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Synthesis, catalytic Si–Si dehydrocoupling, and thermolysis of polyvinylsilanes $[\text{CH}_2\text{CH}(\text{SiH}_2\text{X})]_n$ (X=H, Ph)

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Abstract

Clear honey-like oil $[\text{CH}_2\text{CH}(\text{SiH}_3)]_n$ (PVS) with 40% ceramic yield was crosslinked by Si–Si dehydrocoupling with the catalysts developed recently in our laboratory such as Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Hydride}$ (M = Ti, Zr, Hf; Hydride = Red-Al, *N*-Selectride, Super-Hydride) combination, group 6 metal hexacarbonyl $\text{M}(\text{CO})_6$ (M = Cr, Mo, W), and group 8 metallocene Cp_2M (M = Co, Ni) to give insoluble network of polyethylene–polysilane hybrids. Their thermolysis in argon significantly improved ceramic yields of 62–80%. The thermogravimetric analysis ceramic yields of the crosslinked PVS with the Group 4 metallocene were higher than those with the Group 6 and 8 metal complexes. The most effective dehydrocoupling catalyst was $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ combination. Similarly, white sticky solid $[\text{CH}_2\text{CH}(\text{SiH}_2\text{Ph})]_n$ (PPVS) with 35% ceramic yield was modified by Si–Si dehydrocoupling with the Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Zr) combination catalysts. Thermolysis of the crosslinked PPVS under argon to 800 °C showed improved ceramic yields (47–50%), which were lower than those of crosslinked PVSs due to low degree of crosslinking and high C/Si ratio (C/Si = 8).

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Keywords: Dehydrocoupling; Metallocene; Polyvinylsilane; Crosslinking; Thermolysis

1. Introduction

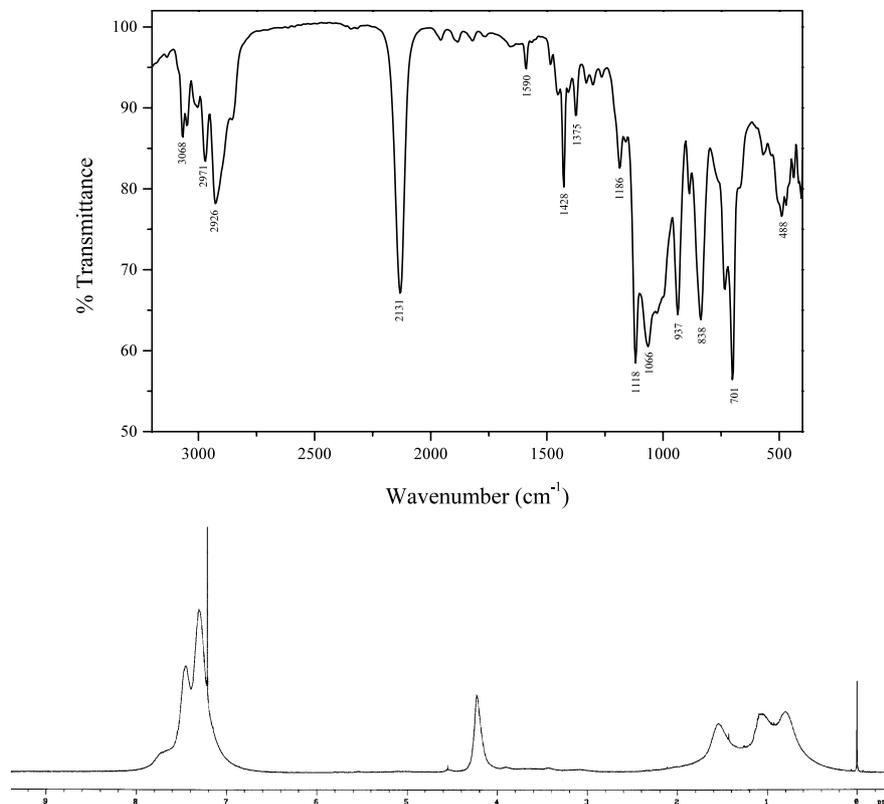
High performance ceramic materials have been given a great deal of interest for potential application as thermomechanical materials due to their stiffness and especially their excellent structural stability under harsh environmental extremes. Oxide ceramics exhibit creep affinity at high temperatures, limiting their application in high energy facilities and the aerospace industry [1]. By comparison, non-oxide ceramics possess increased creep stability at high temperatures, but are not thermomechanically stable in air atmosphere [2]. Silicon-containing non-oxide ceramics such as silicon

