

## Polymerization of Acrylic Acids by Chlorocarbon/Metallocene Combination Initiator<sup>‡</sup>

Hee-Gweon Woo,<sup>\*</sup> Bo-Hye Kim, Myoung-Shik Cho, Min-Sook Kim, Yun-Gil Chung,  
Heui-Suk Ham,<sup>\*</sup> Choon-Scon Paek,<sup>‡</sup> Teak Sung Hwang,<sup>‡</sup> Moo-Jin Jun,<sup>§</sup> and Hong Li<sup>#</sup>

*Department of Chemistry and Institute of Basic Science, Chonnam National University, Kwangju 500-757, Korea*

*<sup>1</sup>Department of Medical Technology, Mokpo Science College, Mokpo 530-730, Korea*

*<sup>‡</sup>Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea*

*<sup>§</sup>Department of Chemistry, Yonsei University, Seoul 120-749, Korea*

*<sup>#</sup>Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China*

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Vinyl monomers undergo addition polymerization by radical, ionic or both initiators, depending on the type of substituent of vinyl derivatives.<sup>1</sup> Poly(acrylic acid)s can be easily prepared by the radical-chain polymerization of acrylic acids, which may occur when radicals are generated by either light absorption or thermal heating. Poly(acrylic acid)s can be used as binding agent for various metal ions and a polymeric support for metal complexes.<sup>2</sup> Transition metals play important role in host-guest self-assembling chemistry,<sup>3</sup> by forming host-guest supramolecular metal complexes by interacting with monomeric, oligomeric, and polymeric ligands.<sup>4</sup>

Halogenated organic chemicals have been employed as effective photoinitiators for the photopolymerization of many vinyl derivatives<sup>5,6</sup> although serious environmental problems can be often created by the halogenated chemicals.<sup>7,8</sup>

Ferrocene (Cp<sub>2</sub>Fe) along with halogenated compounds was thus introduced as both a photopolymerization promoter and a halide-radical trapping sponge.<sup>9</sup> Recently, we first communicated the photopolymerization of methyl methacrylate (MMA) with the CCl<sub>4</sub>/Cp<sub>2</sub>M (M = Fe, Co, Ni) combination initiator, producing polar-substituent-containing polymers with CCl<sub>3</sub>/Cl end groups.<sup>10</sup> The end groups of those polymers can be converted to diverse functional groups by chemical modification. As an extension of our previous reports, here we report the thermal polymerization of acrylic acid (AA) and methacrylic acid (MA), initiated by chlorocarbon/Cp<sub>2</sub>M (M = V, Cr, Mn, Fe, Co, Ni, Ru; Cp' = Cp or Me<sub>3</sub>Cp) combination, to compare their initiating effect in terms of living radical polymerization on the polymerization reactions with the other known organic halide/transition metal complex combination initiators.<sup>11</sup> The chlorocarbons used here include carbon tetrachloride, benzyl chloride, and 1-phenylethyl chloride.

