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Preparation and properties of organic–inorganic hybrid gel films based on polyvinylpolysilsesquioxane synthesized from trimethoxy(vinyl)silane

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Polyvinylpolysilsesquioxane (PVPS) organic–inorganic hybrid gel films comprising polyethylene and siloxane backbone linkages were prepared through two routes: trimethoxy(vinyl)silane (VTS) was first subjected to radical polymerization of the vinyl groups, followed by acid-catalyzed hydrolytic polycondensation of the trimethoxysilyl groups (route A) to afford PVPS; in the second route PVPS was prepared in reverse order (route B). PVPS gel films were transparent and homogeneous. We find that the mechanical and heat-resisting properties correlate both to the degree of polymerization and the degree of cross-linking. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: polyvinylpolysilsesquioxane; gel films; mechanical properties; heat-resisting properties

INTRODUCTION

Organic–inorganic hybrids have received considerable attention as next-generation materials having both rigidity (based on inorganic networks) and flexibility (based on organic networks). In particular, a large number of reports have appeared on polysiloxane hybrids[1,2] prepared as follows: (1) introduction of carbon sources such as sucrose, pitch, carbon black, or phenol resin into a silica matrix by the sol–gel process;[3–6] (2) simultaneous or tandem polymerization of organic monomers in a polysiloxane matrix;[7–16] (3) utilization of π–π interactions between an organic polymer containing phenyl groups and phenylsilsesquioxane;[17–19] (4) trifunctional silanes substituted with polymerizable carbofunctional groups used to form siloxane and carbon–carbon bonding.[20–27] The hybrids prepared by method (1) are physical mixtures of micrometer-sized organic and inorganic components. Hybrid materials prepared by methods (2) and (3) achieve interpenetrating networks at a nanometer scale by physical interactions. In contrast, molecular hybrids with organic–inorganic covalent bonds prepared by the method (4) show complete miscibility of organic and inorganic components at the ångström level.

We reported the relationship between the structure and the mechanical properties of homogeneous and flexible free-standing films of polymethacryloxypropylpolysilsesquioxane prepared by radical polymerization of 3-methacryloxypropyl-(trimethoxy)silane and subsequent polycondensation.[23] In addition, hydrolytic co-polycondensation of tetraethoxysilane with poly(triethoxy(vinyl)silane) forms crack-free coating films.[24] In spite of that, a molecule containing both organic and inorganic functional groups was used as a starting material, these polymer hybrids requiring stepwise polymerization. There are no other polymerization processes reported for preparing these polymer hybrids.

Our primary objective in this paper is to clarify the relationship between chemical structure and properties of polymer hybrids by evaluating the mechanical and heat-resisting properties of the hybrids, which are prepared by stepwise polymerization of vinyl groups and trimethoxysilyl groups of trimethoxy(vinyl)silane (VTS) as a starting material according to Scheme 1. The chemical structure of the free-standing films was controlled by two routes, i.e. A and B. In route A, free-standing films of polyvinylpolysilsesquioxane (PVPS) were prepared by hydrolytic polycondensation of poly(trimethoxy(vinyl)silane) (PVTS), which was synthesized by radical polymerization of VTS. On the other hand,

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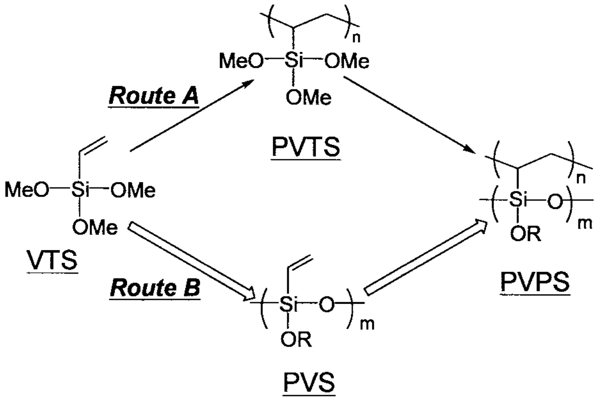

Scheme 1. Preparation of PVPS hybrid gel films.

free-standing films of PVPS were prepared by photoinduced radical polymerization of vinylpolysilsesquioxane (PVS), which was synthesized by hydrolytic polycondensation of VTS in route B.

EXPERIMENTAL

Materials

VTS (b.p. 122.0–123.0 °C) 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 Corp. Bis(2,4,6-trimethylbenzoyl)phenylphosphineoxide (BTPS) was purchased from Ciba Specialty Chemicals K.K. VTS, methanol, THF, triethylamine, and BTPS were distilled before use.[28] DTBP was distilled under reduced pressure before use.[28] The other materials were used as received.