carbide (SiC), silicon nitride (Si_3N_4), and silicon carbonitride ($\text{Si}_x\text{C}_y\text{N}_z$) have received a great deal of attention for diverse applications [3]. *Inter alia*, silicon carbide is of great interest because of its high strength, hardness, chemical resistance, semiconductivity (band gap 2.2 eV (β -SiC), 2.9 eV (α -SiC)), high-temperature stability and X-ray resistance. Thus, SiC ceramic has been widely used as reinforcing materials in advanced ceramics and composites [4]. Silicon carbide is obtained in industrial scale by Acheson process, where high-pure silicon dioxide (99.5%) and petroleum cokes are pyrolyzed together at temperatures as high as 2200–2500 °C [5]. However, the resulting SiC powder is infusible, intractable, and especially not applicable for the preparation of fibers or films.

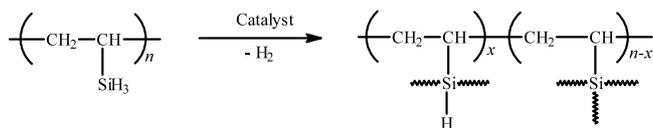
In the mid 1970s, Yajima and coworkers [6] first showed the industrial preparation of SiC fibers, including preparation of polycarbosilane (PCS) precursors via

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Fig. 1. IR and $^1\text{H-NMR}$ spectra of PPVS.

bonds whose thermolysis, due to the nature of the polymer, give only low ceramic yields, can be converted to useful preceramic precursors by appropriate chemical crosslinking treatment of their Si–H bonds because the Si–H bond is a very reactive functional group under thermal conditions or under radiation or under catalysis. For example, PCS for the Nicalon SiC-containing ceramic fiber, which contains Si–H bonds on the main backbone chain as a principal component, may be converted to a more highly cross-linked polymer by exposure to air atmosphere at 300–350 °C. Because polyvinylsilane (PVS) has reactive silyl substituents (SiH_3), it also could be crosslinked effectively by various methods. We crosslinked PVS by Si–Si dehydrocoupling reaction of the silyl groups with the catalyst developed in our laboratory such as Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Hydride}$ ($\text{M} = \text{Ti, Zr, Hf}$; Hydride = Red-Al, N-Selectride, Super-Hydride) combination, with the Group 6 metal carbonyl $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr, Mo, W}$), and with the Group 8 metallocene Cp_2M ($\text{M} = \text{Co, Ni}$) catalysts to produce polyethylene–polysilane hybrids with extended network structure (Scheme 2).



Scheme 2.

It is assumed as shown in Scheme 2 that the insoluble cross-linked PVS could have an extended network structure composed of partially cross-linked silyl groups and fully cross-linked silyl groups in the polymer chain, judged by IR (decrease of intensity of $\nu_{\text{Si-H}}$) and TGA (increase of TGA ceramic yield) analytical data, by solubility change, and by related literatures [9–12].

The catalysts used here as a crosslinking agent of PVS, functioned effectively as dehydrocoupling catalysts of various hydrosilanes [10]. Dehydrocoupling reaction of hydrosilanes by Group 4 metallocene catalysts was first reported by Aitken et al. in 1985 [11a–c]. The dehydrocoupling reaction was further developed by other researchers [11d–e]. The dehydrocoupling reactivity of hydrosilane is well known to decrease dramatically in the order of primary > secondary >> tertiary. Therefore, it was expected that dehydrocoupling crosslinking reaction of PVS having primary silyl group (SiH_3) with various combination catalysts will take place fast at ambient temperature. The dehydrocoupling reaction rate of PPVS with secondary silyl group should be much slower than that of PVS.

