

temperature for 30 min, a solution of **1** (0.13 g, 0.50 mmol) in dry THF was added dropwise for 10 min, and was stirred at room temperature for 20 min. The reaction mixture was poured into ice water, extracted with dichloromethane, washed with brine, dil. sodium hydroxide solution, water, dried, and evaporated *in vacuo* to give a white solid 147 mg (98%) which was recrystallized from carbon tetrachloride, mp 194-196 °C (lit.¹⁸ 191-196 °C), IR (KBr) 3525, 2920, 2860, 1720, 1600, 1490, 1445, 1255, 1215, 1160, 705 cm^{-1} .

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Polymerization of Methyl Methacrylate by Chlorocarbon/Group VIII Metallocene Combination Initiator

Hee-Gweon Woo*, Jin-Young Park, Heui-Suk Ham, Hyoung-Ryun Park, Seung-Deok Cho[†], Young-Hoon Ko[‡], and Whan-Gi Kim[†]

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

[†]*Kumho Petrochemical Co., Ltd., Taejeon 305-600, Korea*

[‡]*Samyang Group R&D Center, Taejeon 305-348, Korea*

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Photochemical or photoinitiated polymerizations occur when radicals are produced by light absorption. Photoinitiation of polymerization offers significant practical advantages: (1) photoinitiation can be spatially directed and turned on or off simply by turning the light source on or off, (2) the photoinitiation rates can be controlled by a combination of the radical source, light intensity and temperature, and (3) photoinitiation can avoid chemical contamination by initiator residues in many cases. Therefore,

photopolymerization technology is conveniently applicable and is heavily employed on a commercial basis today in the areas of surface coatings, photoresists, adhesives, and holography.¹ Photochemical activation of organometallic compounds, leading to catalytically and synthetically useful transformations, has attracted a great deal of attention.² Especially, photochemical properties of millions of cyclopentadienyl complexes, a historically important class of organometallics, have been intensively investigated.³ Many

halogenated organic compounds have been employed as effective photoinitiators for the photopolymerization of many vinyl derivatives although the halogenated organics often create serious environmental problems.⁵ A major problem associated with halogenated photoinitiators is the erosion of reactor system induced by acid hydrogen halide by products during the photopolymerization process. The use of ferrocene (Cp_2Fe) as both a photopolymerization promoter (to activate the halogenated photoinitiator) and a halide-radical trap (to prevent the troublesome acid formation) in combination with halogenated compounds has been found in the literature.⁶ To the best of our knowledge, the other group VIII metallocenes such as cobaltocene (Cp_2Co) and nickelocene (Cp_2Ni) have never been used for this type of photopolymerization of methyl methacrylate (MMA) in spite of their interesting chemical properties⁷ except our recent communication.⁸ In this paper we report the polymerization of MMA, initiated by halocarbon/ Cp_2M ($\text{M} = \text{Fe, Co, Ni}$) combination, to compare their effect on the polymerization reactions. The halocarbons include carbon tetrachloride and 1-phenylethyl chloride.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were performed in prepurified nitrogen or argon 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 $\text{CDCl}_3/\text{CHCl}_3$ as a reference at 7.24 ppm downfield from TMS. Gel permeation chromatography (GPC) was performed on a Waters Millipore GPC liquid chromatography. The calibrant (monodisperse polystyrene) and the sample were taken in THF and separately eluted from an Ultrastaygel GPC column series (sequence 10^3 , 10^4 , 10^5 , 10^6 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570. For the photolysis experiments a Rayonet photochemical reactor model RPR-208 made by the New Southern California Co., which has merry-go-round system in order to uniformly irradiate all samples, was used. The built-in monochromatic W light sources (RUL-300 nm UV lamp; lamp intensity = 6.93×10^{18} hv $\text{mL}^{-1}\text{min}^{-1}$) was positioned approximately 17 cm from the reaction quartz tube. For the thermal polymerization experiments a thermostat bath (model SVM-67) made by the Samik Scientific Co. was employed. MMA was washed twice with aqueous 5% NaOH (to remove inhibitor), washed twice with distilled water, dried over MgSO_4 , and distilled at reduced pressure before use. Cp_2Fe (Aldrich Chemical Co.) was sublimed at reduced pressure before use. Cp_2Co and Cp_2Ni (Aldrich Chemical Co.) were used as received. Carbon tetrachloride and 1-phenylethyl chloride (Aldrich Chemical Co.) were purified by fractional distillation just prior to use.

