Polymer Vol. 39 No. 13, pp. 2941–2949, 1998

0032-3861/98/$19.00+0.00
PII: S0032-3861(97)00614-9

Synthesis and properties of novel thermosetting polysiloxane-*block*-polyimides with vinyl functionality

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(Received 5 March 1997; revised 12 May 1997; accepted 22 July 1997)

A new class of vinyl-functionalized polysiloxane-*block*-polyimides were synthesized and characterized. The copolyimides were derived from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)/bis[4-(3-aminophenoxy)-phenyl]sulfone (BAPSM) combined with two kinds of vinyl-containing diaminopolysiloxanes and imidized by a solution method. They were highly soluble in various organic solvents. The vinyl groups of the copolyimides were reacted with various hydrosilane compounds for crosslinking. The crosslinked products became insoluble in polar solvents and were analysed and characterized by thermomechanical analysis (t.m.a.), dynamic mechanical analysis (d.m.a.), and ^{13}C and ^{29}Si nuclear magnetic resonance (n.m.r.). The tensile modulus of the copolyimides having a polysiloxane composition of 50 wt% increased approximately twofold after the crosslinking reaction, while that of the copolyimides with compositions of 10–30 wt% was similar to that of the original copolyimides. Their thermal expansion coefficient below the glass transition temperature (T_g), $\alpha 1$, was nearly the same as that of the original copolyimides, while the coefficient above T_g, $\alpha 2$, decreased drastically compared with that of the original copolyimides. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: siloxane; polysiloxane-*block*-polyimide; vinyl group)

INTRODUCTION

In recent years, various kinds of polysiloxane-*block*-polyimides have been developed as high performance heat-resistant polymers which can be applied in advanced microelectronics, aerospace and printed circuit industries[1–4]. These copolyimides have also been known to possess additional excellent properties such as oxidative stability, low surface energy, high gas permeability, reasonably good thermal stability, good adhesion and excellent dielectric properties[4–8]. In our previous study, it has been shown that the thermal and mechanical properties as well as the morphology and surface structure of these linear copolyimides are strongly affected by the polysiloxane content and chain length[9,10]. Many of these polysiloxane-*block*-polyimides are soluble in aprotic polar solvents because of the decreased intermolecular interaction in the presence of linear flexible polysiloxane chains[6–8]. However, thermosetting copolyimides containing reactive end-groups were also developed for use as matrix resin of carbon fibre–matrix composites[11–13]. With these two ideas combined, a new class of copolyimides having both flexible segments and reactive side-chains can be designed. These copolyimides may have melt-processability before crosslinking and excellent thermal properties and resistance to various organic reagents after thermosetting and thus should be attractive for use as materials for electric purposes[14]. In the present study, such polysiloxane-*block*-polyimides containing vinyl groups were synthesized by using vinyl-functionalized polysiloxanes, and their thermal and mechanical properties were evaluated[15–17]. These copolyimides are not only thermosetting, but also crosslinked with hydrosilane compounds. The resultant crosslinked copolyimides were analysed by solid state ^{13}C and ^{29}Si c.p./m.a.s. n.m.r. spectroscopies.

EXPERIMENTAL

Materials

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) with a purity of 98.1% was obtained from Daisel Chemical Co., Ltd. (Osaka, Japan). 2,2-Bis[4(3-aminophenoxy)phenyl]sulfone (BAPSM) with a purity of 99.8% was obtained from Wakayama Seika Co., Ltd. (Wakayama, Japan). Bis(γ-aminopropyl)poly(methylvinylsiloxane)s (V1-PSX, $\overline{Mw} = 832$, [equivalent weight of vinyl group] = 806; V2-PSX, $\overline{Mw} = 868$, [equivalent weight of vinyl group] = 380) were provided by Dow Corning Toray Silicone Co., Ltd. (Tokyo, Japan). These oligomers were prepared by the equilibration reaction[18]. All of the above compounds were used without further purification. *N*-Methyl-2-pyrrolidinone (NMP) and xylene were obtained from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan)

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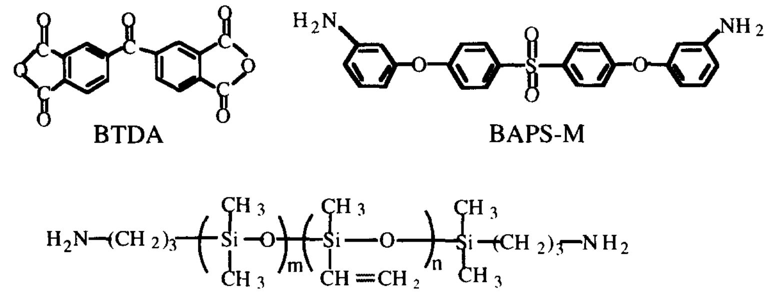


V1-PSX ($\overline{Mw}$=832, $\overline{m}$ = 8, $\overline{n}$ = 1.0)
V2-PSX ($\overline{Mw}$=868, $\overline{m}$ = 7, $\overline{n}$ = 2.0)

