



Preparation and Properties of Organic-Inorganic Hybrid Gel Films Based on Polyvinylpolysilsesquioxane Synthesized from Trimethoxy(vinyl)silane

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Abstract. Polyvinylpolysilsesquioxane (PVPS) organic-inorganic hybrid gel films containing polyethylene and siloxane backbone linkages were prepared through the radical polymerization of trimethoxy(vinyl)silane (VTS) followed by the acid-catalyzed hydrolytic polycondensation of trimethoxysilyl groups. The PVPS gel films were transparent and homogeneous. It was found that the mechanical properties of these films correlate both to the degrees of polymerization and to the extent of cross linking.

Keywords: trimethoxy(vinyl)silane, hydrolytic polycondensation, polyvinylpolysilsesquioxane, organic-inorganic hybrids, gel films, tensile strength, organic-inorganic hybrid

1. Introduction

Organic-inorganic polymer hybrids, which are characterized by the formation of covalent bonds that connect organic and inorganic components, have received considerable attention as next-generation materials having both rigidity and flexibility, based on their inorganic and organic networks, respectively [1–6]. These hybrids are prepared by the tandem or simultaneous polymerization of organic and inorganic components, resulting in the complete miscibility of organic and inorganic components at the nanometre level.

We previously reported the relationship between the structure and the mechanical properties of homogeneous and flexible free-standing films of poly-methacryloxypropylpolysilsesquioxane prepared by the radical polymerization of 3-methacryloxypropyl(trimethoxy)silane and subsequent polycondensation [7, 8]. In addition, we reported the preparation of free-standing films and coating films by the hydrolytic polycondensation of poly(trimethoxy(vinyl)silane) (PVTS) [9–12]. Our primary objective in the present study

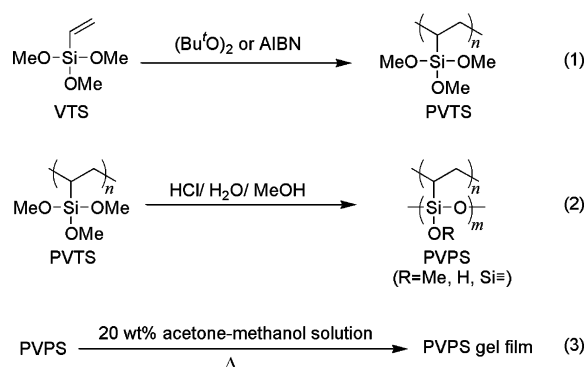
was to clarify the relationship between the chemical structure and the properties of polymer hybrids by evaluating the mechanical properties of the hybrids, which are prepared by the stepwise polymerization of vinyl groups and trimethoxysilyl groups of trimethoxy(vinyl)silane (VTS) as a starting material, according to Scheme 1. Free-standing films of polyvinylpolysilsesquioxane (PVPS) were prepared by the hydrolytic polycondensation of PVTS, which was synthesized by the radical polymerization of VTS.

2. Experimental

2.1. Reagents

VTS was purchased from Dow Corning Toray Silicone Co., Ltd. Methanol, tetrahydrofuran (THF), and triethylamine were obtained from Wako Pure Chemical Industries, Ltd. Di-*t*-butyl peroxide (DTBP) was purchased from NOF Corporation. 1,1'-Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chemical Co., Ltd. VTS, methanol, THF, and triethylamine were distilled before use. The other materials were used as received.

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Scheme 1.

2.2. Preparation of PVPS Organic-Inorganic Hybrids Based on PVTS

2.2.1. Radical Polymerization of VTS. VTS (24.7 g, 0.167 mol) and DTBP or AIBN were placed in a four-necked flask equipped with a condenser and a stirrer, and then were heated to 150°C for 2 h at a rotation rate of 200 rpm under a nitrogen atmosphere. The ratio of VTS and DTBP was varied, as shown in Table 1. The reaction mixture was cooled with an ice bath, and then 30 mL of methanol was added as a polymerization terminator. The mixture was then stirred for 1 h in a cool methanol bath (ca. -30°C) to stop the polymerization. The reaction mixture was evaporated to remove the solvent, affording PVTS as a viscous and colorless liquid.

