

Characterization of polysiloxane-*block*-polyimides with silicate group in the polysiloxane segments

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Abstract

A new class of polysiloxane-*block*-polyimides having silicate in the polysiloxane segments were successfully synthesized and the thermal and mechanical properties of their crosslinking investigated using cast films. The silicate-containing copolyimides were easily derived by hydrosilylation of polysiloxane-*block*-polyimides having vinyl groups in the polysiloxane segments prepared from 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA), 2,2-bis[4-(3-aminophenoxy)phenyl]sulfone (BAPSM) and several kinds of copolyimides with vinyl functionalized diamino-(poly)siloxanes accompanied by solution imidization. During hydrosilylation a small excess of diethoxy(methyl)silane was reacted using hydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 5\text{H}_2\text{O}$) as the catalyst. The copolyimides finally obtained were soluble in various organic solvents and easily hydrolysed to form crosslinked copolyimides during solution casting of films for investigation. The resulting materials have various potential applications as organic-inorganic hybrid materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polysiloxane-*block*-polyimide; Silicate group; Hydrosilylation

1. Introduction

Recently, several kinds of polyimides terminated by silicate groups have been developed and utilized for designing a new class of inorganic-organic hybrid material [1]. The importance of these new materials has recently been recognized because of an increasing demand for high-performance polymers that cannot be produced by conventional methods [2–10]. Organic-inorganic hybrid materials has the potential to realize desired thermal and mechanical properties with the additional benefits of good creep and durability characteristics. The interaction between the organic and inorganic compositions through physical force and chemical bond is important as a method for controlling the structure and properties of the hybrid materials. A standard technique for formation of hybrid material is to use sol-gel chemistry by which inorganic particles with nanometer-to-micrometer scale can be formed in the polymer matrix and vice versa. The process may induce either physical blending of inorganic and organic components or chemical grafting among them [9,10]. In general, alkoxysilane derivatives have been most frequently used for

preparing hybrid materials because they undergo hydrolytic polycondensation to result in the sol-gel process.

On the other hand, polysiloxane-*block*-polyimides have been developed and applied in the advanced microelectronics, aerospace and printed circuit industries, mainly for their high thermal stability and excellent electrical and mechanical properties [11–17]. These copolyimides are known to possess additional characteristic properties such as oxidative stability, low surface energy, high gas permeability, good adhesion, and specific dielectric properties [18]. We have shown that these properties depend mainly on the composition and chain length of the polysiloxane segments [19,20]. Reactive polyimides, thermosetting-type polyimides containing reactive end groups have been developed for use as the matrix resin for carbon fibre-matrix composites [21–24]. More recently, polysiloxane-*block*-polyimides functionalized by the vinyl group in the polysiloxane segments have been synthesized [25]. These copolyimides, consisting of both flexible segments and reactive side chains, are melt-processible and possess excellent thermal properties and resistance to various organic reagents after thermosetting. These properties should be attractive for use in electrical applications. In the present study, based on this background, polysiloxane-*block*-polyimides (SxPI) functionalized with silicate are prepared,

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to develop a new class of thermosetting copolyimides and to construct inorganic–organic hybrid materials.

2. Experimental

2.1. Materials

The chemical structures of the monomers utilized are shown in Fig. 1. A high purity aromatic tetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, purity = 98.1%), was obtained from the Daisel Chemical Co. Ltd (Kyoto, Japan). A high purity aromatic diamine, 2,2-bis[4-(3-aminophenoxy)-phenyl]-sulfone (BAPSM, purity = 99.8%), was obtained from the Wakayama Seika Co. Ltd (Wakayama, Japan). Two kinds of vinyl-containing diamino(poly)siloxanes, V2-PSX ($M_n = 868$, (equivalent weight of vinyl group = 380)) and V4-PSX ($M_n = 890$, (equivalent weight of vinyl group = 120)), were supplied by Dow Corning Toray Silicone Co. Ltd (Tokyo, Japan). Diethoxy(methyl)silane (DEMS) was obtained from Shin-etsu Chemical Co. Ltd (Tokyo, Japan). Hydrogen hexachloroplatinate pentahydrate ($H_2PtCl_6 \cdot 5H_2O$) was purchased from Aldrich Chemical Corp. and stored under an inert atmosphere. The reaction solvents utilized for polyimide synthesis, *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF) and xylene, were supplied by Wako Pure Chemical Industries Ltd (Tokyo, Japan) and Mitsubishi Chemical Co. Ltd. (Tokyo, Japan), respectively. Other reagents were commercially obtained and used without further purification.

2.2. Preparation of VxPI

BTDA was mixed with BAPSM and the diamino(poly)siloxane Vx-PSX (where $x = 2$ or 4) in an appropriate ratio

in a mixture of NMP/xylene (weight ratio 7/3) and reacted at room temperature under a nitrogen atmosphere for 3 h to prepare poly(amic acids) with different compositions of polysiloxane segments. The resulting solutions were heated at 160°C for 10 h under nitrogen flow for solution imidization [18–20,25]. During this reaction, the azeotropically distilled water/xylene mixture was allowed to pool in the Dean–Stark trap and the water by-product was removed. On completion of imidization of the solution, xylene as azeotropic reagent was also removed from the copolyimide solution by distillation. The copolyimides were precipitated into methanol and dried in vacuo at 100°C. The vinyl-containing copolyimides thus prepared are represented as VxPI-y depending on the composition, where $x = 2$ or 4 and y denotes the x value and the composition (by wt%) of the Vx-PSX introduced as the polysiloxane segment.

