antimalarial candidate because structurally similar deoxyartemisinin has been shown to be more active than artemisinin both in vitro (8 times) and in vivo. Third, since the cyclic enol ether 7 can be easily prepared and derivatized, other useful derivatives such as C-4 methylated trioxane are accessible by one additional step. These trioxanes, combined with their antimalarial activities, will be reported in a full paper when ready.

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References

9. All synthesized compounds have the following spectroscopic data. Compound 6: 1H NMR (400 MHz, CDCl3) δ 6.11 (s, 1H), 3.88 (m, 1H), 3.79 (m, 1H), 2.52-2.36 (m, 2H), 2.05-1.90 (m, 4H), 1.85-1.78 (m, 2H), 1.60-1.51 (m, 3H), 1.44 (m, 1H), 1.35 (m, 1H), 0.93 (m, 1H). Compound 7: 1H NMR (400 MHz, CDCl3) δ 6.17 (s, 1H), 3.87 (m, 1H), 3.78 (m, 1H), 2.58-2.42 (m, 2H), 2.15 (s, 3H), 2.04-1.91 (m, 2H), 1.88-1.72 (m, 5H), 1.59-1.32 (m, 3H), 1.16-1.05 (m, 1H), 0.96-0.86 (m, 1H); 13C NMR (75 MHz, CDCl3) δ 208.99, 136.18, 120.00, 63.78, 41.58, 39.39, 35.11, 34.03, 33.18, 30.65, 29.93, 25.93, 25.11. Trioxane 3: 1H NMR (400 MHz, CDCl3) δ 5.19 (s, 1H), 3.96 (m, 1H), 3.75 (m, 1H), 2.49-2.34 (m, 2H), 2.01 (m, 1H), 1.85-1.52 (m, 8H), 1.44 (s, 3H), 1.41-1.28 (m, 1H), 1.2 (m, 1H), 1.13 (m, 1H); 13C NMR (75 MHz, CDCl3) δ 104.04, 91.94, 79.93, 61.26, 46.10, 39.29, 36.41, 32.57, 28.35, 26.96, 26.67, 26.33, 25.00; FT-IR (neat, cm−1) 3013, 2933, 2865, 1453, 1436, 1378, 1088, 1044; Anal calcd for Cl3H4O2: C, 64.98; H, 8.39. Found: C, 65.04; H, 8.45. Trioxane 3a: 1H NMR (400 MHz, CDCl3) δ 4.79 (s, 1H), 4.14 (m, 1H), 3.54 (m, 1H), 2.42 (td, J=14.0, 4.0 Hz, 1H), 2.11 (m, 1H), 1.98-1.81 (m, 3H), 1.75-1.67 (m, 2H), 1.45 (s, 3H), 1.42-1.29 (m, 5H), 1.26-1.18 (m, 2H); 13C NMR (75 MHz, CDCl3) δ 104.30, 97.13, 77.84, 65.65, 43.74, 41.39, 35.14, 28.25, 27.17, 26.40, 26.19, 15.85, 25.21; FT-IR (CHCl3, cm−1) 2978, 2866, 1111, 1076, 1065, 1044, 1016.

Photopolymerization of Acrylic Acids Initiated by CCl4/Group VIII Metallocene

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Photopolymerization technology applicable conveniently is extensively employed this day on a commercial scale in the areas of surface coatings, photoresists, adhesives, and holography.1 Organometallic photochemistry has drawn a great deal of attention because irradiation of organometallic compounds can lead to catalytically and synthetically useful transformations.2 In particular, a historically important class of cyclopentadienyl complexes has been plentifully prepared and their photochemical properties have been intensively investigated.3 Many halogenated organic compounds have been used as effective initiators for the photopolymerization of many vinyl derivatives.4 Practical problems with halogenated photoinitiators are the corrosion of reactor system and some side reactions caused by acid hydrogen halides which are produced as byproducts during the photopolymerization. The use of ferrocene (Cp2Fe) as a photopolymerization promoter (to activate the halogenated photoinitiator) and as a halide radical trap (to prevent the troublesome acid formation) in
Combination with halogenated compounds in the photopolymerization of MMA has been described. To our knowledge, the other group VIII metalloccenes such as cobaltocene (Cp2Co) and nickelocene (Cp2Ni) have never been used for this type of photopolymerization except our recent report on the photopolymerization of MMA initiated by CCl4/group VIII metalloccene. In this communication we wish to report the photopolymerization of acrylic acids such as acrylic acid (AA) and methacrylic acid (MA) initiated by CCl4/group VIII metalloccene to compare with the photopolymerization of MMA initiated by CCl4/group VIII metalloccene.