With the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ combination catalysts ($\text{M} = \text{Ti, Zr, Hf}$), the crosslinked polymers by dehydrocoupling of PVS were isolated in 80–90% yields which were insoluble in most organic solvents. The reactivity of dehydrocoupling on PVS decreased in the order of $\text{Ti} > \text{Zr} > \text{Hf}$. The TGA ceramic yield of the crosslinked

PVS was obtained in the 70–72% range. The IR spectra of the crosslinked PVS showed an intense $\nu_{\text{Si-H}}$ band at ca. 2150 cm^{-1} of which intensity was somewhat decreased as compared with the uncrosslinked PVS, indicating the occurrence of dehydrocoupling of silyl group. In the $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ and $\text{Cp}_2\text{MCl}_2/\text{Super-Hydride}$ combination catalysts ($\text{M} = \text{Ti, Zr, Hf}$), the crosslinked polymers were isolated in 80–90% yield. TGA ceramic residue yields of the crosslinked polymers were obtained in the 66–80% range for all catalysts. The reactivity of dehydrocoupling reaction on PVS decreased in the order of $\text{Ti} > \text{Zr} > \text{Hf}$. The effect of hydrides in the same metallocene compound were investigated. The reactivity decreased with order of $\text{Red-Al} > \text{N-Selectride} > \text{Super-Hydride}$ for Cp_2ZrCl_2 . Dehydrocoupling crosslinking of PVS with 3 mol% of the Group 6 metal hexacarbonyl $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr, Mo, W}$) catalysts was carried out at $80\text{ }^\circ\text{C}$ due to lower dehydrocoupling reactivity than the Group 4 metallocene catalysts at room temperature. The crosslinked polymers were isolated in 91–97% yield. TGA ceramic yields of the crosslinked PVS were obtained in the 62–66% range. The IR spectra of the crosslinked PVS showed an intense $\nu_{\text{Si-H}}$ band at ca. 2150 cm^{-1} of which intensity was somewhat decreased as compared with the uncrosslinked PVS, implying the dehydrocoupling of silyl group. For the Group 8 metallocene Cp_2M ($\text{M} = \text{Co, Ni}$), the crosslinked PVSs were isolated in 90–97% yields. TGA ceramic yield of the crosslinked PVS was 64%. The reactivity of dehydrocoupling reaction on PVS decreased in the order of $\text{Ni} > \text{Co}$. Scanning electron microscopy (SEM) analysis of crosslinked PVS with Cp_2Ni showed gathered structure of leaflets (Fig. 2).

No evidence for an ordered structure was found in the SEM analysis of crosslinked PVS. No appreciable crystalline phase was found in XRD analysis. This polymer has very low surface area (BET method, N_2) of $0.24\text{ m}^2\text{ g}^{-1}$ due to low degree of crosslinking. The characterization results of PVS are summarized in Table 1.

As shown in Table 1, TGA ceramic yields of the crosslinked PVS with the Group 4 metallocene were

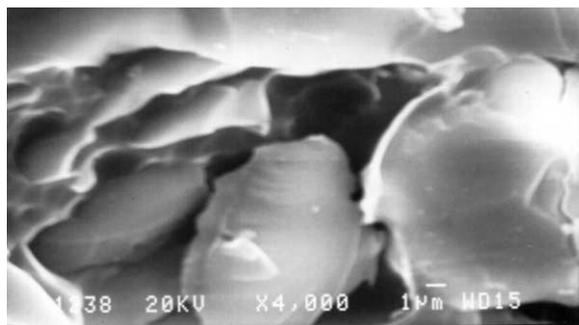


Fig. 2. SEM image of crosslinked PVS (crosslinked with Cp_2Ni) at magnification of 4000.

relatively higher than those with the Group 6 and 8 metal complexes due to higher dehydrocoupling reactivity. Among the Group 4 metallocene combination catalysts, the $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ combination provided highest TGA ceramic yield. Degree of crosslinking is one of the most important factors that affect ceramic yield of preceramic polymers. Therefore, based on TGA ceramic yield, the most effective crosslinking agent is $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ combination catalysts ($\text{M} = \text{Ti, Zr, Hf}$). TGA thermograms of PVS and crosslinked PVS were shown in Fig. 3.

