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Preparations and Properties of Poly(vinylsilane)s

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ABSTRACT: Three kinds of poly(vinylsilane)s, which include oligomers, were prepared by the polymerizations of vinylsilane [$CH_2{=}CHSiH_3$] using a radical initiator catalyst, an anionic catalyst, and a coordinated anionic catalyst (Ziegler−Natta catalyst). A colorless and transparent liquid polymer of molecular weight (M_n) 500−1500, whose structure was $[-CH_2CH(SiH_3)-]_x[-CH_2CH_2SiH_2-]_y$, and a similar liquid polymer of molecular weight (M_n) 500−1500, whose structure was $[-CH(CH_3)SiH_2-]$, were obtained in high yields in the radical and the anionic polymerization, respectively. A white solid polymer, which was slightly soluble in solvent and had the structure $[-CH_2CH(SiH_3)-]$, was obtained in the coordinated anionic polymerization. The reaction mechanisms were proposed on the basis of the reactivity of the silyl group of vinylsilane. The polymers are stable under air and have the reactive Si−H bonds. Silicon carbide was obtained by heating the polymers at high temperature under inert gas.

Introduction

A large number of the polymerization reactions of the vinyl compounds have been studied, and the industrial processes for producing the polymers have been developed. Moreover, there are many reports on the polymerization reactions of silicon-containing vinyl compounds, such as vinyltrialkylsilanes ($CH_2{=}CHSiR_3$) and vinyltrialkoxysilanes [$CH_2{=}CHSi(OR)_3$], in which mainly vinyl polymerization reactions occur.[1−10]

The Si−H bond is very reactive against the C═C, C≡C, C═O, N−H, O−H, O═O, and C−Cl bonds under thermal conditions or under radiation or under catalysts, and some polymers containing the Si−H bond in their molecules have been developed as reactive silicone and ceramic precursors. There are some reports on polymers containing the silylene group ($={SiH_2}$). The polymers having the repeating unit of $-C_6H_4SiH_2-$,[11,12] $-CH_2SiH_2-$, $-CH_2CH_2SiH_2-$,[13,14] $-C{\equiv}CC_6H_4C{\equiv}CSiH_2-$,[15] and $-CH_2CH(SiMeH_2)$[4] have been synthesized.

We selected vinylsilane ($CH_2{=}CHSiH_3$) as a monomer to synthesize a more reactive polymer containing the silyl group ($-SiH_3$) in the molecule. As the monomer is not produced commercially, there are few reports on polymers containing the silyl group. The coordination anionic polymerization reaction of allylsilane ($CH_2{=}CHCH_2SiH_3$) and the copolymerization reactions of vinylsilane and allylsilane with α-olefin were reported.[16−19] The reactivity of the silyl group is different from that of the trialkylsilyl group or trialkoxysilyl group; therefore, we thought that a unique reaction would occur.

We report the polymerization reactions of vinylsilane using a radical initiator catalyst, an anionic catalyst, and a coordinated anionic catalyst and discuss the reaction mechanisms.

Experimental Section

Vinylsilane (molecular weight 58.16, bp −22.8 °C, purity above 99%) was prepared by the reduction of vinyltrichlorosilane with $LiAlH_4$ in n-Bu_2O.[20] The polymerizations were carried out in a 50 or 500 mL autoclave. The catalyst and the solvent were introduced into the autoclave under a nitrogen atmosphere, and vinylsilane was introduced under pressure. The reaction system was then raised to the reaction temperature and reacted. Elemental analysis and infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were employed to determine the structures of the polymers. IR spectra were measured using a JASCO FT/IR-8900. NMR spectra were recorded using a JEOL GS-400, EX-400, and α-400 spectrometers. A nondecoupling sequence was used for ^{1}H NMR, a gated decoupling sequence was used for ^{13}C NMR, and a nondecoupling sequence and inverse-gated decoupling sequence were used for ^{29}Si NMR. Molecular weights were obtained by gel permeation chromatography (GPC) using THF as a solvent with retention times calibrated against polystyrene samples. Thermogravimetric analysis and differential thermal analysis measurement (TG-DTA) under argon and air were used to study the thermal properties of the polymers.

Radical Polymerization. Twelve kinds of radical initiators, such as 2,2-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), and di-*tert*-butyl peroxide (DTBP), were used as radical initiators. The reaction was carried out in neat conditions or in toluene for 8 h. After the reaction, unreacted vinylsilane was removed; then the reaction mixture was removed from the autoclave into air. Copolymerizations were carried out by introducing another vinyl monomer with vinylsilane, as shown in Table 1.

Anionic Polymerization. n-BuLi, $LiAlH_4$, and i-BuOLi were used as catalysts, and the reaction was carried out without solvent. After the reaction, unreacted vinylsilane was removed; then the reaction mixture was removed from the autoclave into air.