2.2.2. Acid-Catalyzed Hydrolytic Polycondensation of PVTS. PVTS (12.35 g, 0.084 mol) and methanol (7 mL) were placed in a four-necked flask equipped

with a stirrer, a nitrogen inlet tube, and a nitrogen outlet tube. The mixture was cooled in an ice bath for 10 min, followed by the addition of water and 6 mol/L hydrochloric acid. The respective amounts of catalyst and water were controlled as shown in Table 2. The mixture was stirred at 0°C for 10 min and then at room temperature for 10 min, followed by stirring at 70°C for 3 h at a rotation rate of 150 rpm under a nitrogen stream flowing at a rate of 360 mL/min. Solvents were removed under reduced pressure to give highly viscous liquid PVPS.

2.2.3. Preparation of PVPS Free-Standing Gel Films.

A 20 wt% acetone-methanol (v/v = 1) solution of PVPS prepared in 2.2.2 was cast on a polymethylpentene (PMP) shale and heated at 80°C for 5–30 days to give PVPS free-standing gel films.

2.3. Instruments and Analysis

²⁹Si NMR spectra of samples dissolved in CDCl₃ (note that all samples were fully soluble in chloroform) were measured on a Jeol JNM-EX400 instrument. Tetramethylsilane (TMS) was used as an internal standard.

Fourier-transformed infrared (FTIR) spectra were taken on a Jeol FT/IR 410 by the KBr disk or the CCl₄ solution method.

Gel permeation chromatography (GPC) was performed by using a high-performance liquid chromatography system (Shimadzu Co. Ltd.) with a Polymer Science Mixed D column.

The tensile strength of the gel films was measured by using an Orientec Tensilon/UTM-II-20 system for a test sample 2 mm wide × 40 mm long.

Table 1. Results on the radical polymerization of VTS^a.

No.	Solvent ^b	Temp. (°C)	Molar ratio of DTBP/VTS	Yield (%)	GPC ^c		DP ^d
					$M_w (\times 10^3)$	M_w/M_n	
1	None	150	0.2	97	11.3	2.7	76
2	None	150	0.05	97	7.4	1.9	50
3	Toluene (5)	110	0.2	61	3.2	1.8	22
4	Toluene (5)	110	0.5	70	1.8	1.7	13
5	Benzene (10)	80	0.4 ^e	58	0.6	1.3	4

^a Scale of operation; VTS 24.7 g (0.167 mol). Time: 2 h.

^b Volume of solvent (mL) is represented in the parentheses.

^c M_w and M_n were calculated based on polystyrene.

^d Degree of polymerization estimated from M_w .

^e AIBN was used instead of DTBP.

Table 2. Preparation of PVPS by hydrolytic polycondensation of PVTS^a.

No.	No. of PVTS	DP (from Table 1)	Molar ratios		GPC ^b		Ratio of siloxane unit ^c				DC ^d (%)
			H ₂ O/Si	HCl/Si	M _w (×10 ³)	M _w /M _n	T ⁰	T ¹	T ²	T ³	
6	1	76	0.13	0.0002	155	28.3	79	21	0	0	7
7	2	50	0.15	0.0002	50	10.5	72	28	0	0	9
8	2	50	0.19	0.0002	170	32.7	65	30	5	0	13
9	2	50	0.20 ^e	0.0002	–	–	–	–	–	–	–
10	3	22	0.27	0.0002	40	8.2	58	30	12	0	18
11	4	13	0.27	0.0002	44	16.5	47	38	15	0	23
12	5	4	0.80	0.040	12	10.0	50	17	19	14	33
13	5	4	0.80	0.050	38	21.0	27	9	28	36	58
14	5	4	1.00	0.053	50	24.2	25	7	24	44	65
15	5	4	1.00 ^e	0.056	–	–	–	–	–	–	–

^a Scale of operation; PVTS 12.35 g (0.0835 mol as Si). Solvent: Methanol 7 mL. Temp.: 70°C, Time: 3 h. Stirring rate: 150 rpm. N₂ flow rate: 360 mL/min.