Preparation of PVPS organic–inorganic hybrids based on PVTS (route A)

Radical polymerization of VTS

VTS (37.05 g, 0.25 mol) and DTBP were placed in a four-necked flask equipped with a condenser and a stirrer, and then heated to 150 °C for 2 h at a rotation rate of 200 rpm under a nitrogen atmosphere. The ratio of VTS to DTBP was varied as shown in Table 1. The reaction mixture was cooled in an ice bath and then 30 ml of methanol as a polymerization terminator was added and stirred for 1 h in a cooled methanol bath (*ca* −30 °C) to stop the polymerization. The reaction mixture was evaporated to remove the solvent to afford PVTS as a viscous colorless liquid.

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, and then cooled in an ice bath for 10 min, followed by the addition of water and 6 mol l^{-1} hydrochloric acid. The amounts of the 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 at a flow rate of 360 ml min^{-1}. Solvents were removed under reduced pressure to give a highly viscous liquid of PVPS.

Table 1. Results for radical polymerization of VTS[a]

No.	Molar ratio DTBP/VTS	Toluene volume (ml)	Yield (%)	GPC[b] $10^{-3}\,M_w$	GPC[b] $10^{-3}\,M_n$	DP[c]
1	0.05	5	41	3.7	1.8	25
2	0.2	5	61	3.2	1.8	22
3	0.4	5	70	2.4	1.7	16
4	0.5	5	70	1.8	1.7	13
5	0.005	0	35	4.1	1.6	28
6	0.02	0	64	4.8	1.7	32
7	0.05	0	97	7.4	1.9	50
8	0.1	0	97	8.0	2.0	54
9	0.2	0	97	11.3	2.7	76
10	0.3	0	97	8.8	2.3	59
11	0.5	0	97	5.8	2.6	39

[a] Scale of operation; VTS 24.7 g (0.167 mol). Temp.: 150 °C; time: 2 h.
[b] Based on polystyrene.
[c] DP estimated from M_W.

Preparation of PVPS free-standing gel films

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

Preparation of PVPS coating films

A 20 wt% acetone–methanol (v/v = 1) solution of PVPS, as prepared above, was filtered with a membrane filter (0.5 μm per diameter) before use. Into the solution, various substrates, such as polypropylene, high-density polyethylene, aluminum, SUS304, glass, and silicon wafer, were dipped and drawn up at a rate of 80 mm min^{-1} and heated at 80 °C for 24 h, followed by heating at 100 °C for a certain period to give PVPS coating films.

Preparation of PVPS organic–inorganic hybrids based on PVS (route B)

Acid-catalyzed hydrolytic polycondensation of VTS

VTS (24.70 g, 0.167 mol) and methanol (14 ml) were placed in a four-necked flask equipped with a stirrer, a nitrogen inlet tube and a nitrogen outlet tube, and then cooled in an ice bath for 10 min, followed by the addition of water and 6 mol l^{-1} hydrochloric acid. The amounts are shown in Table 3. 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 at a flow

Table 2. Preparation of PVPS by hydrolytic polycondensation of PVTS[a]

No.	Precursor no.	Molar ratio H_2O/Si	GPC[b] $10^{-4} M_w$	M_w/M_n	Ratio of siloxane unit[c] T^0	T^1	T^2	DC[d] (%)	State
12	4	0.29	14.0	24.0	46	39	16	23	Viscous liquid
13	4	0.30[e]	—	—	—	—	—	—	White powder
14	2	0.29	13.2	26.7	56	31	13	19	Viscous liquid
15	2	0.30[e]	—	—	—	—	—	—	White powder
16	7	0.13	1.7	5.2	76	24	0	8	Viscous liquid
17	7	0.15	5.0	10.5	72	28	0	9	Viscous liquid
18	7	0.17	8.6	17.3	69	31	0	10	Viscous liquid
19	7	0.19	17.0	32.7	65	30	5	13	Viscous liquid
20	7	0.20[e]	—	—	—	—	—	—	White powder
21	9	0.13	15.5	28.3	79	21	0	7	Viscous liquid
22	9	0.15[e]	—	—	—	—	—	—	White powder

[a] Scale of operation; PVTS 12.35 g (0.0835 mol as Si). HCl/Si = 0.0002. Solvent: methanol 7 ml. Temp.: 70 °C; time: 3 h. Stirring rate: 150 rpm. N_2 flow rate: 360 ml min^{-1}.
[b] Based on polystyrene.
[c] Calculated based on the peak area of ^{29}Si NMR spectrum. T^n: $Si(OSi)_n(OR)_{4-n}$ ($n = 0$–3).
[d] DC of siloxane bonding.
[e] Gelation.