Coordination Anionic Polymerization. Titanium halide catalyst (Toho Chemical Industry Co., Ltd., S21, Ti content 24 wt %) or supported catalyst of titanium compound on anhydrous $MgCl_2$ was employed as catalyst with i-Bu_3Al, and n-heptane was used as the solvent. The supported catalyst was prepared as follows: Twenty grams of anhydrous $MgCl_2$ was ground with 2 mL of p-toluic methyl ester and 2 mL of $(EtO)_4Si$ in a 600 mL ball mill for 20 h. Then 10 g of the grounded mixture, 50 mL of $TiCl_4$, and 100 mL of n-heptane were reacted for 2 h at 80 °C in a 200 mL glass flask; the solid catalyst was then washed by n-heptane. The titanium content of the supported catalyst was 2 wt %.

The reactions were carried out at 70 °C for 6 h. After the reaction, the unreacted vinylsilane was removed; the reaction

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Table 1. Polymerization and Copolymerization of Vinylsilane in the Presence of Radical Initiator

no.	radical initiator, amt (mmol)	vinylsilane amt (mmol)	comonomer, amt (mmol)	reacn temp (°C)	polymer yield[a] (%)	mol wt[b] M_w	M_n	M_w/M_n	content of vinylsilane[c] (%)
1	AIBN, 2.47	130		80	89	2940	1030	2.9	
2	AIBN, 0.65	128		70	75	2620	950	2.8	
3[d]	AIBN, 2.47	130		80	80	2850	1100	2.6	
4	AIBN, 14.89	2810		70	93	2600	980	2.7	
5	BPO, 2.76	138		80	95	1440	510	2.0	
6	DTBP, 0.27	122		130	95	2630	1230	2.1	
7	AIBN, 0.13	60	MA,[f] 68	70	90	127600	12700	10.0	27
8	AIBN, 0.13	65	AN,[g] 67	70	43[e]				22
9	AIBN, 0.10	56	VC,[h] 44	70	49				44
10	AIBN, 0.13	66	MMA,[i] 64	70	74[e]	33200	16200	2.0	12

[a] The yield of the polymer based on the charged monomers. [b] Polystylene equivalent. [c] The content of the vinylsilane unit calculated by the elemental analysis of C, H, and Si. [d] 30 mL of toluene was used as a solvent. [e] Solid polymer. [f] Methyl acrylate. [g] Acrylonitrile. [h] Vinyl chloride. [i] Methyl methacrylate.

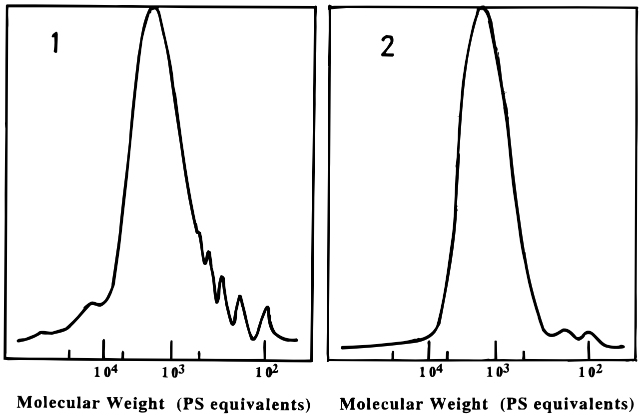


Figure 1. GPC spectra of polymers **1** and **2** obtained using the radical initiator (AIBN) and the anionic catalyst ($LiAlH_4$), respectively.

mixture was poured into methanol, and the precipitate was recovered. Copolymerization was carried out by introducing vinylsilane and propylene.

