

Polymerization of Hydrosilanes and Vinyl Monomers in the Presence of Transition Metal Complex

Myoung-Hee Kim, Jun Lee, Hyo Chang Cha, Joong-Hyeok Shin and Hee-Gweon Woo[†]

Abstract

This minireview provides the chosen examples of our recent discoveries in the polymerization of hydrosilanes, dihydrosilole, lactones, and vinyl derivatives using various catalysts. Hydrosilanes and lactones copolymerize to give poly(lactone-*co*-silane)s with Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) catalyst. Hydrosilanes (including dihydrosilole) reduce noble metal complexes (e.g., AgNO₃, Ag₂SO₄, HAuCl₄, H₂PtCl₆) to give nanoparticles along with silicon polymers such as polysilanes, polysilole, polysiloxanes (and silicas) depending on the reaction conditions. Interestingly, phenylsilane dehydrocoupled to polyphenylsilane in the inert nitrogen atmosphere while phenylsilane dehydrocoupled to silica in the ambient air atmosphere. Cp₂M/CX₄ (M = Fe, Co, Ni; X = Cl, Br, I) combination initiate the polymerization of vinyl monomers. In the photopolymerization of vinyl monomers using Cp₂M/CCL₄ (M = Fe, Co, Ni), the photopolymerization of MMA initiated by Cp₂M/CCL₄ (M = Fe, Co, Ni) shows while the polymerization yield decreases in the order Cp₂Fe > Cp₂Ni > Cp₂Co, the molecular weight decreases in the order Cp₂Co > Cp₂Ni > Cp₂Fe. For the photohomopolymerization and photocopolymerization of MA and AA, the similar trends were observed. The photopolymerizations are not *living*. Many exciting possibilities remain to be examined and some of them are demonstrated in the body of the minireview.

Key words : Poly(caprolactone-*co*-silane)s, Reductive ring-opening, Photopolymerization, Chain initiation, Chain transfer, Poly(hydrosilane), Ferrocene, Cobaltocene, Nickelocene, UV irradiation, Living polymerization, Silver/polymer, Nanocomposites, Dehydrocoupling, Dry Sol-Gel, Organic silica.

1. Introduction

Hydrosilanes undergo versatile reactions in the presence of various catalysts.^[1-3] The reactions include homo/hetero dehydrocoupling, dry sol-gel condensation, etc. Vinyl monomers are easily polymerized by organic radical initiators^[4] and inorganic initiators. In the following sections, this miniaccount provides the selected examples of our recent research developments in the polymerization of hydrosilanes and vinyl monomers in the presence of transition metal complexes. This miniaccount is not meant to be comprehensive, rather, it is focused on the recent research developments discovered in our laboratory.

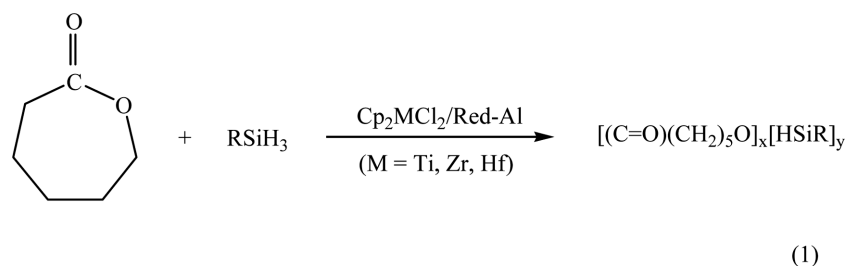
1.1. Copolymerization of ϵ -caprolactone and hydrosilane to poly(caprolactone-*co*-silane)s using Cp₂MCl₂/Red-Al combination catalyst (M = Ti, Zr, Hf)

The non-reductive ring-opening/dehydrocoupling copolymerization of ϵ -caprolactone with various primary hydrosilanes (RSiH₃: phenylsilane, *p*-tolylsilane, benzylsilane, *p*-methylbenzylsilane, and phenethylsilane) and secondary hydrosilanes (RR'SiH₂: phenylmethylsilane and diphenylsilane) using Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination catalyst produced random copolymers, poly(caprolactone-*co*-silane)s in good yield (eq 1).