In a typical experiment, a quartz test tube (1 cm x 20 cm) was loaded with AA (1.44 g, 20 mmol), CCl4 (0.19 mL, 2 mmol), CpFe (0.37 mg, 2 µmol), and benzene (2 mL). The mixture was degassed, sealed, and irradiated with 300 nm UV-light (monochromatic UV lamp intensity, 6.93 x 10^18 hv mL^-1 min^-1) for 2 h. The resulting polymer was taken in methanol, precipitated in hexane, filtered, and dried under vacuum to give 0.46 g (32%) of white solid. Cobaltocene and nickelocene 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 listed in Table 1.

Similarly, the photopolymerization of MA was also carried out to give poly(MA) as white solids. The results are given in Table 2.

We used a fixed mole ratio of monomer: halide: metalloccene (10000:1000:1). CCl4 was used here as both solvent and initiator. The amount of metalloccene used was minimized in order to decrease the contamination of the polymers and the UV-masking action by the metalloccene. We are studying their relative concentration effect on the photopolymerization and will be reported as a separate paper in the future. All of the resulting polymers were soluble in DMF, DMSO, and methanol. Poly(MA)s were produced in higher yields than poly( AA)s in the photopolymerization, as opposed to the expectation based on the steric grounds. However, the molecular weights of poly(AA)s were higher than those of poly(MA)s. The photopolymerization yields of the acrylic acids initiated by CCl4/group VIII metalloccene were generally higher than those of MMA initiated by CCl4/group VIII metalloccene.

Fujisaki et al. suggested that the photopolymerization of MMA may be initiated by ferrocene/CCl4 system as follows:

\[
\text{δ+ δ—} 
\text{Cp2Fe + CCl4 —> Cp2Fe—Cl|CCl4 \xrightarrow{hv} Cp2Fe^+ + Cl^- + CCl4}
\]

\[
\text{MMA + CCl4 \rightarrow poly(MMA)}
\]

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 ferricinium 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 and Table 2, Ph(C = O)CH2Br was ineffectual probably because of the insufficiency of forming the CT complex with ferrocene. CHCl3 was found to be less effective than CCl4. Radicals are particularly strongly stabilized when both an electron-withdrawing and an electron-donating substituent are located at the radical site. Chlorine atom on the radical site could be more stabilizing the corresponding radical center than hydrogen atom. Although the direct C-Cl bond dissociation energy in CHCl3 is not available, the C-Cl bond dissociation energy (73 kcal/mol) in CCl4 is smaller than the C-Cl bond dissociation energy (84 kcal/mol) in CH3Cl. Such arguments were firmly supported by the worldwide replacement of chlorofluorocarbons (CFCs) by hydrochlorofluorocarbons (HCFCs) due to ozone depletion phenomena in the Arctic and Antarctic zones in winter.

The electron configuration is (e_g)^2(e_u)^2 for Cp2Fe (18 electrons), (e_g)^2(e_u)^2 for Cp2Co (19 electrons), and (e_g)^2(e_u)^2 for Cp2Ni (20 electrons). The highest occupied molecular orbitals e_g and e_u are only slightly bonding and therefore removing electrons from them does not greatly destabilize the metalloccenes. The lowest unoccupied molecular orbital e_u 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. The group VIII metalloccenes can be stepwise reduced or oxidized. The photoinitiating ability is linearly related to the magnitude of polymerization yield. We first anticipated the photoinitiating ability of the group VIII metalloccenes should decrease in the order of Cp2Ni/Cp2Co/Cp2 Fe (an oxidation order), based on the 18 electron rule. However, the photoinitiating effect was found to decrease in the order of Cp2Fe>Cp2Ni>Cp2Co. Ferrocene is known to be completely photoinitiert in nonhalogenated solvents.