Table 3. Preparation of PVS by hydrolytic polycondensation of VTS[a]

No.	Molar ratio H_2O/Si	GPC[b] $10^{-3} M_w$	M_w/M_n	Siloxane unit amount[c] T^1	T^2	T^3	DC[d] (%)
30	1.1	1.1	1.4	11	48	41	77
31	1.3	2.1	2.1	3	39	58	85
32	1.45	6.4	2.7	0	28	72	90

[a] Scale of operation; 0.0167 mol as Si. HCl/Si = 0.105. Solvent: methanol 14 ml. Temp.: 70 °C; time: 3 h. Stirring rate: 150 rpm. N_2 flow rate: 360 ml min^{-1}.
[b] Based on polystyrene.
[c] Calculated based on the peak area of ^{29}Si NMR spectrum. T^n: $Si(OSi)_n(OR)_{4-n}$ ($n = 1$–3).
[d] DC of siloxane bonding.

rate of 360 ml min^{-1}. Solvents were removed under reduced pressure to afford a highly viscous liquid of PVS.

Preparation of PVPS free-standing films from PVS by UV irradiation

A 50 wt% acetone solution of PVS containing triethylamine and BTPS as a photoinitiator was cast onto a PMP Petri dish, followed by heating at 80 °C for 10 min to give a film. The film was irradiated with a 400 W high-pressure mercury arc to give free-standing films.

Instruments and analysis

^{29}Si NMR spectra in $CDCl_3$ were measured on a JEOL JNM-EX400 instrument. Tetramethylsilane (TMS) was used as an internal standard.

^{29}Si cross-polarization/magic-angle spinning (CP/MAS) NMR spectra were measured using a JEOL JNM-EX400 instrument. Polydimethylsilane was used as an external standard (−34.5 ppm from TMS).

A ^{1}H hyper decoupled cross-polarization/magic-angle spinning (HPDEC CP/MAS) NMR spectrum was recorded

Table 4. Mechanical properties of PVPS gel films produced via route B[a]

No.	Precursor no.	Irradiation time (min)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	Density (g cm^{-3})
33	30	15	6.1	1.9	380	1.26
34	30	30	8.0	1.6	560	1.28
35	30	60	9.1	1.2	910	1.29
36	30	120	—[b]	—[b]	—[b]	—[b]
37	31	30	10.8	1.1	1030	1.30
38	32	30	12.0	0.9	1320	1.31

[a] Thickness: 0.10 mm. Length × width: 20 mm × 2 mm. Initiator: BTPS. Molar ratio: BTPS/Si = 0.002. Temp.: 25 °C. Atmosphere: nitrogen.
[b] Unable to measure because of crack formation during gelation.

by using a Bruker Avance Wide-bore 300 Solid-state NMR spectrometer.

Fourier-transformed infrared (FTIR) spectra were taken on a JEOL FT/IR 410 by the KBr disk or the CCl_4 solution method.

Gel permeation chromatography (GPC) was performed using a high-performance liquid chromatograph (Nihon Seimitsu Kagaku Co., Ltd.): column (TOSOH G5000HXL/G3000HXL); solvent: THF; detector: RI-3H (Nihon Bunseki Kogyo Co., Ltd.). Monodispersed polystyrenes were used as standards.

The tensile strengths of the gel films were measured using an Orientec Tensilon/UTM-II-20 system on test samples that were 2 mm wide × 40 mm long.

Thermogravimetric differential thermal analysis (TG-DTA) was performed using a TG-DTA2000S equipped with an MTC1000S of Bruker AXS Co., Ltd, under an air atmosphere at a heating rate of 10 °C min^{-1}.

The density of free-standing films was measured according to the Archimedes method at 25 °C with a pycnometer using a 0.005 wt% sodium oleate aqueous solution as the supporting solution.

RESULTS AND DISCUSSION

Synthesis of PVPS organic–inorganic hybrids based on PVTS (route A)

Radical polymerization of VTS

We first synthesized PVTS having various lengths of organic main chains by radical polymerization of VTS using route A.

Table 1 shows the results of radical polymerization of VTS using DTBP as an initiator. The yield of PVTS increases in 5 ml of toluene with increases in the molar ratio of DTBP/VTS, whereas molecular weights and degrees of polymerization (DPs) decrease (Nos 1–4). Bulk polymerization of VTS gives rise to an increase in molecular weight and DP of PVTS with an increase in the molar ratio of DTBP/VTS in the cases of Nos 5–9, whereas decreases in molecular weight and DP were observed in the cases of Nos 10 and 11. The conditions for No. 9 led to a maximum DP. For Nos 7–11, the yield of PVTS shows that polymerization proceeds quantitatively. The variation of molecular weight is due to the low polymerizability of VTS: the small Q value for VTS ($Q = 0.05$)[25] indicates that VTS has a low reactivity in the radical polymerization. In Nos 1, 2, 5–9, large amounts of radical initiators are necessary to start polymerization. When the molar ratio of PTBT/VTS is fully increased, the molecular weight of PVTS is decreased, as seen in the general radical polymerization.