2.3. Hydrosilylation of VxPI

The copolyimides with silicate groups were easily synthesized by hydrosilylation reaction of the polysiloxane-*block*-polyimides (VxPI) containing vinyl groups in the polysiloxane segments (Scheme 1). The copolyimide, VxPI, was dissolved in THF to 10 wt% of the polymer concentration. During stirring of the solution at room temperature under nitrogen flow, a predetermined amount of DEMS was added drop-wise, followed by a small amount of $H_2PtCl_6 \cdot 5H_2O$ (0.1~1.0 wt% versus DEMS); stirring of the solution was continued at room temperature for 12 h. The silicate-functionalized copolyimides thus prepared are represented as SxPI-y-z depending on the composition where x denotes the x value and composition of the original VxPSX and z denotes the ratio of the silicate groups introduced by hydrosilylation relative to the vinyl groups. When SxPI is crosslinked by hydrolytic polycondensation, the original abbreviated name is prefixed by 'C' e.g. C-SxPI-y-z.

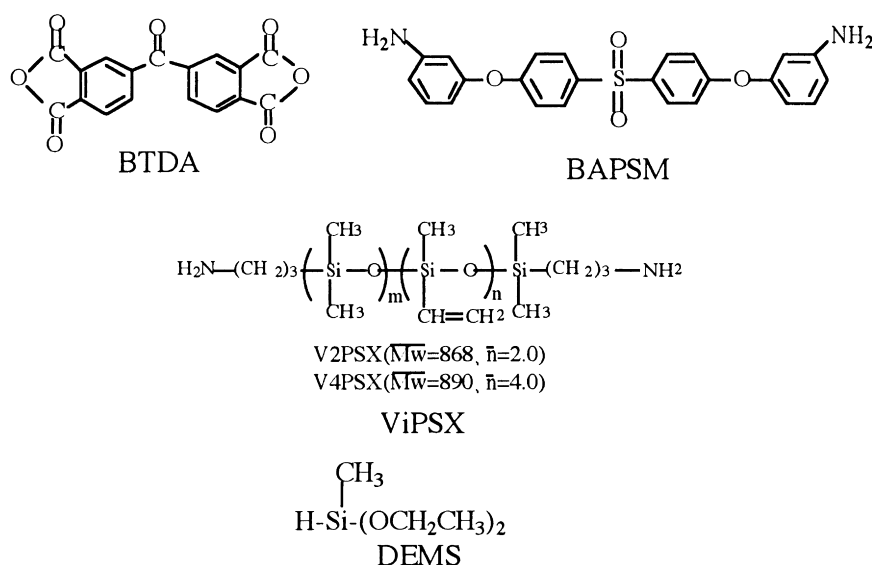
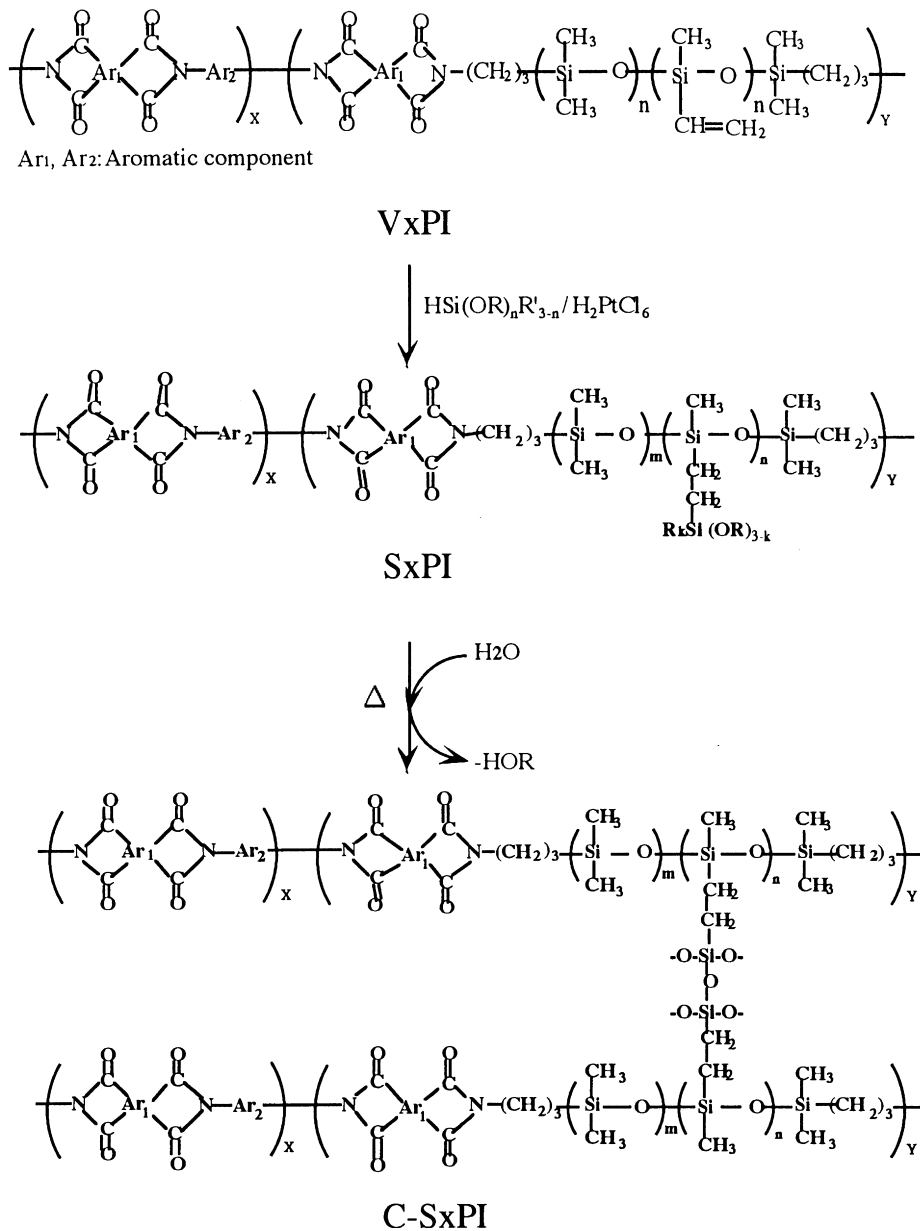