Thermal Polymerization of MMA Initiated by $\text{CCl}_4/\text{Cp}_2\text{M}$ ($\text{M} = \text{Fe, Co, Ni}$). The following procedure is the representative of the thermal polymerization reactions. A test tube (1 cm x 20 cm) containing MMA (2.0 g, 20 mmol),

CCl_4 (0.31 g, 2 mmol), Cp_2Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer was precipitated in hexane, filtered off, and dried *in vacuo* to give 0.90 g (45%) of white solid. The polymer was characterized by ^1H NMR, IR, and GPC techniques. IR (KBr pellet, cm^{-1}): 1728 s ($\nu_{\text{C=O}}$). ^1H NMR (δ , CDCl_3 , 300 MHz): 0.7-1.1 (m, 3H, C- CH_3), 1.7-2.1 (m, 2H, CH_2), 3.6 (m, 3H, OCH_3). GPC: $M_w = 670000$, $M_n = 443000$, $M_w/M_n = 1.5$.

Thermal Polymerization of MMA Initiated by 1-Phenylethyl Chloride/ Cp_2M ($\text{M} = \text{Fe, Co, Ni}$). In a typical experiment, a test tube (1 cm x 20 cm) charged with MMA (2.0 g, 20 mmol), 1-phenylethyl chloride (0.28 g, 2 mmol), Cp_2Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. The resulting polymer was precipitated with hexane, filtered off, and dried under reduced pressure give 1.04 g (52%) of white solid. The IR and ^1H NMR spectra of the poly(MMA) obtained from the thermal polymerization were quite similar to those of the poly(MMA) obtained from the thermal polymerization initiated by $\text{CCl}_4/\text{Cp}_2\text{M}$. GPC: $M_w = 669000$, $M_n = 312000$, $M_w/M_n = 2.1$.

Attempt at Photopolymerization of MMA Initiated by 1-Phenylethyl Chloride/ Cp_2M ($\text{M} = \text{Fe, Co, Ni}$). As a typical experiment, MMA (2.0 g, 20 mmol), 1-phenylethyl chloride (0.28 g, 2 mmol), Cp_2Fe (0.37 mg, 2 μmol) and benzene (2 mL) were added to a quartz test tube (1 cm x 20 cm). The reaction mixture was degassed, sealed, and irradiated with UV-light for 2 h. No polymerization was found after workup.

Results and Discussion

The weight average molecular weights (M_w) of poly(MMA)s produced from the thermal polymerization of MMA, initiated by $\text{CCl}_4/\text{Cp}_2\text{M}$ ($\text{M} = \text{Fe, Co, Ni}$), ranged from 670000 to 960000 with polydispersity index (PDI) equal to 1.3-1.5 in 25-46% yield. The thermal polymerization produced poly(MMA)s with higher molecular weights and with lower PDI in higher yield as compared with the photopolymerization of MMA.⁸ The molecular weights are in the similar molecular weight range of poly(MMA)s produced by the other radical polymerizations of MMA.⁹ The results are summarized in Table 1.

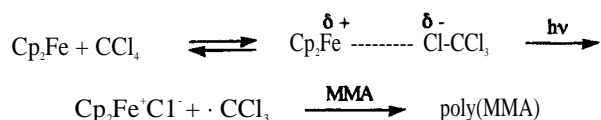
The mole ratio of monomer : halide : metallocene (10000 : 1000 : 1) was fixed in this study. Carbon tetrachloride was employed as both solvent and initiator. The minimum amount of metallocene was used in order to minimize the contamination of the polymer and the UV-masking action by the metallocene. We found in the photopolymerization

Table 1. GPC Characterization of Thermal Polymerization of MMA by $\text{CCl}_4/\text{Cp}_2\text{M}$ Combination Initiator^a

Initiator	Isolated yield (%)	mol wt ^b		
		M_w	M_n	M_w/M_n
$\text{CCl}_4 + \text{Cp}_2\text{Fe}$	46	670000	443000	1.5
$\text{CCl}_4 + \text{Cp}_2\text{Co}$	39	900000	686000	1.3
$\text{CCl}_4 + \text{Cp}_2\text{Ni}$	25	962000	696000	1.4

^aHeating at 70 °C for 24 h. ^bMeasured with GPC in THF.