### Experimental Section

**Materials and Instrumentation.** All polymerization reactions and manipulations were performed in prepurified

nitrogen or argon inert atmosphere using Schlenk techniques. Dry, oxygen-free solvents were used throughout. Glassware was flame-dried or oven-dried prior to use. Infrared spectra were taken using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using DMSO-d<sub>6</sub>/DMSO-H<sub>2</sub>O as a reference at 2.49 ppm downfield from TMS. Carbon-13 NMR spectra were recorded on a Bruker ASX 32 (operating at 75.5 MHz) spectrometer with DMSO-d<sub>6</sub> as a reference at 39.5 ppm. Gel permeation chromatography (GPC) was performed on a Waters Millipore GPC liquid chromatograph. The calibrant monodisperse poly(MA) and the sample were taken in DMF and separately eluted from an Ultrastaygel GPC column series (sequence 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, 10<sup>6</sup> Å columns). Molecular weights were extrapolated from the calibration curve derived from the poly(MA) standard. Data analyses were carried out using a Waters Data Module 570. Reduced viscosity ( $\eta_{red}$ ) and inherent viscosity ( $\eta_{inh}$ ) of different concentration (*c* in g/dL) of polymer solutions in DMF were obtained by measuring three satisfactory readings of the efflux time (polymer, *t*; solvent, *t*<sub>0</sub>) with Ostwald-Fenske viscometer immersed in the constant-temperature bath maintaining at 25 ± 0.01 °C and by substituting the mean of three readings into the known equations.<sup>12</sup> The extrapolation of the two viscosities to the same intercept as *c* approached to zero gave the intrinsic viscosity [ $\eta$ ] in dL/g. For the thermal polymerization experiments a thermostat bath (model SVM-67) manufactured by the Samik Scientific Co. was used. AA and MA were purchased from the Aldrich Chemical Co. and were purified before use by the standard purification procedures.<sup>13</sup> Cp<sub>2</sub>Fe (Aldrich Chemical Co.) was sublimed at reduced pressure before use. Cp<sub>2</sub>V, Cp<sub>2</sub>Cr, Cp<sub>2</sub>Mn, Cp<sub>2</sub>Co, Cp<sub>2</sub>Ni, Cp<sub>2</sub>Ru, (Me<sub>3</sub>Cp)<sub>2</sub>Fe, and (CpFeCpCH<sub>2</sub>)<sub>2</sub> (Aldrich Chemical Co.) were used as received. Carbon tetrachloride, benzyl chloride, and 1-phenylethyl chloride were purchased from the Aldrich Chemical Co. and purified by fractional distillation just prior to use.

**Polymerization of AA Initiated by CCl<sub>4</sub>/Cp<sub>2</sub>M (M = Fe, Co, Ni).** In a typical experiment of thermal polymerization, a glass test tube (1 cm × 20 cm), which is equipped with an adapter to attach to vacuum line, charged with AA (1.44 g, 20 mmol), CCl<sub>4</sub> (0.19 mL, 2 mmol), Cp<sub>2</sub>Fe (0.37 mg, 2

<sup>‡</sup>This paper is dedicated to the late Professor Sang Chul Shim in recognition of his outstanding contribution to photochemistry.

$\mu\text{mol}$ ) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer was dissolved in methanol, precipitated in *n*-hexane, filtered off, and dried under reduced pressure to give 0.81 g (56%) of white solid. The polymer was characterized by  $^1\text{H}$  NMR, IR, and viscosity measurement analytical techniques. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3300 br s ( $\nu_{\text{O-H}}$ ), 1720 s ( $\nu_{\text{C=O}}$ ), 1250 s ( $\nu_{\text{C-O}}$ );  $^1\text{H}$  NMR ( $\delta$ , DMSO- $d_6$ , 300 MHz): 1.2-2.4 (br, 3H, CH-CH<sub>2</sub>), 12.4 (br, 1H, COOH); Intrinsic viscosity: 12.1 dL/g; GPC:  $M_w = 37820$ ,  $M_w/M_n = 1.69$ . Cobaltocene and nickelocene instead of ferrocene were also used with  $\text{CCl}_4$  for the thermal polymerization.

**Polymerization of MA Initiated by  $\text{CCl}_4/\text{Cp}_2\text{M}$  (M = Fe, Co, Ni).** As a representative experiment of thermal polymerization, a glass test tube (1 cm  $\times$  20 cm), which is equipped with an adapter to attach to vacuum line, containing MA (1.72 g, 20 mmol),  $\text{CCl}_4$  (0.19 mL, 2 mmol),  $\text{Cp}_2\text{Fe}$  (0.37 mg, 2  $\mu\text{mol}$ ) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer was taken in methanol, precipitated in *n*-hexane, filtered off, and dried *in vacuo* to afford 1.06 g (62%) of white solid. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3400 br s ( $\nu_{\text{O-H}}$ ), 1720 s ( $\nu_{\text{C=O}}$ ), 1200s ( $\nu_{\text{C-O}}$ );  $^1\text{H}$  NMR ( $\delta$ , DMSO- $d_6$ , 300 MHz): 0.9-1.1 (br, 3H, C-CH<sub>3</sub>), 1.8-2.1 (br, 2H, CHCH<sub>2</sub>), 12.3 (br, 1H, COOH); Intrinsic viscosity: 6.7 dL/g; GPC:  $M_w = 21120$ ,  $M_w/M_n = 1.67$ . Cobaltocene and nickelocene instead of ferrocene were also employed with  $\text{CCl}_4$  for the thermal polymerization.