Fig. 1. Monomer compositions for the synthesis of silicate functionalized copolyimides.



Scheme 1. Synthetic route and possible crosslinking reaction of the copolyimide functionalized with silicate (S_xPI, C-S_xPI).

2.4. Preparation of S_xPI films

A portion of the S_xPI solution obtained after hydrosilylation was cast onto a glass plate and dried by heating at 100°C for 1 h to form a half-dried film. This was peeled off the glass plate, fixed on a stainless frame, and thoroughly dried at 180°C for 30 min and at 250°C for 60 min. The thickness of the film was controlled at a level of $25 \pm 2 \mu\text{m}$. Hydrolysis and polycondensation of the silicates during the heating cycles produced the C-S_xPI films. Their solubility was tested in various solvents at a polymer concentration of 5 wt%. The gel fraction of the S_xPI film finally obtained was determined by its weight decrease after immersion in NMP at room temperature for 24 h.

2.5. Instrumental analysis

Dynamic mechanical analysis (DMA) of the samples was carried out on a Rheovibron DDV-II HP instrument (Orientech Co. Ltd) to establish the crosslinking density. Thermo-mechanical analysis (TMA) was performed with an SSC 5670 Thermomechanical Analysis System (Seiko Electric Co. Ltd), to determine the heat distortion temperature T_{hd} and both thermal expansion coefficients, that below T_{hd} (shown by α_1) and that above T_{hd} (shown by α_2). Thermogravimetric analysis was measured by an SSC5200 (Seiko Electric Co. Ltd). The tensile modulus was measured on an Autograph AG-500A analyser (Shimadzu Co. Ltd) at a cross-head speed of 5 mm min^{-1} . The 400 MHz ¹H- and