Product Characterization. Polymer **1** (radical polymerization): ^1H NMR ($CDCl_3/CDCl_3$, 7.24 ppm) δ 0.5−1.0 (1.9H, $\mathrm{SiC}\mathit{H}$, $\mathrm{SiC}\mathit{H_2}$), 1.0−1.8 (1.8H, $\mathrm{C}\mathit{H_2}\mathrm{CSi}$), 3.2−3.6 (1.6H, $\mathrm{Si}\mathit{H_3}$), 3.6−4.1 (1.0H, $\mathrm{Si}\mathit{H_2}$); ^{13}C NMR ($CDCl_3/CDCl_3$, 77 ppm) δ −8 to +16 ($\mathrm{Si}\mathit{C}\mathrm{H}$, $\mathrm{Si}\mathit{C}\mathrm{H_2}$), 16−40 ($\mathit{C}\mathrm{H_2CSi}$); ^{29}Si NMR ($CDCl_3$/TMS) δ −60 to −45 ($\mathit{Si}\mathrm{H_3}$), −40 to −15 ($\mathit{Si}\mathrm{H_2}$); IR (neat) $\delta(SiH_n)$ 920 cm^{-1}, $\delta(CH)$ 1330 cm^{-1} $\delta(CH_2)$ 1450 cm^{-1}, $\nu(SiH_3, SiH_2)$ 2150 cm^{-1}, $\nu(CH)$ 2850 cm^{-1}, $\nu(CH_2)$ 2900 cm^{-1}. Elemental analysis: C 42.38, H 10.19, Si 47.43 (calculated from the values of C and H); cf. calculated values C 41.31, H 10.40, Si 48.29. Polymer **2** (anionic polymerization): ^1H NMR ($CDCl_3/CDCl_3$, 7.24 ppm) δ 0.3−0.6 (1H, $\mathrm{SiC}\mathit{H}\mathrm{Si}$), 1.1−1.3 (3H, $\mathrm{C}\mathit{H_3}$), 3.7−3.9 (2H, $\mathrm{Si}\mathit{H_2}$); ^{13}C NMR ($CDCl_3/CDCl_3$, 77 ppm) δ −6 to −4 ($\mathrm{Si}\mathit{C}\mathrm{HSi}$), 12−13 ($\mathit{C}\mathrm{H_3}$); ^{29}Si NMR ($CDCl_3$/TMS) δ −20 to −15 ($\mathit{Si}\mathrm{H_2}$); IR (neat) $\delta(SiH_n)$ 930 cm^{-1}, $\delta(CH)$1380 cm^{-1}, $\delta(CH_3)$ 1460 cm^{-1}, $\nu(SiH_n)$ 2110 cm^{-1}, $\nu(CH)$ 2850 cm^{-1}, $\nu(CH_3)$ 2930 cm^{-1}. Elemental analysis: C 42.11, H 10.50, Si 47.36). Polymer **3** (coordinated anionic polymerization): ^1H NMR (1,2,4-trichlorobenzene (abbreviated TCB)/TCB, 7.43 ppm) δ 1.5−1.6 (1H, $\mathrm{C}\mathit{H}$), 1.7−1.9 (2H, $\mathrm{C}\mathit{H_2}$), 3.7−3.8 (3H, $\mathrm{Si}\mathit{H_3}$); ^{13}C NMR (TCB/TCB, 128 ppm) δ 17−19 ($\mathit{C}\mathrm{H}$), 35−37 ($\mathit{C}\mathrm{H_2}$); ^{29}Si NMR (TCB/TMS) δ −51 to −53 ($\mathit{Si}\mathrm{H_3}$); IR (neat) $\delta(SiH_n)$ 910 cm^{-1}, $\delta(CH)$ 1330 cm^{-1}, $\delta(CH_2)$ 1440 cm^{-1}, $\nu(SiH_n)$ 2130 cm^{-1}, $\nu(CH)$ 2830 cm^{-1}, $\nu(CH_2)$ 2880 cm^{-1}. Elemental analysis: C 41.46, H 10.76, Si 47.78).

NMR data were compared and agreed with those of refs 13 and 14.

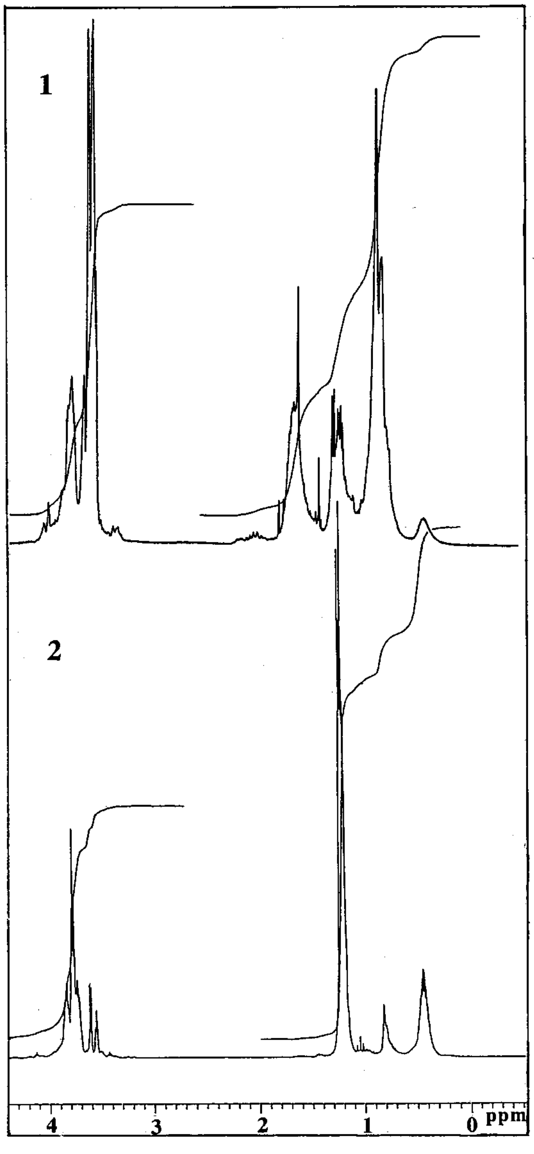


Figure 2. ^1H NMR spectra of polymers **1** and **2** obtained using the radical initiator (AIBN) and the anionic catalyst ($LiAlH_4$), respectively.