In order to prepare a low molecular weight polymer sample for end group analysis, a glass test tube (1 cm  $\times$  20 cm) containing MA (1.72 g, 20 mmol),  $\text{CCl}_4$  (1.9 mL, 20 mmol),  $\text{Cp}_2\text{Fe}$  (0.37 mg, 2  $\mu\text{mol}$ ) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer after the same workup was obtained in 30% yield. IR (KBr pellet,  $\text{cm}^{-1}$ ): 715 w ( $\nu_{\text{C-Cl}}$ );  $^{13}\text{C}$  NMR ( $\delta$ , DMSO- $d_6$ , 75.5 MHz): 75.2 ( $\text{CCl}_3$ ); Intrinsic viscosity: 4.8 dL/g; GPC:  $M_w = 15130$ ,  $M_w/M_n = 1.68$ .

**Copolymerization of AA and MA (1 : 1 mole ratio) Initiated by  $\text{CCl}_4/\text{Cp}'_2\text{M}$  (M = Fe, Co, Ni, V, Cr, Mn, Ru; Cp' = Cp or Me<sub>3</sub>Cp) or  $(\text{CpFeCpCH}_2)_2$ .** As a typical experiment, AA (0.72 g, 10 mmol), MA (0.86 g, 10 mmol),  $\text{CCl}_4$  (0.19 mL, 2 mmol),  $\text{Cp}_2\text{Fe}$  (0.37 mg, 2  $\mu\text{mol}$ ), and benzene (2 mL) were added to a glass test tube (1 cm  $\times$  20 cm) equipped with an adapter to attach to vacuum line. The reaction mixture was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer was dissolved in methanol, precipitated in *n*-hexane, filtered off, and dried *in vacuo* to yield 0.91 g (58%) of white solid. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3350 br s ( $\nu_{\text{O-H}}$ ), 1720 s ( $\nu_{\text{C=O}}$ ), 1230 s ( $\nu_{\text{C-O}}$ );  $^1\text{H}$  NMR ( $\delta$ , DMSO- $d_6$ , 300 MHz): 0.9-1.1 (br, C-CH<sub>3</sub>), 1.2-2.4 (br, CH<sub>2</sub>-CH<sub>2</sub>, CH-CH<sub>2</sub>), 12.4 (br, COOH); Intrinsic viscosity: 9.3 dL/g; GPC:  $M_w = 29760$ ,  $M_w/M_n = 1.70$ . The composition of each monomers in the copolymer was determined by integrating the peak areas for the methyl protons and backbone CH<sub>2</sub>/CH protons in the proton NMR spectrum. A MA : AA ratio of 8.1 : 10.5 was observed from the monomer composition analysis. Other metallocenes instead of ferrocene were also used with  $\text{CCl}_4$  for the thermal copolymerization.