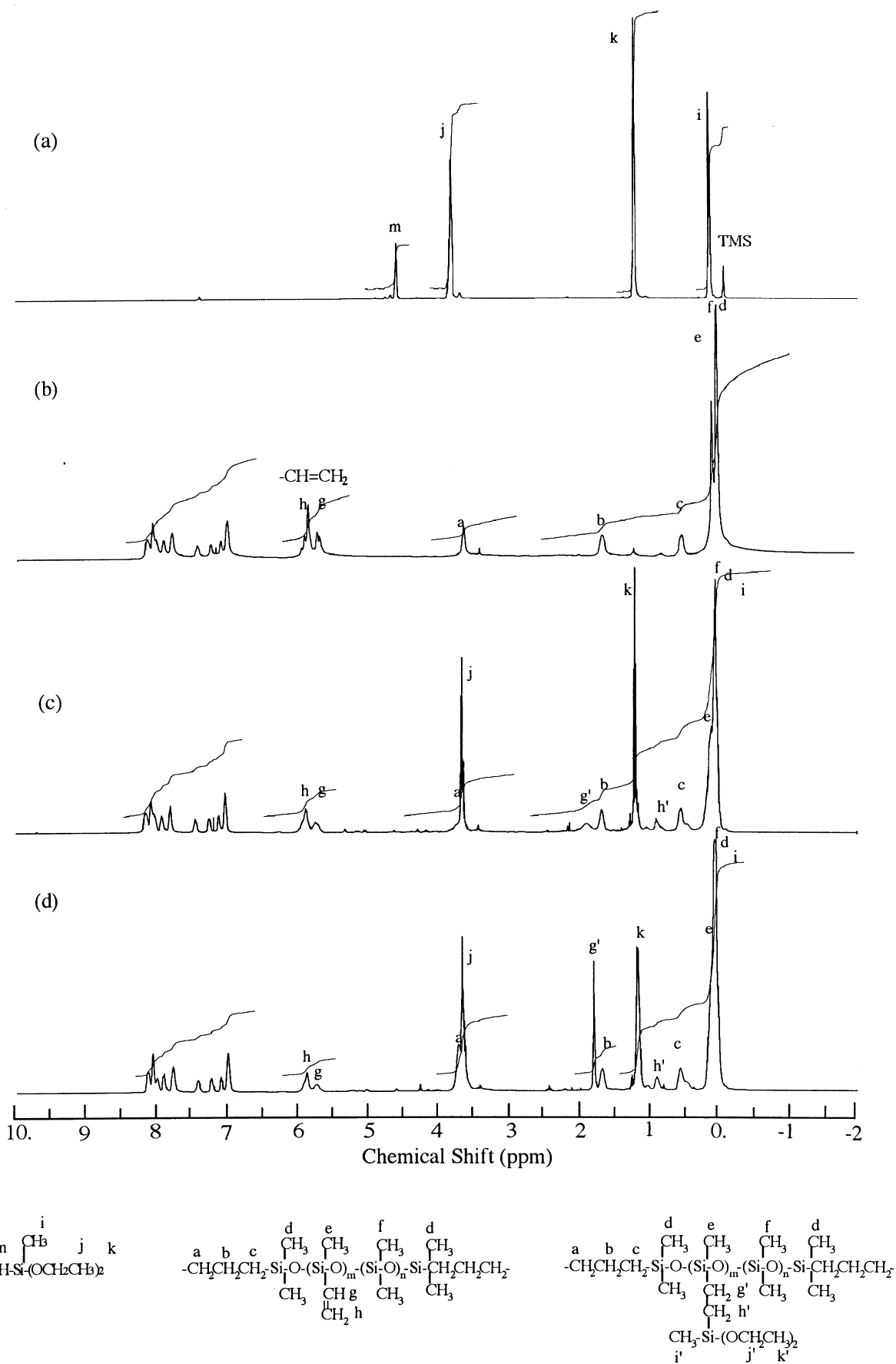


Fig. 2. ¹H-n.m.r. spectra of (a) DEMS; (b) V4PI-50; (c) S4PI-50-1 (6 h of reaction); and (d) S4PI-50-1 (12 h of reaction) in CDCl₃.

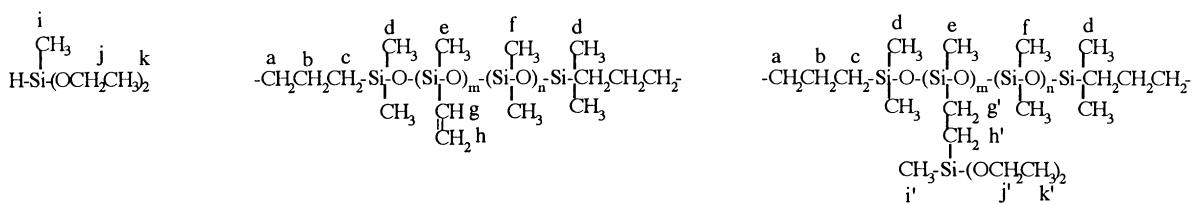
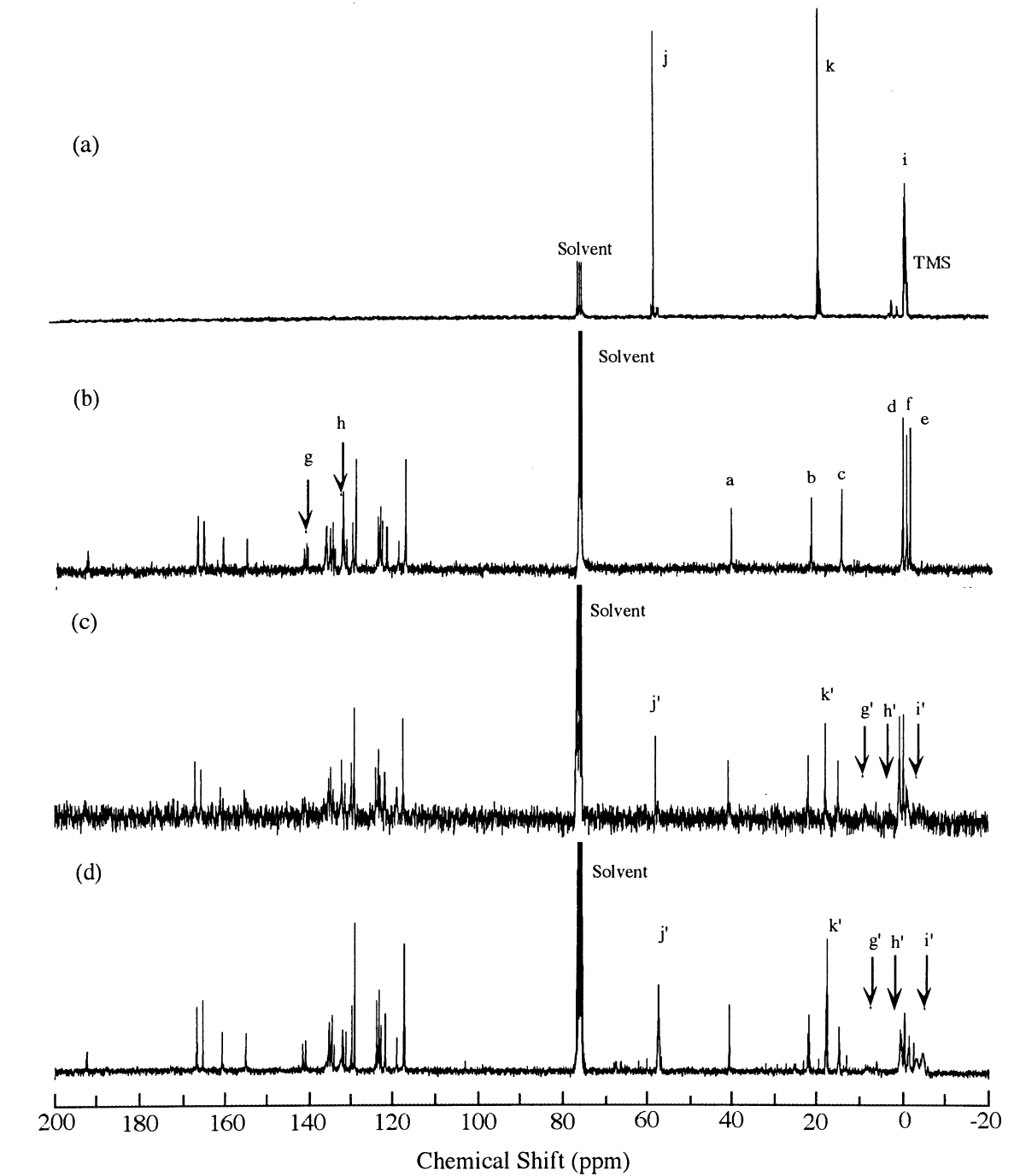