PPVS containing secondary silyl phenyl pendant group could be also crosslinked by various dehydrocoupling catalysts. We examined the crosslinking reaction of PPVS with dehydrocoupling $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M} = \text{Ti, Zr}$) combination catalysts. As expected, dehydrocoupling crosslinking of PPVS with $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ combination catalysts took place very slowly at ambient temperature and upon heating at $80\text{ }^\circ\text{C}$ the reaction mixture became slowly gelatinous. TGA ceramic yields of the crosslinked polymers were obtained in 48% for Ti and 51% for Zr. The relatively low TGA ceramic yield of the crosslinked PPVS is due to low degree of crosslinking and high C/Si ratio ($\text{C/Si} = 8$). The reactivity of dehydrocoupling reaction on PPVS decreased with the order of $\text{Ti} > \text{Zr}$. TGA thermograms of PPVS and crosslinked PPVS were shown in Fig. 4.

In summary, PVSs $[\text{CH}_2\text{CH}(\text{SiH}_2\text{X})]_n$ ($\text{X} = \text{H}$: PVS; $\text{X} = \text{Ph}$: PPVS) were prepared by polymerization of $\text{CH}_2 = \text{CHSi}(\text{OEt})_2\text{X}'$ ($\text{X}' = \text{OEt, Ph}$) in the presence of di-*tert*-butyl peroxide radical initiator followed by reaction of $[\text{CH}_2\text{CHSi}(\text{OEt})_2\text{X}]_n$ ($\text{X}' = \text{OEt, Ph}$) with lithium aluminum hydride in diethyl ether. PVS and PPVS were modified by Si–Si dehydrocoupling crosslinking with the Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{hydride}$ ($\text{M} = \text{Ti, Zr, Hf}$; Hydride = Red-Al, N-Selectride, Super-Hydride), Group 6 metal hexacarbonyl $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr, Mo, W}$), and Group 8 metallocene Cp_2M ($\text{M} = \text{Co, Ni}$) catalysts to give polyethylene–polysilane hybrids with extended network structure. Thermolysis of the crosslinked polymers under nitrogen to $800\text{ }^\circ\text{C}$ showed improved TGA ceramic residue yields. In the dehydrocoupling modification, the Group 4 metallocenes were more effective catalyst than the Group 6 and 8 metal complexes. The most effective dehydrocoupling catalyst was $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ combination.

3. Experimental

All reactions and manipulations were performed under prepurified dry nitrogen atmosphere using Schlenk technique. Solvents such as diethyl ether and toluene were used after distilling from Na/benzophenone. Infrared spectra were obtained using a Nicolet 540 FT-IR spectrometer. $^1\text{H-NMR}$ spectra were acquired

Table 1
Characterization results of dehydrocoupling crosslinking of PVS

Dehydrocoupling catalysts	M	Yield (%) ^a	Gelation time	Ceramic yield (%) at 800 °C ^b
Uncrosslinked PVS	–	–	–	40
<i>Group 4</i> ^c				
Cp ₂ MCl ₂ /Red-Al	Ti	90	1 min	71
	Zr	80	5 min	71
	Hf	83	25 min	72
Cp ₂ MCl ₂ /N-Selectride	Ti	91	4.5 h	79
	Zr	80	5.0 h	80
	Hf	88	5.2 h	78
Cp ₂ MCl ₂ /Super-Hydride	Ti	90	5.5 h	70
	Zr	87	12.5 h	67
	Hf	83	24 h	66
<i>Group 6</i> ^d				
M(CO) ₆	Cr	97	20 h	63
	Mo	94	23 h	65
	W	91	7.5 h	62
<i>Group 8</i> ^c				
Cp ₂ M	Co	97	9 h	64
	Ni	90	45 min	64

^a Insoluble part in common organic solvents.

^b Measured with TGA up to 800 °C.