**Attempted Polymerization of AA and MA Initiated by Halocarbon/ $\text{Cp}_2\text{M}$  (M = Fe, Co, Ni).** In a typical experiment, a glass test tube (1 cm  $\times$  20 cm), which is equipped with an adapter to attach to vacuum line, charged with AA (1.44 g, 20 mmol), 1-phenylethyl chloride (0.28 g, 2 mmol),  $\text{Cp}_2\text{Fe}$  (0.37 mg, 2  $\mu\text{mol}$ ) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The solution was precipitated in *n*-hexane, filtered off, and dried *in vacuo* to afford trace amount (*ca.* 0.01 g) of white solid. Cobaltocene and nickelocene instead of ferrocene with 1-phenylethyl chloride gave the same result. For the thermal polymerization of AA, the other initiating systems of  $\text{Cp}_2\text{M}$ /halocarbon (M = Fe, Co, Ni; halocarbon =  $\text{PhCH}_2\text{Cl}$ ,  $\text{Ph(C=O)CH}_2\text{Br}$ ) yielded the same result. For the thermal polymerization of MA, the initiating systems of  $\text{Cp}_2\text{M}$ /halocarbon (M = Fe, Co, Ni; halocarbon = 1-Phenylethyl chloride,  $\text{PhCH}_2\text{Cl}$ ,  $\text{Ph(C=O)CH}_2\text{Br}$ ) gave the same result.

## Results and Discussion

In order to see the initiating efficiency of the combination initiators on AA, the poly(AA)s with intrinsic viscosities of 12.1-29.7 dL/g ( $M_w = 29760$ -96110,  $M_w/M_n = 1.69$ -1.76) were prepared in 32-56% yields by the thermal polymerization (at 70 °C for 24 h) of AA initiated by  $\text{CCl}_4/\text{Cp}_2\text{M}$  (M = Fe, Co, Ni) combination. The polymerization of AA using the other halocarbons such as  $\text{Ph(C=O)CH}_2\text{Br}$ ,  $\text{PhCH}_2\text{Cl}$ ,  $\text{PhCH(CH}_3\text{)Cl}$  instead of  $\text{CCl}_4$  in combination with  $\text{Cp}_2\text{M}$  (M = Fe, Co, Ni) was also performed to produce trace amount of polymer. The polymerization of AA using  $\text{CCl}_4$  or  $\text{Cp}_2\text{Fe}$  alone as an initiator gave polymer in trace amount. The results are summarized in Table 1.

Similarly, the poly(MA)s with intrinsic viscosities of 6.7-15.4 dL/g ( $M_w = 21120$ -48490,  $M_w/M_n = 1.67$ -1.74) were prepared in 37-62% yields by the thermal polymerization of MA initiated by  $\text{CCl}_4/\text{Cp}_2\text{M}$  (M = Fe, Co, Ni) combination. The polymerization of MA using the other halocarbon such as  $\text{Ph(C=O)CH}_2\text{Br}$ ,  $\text{PhCH}_2\text{Cl}$ ,  $\text{PhCH(CH}_3\text{)Cl}$  instead of  $\text{CCl}_4$  in combination with  $\text{Cp}_2\text{M}$  (M = Fe, Co, Ni) produced trace amount of polymer. The results are given in Table 2.

The thermal copolymerization of AA and MA (monomer feed mole ratio: 1 : 1), initiated by  $\text{CCl}_4/\text{Cp}'_2\text{M}$  (M = Fe, Co,

**Table 1.** Characterization of Polymerization of AA by Chlorocarbon/ $\text{Cp}_2\text{M}$  (M = Fe, Co, Ni) Combination Initiator<sup>a</sup>

Initiator	Isolated yield (%)	Intrinsic viscosity <sup>b</sup> [ $\eta$ ]	Mol wt <sup>c</sup> $M_w$	PDI $M_w/M_n$
$\text{CCl}_4 + \text{Cp}_2\text{Fe}$	56	12.1	37820	1.69
$\text{CCl}_4 + \text{Cp}_2\text{Co}$	41	21.4	68480	1.72
$\text{CCl}_4 + \text{Cp}_2\text{Ni}$	32	29.7	96110	1.76
$\text{Cp}_2\text{Fe}$	trace	—	—	—
$\text{CCl}_4$	trace	—	—	—
$\text{Ph(C=O)CH}_2\text{Br} + \text{Cp}_2\text{M}$	trace	—	—	—
$\text{PhCH}_2\text{Cl} + \text{Cp}_2\text{M}$	trace	—	—	—
$\text{PhCH(CH}_3\text{)Cl} + \text{Cp}_2\text{M}$	trace	—	—	—

<sup>a</sup>Heating at 70 °C for 24 h. <sup>b</sup>Measured in DMF at 25 °C; unit, dL/g. <sup>c</sup>Measured with GPC (vs poly(MA)) in DMF.