Results and Discussion

Radical Polymerization. The reaction results are shown in Table 1. Colorless and transparent liquid oligomer and polymer (abbreviated polymer **1**) of molecular weight (M_n) 500−1500 were obtained in high yield. The GPC spectrum of the polymer **1** obtained using AIBN is shown in Figure 1. ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra are shown in Figures 2−5. The results of NMR spectra, IR, and elemental analysis indicate that polymer **1** has the silyl group (SiH_3) and the silylene group (SiH_2) in the molecule.[13,14] Two

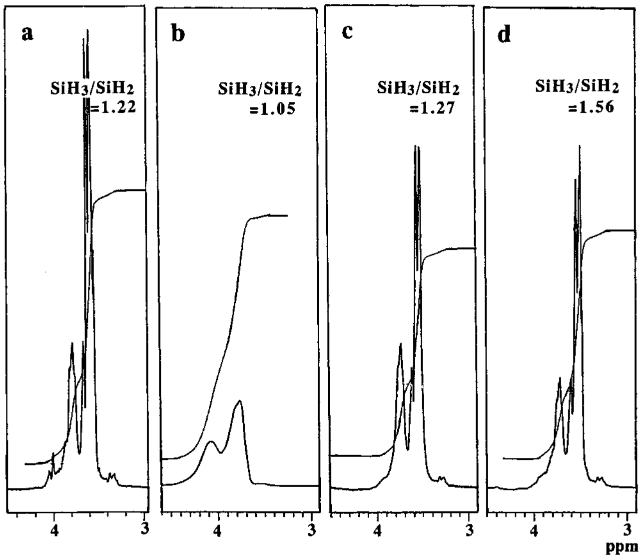
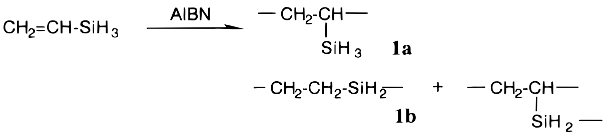


Figure 3. ^{1}H NMR spectra of three fractional portions divided from polymer **1**: (a) polymer **1** (M_w 2600, M_n 980); (b) fraction **1** (M_w 14800, M_n 5190); (c) fraction **2** (M_w 3720, M_n 2150); (d) fraction **3** (M_w 1220, M_n 800). As fraction **1** was insoluble in $CDCl_3$, the spectrum of fraction **1** was measured using C_6D_6 as a solvent and standard.

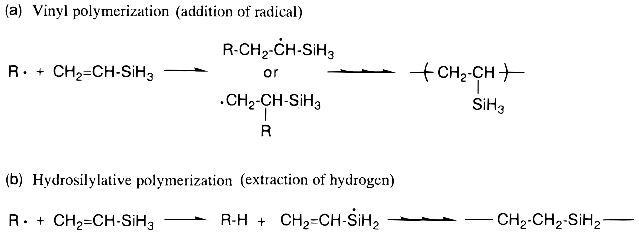
reactions, that is, vinyl polymerization (polymer **1a**) and hydrosilylation polymerization (polymer **1b**, **1c**) occurred.



$$CH_2{=}CH\text{-}SiH_3 \xrightarrow{AIBN} \text{—}CH_2\text{-}\underset{SiH_3}{CH}\text{—}\ \mathbf{1a} \qquad \text{—}CH_2\text{-}CH_2\text{-}SiH_2\text{—}\ \mathbf{1b} + \text{—}CH_2\text{-}\underset{SiH_2\text{—}}{CH}\text{—}\ \mathbf{1c} \tag{1}$$

Figure 3 shows ^{1}H NMR spectra of three fractional portions divided from polymer **1**. The ratio of SiH_3 to SiH_2 decreased with increasing molecular weight, which would be caused partly by the decrease of the end group (SiH_3). Though there is not experimental evidence, the structures of **1a**, **1b**, and **1c** would all be present in the same polymer molecule. The structure of **1c** would be produced by the additional hydrosilylation reaction between the SiH_3 and the C=C bond. The facts that any byproducts such as hydrogen and ethynylsilane were observed in the reaction, and that the result of the elemental analysis is almost the same as the calculated value support this presumption. The polymerization reactions were carried out at various temperatures using 12 kinds of radical initiators, as shown in Figure 8. The ratios of SiH_3/SiH_2 of polymer **1**, which were calculated from ^{1}H NMR spectral data, were increased with decreasing reaction temperature.

Scheme 1. Reaction Mechanism of the Radical Polymerization of Vinylsilane



The polymerization of vinyltrimethylsilane ($CH_2{=}CHSiMe_3$) gave the only vinyl polymerization product [$-CH_2CH_2(SiMe_3)-$]. The hydrosilylations using the radical initiators between hydrosilanes and olefins are well-known reactions.[21] In the case of vinylsilane, the intermolecular hydrosilylation reaction would also proceed, which would be caused by the high reactivity of the Si—H bond with the radical initiator; the abstraction of the hydrogen from the silyl group by the radical initiator (see Scheme 1). The hydrosilylative polymerization reactions of the vinyldialkylsilanes ($CH_2{=}CHSiR_2H$) using the platinum compounds as catalysts were reported to give the polycarbosilanes [$-CH_2CH_2$-SiR_2-, $-CH(CH_3)SiR_2-$].[22,23] Boury et al. obtained the polymer [$(-CH_2CH_2SiH_2-)_x(-CH(CH_3)SiH_2-)_y$] by the hydrosilylative polymerization of vinyldichlorosilane ($CH_2{=}CHSiHCl_2$), followed by reducing it with $LiAlH_4$.[13,14]

