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Photopolymerization of Methyl Methacrylate Initiated by CCl₄/Group VIII Metallocene

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Photopolymerization technology applicable conveniently is amply used on a commercial basis today in the areas of surface coatings, photoresists, adhesives, and holography.[1] Organometallic photochemistry has received a great amount of attention because irradiation of organometallics can lead to catalytically and synthetically useful transformations.[2] *Inter alia*, numerous cyclopentadienyl complexes, a historically important class of organometallics, have been prepared and their photochemical properties have been intensively investigated.[3] A number of halogenated organic compounds have been used as effective photoinitiators.[4] A practical problem with halogenated photoinitiators is the corrosion of reactor system caused by acid hydrogen halides which are produced as byproducts during the photopolymerization. The use of ferrocene (Cp₂Fe) as a photopolymerization catalyst (to activate the halogenated photoinitiator) and as a halide-radical trap (to prevent the troublesome acid formation) in combination with halogenated compounds has been reported.[5] To our knowledge, the other group VIII metallocenes such as cobaltocene (Cp₂Co) and nickelocene (Cp₂Ni) have never been used for this type of photopolymerization. Here we wish to report the photopolymerization of methyl methacrylate (MMA) initiated by CCl₄/group VIII metallocene.

In a typical experiment, a quartz test tube (1 cm×20 cm) charged with MMA (2.14 mL, 20 mmol), CCl₄ (0.19 mL, 2 mmol), Cp₂Fe (0.37 mg, 2 μmol), and benzene (2 mL) was degassed, sealed, and irradiated with 300 nm UV-light (monochromatic UV lamp intensity, 6.93×10^{18} hv mL^{-1} min^{-1})
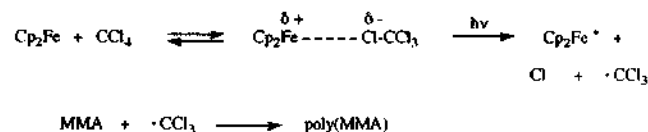
Table 1. GPC Characterization of Photopolymerization of MMA[a]

Initiator	Yield (%)	mol wt[b]		
		M_w	M_n	PDI[c]
CCl₄+Cp₂Fe	22	110600	55700	2.0
CCl₄+Cp₂Co	3	232000	103300	2.3
CCl₄+Cp₂Ni	11	180600	84900	2.1
CHCl₃+Cp₂Fe	10	—	—	—
Ph(C=O)CH₂Br+Cp₂Fe	0	—	—	—
Cp₂Fe	trace	—	—	—
CCl₄	trace	—	—	—

[a] UV-irradiation for 2 h. [b] Measured with GPC in THF. [c] Polydispersity Index, M_w/M_n.

for 2h. The polymer was precipitated in hexane, filtered off, and dried under reduced pressure to give 0.44 g (22%) of white solid.[6] Cobaltocene and nikelocene instead of ferrocene were also used with CCl₄ for the photopolymerization. Other halocarbons such as CHCl₃ and Ph(C=O)CH₂Br were examined as a possible substitute for CCl₄. The results are summarized in Table 1.

We used monomer : halide : metallocene with a fixed mole ratio of 10000 : 1000 : 1. We are studying their relative concentration effect on the photopolymerization and will be reported as a separate paper in the future. Fujisaki *et al.* suggested that the photopolymerization of MMA may be initiated by ferrocene/CCl₄ system as follows:[5b]

$$Cp_2Fe + CCl_4 \rightleftharpoons \overset{\delta+}{Cp_2Fe}\text{-----}\overset{\delta-}{Cl\text{-}CCl_3} \xrightarrow{h\nu} Cp_2Fe^{\cdot} + Cl^- + \cdot CCl_3$$

$$MMA + \cdot CCl_3 \longrightarrow poly(MMA)$$

A charge-transfer (CT) complex formed between ferrocene and CCl₄ by the iron atom serving as an electron donor and the chlorine atom 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 ferricenium chloride. The trichloromethyl radical will finally initiate the photopolymerization. The CT complex formation seems to be a mandatory condition for the photopolymerization. As a control experiment, ferrocene or CCl₄ alone is practically ineffective on the photopolymerization. As shown in Table 1, Ph(C=O)CH₂Br was ineffective because of inability of forming the CT complex with ferrocene. CHCl₃ was found to be less effective than CCl₄ (polymerization yield 10% *vs.* 22%). Radicals are particularly strongly stabilized when both an electron-withdrawing and an electron-donating substituent are located at the radical site.[7] Chlorine atom on the radical site could be more stabilizing the corresponding radical than hydrogen atom. Furthermore, the C-Cl bond dissociation energy in CCl₄ (84 kcal/mol) is smaller than the C-H bond dissociation energy (96 kcal/mol) in CHCl₃.[8] Such arguments were recently supported by the worldwide replacement of chlorofluorocarbons (CFCs) by hydrochlorofluorocarbons (HCFCs) because of ozone depletion in winter.[9]