| Table 1. Characterization of Photopolymerization of AA* |
|---------------------------------|-------|-------|
| initiator | % yield | intrinsic viscosity* [η] |
| CCl4 + Cp2Fe | 32 | 9.4 |
| CCl4 + Cp2Co | 5 | 26.5 |
| CCl4 + Cp2Ni | 12 | 13.4 |
| CHCl3 + Cp2Fe | 15 | — |
| Ph(C = O)CH2Br + Cp2Fe | 0 | — |
| Cp2Fe | 2 | — |
| CCl4 | 2 | — |

*UV-irradiation for 2 h. Measured in DMF at 25 °C; unit, dL/g.

| Table 2. Characterization of Photopolymerization of MA* |
|---------------------------------|-------|-------|
| initiator | % yield | intrinsic viscosity* [η] |
| CCl4 + Cp2Fe | 54 | 2.7 |
| CCl4 + Cp2Co | 5 | 4.0 |
| CCl4 + Cp2Ni | 24 | 3.9 |
| CHCl3 + Cp2Fe | 20 | — |
| Ph(C = O)CH2Br + Cp2Fe | 0 | — |
| Cp2Fe | trace | — |
| CCl4 | trace | — |

*UV-irradiation for 2 h. Measured in DMF at 25 °C; unit, dL/g.
On the other hand, Borrell and Henderson reported that those metalloccenes with an even number of electrons (e.g., 18, 20) were less photoactive, but those with an odd number (e.g., 17, 19) were more photoactive in nonhalogenated solvents. The photoinitiating order appears to coincide with the photostability order in nonhalogenated solvent. We also expected that the molecular weights should decrease in the same order as the order of polymerization yield. 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. However, the molecular weights decreases 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. Ferrocene could accept a chlorine radical forming a ferricenium chloride, but, at the same time, the ferricenium chloride might want to go back by losing the chlorine radical to be stable 18-electron ferrocene. Thus, a growing polymer chain radical containing a $\text{CCl}_3$ as an end group could accept a chlorine radical to cap the radical end of polymer chain.

\[
\text{CCl}_3 \quad \text{AA} \quad \text{C}_1 \text{C} \quad \text{Cp}_2\text{M} \quad \text{C}_1 \text{C} \quad \text{Cp}_2\text{M}
\]

The capping order of metalloccenium chloride could be directly related to the photostability order of metalloccene itself, $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co}$. 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 relationship between polymer molecular weight and monomer conversion. Living polymerization technique allows to precisely control polymer molecular weight distribution and structure. However, the bias of free radicals to undergo self-reaction at diffusion-controlled rates precludes conventionally living polymerization. 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 controlled 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. Matyjaszewski et al. described the atom-transfer radical polymerization initiated by 1-phenylethyl chloride/CuCl/bipyridine combination. The radical polymerization by the initiator combination exhibits a living character with a negligible amount of irreversible transfer and termination and with a narrow molecular weight distribution, $M_d/M_n < 1.5$. In this case, polymer molecular weight linearly increases with monomer conversion. The intrinsic viscosity is directly related to the weight average molecular weight of polymer. Therefore, as shown in Table 1 and Table 2, the reverse linear relationship between polymer molecular weight and monomer conversion could suggest that our photopolymerization is not a living process. Thus, the present chlorine radical transfer from metalloccenium 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 metalloccenium 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. We are checking such a possibility.

In conclusion, we have shown the photopolymerization of AA and MA initiated by $\text{Cp}_2\text{M}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$)/CCl$_3$ combination. Lower-molecular-weight poly(MAs) were produced in higher yields than higher-molecular-weight poly(AAs) in the photopolymerization. It was found that while the polymerization yield decreases in the order of $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co}$, the molecular weight decreases in the order of $\text{Cp}_2\text{Co} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Fe}$. An explanation for the reverse order has been provided.