For all the primary hydrosilanes the polymerization yield and molecular weight decreased in the order Ti > Zr > Hf whereas the TGA residue yield increased in the order Ti < Zr < Hf. The molecular weights with secondary hydrosilanes were higher than those with primary hydrosilanes while a reverse trend was observed for TGA residue yield. A plausible mechanism for the formation of the random copolymers was provided.^[5]

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1.2. Dry Sol-Gel Condensation of $p\text{-X-C}_6\text{H}_4\text{SiH}_3$ (X = H, CH₃, CH₃O, F, Cl) to Organosilica $p\text{-X-C}_6\text{H}_4\text{SiO}_3$ using Nickelocene

The dry sol-gel reaction at toluene in ambient air atmosphere of $p\text{-X-C}_6\text{H}_4\text{SiH}_3$ (X = H, CH₃, CH₃O, F, Cl) to $p\text{-C}_6\text{H}_4\text{SiO}_3$ in high yield, catalyzed by nickelocene, is reported (eq 2).

The highest yield, molecular weight, polydispersity index, and TGA residue yield were obtained for $p\text{-Cl-C}_6\text{H}_4\text{SiH}_3$. Some degree of unreacted Si-H bonds still remained in the gel because of steric reason. All the insoluble gels adopt an amorphous structure with a smooth surface. A plausible mechanism for the dry sol-gel reaction was suggested.^[6]

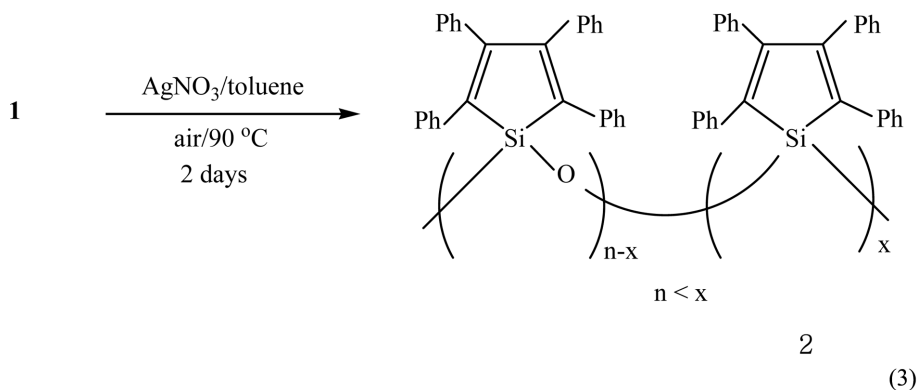
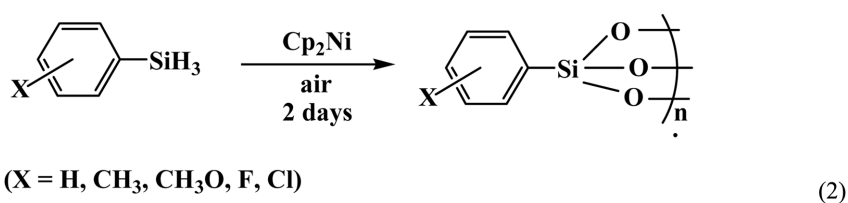
The dry sol-gel copolymerization at toluene in ambient air atmosphere of $p\text{-X-C}_6\text{H}_4\text{SiH}_3$ (X = H, CH₃, CH₃O,

F, Cl) to $p\text{-C}_6\text{H}_4\text{SiO}_3$ in high yield, catalyzed by nickelocene, is also described.^[7]

1.3. Dehydrocoupling of hydrosilanes to polysilanes by the action of noble metal complexes: Catalytic Si-Si/Si-O Dehydrocoupling of 1,1-Dihydroterphenylsilole to Optoelectronic Polysiloles with Colloidal Silver Nanoparticles

The combinative Si-Si/Si-O dehydrocoupling at ambient air atmosphere of 1,1-dihydroterphenylsilole **1** with 2 mol% of AgNO₃ and Ag₂SO₄ in toluene at 90°C produces optoelectronic polysiloles **2** in high yield (eq 3).

