

# Mn<sub>2</sub>(CO)<sub>10</sub>-Induced RAFT Polymerization of Vinyl Acetate, Methyl Acrylate, and Styrene

By Kazuhiko KOUMURA, Kotaro SATOH, and Masami KAMIGAITO\*

A dinuclear manganese complex [Mn<sub>2</sub>(CO)<sub>10</sub>] induced the controlled/living radical polymerization of various conjugated and unconjugated vinyl monomers including vinyl acetate, methyl acrylate, and styrene in conjunction with dithiocarbonyl compounds [R–SC(S)Z] under weak visible light at 40 °C. The obtained polymers had controlled molecular weights, narrow molecular weight distributions, and well-defined chain-end groups originating from R–SC(S)Z, as indicated by SEC, <sup>1</sup>H NMR, and MALDI-TOF-MS analyses. The polymerization most probably proceeds *via* the reversible activation of the C–SC(S)Z bond by •Mn(CO)<sub>5</sub> *via* the metal-catalyzed process and/or by the carbon-centered radical species *via* the addition-fragmentation chain transfer (RAFT) process.

KEY WORDS: Vinyl Acetate / Acrylate / Styrene / Living Radical Polymerization / RAFT Polymerization / Manganese Complex /

Various aspects of the controlled/living radical polymerization have been significantly developed in this decade, including a variety of initiating systems, controllable monomers, polymer structures, fusion with other substances, and applications to functional materials. Among the numerous initiating systems, there are now three representatives in terms of wide applicability and good controllability; *i.e.*, the nitroxide-mediated radical polymerization (NMP),<sup>1,2</sup> metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),<sup>3–17</sup> and reversible addition-fragmentation chain transfer (RAFT)<sup>18</sup> polymerization or macromolecular design *via* interchange of xanthate (MADIX).<sup>19</sup> Although the components and the mechanisms are different, they are all based on the reversible transient activation of the dormant covalent species into the growing radical species. However, each system has its own characteristics or features due to the differences, which suggests that the choice of initiating systems is important depending on the monomers, conditions, purposes, etc.

The metal-catalyzed living radical polymerization or ATRP is one of the best methods in terms of the well-defined architecture of the polymers from a variety of conjugated monomers, such as methacrylates, acrylates, acrylamides, acrylonitrile, and styrenes. This polymerization is generally initiated by the carbon radical generated from the alkyl halide upon the activation of the carbon–halogen bond by the transition metal catalyst, and then proceeds *via* the metal-catalyzed reversible activation of the carbon–halogen terminal into the growing radical species. One growing polymer chain end is thus generated from one carbon–halogen bond, which can permit the well-defined polymer synthesis. Although various transition metals, such as ruthenium,<sup>3</sup> copper,<sup>4,5,7</sup> iron,<sup>8–10</sup> nickel,<sup>6,11,12</sup> rhodium,<sup>13</sup> palladium,<sup>14</sup> molybdenum,<sup>15</sup> cobalt,<sup>16</sup> and rhenium,<sup>17</sup> can be employed, the dormant covalent bonds are mostly chlorides and bromides, and sometimes iodides except for (pseudo)halides like thiocya-

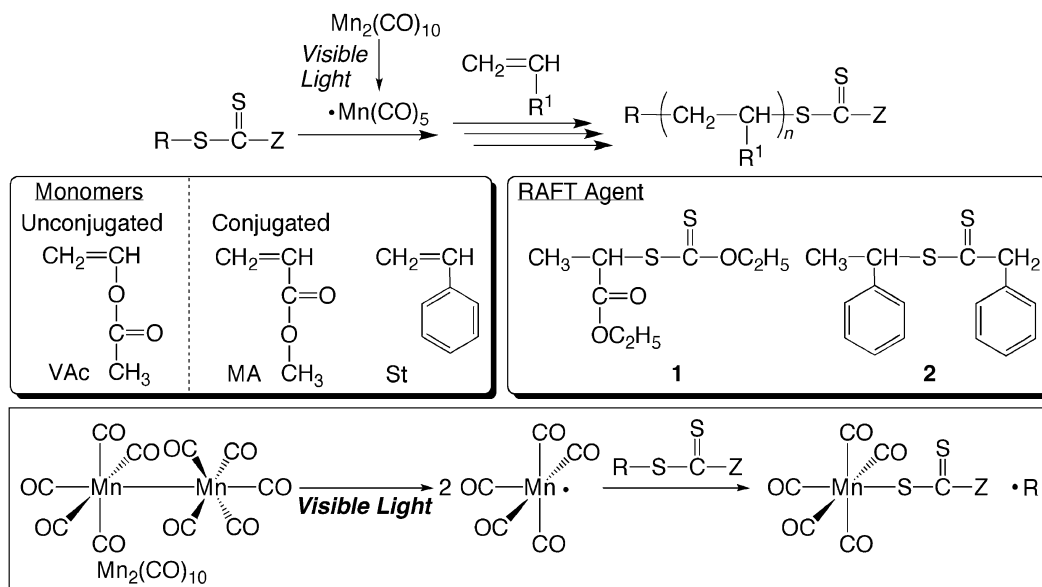
nate.<sup>20</sup> The choice of the metal complexes including metals and ligands as well as the halides is important for the precise control of the polymerizations depending on the monomers.

In contrast, the RAFT/MADIX system with the dithiocarbonyl compounds [R–SC(S)Z] is one of the most widely applicable systems for various monomers including not only conjugated, but also unconjugated monomers like vinyl acetate (VAc).<sup>21–30</sup> The RAFT polymerization is initiated by the formation of a small amount of the oligomer radical chain generated from a radical initiator, such as AIBN, and the monomers. The radical species adds to the RAFT agent [R–SC(S)Z] to form the intermediate radical and then generates the fragment radical species (R•), which results in a polymer chain. The molecular weight of the resulting polymers can be basically determined by the feed ratio of the monomer to the RAFT agent while a slight amount the polymer chain is generated from the radical initiator. The design of the RAFT agents is also important depending on the monomer structures. The dithiocarboxylates, such as dithiophenylacetate (Z = CH<sub>2</sub>Ph) and dithiobenzoate (Z = Ph), are effective for the controlled polymerizations of styrenes and (meth)acrylates<sup>31,32</sup> while xanthate (Z = OR) and dithiocarbamate (Z = NR<sub>2</sub>) are suitable for VAc.<sup>21–30</sup>

Quite recently, we have found that a dinuclear manganese complex [Mn<sub>2</sub>(CO)<sub>10</sub>] induces the fast and efficient controlled/living radical polymerization of various monomers including VAc as well as methyl acrylate (MA) and styrene (St) in conjunction with the appropriate alkyl iodide under weak visible light at 40 °C.<sup>33</sup> This polymerization is triggered by the photochemical homolysis of the Mn–Mn bond to produce the highly active manganese radical [•Mn(CO)<sub>5</sub>],<sup>34,35</sup> which activates the C–I bond derived from the alkyl iodide. One polymer chain is thus generated from one molecule of the iodide initiator. The polymerization is based on the reversible activation of the C–I terminal by •Mn(CO)<sub>5</sub> *via* the metal-

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

\*To whom correspondence should be addressed (Tel: +81-52-789-5400, Fax: +81-52-789-5112, E-mail: kamigaito@apchem.nagoya-u.ac.jp).