**Table 2.** Characterization of Polymerization of MA by Chloro-carbon/Cp<sub>2</sub>M (M = Fe, Co, Ni) Combination Initiator<sup>a</sup>

Initiator	Isolated yield (%)	Intrinsic viscosity <sup>b</sup> [η]	Mol wt <sup>c</sup> M <sub>w</sub>	PDI M <sub>w</sub> /M <sub>n</sub>
CCl <sub>4</sub> + Cp <sub>2</sub> Fe	62	6.7	21120	1.67
CCl <sub>4</sub> + Cp <sub>2</sub> Co	49	9.1	28550	1.70
CCl <sub>4</sub> + Cp <sub>2</sub> Ni	37	15.4	48490	1.74
Cp <sub>2</sub> Fe	trace	—	—	—
CCl <sub>4</sub>	trace	—	—	—
Ph(C=O)CH <sub>2</sub> Br + Cp <sub>2</sub> M	trace	—	—	—
PhCH <sub>2</sub> Cl + Cp <sub>2</sub> M	trace	—	—	—
PhCH(CH <sub>3</sub> )Cl + Cp <sub>2</sub> M	trace	—	—	—

<sup>a</sup>Heating at 70 °C for 24 h. <sup>b</sup>Measured in DMF at 25 °C; unit, dL/g. <sup>c</sup>Measured with GPC (vs poly(MA)) in DMF.

Ni, V, Cr, Mn, Ru, Cp' = Cp or Me<sub>5</sub>Cp), produced poly(AA-co-MA)s. The intrinsic viscosities of resulting poly(AA-co-MA)s ranged from 9.3 to 24.1 dL/g (M<sub>w</sub> = 27930-77100, M<sub>w</sub>/M<sub>n</sub> = 1.65-1.72) in 5-68% yield. A composition analysis of each monomers in the polymer was carried out by integrating the peak areas for the methyl protons and backbone CH<sub>2</sub>/CH protons in the proton NMR spectrum. A MA : AA ratio of 8.1 : 10.5 was observed from the analysis. The results are summarized in Table 3.

Carbon tetrachloride in the polymerization acted as a coinitiator. The minimum amount of metallocene was employed in order to avoid the contamination of the polymer. Therefore, the mole ratio of monomer : chlorocarbon : metallocene (10000 : 1000 : 1) was fixed throughout in this study. As shown in Tables 1-3, the molecular weight (*i.e.*, intrinsic viscosity and M<sub>w</sub>) decreases in the order of Cp<sub>2</sub>Ni > Cp<sub>2</sub>Co > Cp<sub>2</sub>Fe, but the polymerization yield increases in the order of Cp<sub>2</sub>Ni < Cp<sub>2</sub>Co < Cp<sub>2</sub>Fe. The same trend of molecular weight and polymerization yield as the respective homopolymerization of AA and MA was observed in the copolymerization. The thermal polymerization of AA yielded polymers with higher molecular weight in lower yield as compared with that of MA. The thermal copolymerization yielded poly(AA-co-MA)s with higher molecular weight in lower yield as compared with the thermal homopolymerization of MA. By comparison, we reported that molecular

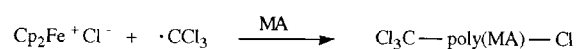
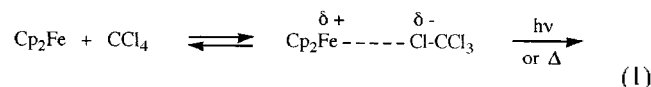
**Table 3.** Characterization of Copolymerization of MA and AA by CCl<sub>4</sub>/Cp<sub>2</sub>M Combination Initiator<sup>a</sup>