The FTIR spectra of VTS and PVTS are given in Fig 1a and b. The absorption bands at 3040 cm^{-1} (ν_{CH}), 1600 cm^{-1} (ν_{CH}), and 1410 cm^{-1} ($\delta_{C=C}$) due to the vinyl group disappear in Fig. 1b, suggesting that the radical polymerization of the vinyl group proceeded.

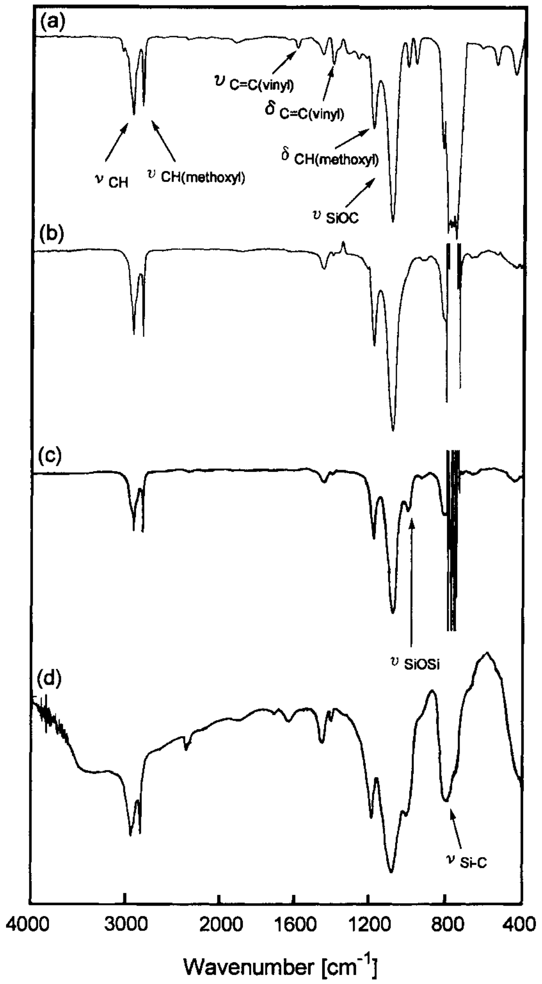

Figure 1. FTIR spectra of VTS (a), PVTS (b), PVPS (c), and PVPS gel film (d) produced via route A.

^{29}Si NMR spectra of VTS and PVTS are shown in Fig. 2. The ^{29}Si NMR spectrum of VTS shows a single peak at −55.6 ppm, whereas the ^{29}Si NMR spectrum of PVTS shows double signals in the ranges of −42.0 to −39.6 ppm and −44.5 to −43.0 ppm due to $-CH[Si(OMe)_3]-$. These two double signals may be due to the sequence of head-to-head and head-to-tail type polymerization, which shows the difficulty in controlling the main chain sequence.

Acid-catalyzed hydrolytic polycondensation of PVTS

Figure 1c shows the FTIR spectrum of PVPS (No. 9). A new absorption band due to $\nu_{Si-O-Si}$ at 1012 cm^{-1} appeared in the spectrum, indicating that siloxane bonds are formed by acid-catalyzed hydrolytic polycondensation of PVTS. The ^{29}Si NMR spectrum of PVPS is given in Fig. 2c. The symbols T^n denote the unit structures of siloxane $RSi(OSi)_n(OR')_{3-n}$ ($n = 0$–3). The ^{29}Si NMR spectrum of PVPS shows new double signals at −50.5 to −48.0 ppm and −47.5 to −45.5 ppm due to the structures T^1 and T^2 respectively, which are due to the two microstructures in PVTS. These results indicate that PVPS

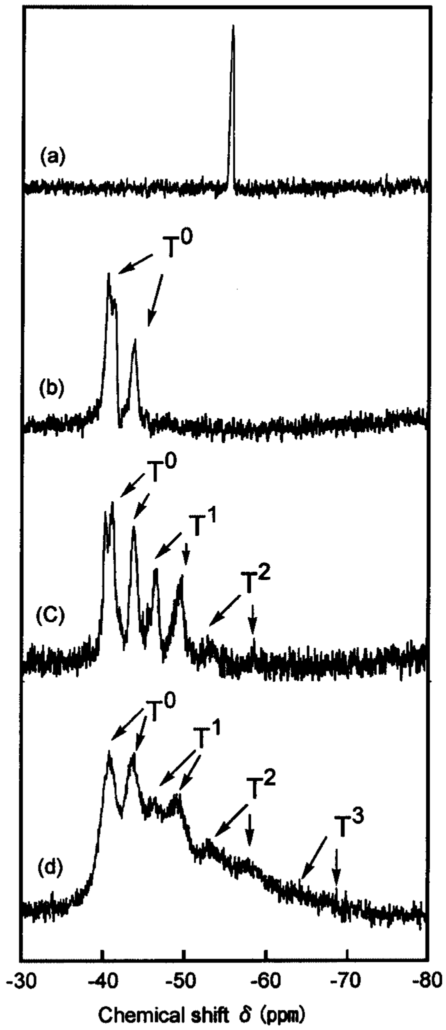

Figure 2. The ^{29}Si NMR spectra of VTS (a), PVTS (b), and PVPS (c) and ^{29}Si CP/MAS NMR spectrum of PVPS gel film (d) produced via route A.

is formed by acid-catalyzed hydrolytic polycondensation of PVTS.