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References

7. Poly(AA): IR (KBr pellet, cm$^{-1}$): 3300 br s (vOH), 1720 s (vC=O), 1250 s (vC=O); $^1$H NMR (δ, DMSO-d$_6$, 300 MHz): 1.2-2.4 (br, 3H, CH$_2$-CH$_2$), 12.4 (br, 1H, COOH); Intrinsic viscosity: 9.4 dL/g.
8. Poly(MA): IR (KBr pellet, cm$^{-1}$): 3400 br s (vOH), 1720 s (vC=O), 1200 s (vC=O); $^1$H NMR (δ, DMSO-d$_6$, 300 MHz): 0.9-1.1 (br, 3H, C-CH$_3$), 1.8-2.1 (br, 2H, CH$_2$), 7.1-7.4 (br, ArH), 12.3 (br, 1H, COOH); Intrinsic viscosity: 2.7 dL/g.
11. Halon Replacements: Technology and Science; Miziolek, A.
Silver(I)/Celite Promoted Oxidative Additions of 1,3-Dicarbonyl Compounds to Olefins. A Facile Synthesis of Dihydrofurans

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The oxidative addition reaction of carbon-centered radicals to alkenes mediated by metal salts (Mn[II], Ce[III], and Co[III]) has received considerable attention over the last decade in organic synthesis for construction of carbon-carbon bonds. Utilization of high valent metal salts in oxidative addition reactions has been particularly efficacious. Among these manganese(III) acetate and cerium(IV) ammonium nitrate (CAN) have been used most efficiently. However, their synthetic exploitations have been limited in the low yield in intermolecular addition reactions, by strong acidic reaction conditions, and by overoxidations due to substitution of acetate or nitroxy groups. Necessity for overcoming these problems has prompted our search for the possibility of using silver(I) metals. In related work, Malek has demonstrated the usefulness of Ag(II) oxide for the generation of a carbon radical and Saegusa has reported the oxidative dimerization of β-diketone by using Ag(I) oxide. It has been reported by Fetizon that silver(I) carbonate/Celite is a valuable reagent for the oxidation of alcohols to aldehydes and ketones in high yield. We report here that Ag(I)/Celite is also an efficient and useful reagent for the oxidative addition of 1,3-dicarbonyl compounds to olefins, which allows the synthesis of dihydrofurans in moderate yield. Silver(I) metal promoted oxidative additions are generally heterogeneous reactions which take place under essentially mild neutral conditions. Two equivalents of silver(I)/Celite are used for completion of the reaction and the reactions are typically carried out by refluxing a solution of a 1,3-dicarbonyl compound with an alkene (5 eq) in an anhydrous solvent. The course of the reaction can be readily monitored by TLC. Isolation of products involves a very simple filtration to remove the reduced silver(0) metal followed by evaporation of solvent. Reaction of 1,3-hexanediol 1 with ethyl vinyl ether was attempted utilizing several silver(I) reagents (Table 1). Both silver(I) oxide and silver(I) carbonate provided the desired dihydrofuran 2 in good yields whereas AgOAc, AgNO3, and AgBF4 gave no reaction. Most interestingly, we found that the readily available reagent, 50% silver(I) oxide/Celite or 50% silver(I) carbonate/Celite, is more efficient than silver(I) metal for the production of dihydrofuran 2 as shown in Table 1. More importantly, the incorporation of Celite resulted in reduced reaction times and improved yields. However, addition of silica gel resulted in a low yield (31%).

In an effort to optimize reaction conditions, we surveyed several solvents for the production of dihydrofuran 2 with the AgO/Celite system (Table 2). Nonpolar solvents such as benzene or heptane gave only low yields (15% or 10%) of dihydrofuran 2 presumably due to the insolubility of silver(I) oxide, while in polar acetonitrile the yield was dramatically improved to 80%.

Examples of the dihydrofurans synthesized via optimized conditions in acetonitrile are shown in Table 3. The structure of the obtained products is easily established spectroscopically. The cis and trans products 7 of entry 5 are identified by observation of coupling constants of 9.0 Hz (cis) and 5.6 Hz (trans) between the two methine protons. While there is no direct precedent for the oxidative addition of 1,3-cyclopentanediene (entry 3) to olefins by using metal salts such