^c [catalyst]/[PVS] = 0.02.

^d [catalyst]/[PVS] = 0.03.

using a Bruker ASX 32 (300 MHz) spectrometer using CDCl₃/CHCl₃ as a reference at 7.24 ppm downfield from TMS. TGA was performed using a Shimadzu TGA-50 Series Thermal Analysis System with a program rate of 10 °C min⁻¹ in argon atmosphere (flow rate, 20 ml min⁻¹). Ceramic residue yield was obtained as the weight percentage of the char remaining after completion of the heating cycle initiated by 100% of the original sample weight. Average molecular weights of

the polymer were determined by Waters Millipore GPC liquid chromatograph with four Ultrastaygel GPC columns series (sequence 500, 10³, 10⁴, 10⁵ Å columns) calibrated with monodisperse polystyrene standards. Scanning electron microscope (SEM) micrograph of the crosslinked polymers were obtained on a JEOL JXA 840. BET surface area was measured using Quntachrome Autosorb-1 Porosimeter. Cp₂MCl₂ (M = Ti, Zr, Hf), M(CO)₆ (M = Cr, Mo, W), Cp₂M

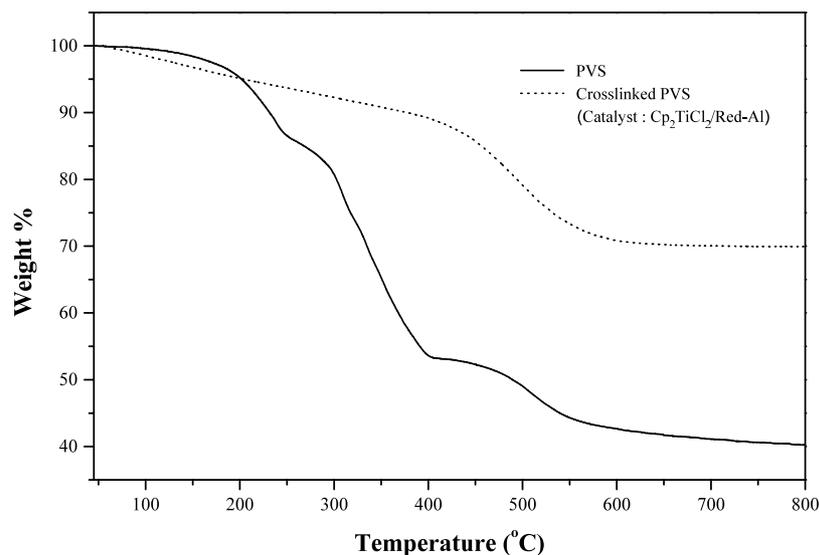


Fig. 3. TGA thermograms of PVS and crosslinked PVS at a heating rate of 20 °C min⁻¹ under an argon flow (20 ml min⁻¹).

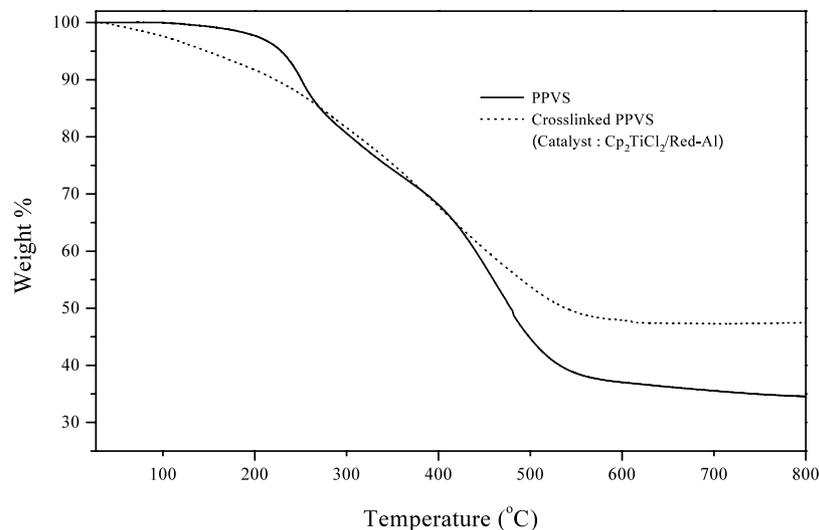


Fig. 4. TGA thermograms of PPVS and crosslinked PPVS at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an argon flow (20 ml min^{-1}).