The results for acid-catalyzed hydrolytic polycondensation of PVTS are listed in Table 2. The T^n(%) values of PVTS and PVPS were calculated based on the equation $[T^n/(T^0 + T^1 + T^2 + T^3)] \times 100$ ($n = 0$–3), where T^n denotes the peak areas of unit structure T^n. The degree of cross-linking (DC) for PVPS and its free-standing films was calculated from the equation $(T^1(\%) + 2T^2(\%) + 3T^3(\%))/3 \times 100$. Acid-catalyzed hydrolytic polycondensation of PVTS, synthesized according to the conditions in Table 1 (No. 7), afforded PVPS with various molecular weights and DCs in the presence of H_2O for molar ratios of H_2O/Si ranging from 0.13 to 0.19 and gave insoluble PVPS as white solids for a molar ratio of H_2O/Si of 0.20. The molar ratio of H_2O/Si that resulted in gelation of PVTS decreased with an increase in DP of PVTS (Nos 12–15 and Nos 19–22), which implies inhibition of acid-catalyzed hydrolytic polycondensation of methoxy groups due to the long organic backbone. The DCs of PVPS (Nos 12, 14, 19, 21) decreased with increasing DP.

Preparation of PVPS organic–inorganic hybrid gel films based on PVTS synthesized according to route A and their mechanical properties

PVPS prepared according to the conditions listed in Table 2 (Nos 16–19 and 21) gave rise to flexible, homogeneous, and transparent free-standing films of 0.05–0.08 mm thickness. The FTIR spectrum of PVPS gel film No. 19 is shown in Fig. 1d. The peak intensity of the gel film due to $\nu_{\text{Si-O-Si}}$ at 1012 cm^{-1} increased when compared with the gel film precursor, PVPS. As shown in Fig. 2d, the ^{29}Si NMR spectrum of the PVPS gel film shows new double signals at −68.0 to −65.5 ppm and −65.0 to −62.0 ppm due to the T^3 structure. Furthermore, structures T^1 and T^2 increased while the T^0 structure decreased. These results indicate that siloxane networks are formed.

Table 5 shows the mechanical properties, the microstructure and the DC of PVPS gel films. Tensile strength and Young's modulus increase and the elongation decreases with an increase in DC of the precursor polymers and in the heating time for Nos 27–29. This is because increases in DC and heating time lead to increases in siloxane bonding, resulting in rigid films. A T^3 structure was observed for No. 24, in which DC increased up to 37% and both the tensile strength and Young's modulus showed maximum values and the elongation displayed a minimum value. The increase in DP of PVTS from 50 to 76 resulted in a decrease in tensile strength and Young's modulus and an increase in elongation (Nos 25 and 26). This is due to the decrease of DC as a result of the long organic backbone, leading to the inhibition of acid-catalyzed hydrolytic polycondensation of methoxy groups.

These results indicate that the hybrid gel films prepared via route A are composed of polyethylene main chains having cross-linked siloxane side chains with only a 20–30% DC at maximum.

Synthesis of PVPS organic–inorganic hybrids (route B)

Acid-catalyzed hydrolytic polycondensation of VTS

To control the DC of PVS, acid-catalyzed polycondensation of VTS was performed in the presence of H_2O in a molar ratios of H_2O/VTS ranging from 1.10 to 1.45. FTIR spectra of VTS and PVS are given in Fig. 3a and b respectively. The peak intensity of the absorption band due to $\delta_{\text{CH(methoxy)}}$ at 1190 cm^{-1} in the spectrum of PVS decreased compared with VTS. In addition, a new absorption band due to $\nu_{\text{Si-O-Si}}$, ranging from 1000 to 1200 cm^{-1}, appeared in the spectrum (Fig. 3b).

Figure 4a and b gives the ^{29}Si NMR spectra for VTS and PVS respectively. Figure 4b shows that a sharp signal at −55.6 ppm due to VTS disappeared and new broad signals appeared at −63.8 ppm due to the T^1 structure, at −72.9 to −71.7 ppm due to the T^2 structure, and at −81.9 to −79.4 ppm due to the T^3 structure.