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The electron configuration is $(e_{2g})^4(a_{1g})^2$ for Cp_2Fe (18 electron), $(e_{2g})^4(a_{1g})^2(e_{1g})^1$ for Cp_2Co (19 electron), and $(e_{2g})^4(a_{1g})^2$ $(e_{1g})^2$ for Cp_2Ni (20 electron). The highest occupied molecular orbitals e_{2g} and a_{1g} are only slightly bonding and therefore removing electrons from them does not greatly destabilize the metallocenes. The lowest unoccupied molecular orbital e_{1g} is not significantly antibonding so when electrons are added to create 19-electron and 20-electron species the stability loss is minimal. Nevertheless, an organometallic complex become most stable when it has 18 electron closed-shell configuration.[10] The group VIII metallocenes can be stepwise reduced or oxidized.[11] The photoinitiating ability is linearly related to the magnitude of polymerization yield. We first expected the photoinitiating ability of the group VIII metallocenes should decrease in the order $Cp_2Ni>Cp_2Co>Cp_2Fe$ (an oxidization order), based on the 18 electron rule. However, the photoinitiating effect was found to decrease in the order $Cp_2Fe>Cp_2Ni>Cp_2Co$. Ferrocene is known to be completely photoinert in nonhalogenated slovents.[12a] On the other hand, Borrell and Henderson reported that those metallocenes with an even number of electrons (e.g., 18, 20) were less photoactive, but those with an odd numbr (e.g., 17, 19) were more photoactive in nonhalogenated slovents.[12b] The photoinitiating order apparently coincides with the photostability order in nonhalogenated solvent. We also anticipated that the molecular weights should decreases in the same order as the polymerization yield order. 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 decreases in the order $Cp_2Co>Cp_2Ni>Cp_2Fe$, exactly opposite to the polymerization yield order. Ferrocene could accept a chlorine atom radical forming a ferricenium chloride, but, at the same time, the ferricenium chloride might want to go back to be stable 18-electron ferrocene. Thus, a growing polymer chain radical containing a CCl_3 end group could accept a chlorine radical to cap the radical end of polymer chain.
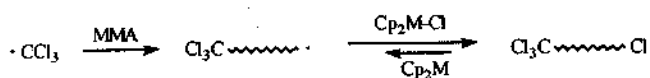
The capping order of metallocenium chloride could be directly related to the photostability order of metallocene itself, $Cp_2Fe>Cp_2Ni>Cp_2Co$. The polymer molecular weight should be, in turn, inversely proportional to the capping order. Typical redox radical telomerization promoted by transition-metal species shows a linear relation between polymer molecular weight and monomer conversion.[13] Matyjaszewski and Wang[14] described the atom-transfer radical polymerization in the presence of 1-phenylethyl chloride/CuCl/bipyridine. The radical polymerization by the catalyst combination exhibits a *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, $M_w/M_n>1.5$ as shown in Table 1 suggests that our photopolymerization is not a *living* process. Thus, the

present chlorine atom radical transfer from metallocenium chloride to polymer chain radical could be an irreversible termination process. A study improving our initiating system to be *living*, the capping process being reversible, is in progress and will be reported in the near future. Finally, we should admit that there is a chance 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] We are checking such a possibility.

In conclusion, we have shown the photopolymerization of MMA initiated by Cp_2M (M=Fe, Co, Ni)/CCl_4. While the polymerization yield decreases in the order $Cp_2Fe>Cp_2Ni>Cp_2Co$, the molecular weight decreases in the order $Cp_2Co>Cp_2Ni>Cp_2Fe$. An explanation for the reverse order has been provided.

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Cobalt-Mediated Olefin Epoxidation and Oxidative DNA Cleavage with Potassium Monopersulfate

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Elucidation of the mechanism of metal-mediated oxidations of organic substrates and oxidative cleavage of DNA has been a subject of recent studies in biological and bioinorganic chemistry.[1] In the studies, water-soluble potassium monopersulfate, $KHSO_5$, has been often used as an oxygen atom donor.[2] For example, Meunier and coworkers showed that metalloporphyrins[3] and metallobleomycins[4] are able to oxygenate organic substrates and cleave DNA with $KHSO_5$ in aqueous medium. They suggested that reactive intermediates responsible for the oxidation reactions are high-valent metal oxo complexes. In this communication, we report that a cobalt salt associated with $KHSO_5$ has the ability of epoxidizing olefins as well as cleaving DNA oxidatively in aqueous solution.