($M = \text{Co}, \text{Ni}$), Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride; 65 wt.% in toluene), Super-Hydride (lithium triethylborohydride; 1.0 M in THF), N-Selectride (sodium tri-*sec*-butylborohydride; 1.0 M in THF), vinyltriethoxysilane, di-*tert*-butyl peroxide (DTBP), LiAlH_4 and HCl (12 M) were purchased from Aldrich Chemical Co. and were used without further purification. Diethoxyphenylvinylsilane was prepared by reaction of phenylmagnesium bromide and vinyltriethoxysilane in THF. PVS [$^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm): δ 0.6–0.9 (1H, CH), 1.0–1.4 (2H, CH_2), 1.4–1.9 (2H, CH_2), 3.4–3.7 (3H, SiH_3); IR (KBr film, neat, cm^{-1}): 2149 ($\nu_{\text{Si-H}}$); GPC (in THF vs polystyrene standard): $M_w = 1300$ ($M_w/M_n = 2.5$); TGA ceramic residue yield: 40%) was prepared according to the literature procedure [12].

3.1. Preparation of PPVS

A 100-ml Schlenk flask was filled with vinyltriethoxysilane (20 g, 90.0 mmol) and DTBP (0.10 g, 0.5 wt.%) under nitrogen stream. Heating at $150\text{--}155\text{ }^{\circ}\text{C}$ for 1 day resulted in a clear, colorless, viscous liquid which was then kept under reduced pressure while heating to $100\text{ }^{\circ}\text{C}$ for 6 h. A solution of 19.0 g (85.5 mmol equivalent) of the resulting residue in 100 ml diethyl ether was added dropwise to an ice-cooled suspension of 4.87 g (128 mmol) of LiAlH_4 in 250 ml of diethyl ether. The reaction mixture was stirred and allowed to warm to room temperature. After it had been stirred for 2 days, the mixture was refluxed for 3 h. The ether solution was then slowly added to ice-cooled 200 ml 2 M-HCl aqueous solution while stirred. The slurry was extracted with diethyl ether in various portions. The ether phases were combined, rinsed with water, were dried over anhydrous MgSO_4 and subsequently removal of ether in vacuo left PPVS 7.0 g (61%) as a white sticky

solid. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm): δ 0.5–1.0 (1H, CH), 1.0–1.3 (1H, CH), 1.3–1.8 (2H, CH_2), 4.0–4.4 (2H, SiH_2), 6.8–7.8 (5H, Ph); IR (KBr pellet, cm^{-1}): 3068 (w), 2969 (w), 2929 (w), 2131 (s, $\nu_{\text{Si-H}}$), 1590 (w), 1428 (s), 1372 (w), 1184 (w), 1119 (s), 1062 (s), 933 (s), 835 (s) 700 (s); GPC (in THF vs polystyrene standard) $M_w = 1611$ ($M_w/M_n = 1.42$); TGA ceramic residue yield: 35%.

3.2. Crosslinking reactions of PVS catalyzed by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$)

The following procedure is the representative of the crosslinking reactions with the Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$) combination catalysts. To a 100-ml Schlenk flask were added Cp_2TiCl_2 (0.030 g, 0.12 mmol) and Red-Al (0.035 ml, 0.12 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 3 min. PVS solution (0.35 g/0.3 ml in toluene) was then slowly injected to the mixture. The reaction mixture turned into deep green immediately evolving hydrogen gas and was solidified with yellow–brown coloration after 1 min. The catalyst was inactivated 1 day later by exposure to the air for a few min. The reaction product was washed well with diethyl ether in various portions and dried under reduced pressure at $50\text{ }^{\circ}\text{C}$ for 1 day to give 0.314 g (90% yield) of pale yellow solid (TGA ceramic residue yield: 71%).