Table 5. Mechanical properties and microstructure of PVPS gel films[a]

No.	Precursor no.	Curing time (days)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	Siloxane unit amount[b] T^0	T^1	T^2	T^3	DC[c] (%)
23	12	10	14.2	8	567	—	—	—	—	—
24	14	10	13.1	14	367	34	28	30	8	37
25	19	10	6.8	14	113	47	31	22	0	25
26	21	10	1.4	23	6	50	32	18	0	23
27	18	10	4.3	18	63	48	32	20	0	24
28	18	20	7.7	8	210	—	—	—	—	—
29	18	30	8.5	5	352	47	31	22	0	25

[a] Thickness: 0.06 mm. Length × width: 20 mm × 2 mm. Curing temp.: 80 °C.
[b] Calculated based on the peak area of ^{29}Si NMR spectrum. T^n: $Si(OSi)_n(OR)_{4-n}$ ($n = 0$–3).
[c] DC of siloxane bonding.

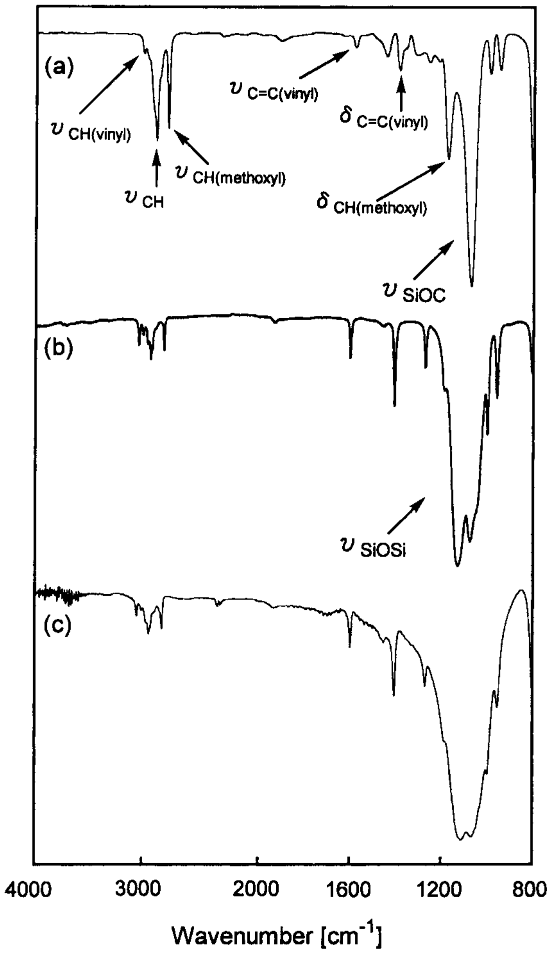

Figure 3. FTIR spectra of VTS (a), PVS (b), and PVPS gel film (c) produced via route B.

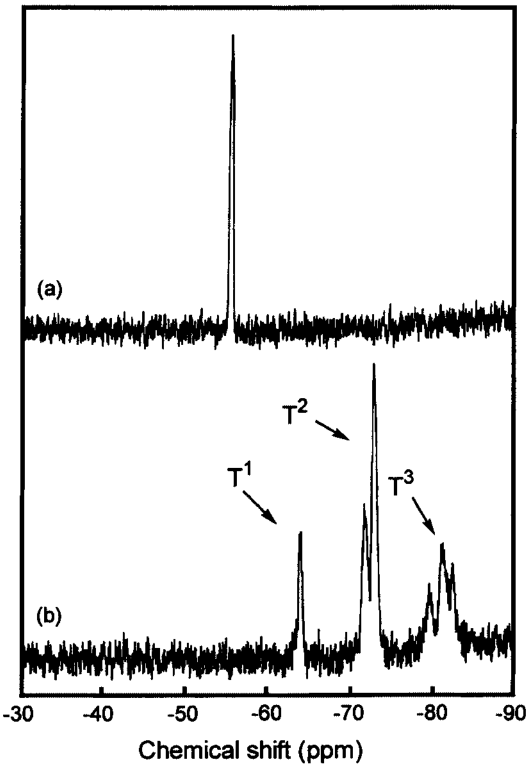

Figure 4. The ^{29}Si NMR spectra of VTS (a) and PVS (b) produced via route B.

The results on the preparation of PVS by hydrolytic polycondensation of VTS are listed in Table 3. Molecular weights, M_w of PVS increased from 1100 to 6400 with an increase in the molar ratio of H_2O/Si from 1.10 to 1.45. This is due to the enhancement of hydrolytic polycondensation. As shown in Table 3, an increase in the molar ratio of H_2O/Si led to decreases of peak areas due to the structures T^1 and T^2 and an increase of peak area due to the T^3 structure, indicating that the DC increased from 77 to 90.