**Scheme 1.** Controlled radical polymerization of various monomers with RAFT agent/ $\text{Mn}_2(\text{CO})_{10}$ .

catalyzed process as well as by the carbon-centered radical species *via* the degenerative iodine transfer process.

In this study, we investigated a combination of the highly active manganese complex with the RAFT/MADIX agent, in which the C–SC(S)Z bond might be activated by  $\cdot\text{Mn}(\text{CO})_5$  *via* the metal-catalyzed process and/or by the carbon-centered radical species *via* the RAFT process, for the controlled/living radical polymerizations of various vinyl monomers, such as VAc, MA, and St (Scheme 1). In contrast to the usual RAFT polymerizations in the presence of an azo-initiator like AIBN, the R–SC(S)Z/ $\text{Mn}_2(\text{CO})_{10}$  system is free from the carbon-centered initiating radical species derived from the azo-initiator that may generate an excess polymer chain. Furthermore, the polymer chains obtained with the R–SC(S)Z/ $\text{Mn}_2(\text{CO})_{10}$  system are free from halogen in contrast to the R–I/ $\text{Mn}_2(\text{CO})_{10}$  system giving polymers with halogen-terminal. A combined system with transition metals and dithiocarbonyl groups has been reported for  $\text{Fe}[\text{SC}(\text{S})\text{NEt}_2]_3$ <sup>36,37</sup> and  $\text{Cu}[\text{SC}(\text{S})\text{NEt}_2]\text{Cl}$ <sup>38</sup> in the presence of an azo- or peroxide-radical initiator, in which the C–SC(S)NEt<sub>2</sub> dormant bond is first generated from the initiating or growing radical species and the higher oxidation state metal [Fe(III) or Cu(II)], which is then activated by the lower oxidation state metal [Fe(II) or Cu(I)]. More recently, a lower oxidation state copper catalyst (CuBr) was employed in conjunction with dithiocarbonyl compounds [R–SC(S)Z; Z = NR', SR', R']<sup>39–42</sup> for conjugated monomers such as St and (meth)acrylates. These polymerizations proceed *via* the ATRP or concurrent ATRP/RAFT process, in which the C–SC(S)Z terminal is activated by CuBr and/or the carbon-centered radical species, to give the polymers with controlled molecular weights. However, an equimolar or higher amount of CuBr relative to the RAFT agent was needed to control the polymerization. We now report that  $\text{Mn}_2(\text{CO})_{10}$  is effective for the halogen-free controlled/living radical polymerization of

VAc and MA in conjunction with a xanthate and dithiocarbonylate, respectively, to give the polymers with controlled molecular weights and a good end-functionality even with the use of a small amount of  $\text{Mn}_2(\text{CO})_{10}$  relative to R–SC(S)Z ( $[\text{Mn}_2(\text{CO})_{10}]_0/[\text{R–SC(S)Z}] \leq 1/5$ ).

## EXPERIMENTAL

### Materials

Vinyl acetate (Wako, >98%), methyl acrylate (Tokyo Kasei, >99%), and styrene (Wako, >99%) were distilled from calcium hydride to remove inhibitors. Ethyl acetate (Kishida, >99%) as a solvent, and *n*-octane (Wako, >98%) as an internal standard for gas chromatography and <sup>1</sup>H NMR spectroscopy were distilled from calcium hydride and bubbled with dry nitrogen for 15 min just before use. *O*-ethyl-*S*-(1-ethoxycarbonyl)ethylthiocarbonate (**1**) was prepared according to the literature.<sup>19</sup> 1-Phenylethyl phenylthioacetate (**2**) was prepared according to the literature.<sup>32</sup>  $\text{Mn}_2(\text{CO})_{10}$  (Aldrich, 98%) and  $\text{Fe}_2\text{Cp}_2(\text{CO})_4$  (Aldrich, 99%) were used as received and handled in unlighted glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere ( $\text{O}_2 < 1$  ppm).

### Polymerization

Polymerization was carried out by the syringe technique under dry nitrogen in oven-dried and sealed glass tubes. A typical example for VAc polymerization with **1**/ $\text{Mn}_2(\text{CO})_{10}$  is given below.  $\text{Mn}_2(\text{CO})_{10}$  (19.4 mg, 0.0498 mmol) was mixed with VAc (4.6 mL, 0.0498 mol), *n*-octane (0.16 mL), and **1** (0.33 mL of 750 mM solution in *n*-octane, 0.248 mmol) sequentially in this order under light shielding condition to give the slightly yellow solution due to the manganese complex. The total volume of the reaction mixture was thus 5.09 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 [3M Filter Light ( $\lambda > 400$  nm)].<sup>33</sup> 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 (118 h, 90.3%). The quenched reaction mixture was diluted with toluene (*ca.* 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 (Mg<sub>0.7</sub>Al<sub>0.3</sub>O<sub>1.15</sub>); 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, and evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers as slightly yellowish white powder (42.1 mg, 78% yield;  $M_n = 18400$ ,  $M_w/M_n = 1.59$ ).

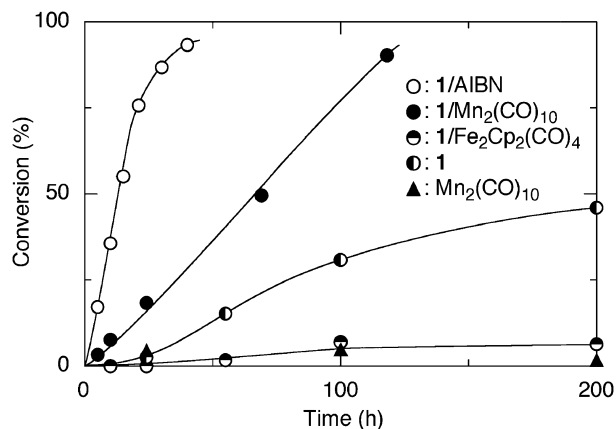
### Measurements

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.  $\times$  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 <sup>1</sup>H NMR spectroscopy (for MA) with *n*-octane as an internal standard. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> at 25 °C on a Varian Gemini 2000 spectrometer, operating at 400 MHz. MALDI-TOF-MS spectra were measured on an Applied Biosystems Voyager-DE STR spectrometer (linear mode) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the ionizing matrix and sodium trifluoroacetate as the ion source. The experiment was carried out at an accelerating potential of 20 kV, where 256 laser shots were accumulated. 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-805L (pore size: 20–1000 Å; 8.0 mm i.d.  $\times$  30 cm)  $\times$  2; flow rate 1.0 mL/min] connected to a SIC WP-03 precision pump and a Shodex RI-71S detector. The columns were calibrated against eight standard polystyrene samples [Shodex:  $M_p = 520$ –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)].