Fig. 3. ^{13}C -n.m.r. spectra of (a) DEMS; (b) V4PI-50; (c) S4PI-50-1 (6 h of reaction); and (d) S4PI-50-1 (12 h of reaction) in CDCl_3 .

100.5 MHz ^{13}C -n.m.r. spectra were measured at room temperature using a JOEL GX400 spectrometer (JOEL, Tokyo, Japan).

3. Results and discussion

The vinyl-containing polysiloxane-*block*-polyimides (VxPI) were prepared by solution imidization of the polyamic acids resulting from the reaction of BTDA, BAPSM and Vx-PSX ($x = 2$ or 4). The fully imidized copolyimides were then subjected to hydrosilylation reaction with DEMS. The amount of DEMS used in the reaction was varied from 1 to 10 relative to the vinyl groups in the PSX segments. The hydrosilylation reaction was accelerated enormously by addition, based on the weight of hydrosilane compound, of 0.1–0.2 wt% of platinum chloride (H_2PtCl_6) [25,26]. As described above, the hydrosilylation products (SxPI) gradually incurred gelation by hydrolytic polycondensation when kept at room temperature for long periods. It was found, however, that they were stable if their solutions were stored in a refrigerator at -20°C . After filtration of the solution, the silicate-functionalized products finally obtained could be isolated by evaporating off the THF solution at $<30^\circ\text{C}$ under vacuum to remove the solvent and unreacted DEMS. The SxPI thus isolated were subjected to the following structural analysis.

3.1. Structure analysis of SxPI

Typical ^1H -n.m.r. spectra of SxPI and the original VxPI in deuterated chloroform (CDCl_3) are shown in Fig. 2. From

the spectra for VxPI, the proton signals of the Si-CH₃ groups (Fig. 2, curves *e,f,d*) were separated into two peaks, the signal at the higher magnetic field was assigned to (CH₂=CH)-Si-CH₃ (curve *e*) while that at the lower magnetic field was assigned to (CH₃)-Si-CH₃ (curves *f,d*) [25]. The signals of (N)-CH₂- (Fig. 2, curve *a*), (C)-CH₂-(C) (curve *b*), and (C)-CH₂-(Si) (curve *c*) were observed at δ 0.6, 1.7, and 3.7 ppm, respectively. The signals of the vinyl group were detected as multiplets at δ 5.7–5.8 and 5.9–6.0 ppm. In SxPI, the intensity of the vinyl signals decreased a little compared with the original peaks, and new signals appeared at δ 0.9, 1.4, 1.9 and 3.7 ppm. These signals were assigned to the ethylene linkage of (Si)-CH₂-CH₂-(Si) (Fig. 2, curves *g',h'*) and the ethyl protons of (Si)-O-CH₂CH₃ (curves *j,k*) which had been introduced by the hydrosilylation. From the integral ratio of the signals at δ 5.7–6.0 and 3.7 ppm the conversion of the vinyl group into the silicate was estimated to be 30–50%. The value was almost identical to the feed ratio of DEMS to the vinyl groups in each experiment, because the hydrosilylation had proceeded only partially.