Initiator	Isolated yield (%)	Intrinsic viscosity <sup>b</sup> [η]	Mol wt <sup>c</sup> M <sub>w</sub>	PDI M <sub>w</sub> /M <sub>n</sub>
CCl <sub>4</sub> + Cp <sub>2</sub> Fe	58	9.3	29760	1.70
CCl <sub>4</sub> + Cp <sub>2</sub> Co	46	14.9	47600	1.71
CCl <sub>4</sub> + Cp <sub>2</sub> Ni	34	21.7	69390	1.72
CCl <sub>4</sub> + (Me <sub>5</sub> Cp) <sub>2</sub> Fe	68	8.9	28120	1.69
CCl <sub>4</sub> + (CpFeCpCH <sub>2</sub> ) <sub>2</sub>	66	9.0	28210	1.68
CCl <sub>4</sub> + Cp <sub>2</sub> V	5	24.1	77100	1.71
CCl <sub>4</sub> + Cp <sub>2</sub> Cr	15	23.2	74230	1.65
CCl <sub>4</sub> + Cp <sub>2</sub> Mn	28	15.4	48920	1.70
CCl <sub>4</sub> + Cp <sub>2</sub> Ru	65	9.0	27930	1.69

<sup>a</sup>Heating at 70 °C for 24 h. <sup>b</sup>Measured in DMF at 25 °C; unit, dL/g. <sup>c</sup>Measured with GPC (vs poly(MA)) in DMF.

weight decreased in the order of Cp<sub>2</sub>Co > Cp<sub>2</sub>Ni > Cp<sub>2</sub>Fe, exactly opposite to the order of polymerization yield. Cp<sub>2</sub>Fe > Cp<sub>2</sub>Ni > Cp<sub>2</sub>Co, in the respective photopolymerizations of AA and MA with CCl<sub>4</sub>/Cp<sub>2</sub>M (M = Fe, Co, Ni)<sup>10b</sup> Interestingly, as shown in Table 3, the polymerization yields with (Me<sub>5</sub>Cp)<sub>2</sub>Fe, (CpFeCpCH<sub>2</sub>)<sub>2</sub>, and Cp<sub>2</sub>Ru were higher than with Cp<sub>2</sub>Fe. In addition, the polymerization yield decreases in the order of Cp<sub>2</sub>Mn > Cp<sub>2</sub>Cr > Cp<sub>2</sub>V. As our constant effort to make a living radical initiator system,<sup>10</sup> the thermal polymerization of AA and MA, initiated by 1-phenylethyl chloride/Cp<sub>2</sub>M (M = Fe, Co, Ni) combination, was performed producing corresponding polymer in trace amount. With other halocarbons such as Ph(C=O)CH<sub>2</sub>Br and PhCH<sub>2</sub>Cl, the similar results were obtained.

We believe that the thermal polymerization of AA and MA with ferrocene/CCl<sub>4</sub> combination initiator might be similarly proceeded by forming a charge-transfer (CT) complex between halocarbon and metallocene as in photopolymerization of AA and MA (eq. 1).<sup>9b,10</sup>



The excited CT complex will then decompose into ferrocenium chloride and trichloromethyl radical which could finally initiate the polymerization of AA and MA.

Endgroup analysis of a low molecular weight poly(MA) with M<sub>w</sub> = 15130, M<sub>w</sub>/M<sub>n</sub> = 1.68 was performed to confirm the suggested polymer structure having the CCl<sub>3</sub> end group using IR and <sup>13</sup>C NMR spectrometers. As expected, a weak band at 715 cm<sup>-1</sup> (ν<sub>C-Cl</sub>) in the IR spectrum and a small peak at 75.2 ppm (CCl<sub>3</sub>) in the <sup>13</sup>C NMR spectrum were observed.