## RESULTS AND DISCUSSION

### Controlled/Living Radical Polymerization of VAc with R–SC(S)OR'/Mn<sub>2</sub>(CO)<sub>10</sub>

The polymerization of VAc was carried out with Mn<sub>2</sub>(CO)<sub>10</sub> or Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>, both of which are efficient for the controlled/



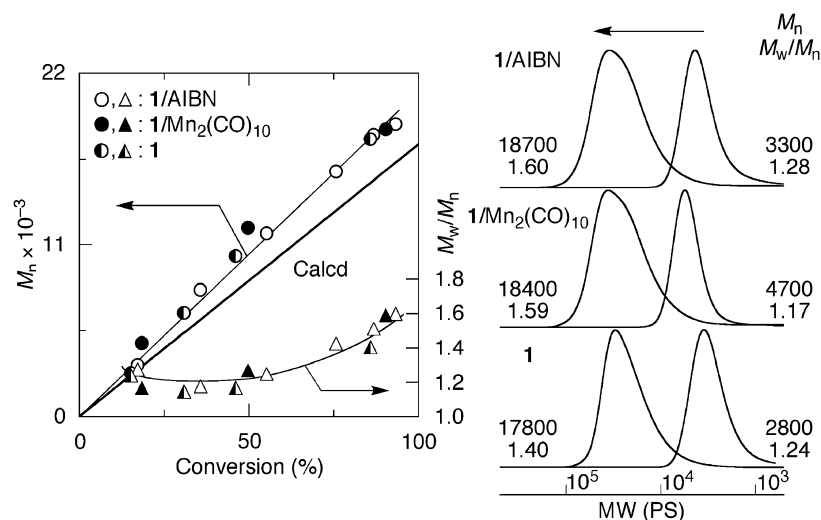
**Figure 1.** Time-conversion curves for the polymerization of vinyl acetate with **1**/AIBN (○), **1**/Mn<sub>2</sub>(CO)<sub>10</sub> (●), **1**/Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> (●), **1** (○), or Mn<sub>2</sub>(CO)<sub>10</sub> (▲) in bulk at 40 °C under visible light; [vinyl acetate]<sub>0</sub> = 9.8 M; [**1**]<sub>0</sub> = 49 mM; [AIBN]<sub>0</sub> = [Mn<sub>2</sub>(CO)<sub>10</sub>]<sub>0</sub> = [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>]<sub>0</sub> = 9.8 mM.

living radical polymerization of VAc in the presence of an alkyl iodide initiator,<sup>33,43</sup> in conjunction with xanthate (**1**) in bulk at 40 °C under weak visible light. The Mn complex induced an almost quantitative polymerization of VAc, although the rate was slower than that with **1**/AIBN under the same conditions (Figure 1). In contrast, the iron complex was not efficient for the polymerization in the presence of xanthate. The manganese complex itself did not induce any polymerization in the absence of **1**, indicating that no polymer chains were generated from Mn<sub>2</sub>(CO)<sub>10</sub>. However, a very slow polymerization proceeded with **1** alone, most probably due to the photolytic activation of the C–SC(S)OR' bond under weak visible light.

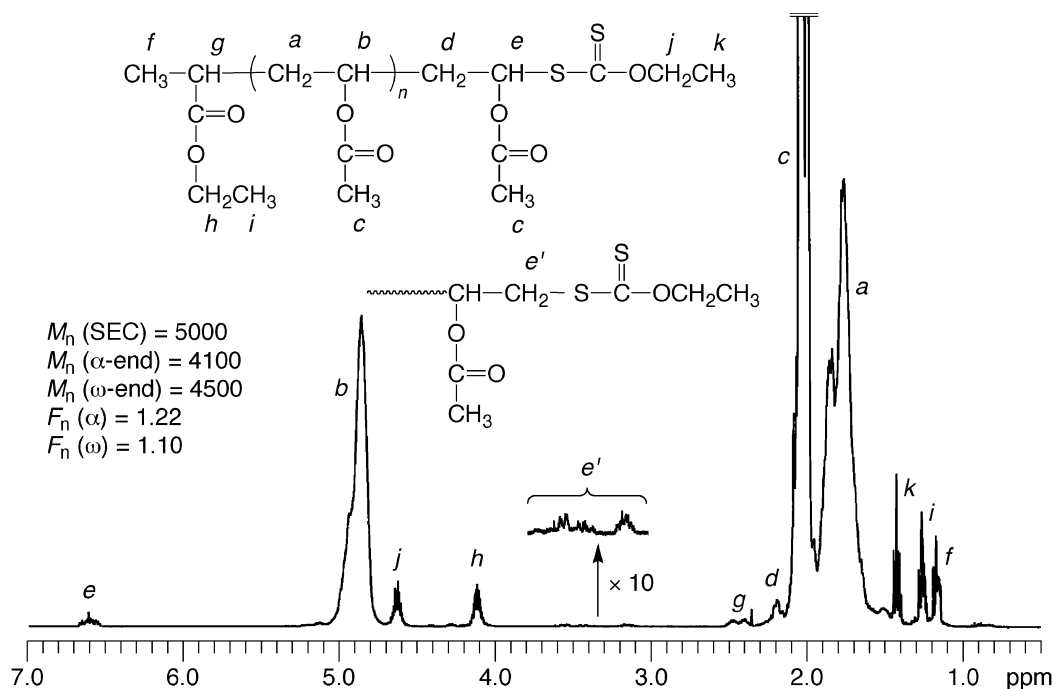
Figure 2 shows the  $M_n$ ,  $M_w/M_n$ , and SEC curves of the obtained poly(VAc). The  $M_n$ , which were based on the polystyrene calibration by SEC, increased in direct proportion to the monomer conversion although they were slightly higher than the calculated values assuming that one **1** molecule generates one polymer chain. The MWDs obtained with **1**/Mn<sub>2</sub>(CO)<sub>10</sub> were almost the same as those with **1**/AIBN. In both cases, as the polymerization proceeded, the SEC curves shifted to the high molecular weights with a slight broadening. One of the main reasons for the broadening is most probably the accumulation of the less reactive primary C–SC(S)OR' terminal originating from the head-to-head addition, which is inherent in the VAc radical polymerization.<sup>44–48</sup> These results suggest that Mn<sub>2</sub>(CO)<sub>10</sub> induces the controlled/living radical polymerization of VAc even in conjunction with a xanthate *via* the reversible activation of the C–SC(S)OR terminal.

