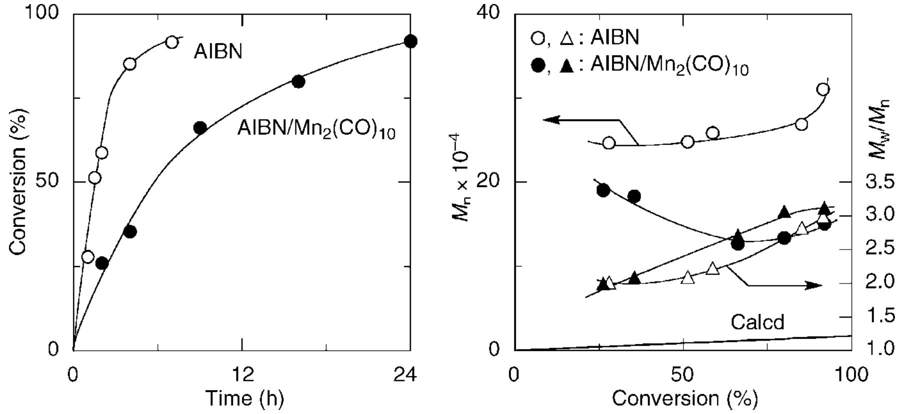


Figure 10. 2,2′-Azobisisobutyronitrile (AIBN)-initiated radical polymerization of vinyl acetate in bulk with or without $Mn_2(CO)_{10}$ at 40 °C under visible light; [vinyl acetate]$_0$ = 9.9 M, [AIBN]$_0$ = 160 mM, $[Mn_2(CO)_{10}]_0$ = 0 or 25 mM.

the Mn−Mn bond of $Mn_2(CO)_{10}$ cleaves upon visible light irradiation.[19] The generated •$Mn(CO)_5$ activates the C−I bond of the initiator to give the carbon-centered radical, and the initiation and the propagation then take place. Because of the facts that the molecular weight was controlled and that the polymer retained the iodide chain ends, the reversible activation of the C−I terminal should occur. There are two possible activation mechanisms for the C−I terminal; that is, metal-catalyzed and degenerative iodine transfer mechanisms.[30−32,37] In the former, the terminal C−I bond is activated by •$Mn(CO)_5$ to generate the growing radical species similar to that for the initiator iodide, although the generated $I{-}Mn(CO)_5$ may or may not give the iodine back to the growing radical species. In the latter mechanism, the reversible C−I bond activation relies on the degenerative iodine transfer process among the polymer chain ends similar to the iodine transfer radical polymerizations.[38,39] To investigate these possibilities and to estimate the contribution of these processes to the controlled radical polymerizations, some model reactions were carried out as follows.

a. Model Reactions for the Mn-Catalyzed C−I Bond Activation. To study the photoinduced activation process of $Mn_2(CO)_{10}$ as well as the C−I bond activation-deactivation processes, $Mn_2(CO)_{10}$ and **1** were mixed in benzene or benzene-d_6 at 40 °C under visible light, and the consumption rates of $Mn_2(CO)_{10}$ and **1** were measured. Figure 8 shows the time-consumption curves of $Mn_2(CO)_{10}$ (A) and **1** (B), which were determined from the decrease in the absorbance of $Mn_2(CO)_{10}$

in the UV−vis spectra of the solution and from the decrease in the peak intensity of **1** by ^{1}H NMR spectroscopy, respectively.

