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Polymerization of Various Vinyl Derivatives Initiated by Chlorocarbon/Group VIII Metallocene Combination

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Vinyl monomers undergo addition polymerization by radical, ionic or both initiators, depending on the type of substituent of vinyl derivatives.[1] *Inter alia*, radical-chain polymerizations occur when radicals are generated by either light absorption or thermal heating. Since photoinitiation of polymerization gives significant practical advantages over the other types of initiation methods, photopolymerization technology is highly used on a commercial scale in the versatile application areas of surface coatings, photoresists, adhesives, and holography.[1]

Halogenated organic chemicals have been employed as effective photoinitiators for the photopolymerization of many vinyl derivatives[2,3] despite of serious environmental problems often created by the halogenated chemicals[4] and even by the CFC substitutes.[5] Notable problems associated with halogenated photoinitiators are the erosion of reactor system and some unwanted side reactions which were induced by acid hydrogen halide byproduct during the photopolymerization process. Thus, ferrocene (Cp_2Fe) along with halogenated compounds was introduced as both a photopolymerization promotor and a halide-radical trapping sponge.[6] Recently, we first communicated the photopolymerization of methyl methacrylate (MMA) and methacrylic acid (MA) with by the CCl_4/Cp_2M (group VIII metallocene, M = Fe, Co, Ni) combination initiator.[7] As an extension of the previous reports, here we report the thermal- and photopolymerization of various vinyl monomers such as MMA, MA, acrylonitrile (AN), styrene (STY), ethyl vinyl ether (EVE), and vinyl acetate (VA) initiated by chlorocarbon/Cp_2M (M = Fe, Co, Ni) combination, to compare their initiating effect in terms of living radical polymerization on the polymerization reactions of vinyl monomers with the other known organic halide/transition metal complex combination initiators. The chlorocarbons used here include carbon tetrachloride 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 $CDCl_3$/$CHCl_3$ as a reference at 7.24 ppm downfield from TMS or using DMSO-d_6/DMSO-H_6 as a reference at 2.49 ppm downfield from TMS. Gel permeation chromatography (GPC) was performed on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were taken in THF and separately eluted from an Ultrastyragel 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. Reduced viscosity (η_{red}) and inherent viscosity (η_{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_o) 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.[8a] The extrapolation of the two viscosities to the same intercept as c approached to zero gave the intrinsic viscosity [η] in dL/g. For the photolysis experiments a Rayonet RPR-208 photochemical reactor 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 UV light sources (RUL-300 nm UV lamp; lamp intensity = 6.93×10^{18} hv mL^{-1} 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. The vinyl monomers were purchased from the Aldrich Chemical Co. were purified before use by the standard purification procedure.[8b] 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 were purchased from the Aldrich Chemical Co. and purified by fractional distillation just prior to use.

Photocopolymerization of MMA and MA (1 : 1 mole ratio) Initiated by CCl_4/Cp_2M (M = Fe, Co, Ni).
As a typical experiment, MMA (1.0 g, 10 mmol), MA (0.86 g, 10 mmol), CCl_4 (0.31 g, 2 mmol), Cp_2Fe (0.37 mg, 2 μmol) and benzene (2 mL) were added to a quartz test tube (1 cm × 20 cm). The reaction mixture was degassed,

sealed, and irradiated with UV-light for 2 h. The resulting polymer was taken in THF, filtered off (to remove poly (MA)), precipitated in benzene (to remove poly(MMA)), and dried *in vacuo* to give 0.67 g (36%) of white solid. The polymer was characterized by ^{1}H NMR, IR, and GPC techniques. IR (KBr pellet, cm^{-1}): 3450 br s (v_{O-H}), 1707 s ($v_{C=O}$). ^{1}H NMR (δ, DMSO-d$_6$, 300 MHz): 0.1-1.1 (br, C-CH$_3$), 1.1-2.1 (br, CH$_2$), 3.5 (br, 3H, OCH$_3$), 12.1 (br, OH), GPC: M_w=2733000, M_n=657000, M_w/M_n=4.2.