The polymers obtained with **1** alone under weak visible light also had controlled molecular weights and similar MWDs, suggesting that **1** might work as a photo iniferter agent, although the reaction was very slow.

The structure of the poly(VAc) obtained with **1**/Mn<sub>2</sub>(CO)<sub>10</sub> was analyzed by <sup>1</sup>H NMR spectroscopy (Figure 3). In addition to the large absorptions attributed to the repeat units of VAc at



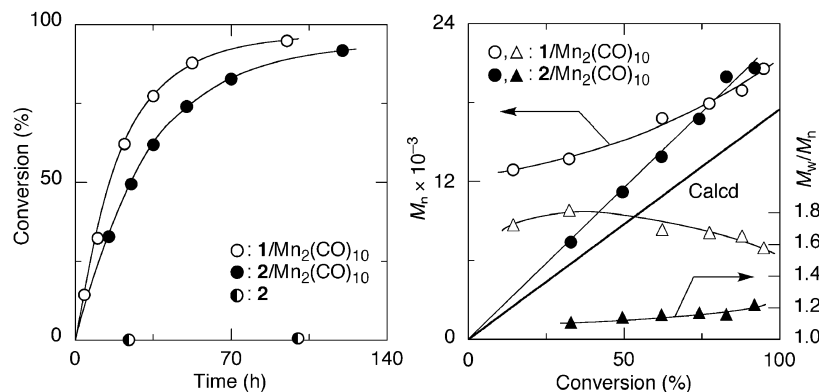
**Figure 2.**  $M_n$ ,  $M_w/M_n$ , and size-exclusion chromatograms of poly(vinyl acetate) obtained with **1**/AIBN (○, △), **1**/ $Mn_2(CO)_{10}$  (●, ▲), or **1** (●, ▲) in bulk at 40 °C under visible light;  $[vinyl\ acetate]_0 = 9.8\ M$ ;  $[1]_0 = 49\ mM$ ;  $[AIBN]_0 = [Mn_2(CO)_{10}]_0 = 9.8\ mM$ . The diagonal bold line indicates the calculated  $M_n$  assuming the formation of one living polymer per one **1** molecule.



**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;  $[vinyl\ acetate]_0 = 9.8\ M$ ;  $[1]_0 = 49\ mM$ ;  $[Mn_2(CO)_{10}]_0 = 9.8\ mM$ .

1.5–2.1 (*a* and *c*) and 4.8–5.2 (*b*) ppm, there are characteristic signals that originated from **1**; *i.e.*, the methyl (*f* and *i*), methylene (*h*), and methine (*g*) protons at the  $\alpha$ -end observed at 1.1–1.3, 4.1, and 2.3–2.5 ppm, respectively. The methyl (*k*) and methylene (*j*) protons at the  $\omega$ -end were also observed at 1.4 and 4.6 ppm, respectively. In addition, the methine (*e*) and methylene (*d*) protons at the xanthate  $\omega$ -terminal VAc unit, which was formed *via* the head-to-tail addition, were observed at 6.6 and 2.2 ppm, respectively. Furthermore, the methylene (*e'*) proton, formed *via* the head-to-head addition, was also

observed at 3.1–3.6 ppm. The number-average content of the head-to-head terminal in one polymer, calculated from the peak intensity ratio of the primary C–S  $\omega$ -end ( $e'/2$ ) to the  $\alpha$ -end ( $h/2$ ), increased as the polymerization proceeded [11% (at 18% monomer conversion) to 93% (at 90% monomer conversion)]. Thus, the accumulation of less reactive primary C–SC(S)OR' bond led to a broadening of the MWDs in the later stage of the polymerization. A similar result was observed in the iodine transfer radical polymerization of VAc.<sup>33,43,49–51</sup>



**Figure 4.** Polymerization of methyl acrylate in ethyl acetate with  $1/\text{Mn}_2(\text{CO})_{10}$  ( $\circ$ ,  $\triangle$ ) or  $2/\text{Mn}_2(\text{CO})_{10}$  ( $\bullet$ ,  $\blacktriangle$ ) at  $40^\circ\text{C}$  under visible light;  $[\text{methyl acrylate}]_0/[\text{MADIX/RAFT agent}]_0/[\text{Mn}_2(\text{CO})_{10}]_0 = 4000/20/4 \text{ mM}$ .

The number-average molecular weights [ $M_n(\text{NMR})$ ] calculated from the  $\alpha$ -( $h/2$ ) and  $\omega$ -end signals ( $j/2$ ) to the main-chain VAc units ( $b$ ) was 4100 and 4500, respectively, which were more or less lower than that by SEC [ $M_n(\text{SEC}) = 5000$ ] based on the polystyrene calibration. The number-average end-functionality ( $F_n$ ) obtained from the  $M_n(\text{NMR})$  and  $M_n(\text{SEC})$  [ $F_n = M_n(\text{SEC})/M_n(\text{NMR}, \alpha\text{- or } \omega\text{-end})$ ] was close to unity for both the  $\alpha$ - and  $\omega$ -terminals:  $F_n(\alpha) = 1.22$  and  $F_n(\omega) = 1.10$ . These results indicate that one poly(VAc) chain was generated from one molecule of **1** and that the xanthate group remained at the  $\omega$ -ends for almost all of the polymer chains without any significant loss during the polymerization. Thus, the Mn-induced controlled/living polymerization proceeds *via* the activation of the C–SC(S)OR' terminal by  $\cdot\text{Mn}(\text{CO})_5$  based on the metal-catalyzed process and/or by the carbon-centered radical species based on the RAFT process.

#### Controlled/Living Radical Polymerization of MA and St with R–SC(S)R'/Mn<sub>2</sub>(CO)<sub>10</sub>

A conjugated monomer, MA, was also polymerized with Mn<sub>2</sub>(CO)<sub>10</sub> in conjunction with **1** or 1-phenylethyl phenyl-dithioacetate (**2**) in ethyl acetate at  $40^\circ\text{C}$  under weak visible light. The MA polymerization proceeded and reached almost quantitative conversions with both RAFT agents when coupled with Mn<sub>2</sub>(CO)<sub>10</sub> (Figure 4). No efficient polymerization of MA with only **2** occurred.