Under visible light, both $Mn_2(CO)_{10}$ and **1** were gradually consumed following first-order kinetics. Upon turning off the light, however, both consumptions ceased immediately, indicating that the thermal homolysis of $Mn_2(CO)_{10}$ was negligible at 40 °C. Thus, the photochemical homolysis of $Mn_2(CO)_{10}$ steadily occurred to generate $\bullet Mn(CO)_5$, which can abstract the iodine atom from **1** to form the carbon-centered radical ($\bullet CH_2CO_2Et$) and $I-Mn(CO)_5$. This indicates that the polymerization is triggered by the continuously supplied $\bullet Mn(CO)_5$ species as the C−I terminal activator. On the other hand, **1** was consumed gradually via the radical−radical coupling reaction under the model reaction conditions along with the accumulation of the $I-Mn(CO)_5$ species. However, the consumption rate of **1** obeyed first order kinetics during the reactions and was not affected by the accumulated $I-Mn(CO)_5$. If the $I-Mn(CO)_5$ species had a strong ability for giving back the iodine atom to $\bullet CH_2CO_2Et$, the consumption rate should have been decreased with an increase in the concentration of $I-Mn(CO)_5$. Thus, the contribution of the deactivation of the growing carbon radical species by $I-Mn(CO)_5$ on regenerating the C−I terminal may not be large.

b. AIBN-Initiated Polymerization of VAc in the Presence of Manganese Complexes. To investigate the direct effects of $I-Mn(CO)_5$ on radical polymerization, the synthesized and isolated $I-Mn(CO)_5$[28] was added into the AIBN-initiated radical polymerization of VAc in bulk at 40 °C under visible light. Upon the addition of $I-Mn(CO)_5$ ($[I-Mn(CO)_5]_0 = 2[AIBN]_0$), the polymerization was retarded (Figure 9). However, the molecular weight of the polymers obtained in the presence of $I-Mn(CO)_5$ was still much higher than the calculated values on the assumption that the reverse mechanism of the metal-catalyzed or atom transfer process took place to produce two polymer chains from one AIBN molecule.[40,41] These results suggest that the deactivation rate by $I-Mn(CO)_5$ was too slow to control the polymerization, in comparison to the fast propagation. Thus, the molecular weight control in the $R-I/Mn_2(CO)_{10}$-based polymerization relies mainly on the degenerative iodine transfer process. A large contribution of the degenerative iodine transfer process is also supported by the fact that bromide based systems with $R-Br/Mn_2(CO)_{10}$ gave uncontrolled and higher molecular weight polymers (see Table S1 in Supporting Information).

Another possible mechanism of the controlled polymerization may be the metal-mediated one, where a possibly in situ generated carbon−manganese bond would be responsible for the control as in the Co-mediated polymerization of VAc with an azo-iniator [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)]/$Co(acac)_2$.[33−35] The polymerization of VAc with AIBN/$Mn_2(CO)_{10}$ was thus investigated (Figure 10). Although the addition of $Mn_2(CO)_{10}$ retarded the AIBN-initiated polymerization, no induction period was observed unlike the cobalt-mediated radical polymerization.[33−35] The obtained molecular weights were much higher than the calculated values assuming that one manganese atom mediates one polymer chain growth, and the MWDs were broad. The molecular weights became slightly lower on addition of $Mn_2(CO)_{10}$ into the AIBN-initiated system, but the effects were too small. These results suggest that the contribution of the manganese-mediated mechanism is negligible in the controlled polymerization with $R-I/Mn_2(CO)_{10}$.

Conclusion

The $Mn_2(CO)_2$-based system was highly effective in fast controlled radical polymerization of vinyl acetate under visible light. The reaction was completed within a few hours even at a low temperature and a low concentration of the manganese complex to give the polymers, whose molecular weight was controlled up to 10^5. The polymerization was photoresponsive; i.e., the polymerization proceeded only during the lighting period while maintaining the molecular weight control during the entire procedures. This system was also applicable to conjugated monomers such as acrylates and styrene with the use of appropriate initiators. The success of the controlled polymerization is due to the gradual supply of the highly active manganese radical species [$\bullet Mn(CO)_5$] and the use of the relatively weak C−I bond, which can be easily activated by $\bullet Mn(CO)_5$ as well as by carbon-centered radical species via the degenerative iodine transfer process.

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Supporting Information Available: Effects of light source and intensity on the polymerization and additional polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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