Polymerization of AN Initiated by CCl$_4$/Cp$_2$M (M = Fe, Co, Ni). The following procedure is the representative of the photopolymerization reactions. A quartz test tube (1 cm × 20 cm) containing AN (1.06 g, 20 mmol), CCl$_4$ (0.31 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and irradiated with UV-light for 2 h. The resulting polymer was precipitated in hexane, filtered off, and dried *in vacuo* to give 0.138 g (13%) of white solid. IR (KBr pellet, cm^{-1}): 2245 s ($v_{C≡N}$). ^{1}H NMR (δ, DMSO-d$_6$, 300 MHz): 1.8-2.2 (br, 2H, CH$_2$), 3.0-3.2 (br, 1H, CH). Intrinsic viscosity (in DMF): 1.9 dL/g.

As a typical experiment of thermal polymerization, test tube (1 cm × 20 cm) containing AN (1.06 g, 20 mmol), CCl$_4$ (0.31 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. No polymerization was found after workup. Similarly, the thermal and photopolymerization of AN by using 1-phenylethyl chloride instead of CCl$_4$ under the same polymerization conditions were unsuccessfully attempted.

Polymerization of STY Initiated by CCl$_4$/Cp$_2$M (M = Fe, Co, Ni). In a typical experiment of thermal polymerization, a test tube (1 cm × 20 cm) charged with STY (2.1 g, 20 mmol), CCl$_4$ (0.19 mL, 2 mmol), Cp$_2$Fe (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 methanol, filtered off, and dried under reduced pressure give 0.32 g (15%) of white solid. IR (KBr pellet, cm^{-1}): 3020 s ($v_{C-H,arom}$), 2920 s ($v_{C-H,alip}$), 1600 s ($v_{c=c}$). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.7-2.2 (br, 2H, CH$_2$), 3.0-3.2 (br, 1H, CH), 7.0-7.5 (br, 5H, C$_6$H$_5$). GPC: M_w=98000, M_n=61000, M_w/M_n=1.6.

As a typical experiment of photopolymerization, a quartz test tube (1 cm × 20 cm) containing STY (2.1 g, 20 mmol), CCl$_4$ (0.19 mL, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and UV-irradiated for 2 h. No polymerization was found after workup.

Polymerization of STY Initiated by 1-Phenylethyl chloride/Cp$_2$M (M = Fe, Co, Ni). In a typical experiment of thermal polymerization, a test tube (1 cm × 20 cm) charged with STY (2.1 g, 20 mmol), 1-phenylethyl chloride (0.28 g, 2 mmol), Cp$_2$Fe (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 methanol, filtered off, and dried under reduced pressure give 0.48 g (23%) of white solid. IR (KBr pellet, cm^{-1}): 3020 s ($v_{C-H,arom}$), 2920 s ($v_{C-H,alip}$), 1600 s ($v_{c=c}$). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.7-2.2 (br, 2H, CH$_2$), 3.0-3.2 (br, 1H, CH), 7.0-7.5 (br, 5H, C$_6$H$_5$). GPC: M_w=488000, M_n=261000, M_w/M_n=1.9.

As a typical experiment of photopolymerization, a quartz test tube (1 cm × 20 cm) containing STY (2.1 g, 20 mmol), 1-phenylethyl chloride (0.28 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2

μmol) and benzene (2 mL) was degassed, sealed, and UV-irradiated for 2 h. No polymerization was found after workup.

Polymerization of Ethyl vinyl ether (EVE) Initiated by CCl$_4$/Cp$_2$M (M = Fe, Co, Ni). As a typical experiment, EVE (1.44 g, 20 mmol), CCl$_4$ (0.31 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) were added to a quartz test tube (1 cm × 20 cm). The reaction mixture was degassed, sealed, and irradiated with UV-light for 2 h. The resulting polymer was taken in methanol, precipitated in hexane, filtered off, and dried *in vacuo* to give 1.14 g (79%) of white solid. IR (KBr pellet, cm^{-1}): 2950 s (v_{C-H}), 1375 m (δ_{C-H}), 1100 s (v_{c-o}). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.18 (br, 3H, OCH$_2$CH_3), 1.61 (br, 2H, backbone CH$_2$), 1.82 (br, 1H, backbone CH), 3.47 (br, 2H, OCH_2CH$_3$). GPC: M_w= 42100, M_n=7800, M_w/M_n=5.4. The photopolymerization of EVE with CCl$_4$/Cp$_2$M (M = Co, Ni) combination did not produce any polymer. The thermal polymerization of EVE with CCl$_4$/Cp$_2$M (M = Fe, Co, Ni) combination did not produce any polymer, either.