Figure 1 Monomers used for synthesis of vinyl-functionalized polysiloxane-*block*-polyimides

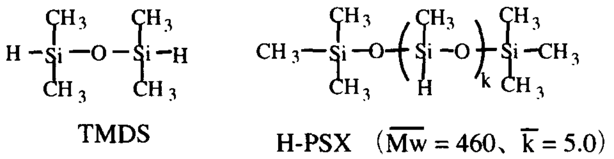


Figure 2 Hydrosiloxane compounds used as hardener

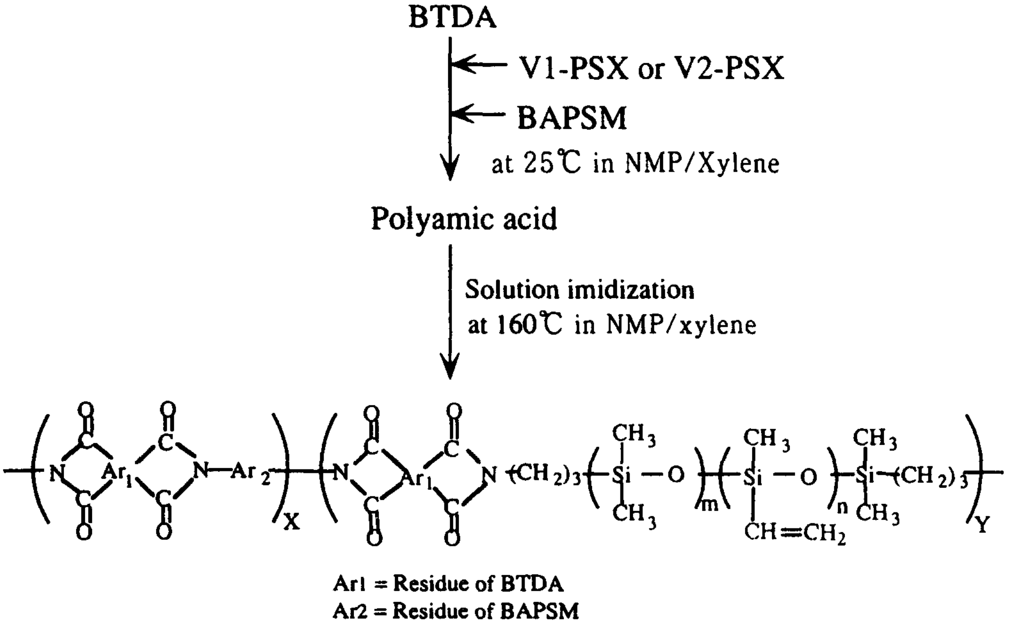
and Mitsubishi Chemical Co., Ltd. (Tokyo, Japan), respectively, and purified by distillation. Hydrosilane compounds, 1,1,3,3-tetramethyldisiloxane (TMDS) and poly(hydromethylsiloxane) (H-PSX, $\overline{Mw}$ = 400), were obtained from Dow Corning Toray Silicone Co., Ltd. (Tokyo, Japan) and used as hardeners. Hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) was purchased from Aldrich and stored under an inert atmosphere. The structures of the representative monomers and hardeners are shown in *Figure 1* and *Figure 2*, respectively.

Preparation of copolyimides

A typical procedure is shown in *Scheme 1*. The whole reaction was carried out in a four-necked round-bottomed separable flask equipped with a thermocouple, a mechanical stirrer, an unversed Dean–Stark trap filled with xylene, a nitrogen gas inlet, a drying tube, and a condenser. A mixture of NMP/xylene (weight ratio = 70/30) was used as the reaction solvent, and its amount was determined so as to adjust the polymer concentration in the finally obtained NMP solution to 25 wt%. The reaction temperature was precisely controlled within ± 2°C in a nitrogen atmosphere for 3 h. Then, solution imidization was followed at 180°C for 5 h with water removed from the azeotropically distilled xylene/water mixture[6–8]. Until 2 h after the imidization reaction had started, a clearly separated water phase was observed in the Dean–Stark trap. After completion of the solution imidization, xylene was distilled off from the reaction solution to give a solution of the fully imidized copolyimide in NMP.