The complexes such as Cp₂Co, Cp₂Ni, Cp₂ZrCl₂/Red-Al, and AgCl were found to be ineffective for the dehydrocoupling of **1**. The polysiloles mainly have Si-Si bonds along with the small portion of Si-O bonds in

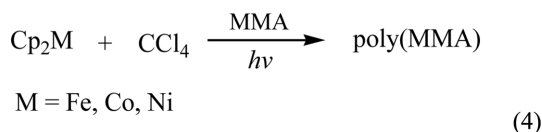


the polymer backbone chain. Interestingly, the Si-O linkage increased with increasing the concentration of catalyst AgNO₃, implying that while Ag(0) species catalyze the Si-Si dehydrocoupling, Ag(I) species catalyze the Si-O dehydrocoupling along with the simultaneous oxidation of NO₃⁻ ion to NO₂. The silver complexes transformed to colloidal silver nanoparticles during the catalytic reaction. The Si-Si/Si-O dehydrocoupling of **1** with AgNO₃ even at dry nitrogen atmosphere is occurred, supporting that the oxidation of NO₃⁻ ion to NO₂ is only the possible oxygen source, but not from the adventitious moisture in air. σ -, β -, and γ -Cyclodextrins considerably deteriorated the dehydrocoupling of **1** probably due to both the formation of insoluble inclusion complexes in toluene and the encapsulation of SiH₂ moiety. The resulting silole polymer **2** emits green light at 520 nm and is electroluminescent at 520 nm.^[8a]

Similarly, **1** also dehydrocoupled to **2** by the reduction of noble metal complexes such as Ag₂SO₄, HAuCl₄, H₂PtCl₆.^[8b] Primary hydrosilanes (i.e., RSiH₃) dehydrocoupled to polysilanes by the reduction of noble metal complexes such as AgNO₃, Ag₂SO₄, HAuCl₄, H₂PtCl₆.^[8c]

1.4. Photopolymerization of vinyl derivatives using Cp₂M/CX₄ (M = Fe, Co, Ni; X = Cl, Br, I)

Organometallic photochemistry has received a great amount of attention because irradiation of organometallics can lead to catalytically and synthetically useful transformations.^[9] In particular, numerous cyclopentadienyl complexes, a historically important class of organometallics, have been prepared and their photochemical properties have been intensively investigated.^[10] A number of halogenated organic compounds have been



used as effective photoinitiators.^[11] 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.^[12] We first used the other group VIII metallocenes such as cobaltocene (Cp₂Co) and nickelocene (Cp₂Ni) for this type of photopolymerization (eq. 4).^[13]

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 μ mol), and benzene (2 mL) was degassed, sealed, and irradiated with 300 nm UV-light (monochromatic UV lamp intensity, 6.93×10¹⁸ hv mL⁻¹ min⁻¹) for 2 hrs. The polymer was precipitated in hexane, filtered off, and dried under reduced pressure to give 0.44 g (22%) of white solid. Cobaltocene and nickelocene instead of ferrocene were also used with CCl₄ for the photopolymerization. Other halocarbons such as chloroform and Ph(C=O)CH₂Br were also examined as a possible substitute for CCl₄. We used monomer:halide:metallocene with a fixed mole ratio of 10,000:1,000:1. The results are summarized in Table 1.

Fujisaki and coworkers suggested that the photopolymerization of MMA may be initiated by Cp₂Fe/ CCl₄

Table 1. GPC Characterization of Photopolymerization of MMA^a

Initiator	Yield (%)	mol wt ^b		
		<i>M_w</i>	<i>M_n</i>	PDI ^c
CCl ₄ + Cp ₂ Fe	22	110600	55700	2.0
CCl ₄ + Cp ₂ Co	3	232000	103300	2.3
CCl ₄ + Cp ₂ Ni	11	180600	84900	2.1
CHCl ₃ + Cp ₂ Fe	10	-	-	-
Ph(C=O)CH ₂ Br+ Cp ₂ Fe	0	-	-	-
Cp ₂ Fe	trace	-	-	-
CCl ₄	trace	-	-	-

^aUV-irradiation for 2hrs. ^bMeasured with GPC in THF. ^cPolydispersity Index, *M_w*/*M_n*.