Attempted Polymerization of Vinyl acetate (VA) Initiated by CCl$_4$/Cp$_2$M (M = Fe, Co, Ni). The following procedure is the representative of the photopolymerization reactions. A quartz test tube (1 cm × 20 cm) containing VA (1.72 g, 20 mmol), CCl$_4$ (0.31 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and irradiated with UV-light for 2 h. No polymerization was found. As a typical experiment of the thermal polymerization, test tube (1 cm × 20 cm) containing VA (1.72 g, 20 mmol), CCl$_4$ (0.31 g, 2 mmol), Cp$_2$Fe (0.37 mg, 2 μmol) and benzene (2 mL) was degassed, sealed, and heated at 70 °C for 24 h. No polymerization was found after workup.

Results and Discussion

Poly(MA) is hardly soluble in benzen, THF and CHCl$_3$, but soluble in methanol, DMF and DMSO. In contrast, poly (MMA) is hardly soluble in methanol, but soluble in benzene, THF and CHCl$_3$.[7,8c] Copolymerizaton is useful to improve the adhesion, compatibility, and solubility of polymers. In their solubility behavior copolymer resemble more or less the properties of the dominating monomer. Poly (MMA-*co*-MA) is hardly soluble in benezene, but soluble in THF and CHCl$_3$.[9] The photopolymerization of MMA and MA (1:1 mole ratio), initiated by CCl$_4$/Cp$_2$M (M = Fe, Co, Ni), produced poly(MMA-*co*-MA)s. The copolymer was purified by dissolving them in THF, filtering (to remove poly (MA)), and precipitating with benzene (to remove poly (MMA)). The homopolymers were not obtained in appreciable amounts from the workup procedure. The weight average molecular weights (M_w) of resulting poly(MMA-*co*-MA)s ranged from 2.7 × 10^6 to 3.5 × 10^6 with polydispersity index (PDI, M_w/M_n) equal to 3.9-7.2 in 20-36% yield. The thermal copolymerization of MMA and MA (1:1 mole ratio) with either CCl$_4$/Cp$_2$M (M = Fe, Co, Ni) or 1-phenylethylchloride/Cp$_2$M (M = Fe, Co, Ni) was not occurred. The results are summarized in Table 1.
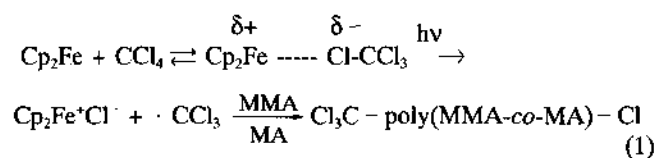
Carbon tetrachloride in the polymerization acted as both solvent and initiator. The minimum amount of metallocene was employed in order to avoid both the contamination of the polymer and the UV-masking action of the photopoly-

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Table 1. GPC Characterization of Copolymerization of MMA and MA by Chlorocarbon/Cp₂M (M = Fe, Co, Ni) Combination Initiator

Initiator	Isolated yield (%)	mol wt[c]		
		M_w	M_n	M_w/M_n
CCl₄+Cp₂Fe[a]	36	2733000	657000	4.2
CCl₄+Cp₂Co[a]	20	3474000	487000	7.2
CCl₄+Cp₂Ni[a]	25	3062000	785000	3.9
CCl₄+Cp₂M[b]	0	–	–	–
1-phenylethyl chloride +Cp₂M[a,b] (M = Fe, Co, Ni)	0	–	–	–

[a] UV-irradiation for 2 h; MMA : MA=1 : 1 mole ratio. [b] Heating at 70 °C for 24 h; MMA : MA=1 : 1 mole ratio. [c] Measured with GPC (vs polystyrene) in THF.

Table 2. Characterization of Polymerization of Acrylonitrile by Chlorocarbon/Cp₂M (M = Fe, Co, Ni) Combination Initiator

Initiator	Isolated yield (%)	Intrinsic viscosity[c] [η]
CCl₄+Cp₂Fe[a]	13	1.9
CCl₄+Cp₂Co[a]	6	3.5
CCl₄+Cp₂Ni[a]	9	2.1
CCl₄+Cp₂M[b] (M = Fe, Co, Ni)	0	–
1-phenylethyl chloride+Cp₂M[a,b] (M = Fe, Co, Ni)	0	–

[a] UV-irradiation for 2 h. [b] Heating at 70 °C for 24 h. [c] Measured in DMF at 25 °C; unit, dL/g.