Preparation of PVPS hybrid gel films by UV irradiation of PVS

Photopolymerization of PVS in the absence of a photoinitiator failed in spite of UV irradiation for 5 h. Therefore, it was performed in the presence of BTPS as a photoinitiator.

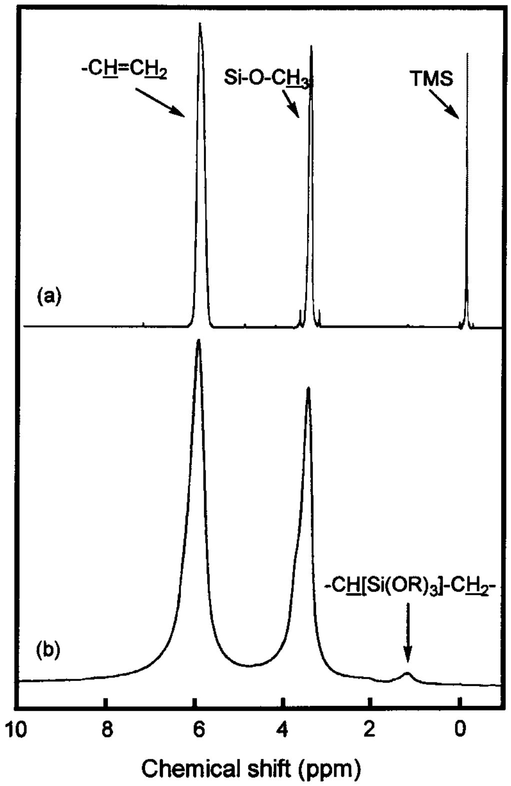

Figure 5. The ^{1}H NMR spectrum of PVS (a) and ^{1}H HPDEC NMR spectrum of PVPS (b) gel film produced via route B.

Appropriate choice of loading of photoinitiator and UV irradiation time led to transparent, homogeneous, and sturdy free-standing films (Nos 33–38). These results are summarized in Table 4. The curing rate increased with increasing concentration of photoinitiator, resulting in an increase in the hardness of the films. The hardness of the films also increased with an increase of irradiation time, resulting in crack formation. An FTIR spectrum of PVPS gel film is shown in Fig. 3c. No alteration of the peak intensity of absorption bands due to ν_{CH} at 3060 cm^{-1}, ν_{CH} at 3020 cm^{-1}, $\nu_{C=C}$ at 1600 cm^{-1}, and $\delta_{C=C}$ at 1410 cm^{-1} of vinyl group was observed. The ^{1}H NMR spectra of the PVS and PVPS gel films are given in Fig. 5a and b respectively. In the spectrum of the PVPS gel film, a new signal at 1.19 ppm due to the ethylene group appeared, suggesting that radical polymerization of the vinyl group proceeded. However, the peak intensity of the signal due to the ethylene group is weaker than that due to the residual vinyl group. These results indicate that UV irradiation of PVS gave rise to radical polymerization of vinyl groups, whereas the yield of polymer was low according to the ^{1}H NMR spectrum of the PVPS gel film in which the peak intensity of the residual vinyl groups was strong.

Mechanical properties of PVPS organic–inorganic hybrids (route B)

The tensile strength of the PVPS gel films is summarized in Table 3. The tensile strength and Young's modulus of the gel films increased and the elongation decreased with increase of UV irradiation time and DC of the precursor. The density of the films increased from 1.26 to 1.29 g cm^{-3} with an increase of irradiation time (Nos 33–35). In addition, the density of the films increased from 1.28 (No. 34) to 1.31 g cm^{-3} (No. 38) with an increase of DC of precursors in the cases of Nos 35, 37, and 38. These results indicate that increasing the UV irradiation time and the DC of precursors gives rise to films with high density, leading to sturdier films.

The films prepared via route B are sturdy and brittle because of their high DC, although the DP of organic groups is low.

Comparison of properties of gel films prepared by routes A and B

The tensile strength and Young's modulus of the gel films prepared by route B are much greater than those of gel films prepared by route A, as shown in Tables 4 and 5. On the other hand, the elongation of the gel films prepared by route B is smaller than those prepared by route A. This is because of the DCs of gel films via route A and route B are 20–30% and 77–90% respectively. Therefore, the gel films via route A have a flexibility, reflecting the properties of the polyethylene backbone linkages, whereas gel films via route B have a toughness and a brittleness based on the properties of the siloxane network. Moreover, the density of the gel films prepared via route B is higher than for films prepared via route A, due to the densification of films via route B.