^{13}C -n.m.r. spectra of both VxPI and SxPI are shown in Fig. 3. For VxPI, the carbon signals of the vinyl group appeared at δ 131.8 and 136.4 ppm, and those of the three Si-CH₃ groups appeared at δ -1.6, 0.6 and 1.3 ppm. For SxPI new carbon signals were detected at δ 58, 18, 5–0, and 0–6 ppm. These signals were attributed to the [diethoxy-(methyl)silyl]ethyl groups (Si-CH₃, (Fig. 3, curve *i*)), ethoxy groups (curves *j,k*), and ethylene linkage (curves *g',h'*) introduced by the hydrosilylation. These data also support the partial introduction of the silicate group into the siloxane segments of VxPI.

Table 1
Composition of VxPI and SxPI and solubility of the C-SxPI films

Polymer	Siloxane Component (wt%)		Silicate ^a (mol/mol)	Solvent solubility ^b		
				NMP	THF	CHCl ₃
V2PI-10	V2-PSX	10	0	S	S	S
C-S2PI-10-2		10	2.0	IS	IS	IS
C-S2PI-10-5		10	5.0	IS	IS	IS
V2PI-30		30	0	S	S	S
C-S2PI-30-2		30	2.0	IS	IS	IS
C-S2PI-30-5		30	5.0	IS	IS	IS
C-S2PI-30-10		30	10.0	IS	IS	IS
V2PI-50		50	0	S	S	S
C-S2PI-50-2		50	2.0	IS	IS	IS
C-S2PI-50-5		50	5.0	IS	IS	IS
V4PI-30	V4-PSX	30	0	S	S	S
C-S4PI-30-1		30	1.0	IS	IS	IS
C-S4PI-30-2		30	2.0	IS	IS	IS
C-S4PI-30-5		30	5.0	IS	IS	IS
V4PI-50		50	0	S	S	S
C-S4PI-50-1		50	1.0	IS	IS	IS
C-S4PI-50-2		50	2.0	IS	IS	IS

^a [DEMS] = [DEMS(mol%)]/[vinyl group (mol%)]

^b S, soluble; IS, insoluble

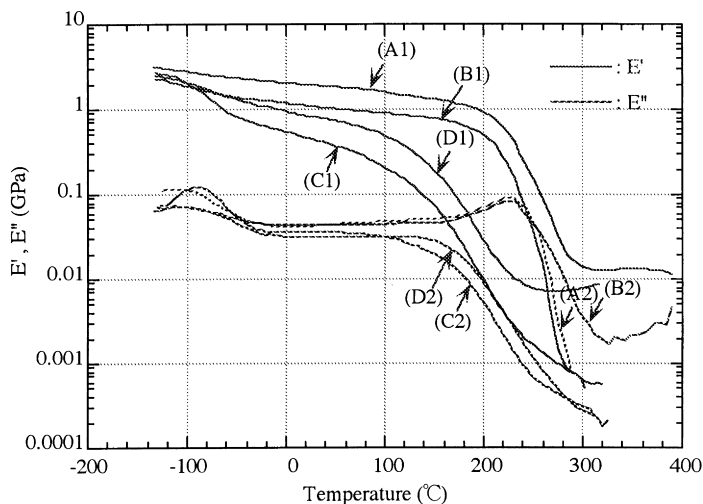


Fig. 4. Temperature-dependent changes in storage modulus (E') and loss modulus (E'') of the copolyimide films of V4PI-30 ((A1), (A2)); C-S4PI-30-10 ((B1), (B2)); V4PI-50 ((C1), (C2)); and C-S4PI-50-2 ((D1), (D2)).

3.2. Solubility and thermal and mechanical properties of the C-SxPI

The solubility of VxPI and C-SxPI with different Vx-PSX and silicate compositions are compared in Table 1. VxPI is as soluble in various organic solvents as other linear polysiloxane-*block*-polyimide derivatives, mainly due to the lower intermolecular interaction between the polysiloxane segments [16–20]. When SxPI was isolated from the NMP solution by the ordinary reprecipitation method in air, the polymer solubility was decreased because of the crosslinking reaction through the hydrolytic polycondensation of the silicate groups. However, addition of THF or CHCl_3 into the NMP solution of SxPI did not induce any precipitation of the polymer. When this solution was preserved at room temperature for 3–7 days, gelation proceeded spontaneously, probably because of the gradual hydrolysis of the silicate units introduced. Therefore, the solubility of

SxPI seems to be identical to that of the original VxPI. The C-SxPI films formed by casting the SxPI solution exhibited extremely poor solubility in various organic polar solvents as summarized in Table 1 [18–20,25,27]. The insolubility, even in NMP, suggested that the crosslinking had been driven through covalent bond formation as shown in Scheme 1.