Table 3. GPC Characterization of Polymerization of Styrene by CCl₄/Cp₂M (M = Fe, Co, Ni) Combination Initiator

Initiator	Isolated yield (%)	mol wt[c]		
		M_w	M_n	M_w/M_n
CCl₄+Cp₂Fe[a]	15	98000	61000	1.6
CCl₄+Cp₂Co[a]	11	103000	62000	1.7
CCl₄+Cp₂Ni[a]	8	108000	68000	1.6
CCl₄+Cp₂M[b] (M = Fe, Co,	0			

[a] Heating at 70 °C for 24 h. [b] UV-irradiation for 2 h. [c] Measured with GPC (vs polystyrene) in THF.

merization by the metallocene. Therefore, the mole ratio of monomer : chlorocarbon : metallocene (10000 : 1000 : 1) was fixed throughout in this study. The photocopolymerization yielded poly(MMA-co-MA)s with higher molecular weights and with higher PDI in higher yield as compared with the photohomopolymerization of MMA.[7a] The molecular weights are in the similar molecular weight range of poly (MMA-co-MA)s produced by the plasma-induced radical copolymerization of MMA and MA.[9] We reported that molecular weights decrease in the order of Cp₂Co > Cp₂Ni > Cp₂Fe, exactly opposite to the order of polymerization yield, Cp₂Fe > Cp₂Ni > Cp₂Co, in the respective photohomopolymerizations of MMA and MA with CCl₄/Cp₂M (M = Fe, Co, Ni).[7] As seen in Table 1, the same trend of molecular weights and polymerization yield as the respective homopolymerization was observed in the copolymerization. We believe that the photocopolymerization of MMA and MA with ferrocene/CCl₄ combination initiator might be proceeded by forming a charge-transfer (CT) complex between halocarbon and metallocene (eq. 1).[7]

$$\text{Cp}_2\text{Fe} + \text{CCl}_4 \rightleftarrows \overset{\delta+}{\text{Cp}_2\text{Fe}} \cdots \overset{\delta-}{\text{Cl-CCl}_3} \overset{h\nu}{\longrightarrow}$$

$$\text{Cp}_2\text{Fe}^+\text{Cl}^- + \cdot\text{CCl}_3 \xrightarrow{\frac{\text{MMA}}{\text{MA}}} \text{Cl}_3\text{C} - \text{poly(MMA-co-MA)} - \text{Cl}$$
(1)

The CT complex formation seems to be essential to the photopolymerization.[7] The photochemically excited CT complex will then decompose into ferricenium chloride and trichloromethyl radical which could finally initiate the photocopolymerization of MMA and MA.

In order to see the initiating efficiency of the combination initiator on acrylonitrile (AN), the poly(AN)s with intrinsic viscosities of 1.9-3.5 dL/g were prepared in 6-13% yields by the photopolymerization of AN initiated by CCl₄/Cp₂M (M= Fe, Co, Ni) combination. The results are given in Table 2.

The thermal polymerization at 70 °C for 24 h of AN with the CCl₄/Cp₂M (M = Fe, Co, Ni) combination initiator was unsuccessfully attempted. In addition, the thermal and photopolymerization using the 1-phenylethyl chloride/Cp₂M (M = Fe, Co, Ni) combination initiator were performed, but came to nothing. We found the same trend in Table 2 as in Table 1 that the molecular weights decrease in the order of

Cp₂Co > Cp₂Ni > Cp₂Fe, but the polymerization yield increase in the order of Cp₂Co < Cp₂Ni < Cp₂Fe in the photopolymerizations of AN with CCl₄/Cp₂M (M = Fe, Co, Ni). The intrinsic viscosity is directly related to the weight average molecular weight of polymer.[8]

The weight average molecular weights (M_w) of poly(STY) s yielded from the thermal polymerization at 70 °C for 24 h of styrene (STY), initiated by CCl₄/Cp₂M (M = Fe, Co, Ni), ranged from 9.8×10^3 to 1.1×10^5 with polydispersity index equal to 1.6-1.7 in 8-15% yield. The results are summarized in Table 3.