The poly(MA) obtained with  $1/\text{Mn}_2(\text{CO})_{10}$  had relatively higher molecular weights than the calculated ones in the early stage of the polymerization and broad MWDs during the polymerization ( $M_w/M_n \sim 1.6$ ). However, when coupled with **2**, the  $M_n$ , which was based on the PMMA calibration by SEC, increased in direct proportion to the monomer conversion and were slightly higher than the calculated values. The MWDs were narrow throughout the polymerizations ( $M_w/M_n \sim 1.2$ ). These are due to a more reactive C–SC(S)R' bond derived from **2** to the manganese radical species and/or a higher chain transfer constant of **2** than that of **1**, as observed in the RAFT polymerizations.<sup>52</sup> Thus, **2** proved a better RAFT agent for the controlled/living radical polymerization of MA with Mn<sub>2</sub>(CO)<sub>10</sub> as in the usual azo-based RAFT polymerizations.<sup>31,32</sup>

To investigate the effects of the metal catalyst concentration, the MA polymerizations were carried out with  $2/\text{Mn}_2(\text{CO})_{10}$  by varying the concentration of Mn<sub>2</sub>(CO)<sub>10</sub> (Table I). Even at a low concentration of Mn<sub>2</sub>(CO)<sub>10</sub> ( $[2]_0/[\text{Mn}_2(\text{CO})_{10}]_0 = 20$ ), the polymerization proceeded and gave the polymers with controlled molecular weights (Figure 5). The MWDs of the obtained polymers became narrower with the decreasing Mn concentration (see also entries 2–4 in Table I). A similar result was obtained for the R–I/Mn<sub>2</sub>(CO)<sub>10</sub>-induced polymerization. The control of the molecular weights was similarly achieved as with  $2/\text{AIBN}$  (Figure 5 and entries 6–8 in Table I). The molecular weights can be varied by the feed ratios of MA to **2** (entries 2–5), which also suggests that the controlled/living polymerization proceeds *via* the reversible activation of the C–SC(S)R' terminal derived from **2**.

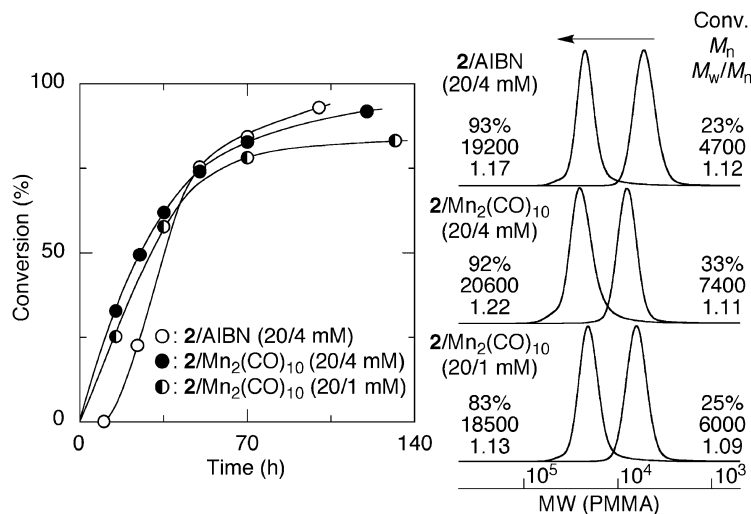
The polymerizations of St with dithiocarbonyl compounds/Mn<sub>2</sub>(CO)<sub>10</sub> were also examined and summarized in Table I. The xanthate system was not effective as indicated by the low monomer conversion as well as the higher molecular weights (entry 9). The  $M_n$ 's of the polystyrene obtained with  $2/\text{Mn}_2(\text{CO})_{10}$  were in good agreement with the calculated values (entries 10 and 11). However, the polymerization of St with  $2/\text{Mn}_2(\text{CO})_{10}$  was generally quite slow. Thus, further optimization of the polymerization conditions including the RAFT agent structure is necessary to more finely control the polymerization of St with Mn<sub>2</sub>(CO)<sub>10</sub>.

The obtained poly(MA) was also analyzed by <sup>1</sup>H NMR spectroscopy. Figure 6 shows the <sup>1</sup>H NMR spectrum of poly(MA) obtained with  $2/\text{Mn}_2(\text{CO})_{10}$ . The polymer gave the characteristic signals of poly(MA); *i.e.*, methyl ester groups ( $c$ ) and main-chain protons ( $b$  and  $c$ ). In addition to these large absorptions, methyl ( $e$ ) and methine ( $f$ ) protons at the  $\alpha$ -end, methylene ( $h$ ) protons at the  $\omega$ -end, and phenyl groups ( $g$  and  $i$ ) at both ends were observed. The  $M_n$  values of poly(MA) calculated from the  $\alpha$ -( $f$ ) and  $\omega$ -( $h/2$ ) end to the main-chain MA units ( $c/3$ ) was 3800 and 4100, respectively, in good agreement with that by SEC [ $M_n(\text{SEC}) = 4200$ ]. The  $F_n$  values of  $\alpha$ -[ $F_n(\alpha) = 1.12$ ] and  $\omega$ -[ $F_n(\omega) = 1.08$ ] were close to unity, which indicated that one molecule of the RAFT agent generates

**Table I.** Polymerization of various monomers with RAFT/MADIX agent/ $\text{Mn}_2(\text{CO})_{10}$  or AIBN<sup>a</sup>

entry	Monomer	Initiating System	[RAFT/MADIX] <sub>0</sub> (mM)	[ $\text{Mn}_2(\text{CO})_{10}$ ] <sub>0</sub> or [AIBN] <sub>0</sub> (mM)	Time (h)	Conv., <sup>b</sup> (%)	$M_n$ (calcd) <sup>d</sup>	$M_n$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
1	MA	1/ $\text{Mn}_2(\text{CO})_{10}$	20	4	95	95	16600	20600	1.58
2	MA	2/ $\text{Mn}_2(\text{CO})_{10}$	20	10	140	88	15400	23200	1.52
3	MA	2/ $\text{Mn}_2(\text{CO})_{10}$	20	4	120	92	16100	20600	1.22
4	MA	2/ $\text{Mn}_2(\text{CO})_{10}$	20	1	132	83	14600	18500	1.13
5 <sup>e</sup>	MA	2/ $\text{Mn}_2(\text{CO})_{10}$	80	16	132	95	4400	5400	1.17
6	MA	2/AIBN	20	10	48	91	15900	18800	1.19
7	MA	2/AIBN	20	4	100	93	16300	19200	1.17
8 <sup>e</sup>	MA	2/AIBN	80	16	115	94	4300	4800	1.14
9	MA	2	20	0	240	<1			
10	St	1/ $\text{Mn}_2(\text{CO})_{10}$	41	8.2	340	13	2900	19200	2.18
11	St	2/ $\text{Mn}_2(\text{CO})_{10}$	41	20	48	92	19400	20700	1.86
12	St	2/ $\text{Mn}_2(\text{CO})_{10}$	41	8.2	805	74	13300	15800	1.25
13	St	2/AIBN	41	20	240	97	20400	18400	1.10
14	St	2	20	0	200	<10			

<sup>a</sup>Polymerization conditions:  $[\text{monomer}]_0/[\text{RAFT/MADIX}]_0 = 200$ ,  $[\text{methyl acrylate}]_0 = 4.0\text{M}$  in ethyl acetate,  $[\text{styrene}]_0 = 8.2\text{M}$  in bulk at 40 °C under visible light. <sup>b</sup>The monomer conversion was determined by <sup>1</sup>H NMR (for MA) or gas chromatography (for St). <sup>c</sup> $M_n(\text{calcd}) = \text{MW}(\text{monomer}) \times [\text{monomer}]_0/[\text{RAFT/MADIX}]_0 \times \text{conv.} + \text{MW}(\text{RAFT/MADIX})$ . <sup>d</sup>The number-average molecular weight ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) were determined by size-exclusion chromatography in THF (poly(methyl methacrylate) standard for MA, and polystyrene standard for St). <sup>e</sup> $[\text{monomer}]_0/[\text{RAFT/MADIX}]_0 = 50$ .