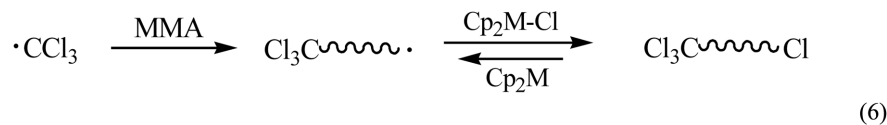
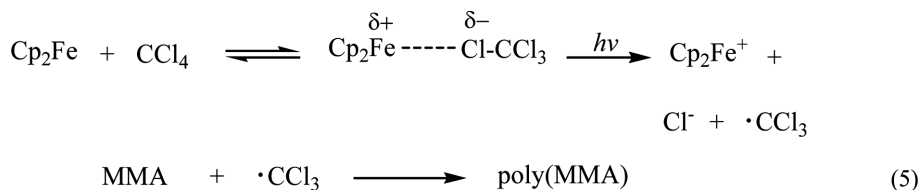
system as follows (eq. 5):^[12b]

A charge-transfer (CT) complex formed between ferrocene and CCl_4 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 ($\text{Cp}_2\text{Fe}^+\text{Cl}^-$). The trichloromethyl radical will finally initiate the photopolymerization. The CT complex formation seems to be a mandatory condition for the photopolymerization. As shown in Table 1, ferrocene or CCl_4 alone is practically ineffective on the photopolymerization. $\text{Ph}(\text{C}=\text{O})\text{CH}_2\text{Br}$ is ineffective because of inability of forming the CT complex with ferrocene. CHCl_3 is less effective than CCl_4 . Chlorine atom on the radical site could be more stabilizing the corresponding radical than hydrogen atom.^[14] The C-Cl bond dissociation energy in CCl_4 (84 kcal/mol) is smaller than the C-H bond dissociation energy (96 kcal/mol) in CHCl_3 .^[15] Such arguments were supported by the worldwide replacement of chlorofluorocarbons (CFCs) by hydrochlorofluorocarbons (HCFCs) because of ozone depletion in winter.^[16]

The electron configuration is $(e_{2g})^4(a_{1g})^2$ for 18 electron ferrocene, $(e_{2g})^4(a_{1g})^2(e_{1g})^1$ for 19 electron cobaltocene, $(e_{2g})^4(a_{1g})^2(e_{1g})^2$ for 20 electron nickelocene. The highest occupied molecular orbitals e_{2g} and a_{1g} are only slightly bonding and therefore removing electron 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 although an organometallic complex become most stable when it has 18 electron closed-shell config-

uration. The group VIII metallocenes can be stepwise reduced or oxidized. 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 $\text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co} > \text{Cp}_2\text{Fe}$ (an oxidation order), based on the 18 electron rule. However, as seen in Table 2, the photoinitiating effect decreases in the order $\text{Cp}_2\text{Fe} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Co}$. Ferrocene is known to be completely photoinert in nonhalogenated solvents.^[17a] It is known that those metallocenes with an even number of electrons (e.g., 18, 20) are less photoactive, but those with an odd number (e.g., 17, 19) are more photoactive in nonhalogenated solvents.^[17b] Thus, the photoinitiating order apparently coincides with the photostability order in nonhalogenated solvents. We also anticipated that the polymer molecular weights should decrease in the same order as the polymerization yield order because it is known that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization of vinyl monomers.^[4] However, the molecular weights decrease in the order $\text{Cp}_2\text{Co} > \text{Cp}_2\text{Ni} > \text{Cp}_2\text{Fe}$, 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 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 (eq. 6)

The capping order of metallocenium chloride could be directly related to the photostability order of metallocene 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. Matyjaszewski and cow-



orker reported the atom-transfer radical polymerization (ATRP) in the presence of 1-phenylethyl chloride/CuCl/bipyridine.^[18] The ATRP exhibits a *living* character with a negligible amount of irreversible transfer and termination and with a narrow molecular weight distribution, $M_w/M_n < 1.5$. The molecular weight distribution, $M_w/M_n > 1.5$ as shown in Table 1 suggests that our current photopolymerization is not a *living* process. Thus, the current chlorine atom radical transfer from metalocenium chloride to polymer chain radical could be an irreversible termination process.