Polymer **1** was soluble in benzene, THF, chloroform, pentane, and ethyl acetate, but insoluble in methanol and acetonitrile. Polymer **1** was stable and could be kept for a long time under air. From the results of the TG-DTA measurements under air, there was no weight loss until 80 °C and a large exothermic peak was observed around 180 °C. An oxidation reaction of the silyl and silylene groups should have occurred to form the siloxane bond (Si—O—Si). The results of TG-DTA measurements under inactive gas are shown in Figure 9.

The results of the copolymerizations between vinylsilane and another vinyl monomer are shown in Table

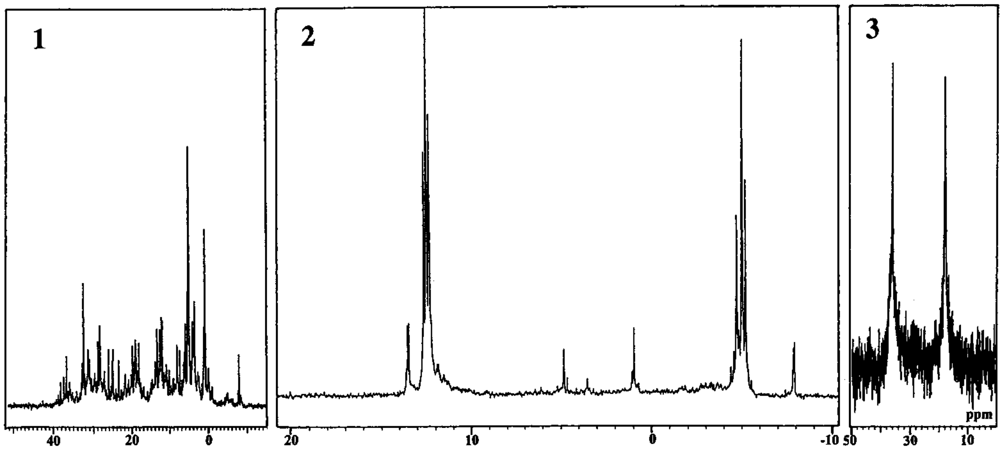


Figure 4. ^{13}C NMR spectra of polymers **1**−**3** obtained using the radical initiator (AIBN), the anionic catalyst ($LiAlH_4$), and the coordinated anionic catalyst (supported catalyst), respectively.

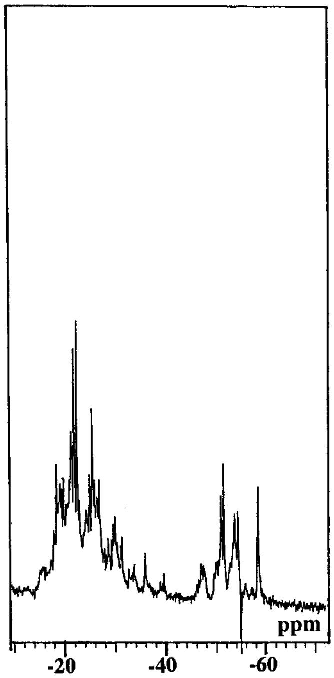
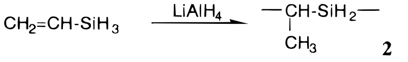


Figure 5. ^{29}Si NMR spectra of polymer **1** obtained using the radical initiator (AIBN).

1 (expt nos. 7−10). The elemental analysis, IR, and NMR spectra indicated that the SiH_3, SiH_2, and SiH groups were included in the polymers; therefore the copolymerizations would proceed. Further studies are needed to clarify the copolymerizations.

Anionic Polymerization. The results are shown in Table 2. Colorless and transparent liquid oligomer and polymer (abbreviated polymer **2**) of molecular weight (M_n) 500−1500 were obtained in high yield. The GPC spectrum of polymer **2** is shown in Figure 1. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra are shown in Figures 2, 4, and 6, respectively. From the chemical shifts[13,14] and the spin−spin couplings of the ^{29}Si NMR spectrum (nondecoupling sequence) in Figure 6a, two signals at −20 to −15 ppm and −60 to −45 ppm would be assigned to SiH_2 and SiH_3 (end group of the molecule). The results of elemental analysis and all of the spectral data indicate that polymer **2** has the following structure:



$$\mathrm{CH_2{=}CH\text{-}SiH_3} \xrightarrow{\mathrm{LiAlH_4}} \text{—}\underset{\mathrm{CH_3}}{\mathrm{CH}}\text{-}\mathrm{SiH_2}\text{—} \quad \mathbf{2} \qquad (2)$$

The properties are similar to those of polymer **1**. In TG-DTA curves in Figure 9, the initiation temperature of thermal degradation of polymer **2** is higher than that of polymer **1**. The results suggest that the polymer chain of the Si−C unit would be more thermally stable than that of the Si−C−C unit.