Unlike main group of organic compounds generally satisfying octet rule,<sup>14a</sup> organometallic complexes using d-orbitals become generally most stable when they have 18-electron closed-shell configuration.<sup>14b,c</sup> The group VIII metallocenes are known to proceed reduction or oxidation stepwisely.<sup>15</sup> In this case it is believed that the metallocenes are oxidized by accepting a halogen radical in the polymerization. The initiating capability should be linearly related to the magnitude of polymerization yield. We first expected that the thermal initiating ability of the group VIII metallocenes should decrease in the oxidation order of Cp<sub>2</sub>Ni > Cp<sub>2</sub>Co > Cp<sub>2</sub>Fe according to the 18 electron rule.<sup>14c</sup> However, it turned out that the thermal initiating efficiency decreased in the order of Cp<sub>2</sub>Fe > Cp<sub>2</sub>Co > Cp<sub>2</sub>Ni as shown in Tables 1-3. The order of thermal initiating efficiency is in accord with the order of their thermal stability. By contrast, the photo initiating efficiency was found to decrease in the order of Cp<sub>2</sub>Fe > Cp<sub>2</sub>Ni > Cp<sub>2</sub>Co.<sup>10</sup> The order of photoinitiating efficiency coincides with the photostability order. The capping efficiency order of metallocenium chloride could be directly related to the thermal stability order of metallocene itself.<sup>10</sup> The polymer molecular weight should be, in turn,

inversely proportional to the capping order.<sup>16</sup> Interestingly, the copolymerization yields with  $(Me_3Cp)_2Fe$ ,  $(CpFeCpCH_2)_2$ , and  $Cp_2Ru$  were found to be higher than that with  $Cp_2Fe$  probably because of their higher oxidizing capability attributed to higher electron density on the metals. Furthermore, the polymerization yield decreases in the order of  $Cp_2Mn > Cp_2Cr > Cp_2V$  because of their oxidizing capability.

Living radical polymerization technique has advantages in precisely controlling the molecular weight distribution and structure of polymer.<sup>11,17-20</sup> Unlike the atom-transfer radical polymerization by 1-phenylethyl chloride/ $CuCl$ /bipyridine combination initiator,<sup>18-20</sup> for the thermal polymerization of AA and MA as shown in Tables 1-3, the reverse relationship of polymer molecular weights and polymerization yield was found. Based on the polydispersity index ( $M_w/M_n$ ) > 1.5 as shown in Table 1-3, the polymerization reactions seem not to be progressed by living process.<sup>10</sup> The reactions of poly(AA), poly(MA), and poly(AA-co-MA) with supramolecular host-guest complex are in progress and the results will be published elsewhere in due course.<sup>21</sup>

In conclusion, this work describes the thermal homo- and co-polymerization of AA and MA with group VIII metallocene/halocarbon initiator combination. For the polymerization of AA and MA initiated by  $CCl_4/Cp_2M$  ( $M = Fe, Co, Ni$ ), while the polymerization yield decreases in the order of  $Cp_2Fe > Cp_2Co > Cp_2Ni$ , the molecular weight decreases in the order of  $Cp_2Ni > Cp_2Co > Cp_2Fe$ . An explanation for the reverse order has been provided. The polymerization yields with  $(Me_3Cp)_2Fe$ ,  $(CpFeCpCH_2)_2$ , and  $Cp_2Ru$  were higher than with  $Cp_2Fe$ . The polymerization yield decreases in the order of  $Cp_2Mn > Cp_2Cr > Cp_2V$ . The thermal polymerization of AA and MA using other halocarbon such as 1-phenylethyl chloride, benzyl chloride, 2-bromoacetophenone instead of  $CCl_4$  in combination with  $Cp_2Fe$  produced polymer in trace amount. The polymerization reactions described above were found not to be living based on the polydispersity index ( $M_w/M_n$ ) > 1.5.

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