3.3. Crosslinking reactions of PVS catalyzed by $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$)

The following procedure is the representative of the crosslinking reactions with the Group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{N-Selectride}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$) combination catalysts. PVS (0.35 g, 0.12 mol) in 0.30 ml of toluene was added to a Schlenk flask containing Cp_2TiCl_2

(0.030, 0.12 mmol) and N-Selectride (0.024 ml, 0.24 mmol). The reaction mixture turned into deep green immediately evolving hydrogen gas and was solidified with dark green coloration after 4.5 h. After 1 day the catalyst was inactivated by exposure to the air for a few minutes. The reaction product was rinsed well with diethyl ether in various portions and dried under reduced pressure at 50 °C for 1 day to give 0.317 g (91% yield) of pale yellow solid (TGA ceramic residue yield: 79%).

3.4. Crosslinking reactions of PVS catalyzed by $Cp_2MCl_2/Super-Hydride$ ($M = Ti, Zr, Hf$)

In a typical reaction, to a 100-ml Schlenk flask were added Cp_2TiCl_2 (0.030 g, 0.12 mmol) and Super-Hydride (0.024 ml, 0.24 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 3 min. PVS solution (0.35 g/0.3 ml in toluene) was then slowly injected. The reaction mixture turned into deep green immediately evolving hydrogen gas and was solidified with orange coloration after 5.5 h. The catalyst was inactivated 24 h later by exposure to the air for a few min. The reaction product was washed well with diethyl ether in various portions and dried under reduced pressure at 50 °C for 1 day to afford 0.314 g (90% yield) of pale yellow solid (TGA ceramic residue yield: 70%).

3.5. Crosslinking reactions of PVS catalyzed by $M(CO)_6$ ($M = Cr, Mo, W$)

As a typical reaction, to a 100-ml Schlenk flask was added $Cr(CO)_6$ (0.026 g, 0.18 mmol) under nitrogen atmosphere, and PVS (0.35 g, 6.02 mmol) in 2 ml of dioxane was then charged. The reaction mixture was slowly heated up 80 °C in order to minimize the sublimation of $Cr(CO)_6$ and was solidified with light yellow coloration after 20 h. After 24 h, the resulting mixture was rinsed well with diethyl ether in various portions and dried under reduced pressure at 50 °C for 1 day to provide 0.340 g (97% yield) of light yellow solid (TGA ceramic residue yield: 63%).

3.6. Crosslinking reactions of PVS catalyzed by Cp_2M ($M = Co, Ni$)

The following procedure is the representative of the crosslinking reactions with the Group 8 metallocene Cp_2M ($M = Co, Ni$) catalysts. To a 100-ml Schlenk flask was added Cp_2Ni (0.023 g, 0.12 mmol) under nitrogen atmosphere, and then, PVS solution (0.35 g/0.3 ml in toluene) was slowly injected. The reaction mixture turned into light green immediately evolving hydrogen gas and was solidified with brown coloration after 45 min. The reaction product was washed well with diethyl

ether in various portions and dried under reduced pressure at 50 °C for 1 day to yield 0.314 g (90% yield) of beige solid (TGA ceramic residue yield: 64%).

3.7. Crosslinking reactions of PPVS catalyzed by $Cp_2MCl_2/Red-Al$ ($M = Ti, Zr$)

As a typical reaction, to a 100-ml Schlenk flask were charged Cp_2TiCl_2 (0.013 g, 0.053 mmol) and Red-Al (0.016 ml, 0.053 mmol) under nitrogen atmosphere, and PPVS (0.35 g, 2.65 mmol) in 1 ml of toluene was slowly syringed. The reaction mixture turned into deep brownish green immediately evolving hydrogen gas. After 5 min, the reaction mixture was slowly heated up to 80 °C and was solidified with brownish yellow coloration after 30 h. The resulting mixture was rinsed well with diethyl ether in various portions and dried under reduced pressure at 50 °C for 1 day to give 0.330 g (94% yield) of pale yellow solid (TGA ceramic residue yield: 48%).

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