Oku et al. reported that the polymerization of vinyltrimethylsilane ($CH_2{=}CHSiMe_3$) in the presence of *s*-BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine gave the only vinyl polymerization product [$-CH_2CH_2(SiMe_3)-$] accompanied by the transfer reaction.[24−26] In the case of vinylsilane, the polymerization would proceed by the mechanism shown in Scheme 2. The addition reaction of an anion to the silyl group yields a pentacoordinated silicon anion, and a hydrogen transfer reaction would have occurred. The pentacoordinated silicon anions are well-known[27−30] and have been thought as the suitable intermediates for some reactions.[31,32] The mechanism is supported by the following facts: The steric hindrance around the silicon is small, and the silicon would be easily attacked by the anion. Moreover, the bond energy of the Si−H bond is small; therefore, an intramolecular translation of hydrogen would easily occur to give the α-anion (α to silicon), which is considered as the stable anion by the effect of $p-\sigma^*$ conjugation.[33] In the case of vinyltrimethylsilane, the C=C bond would be more easily attacked by the anion than the silicon because of the large steric hindrance around the silicon. Even if the silicon is attacked by the anion, the resulting anion would not be able to attack the other monomer and the catalyst anion would be released; the reversible reaction would occur ($Si + R^- \rightleftharpoons [Si-R]^-$).

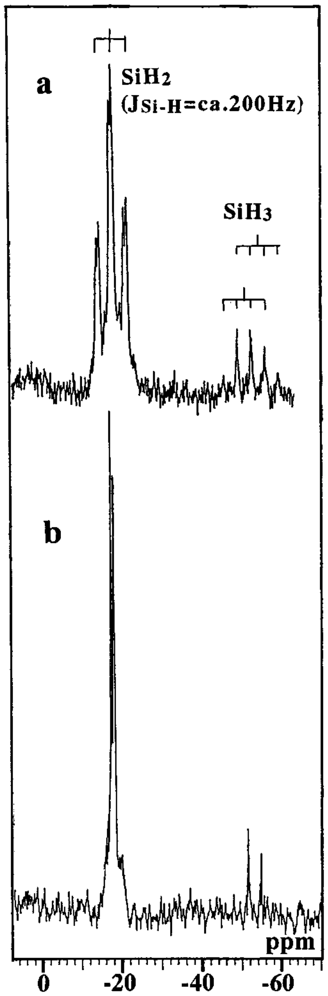


Figure 6. ^{29}Si NMR spectra of polymer **2** obtained using the anionic catalyst ($LiAlH_4$): (a) nondecoupling sequence; (b) inverse-gated decoupling sequence

Coordination Anionic Polymerization. The results are shown in Table 3. A white solid polymer (abbreviated polymer **3**) and a small amount of liquid olygomer (M_n 200−2000) were obtained. The supported catalyst gave a higher polymer yield than the titanium halide catalyst (expt nos. 1 and 2 in Table 3). However, the polymer amount of poly(vinylsilane) per unit catalyst weight (44 g/g of cat., 2200 g/g of Ti) is lower than that of polypropylene (usually above 2000 g/g of cat.). The reactivity and polymer yield of the copolymerization of vinylsilane with propyrene was also low (see expt no.

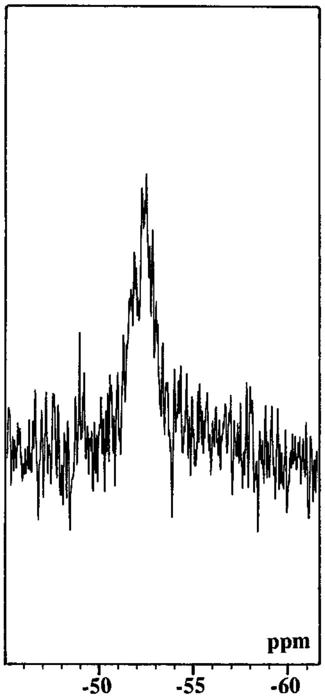


Figure 7. ^{29}Si NMR spectra of polymer **3** obtained using the coordinated anionic catalyst (supported catalyst).