We witnessed the different trend in Table 3 from in Table 1 and Table 2 that the molecular weights decrease in the order of Cp₂Ni > Cp₂Co > Cp₂Fe, but the polymerization yield increase in the order of Cp₂Ni < Cp₂Co < Cp₂Fe in the thermal polymerizations of STY with CCl₄/Cp₂M (M = Fe, Co, Ni). Unlike MMA, MA, and AN, the photopolymerization of STY using the CCl₄/Cp₂M (M = Fe, Co, Ni) combination initiator was not occured. As our constant effort to make a living radical initiator system, the thermal polymerization of STY, initiated by 1-phenylethyl chloride/Cp₂M (M = Fe, Co, Ni) combination, was performed, producing poly(STY)s with weight average molecular weight (M_w) of $4.8 \times 10^5 - 5.4 \times 10^5$ and with PDI of 1.8-1.9 in 17-23% yields. No photopolymerization of STY using the 1-phenylethyl chloride/Cp₂M (M = Fe, Co, Ni) combination initiator was observed. The results are given in Table 4.

Unlike organic compound generally satisfying octet rule,[10a] an organometallic complex become generally most stable when it has an 18-electron closed-shell configuration.[10b,c] The group VIII metallocenes are known to be stepwise reduced or oxidized,[11] and the metallocenes can be oxidized by accepting a halogen radical in the polymerization. The in-

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Table 4. GPC Characterization of Polymerization of Styrene by 1-Phenylethyl Chloride/Cp$_2$M (M = Fe, Co, Ni) Combination Initiator
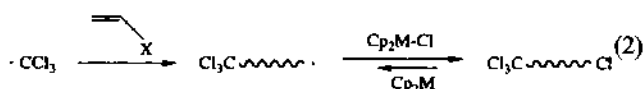
Initiator	Isolated yield (%)	mol wt[c]		
		M_w	M_n	M_w/M_n
1-phenylethyl chloride+ Cp$_2$Fe[a]	23	488000	261000	1.9
1-phenylethyl chloride+ Cp$_2$Co[a]	20	495000	270000	1.8
1-phenylethyl chloride+ Cp$_2$Ni[a]	17	537000	291000	1.8
1-phenylethyl chloride+ Cp$_2$M[b] (M = Fe, Co, Ni)	0			

[a] Heating at 70 °C for 24 h. [b] UV-irradiation for 2 h. [c] Measured with GPC (vs polystyrene) in THF.

itiating capability should be linearly related to the magnitude of polymeization yield. We first anticipated that the photoinitiating ability of the group VIII metallocenes should decrease in the oxidation order of Cp$_2$Ni > Cp$_2$Co > Cp$_2$Fe, according to the 18 electron rule. However, the photoinitiating efficiency was found to decrease in the order of Cp$_2$Fe > Cp$_2$Ni > Cp$_2$Co as shown in Table 1 and Table 2. In fact, the order of photoinitiating efficiency coincides with the photostability order. By contrast, the thermal initiating efficiency was found to decrease in the order of Cp$_2$Fe > Cp$_2$Co > Cp$_2$Ni as shown in Table 3. The order of thermal initiating efficiency coincides with the order of their thermal stability.

We provide a speculation to rationalize the experimental results (*vide infra*). Ferrocene could accept a chlorine radical to form a 19-electron ferricenium chloride which may, at the same time, want to go back by losing the chlorine radical to the stable 18-electron ferrocene. Thus, a growing polymer chain radical containig 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 back under the photochemical condition because the substitution of alkyl group on the halocarbon should decrease the tendency of forming a CT complex (eq. 2).