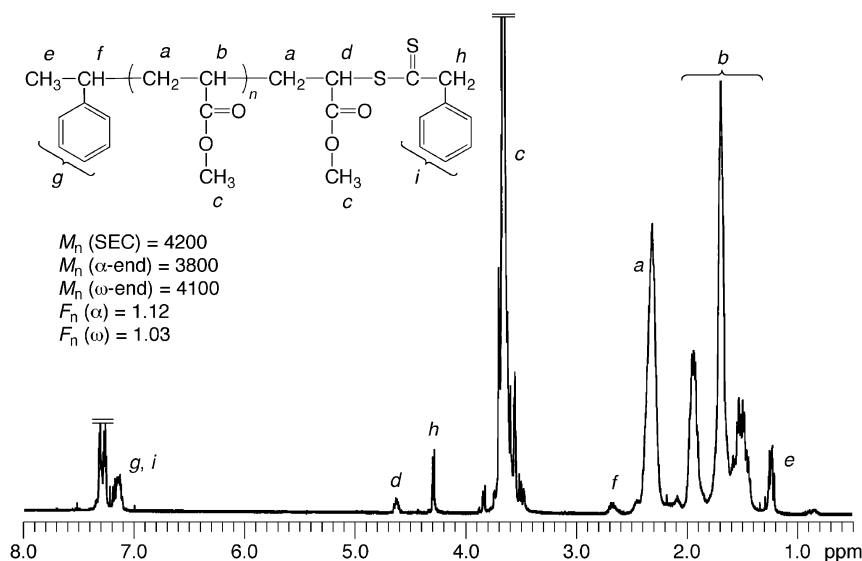
**Figure 5.** Polymerization of methyl acrylate in ethyl acetate with 2/AIBN or 2/ $\text{Mn}_2(\text{CO})_{10}$  at 40 °C under visible light;  $[\text{methyl acrylate}]_0/[2]_0/[AIBN]_0 = 4000/20/4\text{ mM}$  (○),  $[\text{methyl acrylate}]_0/[2]_0/[Mn_2(\text{CO})_{10}]_0 = 4000/20/4\text{ mM}$  (●), 4000/20/1 mM (●).

one polymer chain to give the polymers with controlled molecular weights.

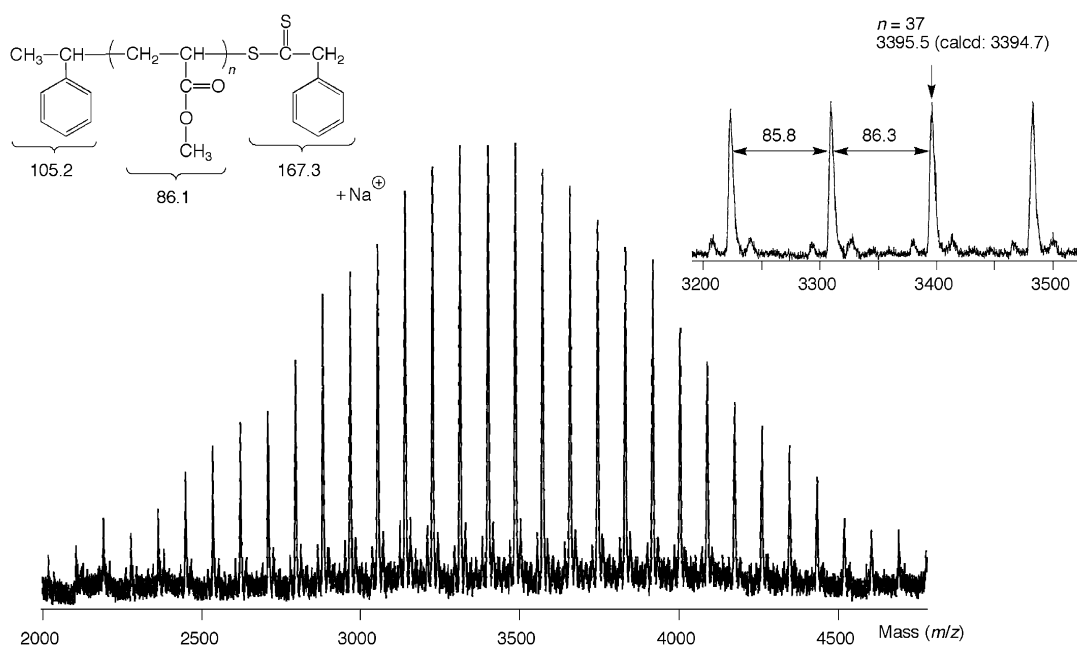
The poly(MA) obtained with 2/ $\text{Mn}_2(\text{CO})_{10}$  was also analyzed by MALDI-TOF-MS in the presence of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix and  $\text{CF}_3\text{CO}_2\text{Na}$  as the ionizing agent (Figure 7). The spectrum consists of a series of peaks, each separated by 86 Da intervals, which corresponds to the formula weight of the MA monomer. The molecular weight of each individual peak was very close to the calculated value for  $[\text{CH}_3\text{CH}(\text{Ph})-(\text{MA})_n-\text{SC}(=\text{S})\text{CH}_2\text{Ph}/\text{Na}^+]$ ; *i.e.*, poly(MA) processing one 2 molecule moiety at the  $\alpha$ - and  $\omega$ -ends, and the sodium ion from the salt for the MS analysis. This again indicates that the 2/ $\text{Mn}_2(\text{CO})_{10}$  system produces the poly(MA) with well-defined terminal groups.