^b M_w and M_n were calculated based on polystyrene.

^c Calculated based on the peak area of ²⁹Si NMR spectrum. Tⁿ: Si(OSi)_n(OR)_{4-n} (n = 0–3).

^d Degree of condensation of siloxane bonding.

^e Gelation.

3. Results and Discussion

3.1. Radical Polymerization of VTS

PVTS with organic backbones of various lengths were synthesized by radical polymerization of VTS. Table 1 shows the results of the radical polymerization of VTS using DTBP or AIBN as an initiator. In cases No. 1 and 2, bulk polymerization of VTS gave rise to a decrease in molecular weight and DP with a decrease in the molar ratio (DTBP/VTS). In cases No. 3 and 4, the yield of PVTS increased in 5 mL of toluene with an increase in the molar ratio (DTBP/VTS), whereas the molecular weight and DP decreased. In case No. 5, the molecular weight and DP decreased when the polymerization was carried out in benzene in the presence of AIBN at 80°C, since the polymerization was performed under mild condition by decreasing the reactivity of the initiator, temperature and concentration. The variation in molecular weight was due to the low polymerizability of VTS: the small Q value in Q-e scheme for VTS ($Q = 0.05$) [13] indicates that VTS is not highly reactive under conditions involving radical polymerization.

The FT-IR spectra of all PVTS samples showed the disappearance of the absorption bands at 3040 cm⁻¹ (ν_{CH}), 1600 cm⁻¹ (ν_{CH}), and 1410 cm⁻¹ ($\delta_{\text{C}=\text{C}}$) due to the vinyl group [12], suggesting that radical polymerization of the vinyl group had proceeded.

The ²⁹Si NMR spectrum of VTS showed a single peak at -55.6 ppm, whereas the ²⁹Si NMR spectrum of PVTS showed double signals in the ranges of -42.0 to -39.6 ppm and -44.5 to -43.0 ppm, due to -CH₂Si(OMe)₃-. These two double signals may have been the result of head-to-head and head-to-tail-type polymerization sequencing, which would indicate that there had been some difficulty in controlling the main chain sequence.

3.2. Acid-Catalyzed Hydrolytic Polycondensation of PVTS

The hydrolytic polycondensation of PVTS was confirmed by the both FT-IR and ²⁹Si NMR spectral changes. A new absorption band due to $\nu_{\text{Si-O-Si}}$ at 1012 cm⁻¹ appeared in the FT-IR spectrum, indicating that siloxane bonds were formed by the acid-catalyzed hydrolytic polycondensation of PVTS. The ²⁹Si NMR spectrum of PVPS showed new double signals at -50.5 to -45.5 ppm and -59.5 to -51.5 ppm, due to the formation of T¹ and T² structures, respectively, as shown in Fig. 1. These results indicate that PVPS is formed by the acid-catalyzed hydrolytic polycondensation of PVTS. (The symbol Tⁿ denotes the unit structures of siloxane RSi(OSi)_n(OR')_{3-n} (n = 0–3).)

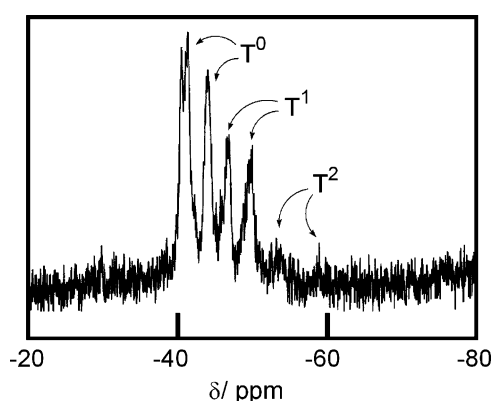


Figure 1. ^{29}Si NMR spectrum of PVPS.