The capping efficiency order of metallocenium chloride

$$ \cdot CCl_3 \xrightarrow{\;\;X\;\;} Cl_3C\text{\tiny{vvvvv}}\cdot \xrightleftharpoons[Cp_2M]{Cp_2M\text{-}Cl} Cl_3C\text{\tiny{vvvvv}}Cl \tag{2} $$

could be directly related to the photo or thermal stability order of metallocene itself, depending on the polymerization condition. The polymer molecular weight should be, in turn, inversely proportional to the capping order.[12]

Living radical polymerization technique has advantages in precisely controlling the molecular weight distribution and structure of polymer.[13-16] Unlike the atom-transfer radical polymerization by 1-phenylethyl chloride/CuCl/bipyridine combination initiator,[14-16] as shown in Table 1-4, for the photo and thermal polymerization of various vinyl monomers, the polydispersity index $M_w/M_n > 1.5$ and the reverse relationship of molecular weights and polymerization yield was found. Polymer molecular weight did not linearly increase

with monomer conversion, either. The polymerization reactions seem not to be a *living* process.[7] The thermal and photopolymerization of EVE initiated by CCl$_4$/Cp$_2$M combination did not take place except the photopolymerization of EVE with CCl$_4$/Cp$_2$Fe combination initiator. The thermal and photopolymerization of VA with CCl$_4$/Cp$_2$M combination initiator did not happen at all.

In conclusion, this work describes the polymerization of various vinyl monomers such as MMA, MA, AN and STY with group VIII metallocene/halocarbon initiator combination. For the photocopolymerization of MMA and MA (1 : 1 mole ratio) initiated by CCl$_4$/Cp$_2$M, while the polymerization yield decreases in the order of Cp$_2$Fe > Cp$_2$Ni > Cp$_2$Co, the molecular weight decreases in the order of Cp$_2$Co > Cp$_2$Ni > Cp$_2$Fe as observed in the respective photohomopolymerization of MMA and MA. For the photopolymerization of AN initiated by by CCl$_4$/Cp$_2$M, the same trend was also observed. The thermal polymerization of AN initiated by CCl$_4$/Cp$_2$M combination was not occurred. The thermal and photopolymerization of AN initiated by the 1-phenylethyl chloride/Cp$_2$M combination were not occurred, either. For the thermal polymerization of STY initiated by CCl$_4$/Cp$_2$M or 1-phenylethyl chloride/ Cp$_2$M, while the polymerization yield decreases in the order of Cp$_2$Fe > Cp$_2$Co > Cp$_2$Ni, the molecular weight decreases in the order of Cp$_2$Ni > Cp$_2$Co > Cp$_2$Fe. The photopolymerization of STY initiated by CCl$_4$/Cp$_2$M or 1-phenylethyl chloride/Cp$_2$M combination was not occurred. An explanation for the reverse order has been provided. The thermal and photopolymerization of EVE initiatied only by CCl$_4$/ Cp$_2$Fe combination took place. The thermal and photopolymerization of VA with CCl$_4$/Cp$_2$M combination initiator did not happen at all. All the polymerization reactions described above were found to be not *living*.

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Transient Photoinduced Charge Carrier Dynamics of Glassy Carbon Film

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Conjugated organic polymers have been intensively investigated in the past few years because of their electrical and optical properties. Of special interests are electroluminescence, photoconductivity, photovoltaic effect, and the electrical conductivity of polymers. Moreover, because of their often large nonlinear optical susceptibilities and their roles as model compounds for quasi-one-dimensional semiconductors, considerable interests have been directed to the studies of electrical and optical properties with long conjugated chain polymers, such as polyacetylenes,[1] polydiacetylenes,[2,3] polythiophenes,[3,4] poly(phenylenevinylene)s,[5] poly(2,5-diethynylthiophene),[6] etc. To understand the electrical conductivities of conjugated polymers as well as their promising optical and nonlinear optical properties, the charge carrier generation and transporting behaviors in these polymers have become the subject of interests. Also, since

the charge carrier dynamics procede in fast-time regions, generally from femtoseconds to milliseconds,[7] pulsed laser spectroscopy has become a powerful tool to investigate these charge carrier generation and transporting mechanisms.

Glassy carbon (GC) polymer which is investigated in the present study is the electrode material which is commercially being utilized. To our knowledge, however the detailed conduction mechanisms of GC have not been reported yet. Therefore, in this study, we have investigated the conduction mechanism of the synthesized GC film with steady-state absorption and nanosecond time-resolved transient photoconductivity (PC) measurement. The result of the transient PC measurement of the GC film shows tens of nanoseconds PC decay signal and the steady-state absorption spectrum of the GC shows a broad band structure peaked approximately at 592 nm in the visible wavelength range. To discuss these experimental results, we have compared them with the reported spectroscopic results of pyrene

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