## CONCLUSION

The dinuclear manganese complex,  $[\text{Mn}_2(\text{CO})_{10}]$ , was also effective in conjunction with dithiocarbonyl compounds  $[\text{R}-\text{SC}(\text{S})\text{Z}]$  to induce the controlled/living radical polymerization of various conjugated and non-conjugated vinyl monomers under weak visible light. The polymerization is based on the reversible activation of the C–SC(S)Z bond by  $\cdot\text{Mn}(\text{CO})_5$  via the metal-catalyzed process and/or by the carbon-centered radical species via the RAFT process to produce polymers with controlled molecular weights and well-defined chain-end groups originating from R–SC(S)Z. Although advantages of  $\text{Mn}_2(\text{CO})_{10}$  over AIBN in combination with R–SC(S)Z have not yet been clarified, this study indicates that  $\text{Mn}_2(\text{CO})_{10}$  can



**Figure 6.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 25 °C) of poly(methyl acrylate) obtained with 2/Mn<sub>2</sub>(CO)<sub>10</sub> in bulk at 40 °C under visible light; [methyl acrylate]<sub>0</sub> = 4.0 M; [2]<sub>0</sub> = 80 mM; [Mn<sub>2</sub>(CO)<sub>10</sub>]<sub>0</sub> = 16 mM.



**Figure 7.** MALDI-TOF-MS spectrum of poly(methyl acrylate) ( $M_n$  = 4200,  $M_w/M_n$  = 1.10) obtained with 2/Mn<sub>2</sub>(CO)<sub>10</sub> in bulk at 40 °C under visible light; [methyl acrylate]<sub>0</sub> = 4.0 M; [2]<sub>0</sub> = 80 mM; [Mn<sub>2</sub>(CO)<sub>10</sub>]<sub>0</sub> = 16 mM.

be employed as an activating agent and/or non-carbon-centered radical generator without losing its activity even in the presence of dithiocarbonyl compounds.

**Acknowledgment.** This work was supported in part by a Grant-in-Aid for Young Scientists (S) (No. 19675003) by the Japan Society for the Promotion of Science, a Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformation of Carbon Resources” (No. 17065008) from the Ministry of Education, Culture, Sports, Science, and

Technology, Japan, and the Global COE Program “Elucidation and Design of Materials and Molecular Functions.”

Received: March 23, 2009

Accepted: April 13, 2009

Published: June 3, 2009

## REFERENCES

- a) C. J. Hawker, *J. Am. Chem. Soc.*, **116**, 11185 (1994).  
 b) C. J. Hawker, A. W. Bosman, and E. Harth, *Chem. Rev.*, **101**, 3661

- (2001).
2. A. Studer and T. Schulte, *Chem. Rec.*, **5**, 27 (2005).
  3. a) M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules*, **28**, 1721 (1995).  
b) M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rev.*, **101**, 3689 (2001).  
c) M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rec.*, **4**, 159 (2004).  
d) M. Ouchi, T. Terashima, and M. Sawamoto, *Acc. Chem. Res.*, **41**, 1120 (2008).
  4. a) J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).  
b) K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).  
c) N. V. Tsarevsky and K. Matyjaszewski, *Chem. Rev.*, **107**, 2270 (2007).  
d) W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.*, **32**, 93 (2007).
  5. V. Percec and B. Barboiu, *Macromolecules*, **28**, 7970 (1995).
  6. C. Granel, Ph. Dubois, R. Jérôme, and Ph. Teyssié, *Macromolecules*, **29**, 8576 (1996).
  7. D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, and A. J. Shooer, *Macromolecules*, **30**, 2190 (1997).
  8. a) T. Ando, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **30**, 4507 (1997).  
b) Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **32**, 6877 (1999).  
c) Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **33**, 3543 (2000).  
d) M. Kamigaito, I. Onishi, S. Kimura, and M. Sawamoto, *Chem. Commun.*, 2694 (2002).
  9. a) K. Matyjaszewski, M. Wei, J. Xia, and N. E. McDermott, *Macromolecules*, **30**, 8161 (1997).  
b) M. Teodorescu, S. G. Gaynor, and K. Matyjaszewski, *Macromolecules*, **33**, 2335 (2000).
  10. a) J. Louie and R. H. Grubbs, *Chem. Commun.*, 1479 (2000).  
b) S. Zhu, D. Yan, G. Zhang, and M. Li, *Macromol. Chem. Phys.*, **201**, 2666 (2000).  
c) V. C. Gibson, R. K. O'Reilly, W. Reed, D. F. Wass, A. J. P. White, and D. J. Williams, *Chem. Commun.*, 1850 (2002).  
d) R. K. O'Reilly, V. C. Gibson, A. J. P. White, and D. J. Williams, *J. Am. Chem. Soc.*, **125**, 8450 (2003).  
e) R. K. O'Reilly, V. C. Gibson, A. J. P. White, and D. J. Williams, *Polyhedron*, **23**, 2921 (2004).  
f) S. Niibayashi, H. Hayakawa, R.-H. Jina, and H. Nagashima, *Chem. Commun.*, 1855 (2007).
  11. a) H. Uegaki, Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **30**, 2249 (1997).  
b) H. Uegaki, Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **31**, 6756 (1998).  
c) H. Uegaki, M. Kamigaito, and M. Sawamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 3003 (1999).
  12. a) P. Li and K. Y. Qiu, *Polymer*, **43**, 5873 (2002).  
b) R. K. O'Reilly, M. P. Shaver, and V. C. Gibson, *Inorg. Chim. Acta*, **359**, 4417 (2006).
  13. a) V. Percec, B. Barboiu, A. Neumann, J. C. Ronda, and M. Zhao, *Macromolecules*, **29**, 3665 (1996).  
b) G. Moineau, C. Granel, Ph. Dubois, R. Jérôme, and Ph. Teyssié, *Macromolecules*, **31**, 542 (1998).  
c) M. G. L. Petrucci, A.-M. Lebuis, and A. K. Kakkar, *Organometallics*, **17**, 4966 (1998).
  14. Ph. Lecomte, I. Drapier, Ph. Dubois, R. Jérôme, and Ph. Teyssié, *Macromolecules*, **30**, 7631 (1997).
  15. a) J. A. M. Brandts, P. van de Geijn, E. E. van Faassen, J. Boersma, and G. van Koten, *J. Organomet. Chem.*, **584**, 246 (1999).  
b) E. Le Grogneec, J. Claverie, and R. Poli, *J. Am. Chem. Soc.*, **123**, 9513 (2001).  
c) F. Stoffelbach, D. M. Haddleton, and R. Poli, *Eur. Polym. J.*, **39**, 2099 (2003).
  - d) J. A. Mata, S. Maria, J.-C. Daran, and R. Poli, *Eur. J. Inorg. Chem.*, 2624 (2006).
  16. a) B. Wang, Y. Zhuang, X. Luo, S. Xu, and X. Zhou, *Macromolecules*, **36**, 9684 (2003).  
b) M.-S. Weiser and R. Mülhaupt, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 3804 (2005).  
c) K. Matsubara and M. Matsumoto, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 4222 (2006).
  17. a) Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **32**, 2420 (1999).  
b) S. Komiya, T. Chigira, T. Suzuki, and M. Hirano, *Chem. Lett.*, **28**, 347 (1999).
  18. a) J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, and S. H. Thang, *Macromolecules*, **31**, 5559 (1998).  
b) G. Moad, E. Rizzardo, and S. H. Thang, *Aust. J. Chem.*, **58**, 379 (2005).  
c) G. Moad, E. Rizzardo, and S. H. Thang, *Polymer*, **49**, 1079 (2008).  
d) G. Moad, E. Rizzardo, and S. H. Thang, *Acc. Chem. Res.*, **41**, 1133 (2008).
  19. M. Destarac, C. Brochon, J.-M. Catala, A. Wilczewska, and S. Z. Zard, *Macromol. Chem. Phys.*, **203**, 2281 (2002).
  20. a) K. A. Davis and K. Matyjaszewski, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **41**, 449 (2004).  
b) W. Tang and K. Matyjaszewski, *Macromolecules*, **40**, 1858 (2007).
  21. E. Rizzardo, J. Chiefari, R. T. A. Mayadunne, G. Moad, and S. H. Thang, "ACS Symposium Series", vol. 768, American Chemical Society Publication, 2000, p 278.
  22. D. Charnot, P. Corpart, H. Adam, S. Zard, T. Biadatti, and G. Bouhadir, *Macromol. Symp.*, **150**, 23 (2000).
  23. M. Destarac, D. Charnot, X. Frank, and S. Z. Zard, *Macromol. Rapid Commun.*, **21**, 1035 (2000).
  24. M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana, and C. Barner-Kowollik, *Macromol. Chem. Phys.*, **204**, 1160 (2003).
  25. M. L. Coote and L. Radom, *Macromolecules*, **37**, 590 (2004).
  26. A. Favier, C. Barner-Kowollik, T. Davis, and M. H. Stenzel, *Macromol. Chem. Phys.*, **205**, 925 (2004).
  27. R. W. Simms, T. P. Davis, and M. F. Cunningham, *Macromol. Rapid Commun.*, **26**, 592 (2005).
  28. D. Boschmann and P. Vana, *Polym. Bull.*, **53**, 231 (2005).
  29. J. P. Russum, N. D. Barbre, C. W. Jones, and F. J. Schork, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2188 (2005).
  30. F. Chen, Z. Cheng, J. Zhu, W. Zhang, and X. Zhu, *Eur. Polym. J.*, **44**, 1789 (2008).
  31. Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo, and S. H. Thang, *Macromolecules*, **36**, 2256 (2003).
  32. J. F. Quinn, E. Rizzardo, and T. P. Davis, *Chem. Commun.*, 1044 (2001).
  33. K. Koumura, K. Satoh, and M. Kamigaito, *Macromolecules*, **41**, 7359 (2008).
  34. a) E. W. Abel and F. G. A. Stone, *Q. Rev., Chem. Soc.*, **23**, 325 (1969).  
b) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).  
c) T. J. Meyer and J. V. Caspar, *Chem. Rev.*, **85**, 187 (1985).  
d) A. E. Stiegman and D. R. Tyler, *Coord. Chem. Rev.*, **63**, 217 (1985).  
e) B. C. Gilbert and A. F. Parsons, *J. Chem. Soc., Perkin Trans. 2*, 367 (2002).  
f) T. E. Bitterwolf, *J. Organomet. Chem.*, **689**, 3939 (2004).
  35. a) S. A. Hallock and A. Wojcicki, *J. Organomet. Chem.*, **54**, C27 (1973).  
b) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).  
c) S. B. McCullen and T. L. Brown, *Inorg. Chem.*, **20**, 3528 (1981).  
d) T. Kondo, Y. Sone, Y. Tsuji, and Y. Watanabe, *J. Organomet. Chem.*, **473**, 163 (1994).