The TG-DTA traces of PVPS gel films via route A (Nos 27 and 29) are given in Fig. 6. A marked weight loss of the gel film No. 29 was observed at temperatures from 270 to 760 °C. During the period of this weight loss, endothermic peaks were observed at temperatures of 270 and 430 °C. The weight loss of gel film No. 27 was detected in a similar manner as above. The T_g values[5] of the gel films of Nos 27 and 29 were 262 °C and 271 °C respectively. The weight losses of gel films of Nos 27 and 29 were 54% and 45% respectively at 1400 °C. These results demonstrate the improvement of heat-resisting properties of gel films with an increase in DC.

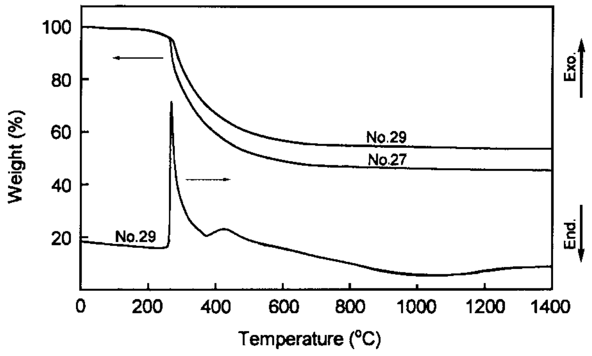

Figure 6. TG-DTA traces of PVPS gel films under air atmosphere produced via route A.

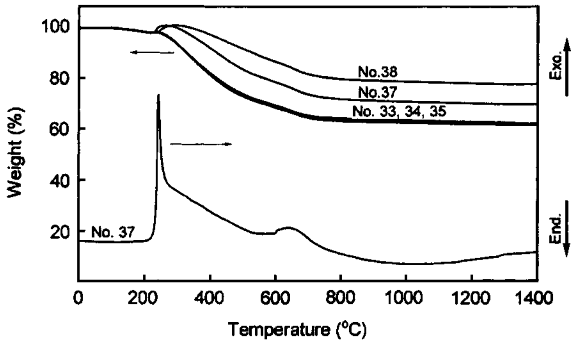

Figure 7. TG-DTA traces of PVPS gel films under air atmosphere produced via route B.

TG-DTA curves of PVPS gel films via Route B (Nos 33–35, 37, 38) are shown in Fig. 7. A weight loss for gel film No. 37 was observed up to 720 °C, after an increment of weight accompanied by an endothermic reaction was observed at temperatures of 240 to 260 °C. The weights of the gel films Nos 33–35, 38 decreased in a similar manner as above. Similar TG traces were observed in the case of Nos 33–35, despite the different periods of UV irradiation. The T_g values[5] of Nos 33–35 were 320 °C, and those of Nos 37 and 38 were 380 °C and 430 °C respectively. Furthermore, the weight losses of the gel films of Nos 33–35 were 38%, and those of Nos 37 and 38 were 27% and 22% respectively. These results indicate that the heat-resisting properties of the gel films are improved with an increase of DC and are independent of UV irradiation time.

The gel films produced via route B showed higher T_g[5] and lower weight loss at 1400 °C because of their higher DC when compared with those produced via route A.

These results indicate that the heat-resisting properties of gel films depend markedly on the DC. In addition, these gel films have special properties that cannot be expected from polyethylene itself. This is because of the fact that the gel films are hybrids consisting of polyethylene and polysiloxane backbone linkages, leading to the properties that T_g values[5] are above 270 °C and the weight losses are less than 55% at 1400 °C.

CONCLUSIONS

PVPS gel films were prepared by two routes, A and B. In route A, VTS was firstly subjected to radical polymerization to form PVTS, followed by acid-catalyzed hydrolytic polycondensation of PVTS to give PVPS gel films. In route B, hand, PVPS gel films were prepared by photoinduced radical polymerization of PVS, which was synthesized by acid-catalyzed polycondensation of VTS.

In route A, PVTSs with various DPs were obtained by radical polymerization of VTS using various molar concentrations of DTBP as an initiator. The acid-catalyzed hydrolytic polycondensation of these PVTSs gave rise to PVPSs with various DPs and DCs. Heat treatment of these PVPSs provided transparent, homogeneous and flexible hybrid gel films. The tensile strength and Young's modulus of the gel films increased with an increase of DC, whereas elongation decreased. On the other hand, the tensile strength and Young's modulus of the gel films decreased with an increase in DP, whereas elongation increased.

In route B, PVS with various DCs were prepared by acid-catalyzed hydrolytic polycondensation of VTS. UV irradiation of the PVS led to transparent (or yellowish), homogeneous and tough PVPS hybrid gel films. The tensile strength and Young's modulus of the gel films increased with an increase of time of UV irradiation and DC of the precursor polymer, whereas elongation decreased.

The gel films produced via route B showed higher density, tensile strength and Young's modulus, and smaller elongation, compared with those produced via route A. In addition, it was revealed that the heat-resisting properties of gel films depend markedly on the DC.

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