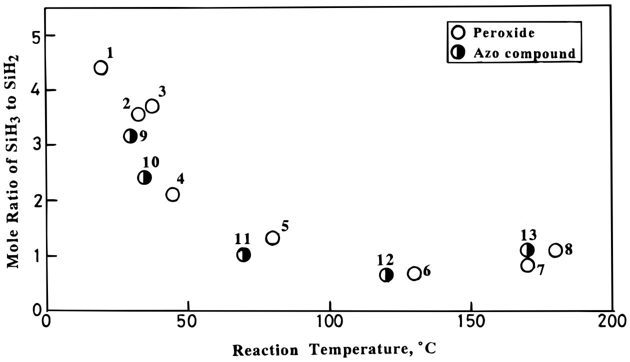


Figure 8. Mole ratios of SiH_3 to SiH_2 in polymer **1** versus the reaction temperatures. 100−300 mmol of vinylsilane and 0.5−1.5 mmol (5 mol % vs vinylsilane) of the radical initiators were reacted for 8 h (**2**−**8**, **10**−**13**) or 20 h (**1**, **9**). The radical initiators were acetyl cyclohexylsulfonyl peroxide (**1**, **2**), isobutyryl peroxide (**3**), bis-4-*tert*-butylcyclohexyl peroxydicarbonate (**4**), BPO (**5**), DTBP (**6**), cumene hydroperoxide (**7**), *tert*-butyl hydroperoxide (**8**), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (**9**, **10**), AIBN (**11**), 2,2′-azobis(2,4,4-trimethylpentane)-(azodi-*tert*-octane) (**12**), and 2,2′-azobis(2-methylpropane)-(azodi-*tert*-butane) (**13**).

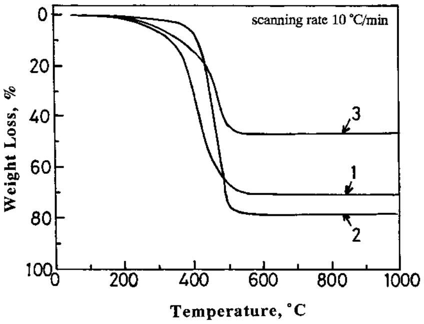


Figure 9. TGA curves of the poly(vinylsilane)s under argon.

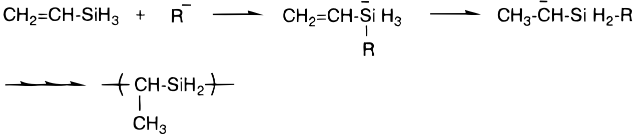
3 in Table 3 and ref 19). The active sites of the catalyst (Ti component) would be poisoned by vinylsilane to form the Ti−Si bond, and the catalytic activity was decreased.

Table 2. Polymerization of Vinylsilane in the Presence of Anionic Catalyst

no.	catalyst, amt (mmol)	vinylsilane amt (mmol)	reacn temp (°C)	reacn time (h)	polymer yield[a] (%)	mol wt[b] M_w	mol wt[b] M_n	mol wt[b] M_w/M_n
1	*n*-BuLi, 6.78	133	30	18	93	4310	1130	3.8
2	$LiAlH_4$, 1.17	117	120	20	87	2700	1490	1.8
3	*i*-BuOLi, 9.89	194	120	20	86	2900	500	5.8

[a] The yields of the polymer were calculated on the basis of the charged monomers. [b] Polystyrene equivalent.

Scheme 2. Reaction Mechanism of the Anionic Polymerization of Vinylsilane



$$CH_2{=}CH\text{-}SiH_3 + R^- \longrightarrow CH_2{=}CH\text{-}\underset{R}{\overset{-}{Si}}H_3 \longrightarrow CH_3\text{-}\overset{-}{C}H\text{-}SiH_2\text{-}R \longrightarrow \left(\underset{CH_3}{CH}\text{-}SiH_2\right)$$

Table 3. Polymerization of Vinylsilane in the Presence of Ziegler−Natta Catalyst

no.	catalyst, amt (mg)	*i*-Bu_3Al amt (mmol)	vinylsilane amt (mmol)	heptane vol (mL)	polymer[a] amt (g)	polymer[a] yield (%)	polymer per unit g/g of cat	polymer per unit g/g of Ti
1	$TiCl_3$, 1780	23.8	1160	250	12.1	18	7	29
2	$TiCl_3$, 774 (supported on $MgCl_2$)	10.8	1470	240	33.9	40	44	2200
3	$TiCl_3$, 494	5.0	126[b]	21	0.4	5[c]	1	4

[a] Solid polymer. [b] 32 mmol of propylene was also used as a comonomer. [c] The content of the vinylsilane unit calculated by the elemental analysis of C, H, and Si was 20 wt %.

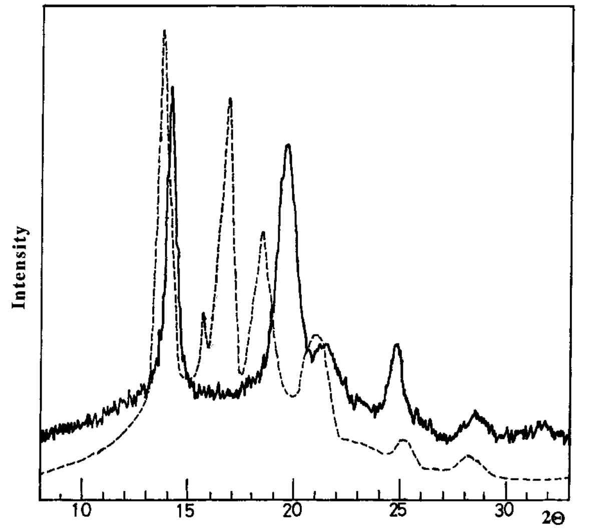
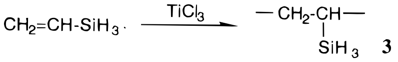


Figure 10. X-ray diffraction patterns of (—) polymer **3** and (- - -) polypropylene.