- e) B. C. Gilbert, W. Kalz, C. I. Lindsay, P. T. McGrail, A. F. Parsons, and D. T. E. Whittaker, *Tetrahedron Lett.*, **40**, 6095 (1999).
- f) N. Huther, P. T. McGrail, and A. F. Parsons, *Tetrahedron Lett.*, **43**, 2535 (2002).
- g) N. Huther, P. T. McGrail, and A. F. Parsons, *Eur. J. Org. Chem.*, 1740 (2004).
36. M. Nishimura, M. Kamigaito, and M. Sawamoto, The 218th ACS National Meeting, Polymer Preprints, New Orleans, LA, USA, 470 (1999).
37. D.-Q. Qin, S.-H. Qin, and K.-Y. Qiu, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 3464 (2001).
38. a) P. Li and K.-Y. Qiu, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 2093 (2002).  
b) P. Li, S.-H. Qin, D.-Q. Qin, and K.-Y. Qiu, *Polym. Int.*, **53**, 756 (2004).
39. a) W. Zhang, N. Zhou, J. Zhu, B. Sun, and X. Zhu, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 510 (2006).  
b) W. Zhang, X. Zhu, Z. Cheng, and J. Zhu, *J. Appl. Polym. Sci.*, **106**, 230 (2007).
40. Y. Kwak and K. Matyjaszewski, *Macromolecules*, **41**, 6627 (2008).
41. R. Nicolaÿ, Y. Kwak, and K. Matyjaszewski, *Macromolecules*, **41**, 4585 (2008).
42. Y. Kwak, R. Nicolaÿ, and K. Matyjaszewski, *Macromolecules*, **41**, 6602 (2008).
43. M. Wakioka, K.-Y. Baek, T. Ando, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **35**, 330 (2002).
44. D. W. Ovenall, *Macromolecules*, **17**, 1458 (1984).
45. R. L. Adelman and R. C. Ferguson, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 891 (1975).
46. F. F. Vercauteren and W. A. B. Donners, *Polymer*, **27**, 993 (1986).
47. S. Amiya and M. Uetsuki, *Macromolecules*, **15**, 166 (1982).
48. S. Amiya and M. Uetsuki, *Anal. Sci.*, **1**, 91 (1985).
49. a) N. Ueda, M. Kamigaito, and M. Sawamoto, The 37th IUPAC International Symposium on Macromolecules, Preprints, Gold Coast, Australia, 237 (1998).  
b) N. Ueda, JP Patents 10 060 021 (1996).  
c) N. Ueda, JP Patents 11 147 914 (1997).  
d) N. Ueda, JP Patents 11 171 926 (1997).
50. M. C. Iovu and K. Matyjaszewski, *Macromolecules*, **36**, 9346 (2003).
51. K. Koumura, K. Satoh, M. Kamigaito, and Y. Okamoto, *Macromolecules*, **39**, 4054 (2006).
52. M. Destarac, W. Bzducha, D. Taton, I. Gauthier-Gillaizeau, and S. Z. Zard, *Macromol. Rapid Commun.*, **23**, 1049 (2002).