The typical DMA curves of the V4PI and C-S4PI films are compared in Figs 4 and 5. The original copolyimide films of V4PI-30 and V4PI-50 exhibited the typical behaviour of linear thermoplastic polyimides in losing their storage modulus above the softening point, whereas the films of C-S4PI-30-10 and C-S4PI-50-2 retained their storage modulus even at temperatures higher than 300°C. The loss moduli of C-S4PI-30-10 and C-S4PI-50-2 were a little lower than those corresponding to V4PI-30 and V4PI-50, respectively. These data suggest that the V4-PSX segments involved in S4PI were crosslinked as intended. Two

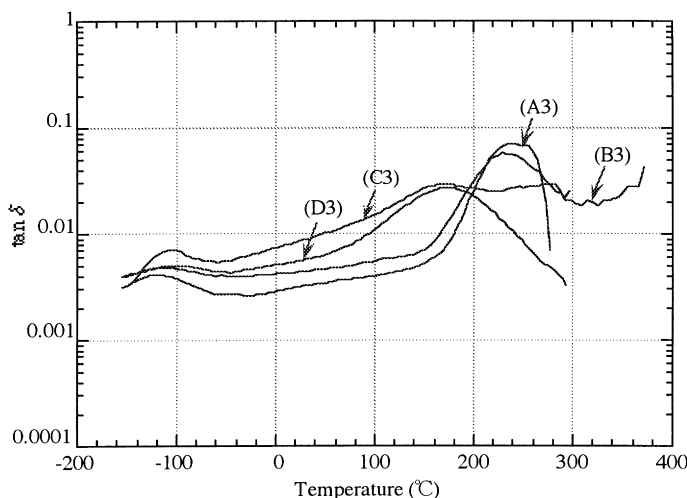


Fig. 5. Temperature-dependent changes in loss tangent ($\tan \delta$) of the copolyimide films of V4PI-30 (A3); C-S4PI-30-10 (B3); V4PI-50 (C3); and C-S4PI-50-2 (D3).

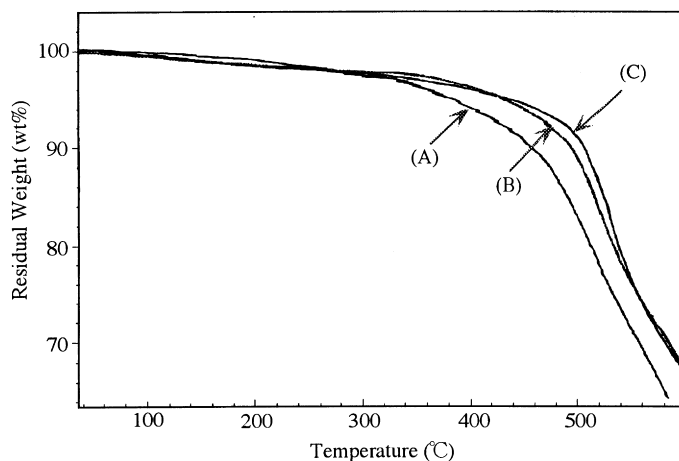


Fig. 6. Results of thermogravimetric analysis of: (A) V4PI-30; (B) C-S4PI-30-1; and (C) C-S4PI-30-5.

different peaks were exhibited on the $\tan \delta$ and loss modulus curves of both V4PI-30 and V4PI-50. The peak in the lower temperature range (T_{g1}) can be attributed to the polysiloxane phase and the peak in the higher temperature range (T_{g2}) can be attributed to the polyimide phase. This may be an indication of a phase-separated structure in these polymers which should be favourable for silanol coupling among the silicate side chains. In the crosslinked films the peak at the low temperature became smaller, while that at the high temperature did not change significantly. Therefore, the phase-separation structure should have been retained even after the crosslinking.

Comparison of the TGA curves of V4PI-30, C-S4PI-30-1 and C-S4PI-30-2 (Fig. 6) suggests that the thermal stability of the copolyimides improves significantly with the progress of the crosslinking reaction. Similar results were obtained in

the other series of VxPI and CSxPI films. The structure crosslinked by covalent bonds (Scheme 1) is effective for resisting mass diffusion at high temperature.

The thermal and mechanical properties of the VxPI and C-SxPI films with different compositions are summarized in Table 2. The T_{hd} of the C-SxPI films seemed to shift to a slightly higher temperature region compared with the T_{hd} of VxPI. The α_1 and α_2 of the C-SxPI films having 30 and 50 wt% of Vx-PSX became considerably lower than those of the corresponding VxPI films due to the formation of a crosslinked structure. The tensile modulus and strength of the CSxPI films with 10 and 30 wt% of Vx-PSX were almost comparable with those of the corresponding VxPI films. In this case the crosslinking effect may not have suppressed its plasticizing effect. In contrast, the tensile strength and modulus of the C-SxPI having 50 wt% of

Table 2
Comparison of thermal and mechanical properties of VxPI and C-SxPI films

Polymer	T_{hd}^a (°C)	α_1^b (ppm/°C)	α_2^c (ppm/°C)	Tensile strength ^d (MPa)	Tensile modulus ^d (GPa)
V2PI-10	192	116	> 5000	79.4	2.62
C-S2PI-10-2	199	130	2300	83.3	2.65
C-S2PI-10-5	198	128	2980	75.5	2.68
V2PI-30	150	155	> 5000	41.2	1.17
C-S2PI-30-2	158	132	601	35.3	1.23
C-S2PI-30-5	150	140	738	45.1	1.22
C-S2PI-30-10	150	128	870	44.1	1.24
V2PI-50	98	2728	> 5000	11.8	0.35
C-S2PI-50-2	100	204	354	23.5	0.61
C-S2PI-50-5	100	189	359	22.5	0.59
V4PI-30	154	155	> 5000	47.0	1.22
C-S4PI-30-1	156	105	740	50.0	1.35
C-S4PI-30-2	156	109	362	50.0	1.37
C-S4PI-30-5	157	106	250	57.8	1.48
V4PI-50	97	2803	> 5000	11.8	0.36
C-S4PI-50-1	102	201	348	27.4	0.59
C-S4PI-50-2	102	185	340	29.4	0.61

^a Determined by TMA

^b Determined by TMA (10°C/min, under N₂, temperature range 50–100°C)

^c Determined by TMA (10°C/min, under N₂, temperature range $T_g \sim T_g + 50^\circ\text{C}$)

^d Measured by Autograph 2000A (cross head speed 3 mm min⁻¹).