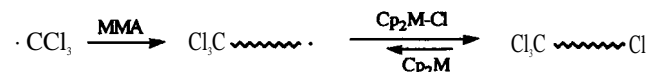
of MMA with $\text{CCl}_4/\text{Cp}_2\text{M}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) that molecular weights decrease in the order of $\text{Cp}_2\text{Co} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Fe}$, exactly opposite to the order of polymerization yield, $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co}$.⁸ Fujisaki and coworker proposed a mechanism for the photopolymerization of MMA with ferrocene/ CCl_4 combination initiator *via* a charge-transfer (CT) complex formation.^{6b}



A CT complex formed between ferrocene and CCl_4 by the iron atom serving as an electron donor and the chlorine atom serving as an electron acceptor. The primary process of photochemical initiation of the polymerization could be the absorption of light by this CT complex which will then dissociate into trichloromethyl radical and an oxidized form of ferricenium chloride. The trichloromethyl radical could eventually initiate the photopolymerization. The CT complex formation between halocarbon and metallocene appears to be an essential condition for the photopolymerization.⁸

Generally, an organometallic complex become most stable when it has an 18 electron closed-shell configuration.¹⁰ The group VIII metallocenes are known to be stepwise reduced or oxidized,¹¹ and 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 anticipated that the photoinitiating ability of the group VIII metallocenes should decrease in the oxidation order of $\text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co} > \text{Cp}_2\text{Fe}$, according to the 18 electron rule. However, the photoinitiating efficiency was found to decrease in the order of $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co}$. The order of photoinitiating efficiency coincides with the photostability order.⁸ By contrast, the thermal initiating efficiency was found to decrease in the order of $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Co} > \text{Cp}_2\text{Ni}$ as shown in Table 1. The order of thermal initiating efficiency coincides with the order of their stability. We expected that the molecular weights should decrease as in the same order of polymerization yield since it is known that high-molecular-weight polymer is formed instantly and that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization of vinyl monomers.¹ However, the molecular weights were found to decrease in the order of $\text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co} > \text{Cp}_2\text{Fe}$, exactly opposite to the order of polymerization yield. At present we are not sure if a charge-transfer (CT) complex forms between ferrocene and CCl_4 prior to its dissociation into trichloromethyl radical and ferricenium chloride in the thermal polymerization as in the photopolymerization. *Albeit* the following explanation is only a speculation, we may rationalize the facts (*vide infra*). Ferrocene could accept a chlorine radical to form a 19-electron ferricenium chloride which might concomitantly want to go back by losing the chlorine radical to the stable 18-electron ferrocene. Thus, a growing polymer chain radical containing a CCl_3 end group could take a chlorine radical back to cap the radical end of polymer chain. The resulting polymer may resist losing a chlorine atom again under the photochemical condition because the substitution of alkyl

group on the halocarbon decrease the tendency of forming a CT complex.



The capping efficiency order of metallocenium chloride could be directly related to the thermal stability order of metallocene itself, $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Co} > \text{Cp}_2\text{Ni}$. The polymer molecular weight should be, in turn, inversely proportional to the capping order. Typical redox radical telomerizations promoted by transition-metal species are reported to show a linear relationship between polymer molecular weight and monomer conversion.¹²