The results of the acid-catalyzed hydrolytic polycondensation of PVTS are listed in Table 2. The $T^n(\%)$ s of PVTS and PVPS were calculated based on the equation $T^n/(T^0 + T^1 + T^2 + T^3) \times 100$, where T^n denotes the peak areas of the unit structure T^n ($n = 0-3$). The degrees of cross-linking (DC) of PVPS and its free-standing films were calculated from the equation $(T^1 + 2T^2 + 3T^3)/3 \times 100$. The DC of PVPS No. 6 was as low as 7%, although it exhibited a high M_w . The DC of PVPS increased with decreasing DP and increasing molar ratios of $\text{H}_2\text{O}/\text{Si}$ and HCl/Si . When the molar ratio $\text{H}_2\text{O}/\text{Si}$ was increased from 0.15 to 0.20, PVPS sols were obtained in Nos. 7 and 8, while an insoluble PVPS product (white solid) was formed in No. 9. The same tendency was observed in Nos. 12–15. It can be seen that the M_w of PVPS was about 50000 in cases 7, 10, 11, and 14; this effect was the result of decreasing molar ratios of $\text{H}_2\text{O}/\text{Si}$ and HCl/Si with an increasing DP. The increasing DP implies the inhibi-

tion of acid-catalyzed hydrolytic polycondensation of methoxy groups due to the presence of a long organic backbone.

3.3. Preparation of PVPS Organic-Inorganic Hybrid Gel Films Based on PVTS and the Mechanical Properties of PVPS Gel Films

PVPS was prepared according to the conditions listed in Table 2 (Nos. 7, 10–14), and this method of preparation gave rise to flexible, homogeneous, and transparent free-standing films of approximately 0.1 mm thickness. In the FT-IR spectrum of the PVPS gel film, the peak intensity due to $\nu_{\text{Si-O-Si}}$ at 1012 cm^{-1} increased when compared to the gel film precursor, PVPS. In the ^{29}Si NMR spectrum of the PVPS gel film, new double signals at -68.0 – -65.5 ppm and -65.0 – -62.0 ppm appeared, which were due to the T^3 structure. On aging of the gel films, the peak intensities due to structures T^1 and T^2 increased, while the peak intensity of the T^0 structure decreased, which indicated that siloxane networks had been formed.

The mechanical properties of the PVPS gel films are shown in Table 3. The tensile strength of PVPS gel films was 3.00–6.71 MPa. The elongation of the PVPS gel films prior to rupture was ca. 20 % in cases 16–18, whereas it was 6.0–1.7% in cases 19–21. The Young's modulus was 21.0–231.9 MPa.

Since PVPS gel films were considered as materials of polyethylene and silica gel, the mechanical properties of PVPS gel films can be represented by the nature of these components. The tensile strength was independent of the DP and M_w of PVPS, because the gel films are composed of inorganic and organic components

Table 3. Mechanical properties of PVPS gel films.

		PVPS precursor polymer				PVPS gel film		
		GPC ^a		DP (%)	DC (%)	Tensile strength/MPa	Elongation (%)	Young's modulus/MPa
No.	No.	$M_w (\times 10^3)$	M_w/M_n					
16	7	50	10.5	50	9	3.00	20.0	21.0
17	10	40	8.2	22	18	4.90	21.9	81.4
18	11	44	16.5	13	23	5.80	19.3	121.4
19	12	12	10.0	4	33	5.56	6.0	63.4
20	13	38	21.0	4	58	6.71	2.9	231.9
21	14	50	24.2	4	65	4.96	1.7	184.6