In a typical experiment, $KHSO_5$ (10 mM) was added to a reaction solution containing $Co(NO_3)_2$ (0.1 mM), CBZ (CBZ=carbamazepine, 1 mM, introduced as a 10 mM solution in methanol), and benzophenone (internal standard, 1 mM, introduced as a 10 mM solution in methanol) in 5 mL of water. The reaction mixture was stirred for 1 h at room temperature and analyzed by HPLC. We found that the conversion of CBZ was above 95%, and the yield of CBZ-oxide[5] product was 75% under our reaction conditions (eq. 1). Formation of CBZ-oxide was not detected in the absence of either cobalt salt or $KHSO_5$.[6] Other metal salts such as Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} were inactive in the CBZ epoxidation reaction, and other oxidants such as H_2O_2, *t*-BuOOH, and PhIO did not give the epoxide product either.

We then studied oxidative cleavage of DNA using the $M^{2+}/KHSO_5$ system. The cleavage of DNA was followed by monitoring the conversion of supercoiled pBR-322 DNA
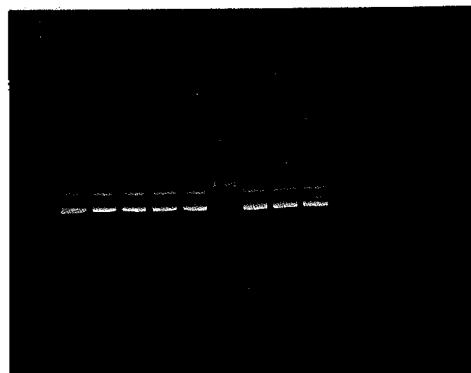
Figure 1. Cleavage of pBR 322 plasmid DNA (form I) by Co^{2+}/$KHSO_5$. Reactions were initiated with the addition of $KHSO_5$ in 50 mM phosphate buffer at pH 6.0. Preincubation of DNA with metal salts was performed for 10 min at 25 °C. Digestion time with $KHSO_5$ was 1 min. Conversion of form I to form II DNA was detected by gel electrophoresis on 1% agarose with ethidium bromide staining. Lane 1, reaction control, DNA (22.7 μM in base pairs) alone; lane 2, reaction control. $Co(NO_3)_2$ (22.7 μM); lane 3, reaction control, $KHSO_5$ (113.5 μM); lane 4, cleavage reaction [$Mn(CH_3CO_3)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)]; lane 5, cleavage reaction [$Fe(ClO_4)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)]; lane 6, cleavage reaction [$Co(NO_3)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)]; lane 7, cleavage reaction [$Ni(NO_3)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)]; lane 8, cleavage reaction [$Cu(CF_3SO_3)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)]; lane 9, cleavage reaction [$Zn(CF_3SO_3)_2$ (22.7 μM), $KHSO_5$ (113.5 μM)].
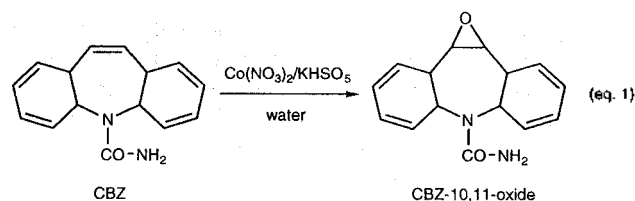
(form I) to an open circle (form II).[7] As shown in Figure 1, among the tested metal salts, only the cobalt salt showed the activity of cleaving DNA efficiently. This reactivity pattern was the same as that observed in the CBZ epoxidation reaction, suggesting that there is close correlation between the olefin epoxidation and the DNA cleavage by metal salt and KH_5O_5.

Cobalt-HSO_5 complex, 1, and high-valent cobalt oxo complex, 2, are proposed to be a possible intermediate for the oxidation of substrates (see Scheme 1). Since Meunier *et al.* reported that the reactive oxidizing agent generated in water-soluble manganese porphyrin-catalyzed CBZ epoxidation by $KHSO_5$ was high-valent manganese oxo complex and that the manganese oxo complex readily exchanged its oxygen atom with that of solvent water,[3b] we attempted CBZ epoxidation by $Co^{2+}/KHS^{16}O_5$ in $H_2^{18}O$ solution.[8] When the origin of the oxygen atom incorporated into the CBZ-oxide product was analyzed,[9] we found that the oxygen atom came from the oxidant, not from the solvent water, under our reaction conditions. This result is in sharp contrast to