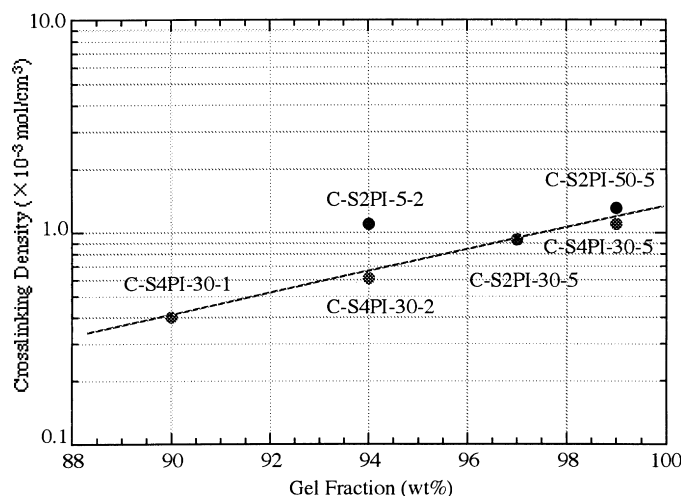


Fig. 7. Plot of crosslinking density versus gel fraction for the C-SxPI films.

V_x-PSX were much higher than those of the corresponding V_xPI films. This may be because their polysiloxane segments were well phase-separated from the polyimide segments and highly crosslinked by the hydrolytic polycondensation of the silicate groups [25]. The increase in the silicate/vinyl ratio in SxPI produced little effect on the thermal and mechanical properties of the C-SxPI films. An effect could be obtained when 1 to 2 mol% of the vinyl groups of V_xPI were converted to silicate units at a relatively higher composition of V_x-PSX in the copolymers.

3.3. Effect of crosslinking density

The gel fraction of each C-SxPI film was measured and plotted against the crosslinking density calculated from the results of DMA using Mooney–Rivlin's equation [28]. As shown in Fig. 7, the gel fraction increased with increasing crosslinking density. It is known that the gel fraction exceeded 90 wt% above a crosslinking density of 0.4 mmol cm^{-3} . The crosslinking density increased with increasing compositions of V_x-PSX and silicate content, though this relation was far from linear, particularly with regard to the silicate content.

For promoting the crosslinking density of the C-SxPI films some water was added to the SxPI solution prior to casting. The effect of the water addition on the thermal properties of the resultant C-SxPI films are shown in Table 3. The hydrolytic polycondensation of the silicate groups was enhanced by the added water and the following heat treatment, the resulting films exhibiting lower α_2 and higher crosslinking density. Their crosslinking density increased considerably, supporting the accelerated silanol coupling reaction. Furthermore, addition of acid for catalysis may also be effective in enhancing crosslinking, as observed in the polycondensation of silicate compounds [1–10].

4. Conclusions

SxPI films having different compositions were successfully prepared by hydrosilylation of V_xPI and DEMS. The structure of SxPI isolated by careful preparation was confirmed by ¹H- and ¹³C-n.m.r. spectroscopy. The hydrolytic polycondensation of the silicate units introduced into SxPI was readily induced by spontaneous hydrolysis and

Table 3
Effect of water addition and heating on the thermal properties of C-SxPI film

Polymer	Amount of H ₂ O ^a (mol%)	α_1^b (ppm/°C)	α_2^c (ppm/°C)	Crosslinking density ^d $\rho (\times 10^{-3} \text{ mol cm}^{-3})$
C-S4PI-30-2	0	105	740	0.40
C-S4PI-30-2'	20	108	243	0.89
C-S4PI-30-5	0	109	362	0.61
C-S4PI-30-5'	20	106	161	1.66
C-S4PI-30-10	0	106	250	1.10
C-S4PI-30-10'	20	115	108	1.68

^a Heating cycle was carried out for 1 h at 250°C under nitrogen atmosphere

^b Determined by TMA ($10^\circ\text{C min}^{-1}$, under N₂, temperature range 50–100°C)

^c Determined by TMA ($10^\circ\text{C min}^{-1}$, under N₂, temperature range $T_g - T_g + 50^\circ\text{C}$)

^d Calculated using Mooney–Rivlin's equation $E = 3dRT/Mc = 3\rho RT$, $\rho = d/Mc$

condensation of the silicate groups during the heating cycle of film preparation under ambient conditions. The thermal and mechanical properties of the C-SxPI films crosslinked with silicate units were well characterized. It was found that these properties can be controlled by changing the polysiloxane composition and silicate content. These materials may be useful for preparing inorganic–organic hybrid networks.

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