^a M_w and M_n were calculated based on polystyrene.

such as siloxane and polyethylene. The elongation decreased in Nos. 19–21, which was due to the progress of siloxane network formation because of the low DP, i.e., the hydrolytic polycondensation of the methoxy group is favored to form a denser siloxane network, in cases when the polyethylene chain is short. The Young's modulus increased when the DP decreased or when the DC increased. Since the long polyethylene chain acts as a bulky organic group in the hydrolytic polycondensation process, the mechanical properties of gel films of high DP are mainly governed by the polyethylene chain, resulting in high elongation and low tensile strength. In contrast, rigid and tough gel films are obtained when the DP is low.

4. Conclusions

Polyvinyl(trimethoxy)silanes (PVTS) with various degrees of polymerization (DPs) were obtained by the radical polymerization of trimethoxy(vinyl)silane (VTS) using various molar concentrations of di-*t*-butyl peroxide or 1,1'-azobisisobutyronitrile as an initiator. The acid-catalyzed hydrolytic polycondensation of these PVTSs gave rise to polyvinylpolysilsesquioxanes (PVPS) with various DPs and degrees of condensation (DC). PVPSs provided transparent, homogeneous, and flexible hybrid gel films. The tensile strength and Young's modulus of the gel films increased with an increase in DC, whereas elongation decreased under these conditions. On the other hand, the tensile strength and Young's modulus of the gel films de-

creased with an increase in DP, whereas elongation increased.

References

1. J.E. Mark, C.Y.-C. Lee, and P.A. Bianconi (Eds.), *Hybrid Organic-Inorganic Composites* (American Chemical Society, Washington, 1995).
2. B. K. Coltrain, C. Sanchez, D.W. Schaefer, and L. Garth (Eds.), *Better Ceramics Through Chemistry VII: Organic Inorganic Hybrid Materials* (Wilkes, Materials Research Society, Warrendale, PA, 1996).
3. R.M. Laine, C. Sanchez, E. Giannelis, and C.J. Brinker (Eds.), *Organic/Inorganic Hybrid Materials* (Materials Research Society, Warrendale, PA, 1998).
4. L.C. Klein, L. Francis, M.R. DeGuire, and J.E. Mark (Eds.), *Organic/Inorganic Hybrid Materials II* (Materials Research Society, Warrendale, PA, 1999).
5. R.M. Laine, C. Sanchez, E. Giannelis, and C.J. Brinker (Eds.), *Organic/Inorganic Hybrid Materials '2000* (Materials Research Society Symposia Proceedings, Material Research Society, Warrendale, PA, 2001), Vol. 628.
6. R.M. Laine, C. Sanchez, S. Yang, and C.J. Brinker (Eds.), *Organic/Inorganic Hybrid Materials* (Materials Research Society, Warrendale, PA, 2002).
7. Y. Abe, Y. Honda, and T. Gunji, *Appl. Organometal. Chem.* **12**, 749 (1998).
8. T. Gunji, Y. Makabe, N. Takamura, and Y. Abe, *Appl. Organometal. Chem.* **15**, 683 (2001).
9. N. Takamura, T. Gunji, H. Hatano, and Y. Abe, *J. Polym. Sci.: Part A: Polym. Chem.* **37**, 1017 (1999).
10. N. Takamura, K. Taguchi, T. Gunji, and Y. Abe, *J. Sol-Gel Sci. & Tech.* **16**, 227 (1999).
11. Y. Abe, K. Kagayama, N. Takamura, T. Gunji, T. Yoshihara, and N. Takahashi, *J. Non-Crystal. Solids* **261**, 39 (2000).
12. N. Takamura, H. Okonogi, T. Gunji, and Y. Abe, *Kobunshi Ronbunshu* **57**, 198 (2000).
13. L. J. Young, *J. Polym. Sci.* **54**, 411 (1961).