Polymer **3** is insoluble in benzene, THF, and NMP but soluble in TCB and hot tetralene. The results of elementary analysis and all of the spectral data (see Figures 4 and 7) indicate that the vinyl polymerization has occurred.



$$CH_2{=}CH\text{-}SiH_3 \xrightarrow{TiCl_3} -CH_2\text{-}\underset{SiH_3}{CH}- \quad \mathbf{3} \tag{3}$$

X-ray diffraction patterns of polymer **3** are shown in Figure 10. The crystallinity of polymer **3** was about 60%. The diffraction pattern of polymer **3** is analogous to that of polypropylene, except for the values of 2θ of

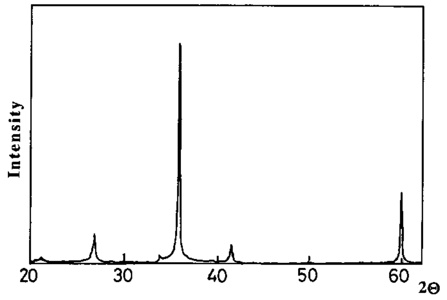


Figure 11. X-ray diffraction pattern of polymer **2** heated at 2000 °C under argon.

Table 4. Ceramics Yields of Poly(vinylsilane)s

	ceramics yields	
polymer	wt %	mol %[b]
polymer **1** (radical)	32	46
polymer **2** (anionic)	25	36
polymer **3** (coordinated anionic)	47 (68)[c]	68 (98)[c]

[a] Polymers were treated at temperatures of 20−1400 °C (5 °C/min) under argon. [b] Calculated on the basis of the Si atom. [c] Increasing temperature was 5 °C/h.

the peaks. The values of 2θ of polymer **3** are greater than those of polypropylene. The silyl group is larger than the methyl group, so the spacing of the crystal of polymer **3** would be larger than that of polypropylene. An endothermic peak assigned to a melting point was observed around 175 °C in the DSC (differential thermal analysis) curve (cf. melting point of polypropylene: 162 °C). From the TG-DTA measurements under air, a large exothermic peak was observed around 145 °C under air, which would be caused by an oxidation reaction of the silyl group to form the siloxane bond. There was no weight loss until 270 °C under argon (Figure 9).

Much effort has been made to introduce the polar functional groups into the nonpolar polyolefins such as polypropylene and polyethylene, and many catalysts and the comonomers have been studied, because the Ziegler−Natta catalyst does not show a catalytic activity against the polymerization of a vinyl compound having a polar group in a molecule.[34] All catalysts and monomers were insufficient.[35,36] The polarity of vinylsilane is low; therefore, vinylsilane might react in the presence of the Ziegler−Natta catalyst. We could make many functional polyolefins using the high reactivity of the silyl groups introduced into the polyolefins.[19]

Preparation of Silicon Carbide from Poly(vinylsilane)s. Silicon carbide (β-SiC) was obtained when the previous three poly(vinylsilane)s were heated at elevated temperature under an unreactive gas such as argon (see Figure 11 and Table 4). The ceramic yield would depend on intermolecular cross-linking reactions, which would be induced by the radicals produced by the thermal cleavage of the favorable Si−H bond. A more highly cross-linked structure would give a higher ceramic yield. Therefore, a pyrolytic conversion of the poly(vinylsilane)s under more proper conditions might give higher ceramic yields than the values in Table 4. As the poly(vinylsilane)s have more reactive silyl or silylene groups, the cross-linking reaction in the poly(vinylsilane) would proceed more easily. Very strong silicon carbide fibers have been synthesized from the blended precursor of polymer **1** with the polycarbosilane, which is prepared by the thermal cracking of permethylpolysilane and has the $Si(CH_3)HCH_2$ unit in the molecule,[37] by melt-spinning, thermal oxidation cross-linking, and heating above 1000 °C.[38]

Summary

Three kinds of poly(vinylsilane)s, which include oligomers and were different from each other in their structures, were prepared by the polymerization of vinylsilane [$CH_2{=}CHSiH_3$] using a radical initiator catalyst, an anionic catalyst, and a coordinated anionic catalyst (Ziegler−Natta catalyst). A colorless and transparent liquid polymer of molecular weight (M_n) 500−1500, whose structure was $[-CH_2CH(SiH_3)-]_x[-CH_2\text{-}CH_2SiH_2-]_y$, and a similar liquid polymer of molecular weight (M_n) 500−1500, whose structure was $[-CH(CH_3)SiH_2-]$, were obtained in high yields in the radical and the anionic polymerizations, respectively. A white solid polymer, which was slightly soluble in solvent and whose structure was $[-CH_2CH(SiH_3)-]$, was obtained in the coordinated anionic polymerization. The reaction mechanisms were proposed on the basis of the reactivity of the silyl group of vinylsilane. The polymers are stable under air. Silicon carbide was obtained by heating the polymers at high temperature under inert gas.

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