As described above, the photopolymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) shows while the polymerization yield decreases in the order $Cp_2Fe > Cp_2Ni > Cp_2Co$, the molecular weight decreases in the order $Cp_2Co > Cp_2Ni > Cp_2Fe$.^[13] The photopolymerizations of methacrylic acid (MA) and acrylic acid (AA) initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) show the similar trends (polymerization yield and polymer molecular weight) to the photopolymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$).^[19] Similarly, the photocopolymerization of MMA and MA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) shows that the polymerization yield decreases in the order $Cp_2Fe > Cp_2Ni > Cp_2Co$ whereas the molecular weight decreases in the order $Cp_2Co > Cp_2Ni > Cp_2Fe$.^[20] The photopolymerizations of acrylonitrile (AN) initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) show the similar trends (polymerization yield and polymer molecular weight) to the photopolymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$).^[20] The photopolymerizations of styrene (STY) and vinyl acetate (VA) are not occurred in the presence of).^[20] In comparison, the thermal polymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) shows that while the polymerization yield decreases in the order $Cp_2Fe > Cp_2Co > Cp_2Ni$, the molecular weight decreases in the order $Cp_2Ni > Cp_2Co > Cp_2Fe$.^[21] The thermal polymerization is not *living*. The thermal polymerization of styrene initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) also shows the similar trends to that of MMA.^[20] The thermal copolymerization of MMA and MA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) shows the similar trends to that of MMA. For the thermal copolymerization of MMA and MA with the initiation system Cp_2M/CCl_4 ($M = V, Cr, Mn$), the polymerization yield decreases in the order $Cp_2Mn > Cp_2Cr > Cp_2V$.^[22] The photopolymerizations of MMA initiated by $Cp_2M/$

CX_4 ($M = Fe, Co, Ni$; $X = Cl, Br, I$) show the similar trends (in terms of polymerization yield and polymer molecular weight) to the photopolymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$). The initiating efficiency increases in the order: $Cl_4 < CBr_4 < CCl_4$ probably due to steric effect of CX_3 moiety in spite of bond strength order $C-I < C-Br < C-Cl$.^[23]

2. Conclusions

This minireview describes the polymerization of vinyl monomers, lactones, and hydrosilanes (and dihydrosilole) with various initiators such as Cp_2M/CX_4 ($M = Fe, Co, Ni$; $X = Cl, Br, I$), $Cp_2MCl_2/Red-Al$ ($M = Ti, Zr, Hf$), nickelocene, and noble metal complexes. Hydrosilanes copolymerize with lactones to produce poly(lactone-*co*-silane)s in the presence of $Cp_2MCl_2/Red-Al$ ($M = Ti, Zr, Hf$) catalyst. Hydrosilanes (including dihydrosilole) reduce noble metal complexes (e.g., $AgNO_3$, Ag_2SO_4 , $HAuCl_4$, H_2PtCl_6) to give metal nanoparticles along with silicon polymers such as polysilanes, polysilole, polysiloxanes (and silicas) depending on the reaction conditions. Interestingly, phenylsilane dehydrocoupled to polyphenylsilane in the inert nitrogen atmosphere while phenylsilane dehydrocoupled to silica in the ambient air atmosphere. In the photopolymerization of vinyl monomers using Cp_2M/CCl_4 ($M = Fe, Co, Ni$), the photopolymerization of MMA initiated by Cp_2M/CCl_4 ($M = Fe, Co, Ni$) shows while the polymerization yield decreases in the order $Cp_2Fe > Cp_2Ni > Cp_2Co$, the molecular weight decreases in the order $Cp_2Co > Cp_2Ni > Cp_2Fe$. For the photopolymerization and photocopolymerization of MA and AA, the similar trends were observed. The initiating efficiency increases in the order: $Cl_4 < CBr_4 < CCl_4$ probably due to steric effect of CX_3 moiety in spite of bond strength order $C-I < C-Br < C-Cl$. Furthermore, the photopolymerizations are not living. Hydrosilanes reduce noble metal complexes (e.g., $AgNO_3$, Ag_2SO_4 , $HAuCl_4$, H_2PtCl_6) to give nanoparticles along with silicon polymers such as polysilanes, and polysiloxanes.

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