Living polymerization technique allows to precise control of polymer molecular weight distribution and structure. The bias of free radicals to undergo self-reaction at diffusion-controlled rates precludes conventionally *living* polymerization. However, radical polymerization may be considered *living* if the following conditions are met: (1) the radicals must be long-lived and slow to initiate polymerization, (2) the interruption of chain growth should be occurred by radical combination and group transfer, and (3) the bond to the end group formed in the termination reaction must be labile. Rizzardo *et al.* reported alkoxyamine-initiated living radical polymerization.¹³ Matyjaszewski and coworker¹⁴ described the atom-transfer radical polymerization by 1-phenylethyl chloride/ $\text{CuCl}/\text{bipyridine}$ combination initiator. The radical polymerization by the initiator combination exhibits a distinctive *living* character with a negligible amount of irreversible transfer and termination and with a narrow molecular weight distribution, $M_w/M_n < 1.5$. In this case, polymer molecular weight linearly increases with monomer conversion. On the other hand, as shown in Table 1, for the thermal polymerization of MMA the polydispersity index was $M_w/M_n < 1.5$, but the reverse relationship of molecular weights and polymerization yield was also found as the photopolymerization of MMA. Furthermore, polymer molecular weight did not linearly increase with monomer conversion. The polymerization seems not to be a *living* process in spite of the lower PDI values. Thus, the present chlorine atom radical transfer from metallocenium chloride to polymer chain radical could be an irreversible termination process in the thermal and photopolymerization of MMA initiated by $\text{CCl}_4/\text{Cp}_2\text{M}$ combination. We are presently uncertain of the low PDI values in spite of the fact that CCl_4 is used as a chain transfer agent.^{1b}

As a part of our constant effort to devise a living initiator system, the thermal polymerization of MMA, initiated by 1-phenylethyl chloride/ Cp_2M ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) combination, was carried out, producing poly(MMA)s with weight average molecular weights (M_w) of 669000-1153000 and with PDI of 1.6-2.1 in 12-52% yields. The photopolymerization of MMA using the 1-phenylethyl chloride/ Cp_2M ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) combination initiator was unsuccessfully attempted. The results are given in Table 2.

Unlike the atom-transfer radical polymerization by 1-phenylethyl chloride/ $\text{CuCl}/\text{bipyridine}$ combination initiator,¹⁴ the trend of polymerization yields versus molecular weights was same as in the thermal polymerization of MMA initiated by $\text{CCl}_4/\text{Cp}_2\text{M}$. Again, the polydispersity index M_w/M_n

Table 2. GPC Characterization of Polymerization of MMA by 1-Phenylethyl Chloride/Cp₂M Combination Initiator

Initiator	Isolated yield (%)	mol wt ^c		
		M _w	M _n	M _w /M _n
1-phenylethyl chloride + Cp ₂ Fe ^a	52	669000	312000	2.1
1-phenylethyl chloride + Cp ₂ Co ^a	36	941000	532000	1.8
1-phenylethyl chloride + Cp ₂ Ni ^a	12	1153000	703000	1.6
1-phenylethyl chloride + Cp ₂ M ^b (M=Fe, Co, Ni)	0			

^aHeating at 70 °C for 24 h. ^bUV-irradiation for 2 h. ^cMeasured with GPC in THF.

$M_w > 1.5$ implies that the system may not be *living*. A study improving our initiating system to be *living*, the capping process being reversible, and clarifying the solvent effect on the polymer molecular weight, is in progress and will be reported as a separate paper.¹⁵ Finally, there is a possibility that metallocenium chloride might not be a spectator, but might act as a photoinitiator. In fact, cationic organometallic compounds of many types are known to be efficient photoinitiators of cationic polymerization.² However, the possibility could be removed because ferrocenium hexafluorophosphate was found to show no appreciable photoinitiating activity under the present polymerization condition.

In conclusion, this work describes the polymerization of MMA initiated by group VIII metallocene/halocarbon combination. For the thermal polymerization of MMA initiated by CCl₄/Cp₂M, while the polymerization yield decreases in the order of Cp₂Fe > Cp₂Co > Cp₂Ni, the molecular weight decreases in the order of Cp₂Ni > Cp₂Co > Cp₂Fe. For the thermal polymerization of MMA initiated by 1-phenylethyl chloride/Cp₂M, the trend of polymerization yields versus molecular weights was same as that of the thermal polymerization of MMA initiated by CCl₄/Cp₂M. The photopolymerization of MMA initiated by 1-phenylethyl chloride/Cp₂M was not occurred. An explanation for the reverse order has been provided. The polymerization reactions turn out to be not *living*.

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