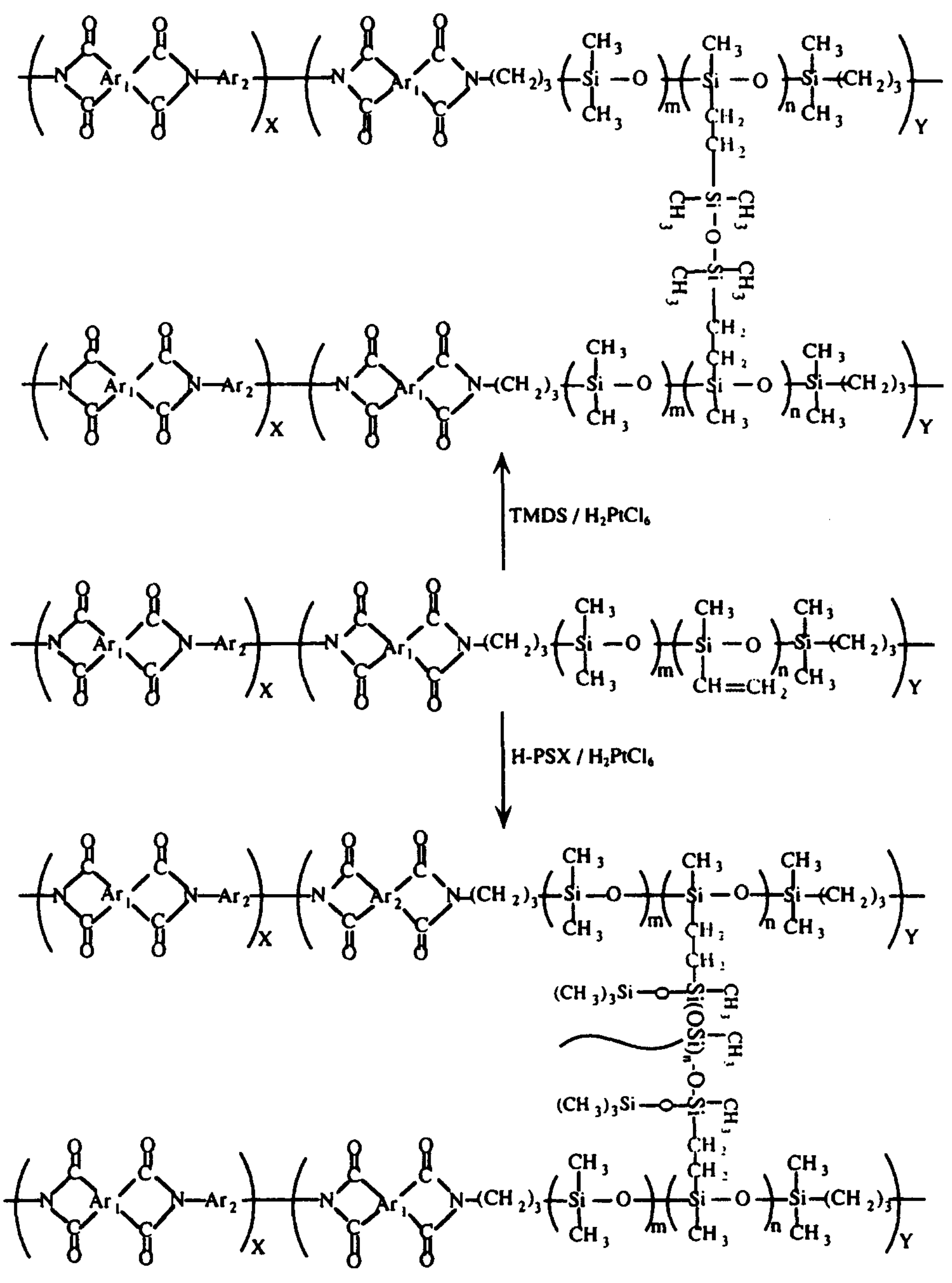
Reaction of copolyimides and hydrosilane compounds

The reaction solution containing the fully imidized copolyimide obtained above was diluted with NMP to a polymer concentration of 20 wt%. The solution was stirred under nitrogen flow at 25°C, and the hydrosilane, TMDS or H-PSX, was added dropwise. Then, a small amount of $H_2PtCl_6{\cdot}6H_2O$ (0.1–0.2 wt% relative to hydrosilane) was added. The hydrosilylation reaction was continued at 25°C



Ar1 = Residue of BTDA
Ar2 = Residue of BAPSM

Scheme 1 Synthesis of vinyl-functionalized polysiloxane-*block*-polyimides of V1-PI (V1-PSX based) and V2-PI (V2-PSX based) series via solution imidization



Scheme 2 Cross-linking reactions of vinyl-functionalized polysiloxane-*block*-polyimides with hydrosilane compounds

for 5 h under a nitrogen atmosphere. The possible hydrosilylations between the copolyimides and the hardeners are shown in *Scheme 2*.

Preparation of copolyimide films

A 20 wt% solution of the copolyimide in NMP was cast onto a glass plate and solidified by heating at 100°C for 1 h. The half-dried film was peeled off from the substrate, fixed on a stainless steel frame, and heated at 180°C for 30 min to form a voidless transparent film. The thickness of the film was controlled at the level of 25 ± 2 μm. The resultant film was then subjected to crosslinking by heat treatment with a heating cycle of 100°C for 30 min, 150°C for 30 min, and 200°C for 60 min. The films of the copolyimides crosslinked with hydrosilane were also prepared likewise.

Instrumental analyses

Dynamic mechanical analysis (d.m.a.) was conducted on a Reobivron DDV-II EP (Orientech Co., Ltd.) analyser to determine the crosslinking density of the copolyimides. Thermogravimetric analysis (t.g.a.) and thermomechanical analysis (t.m.a.) were performed with an SSC-5200 thermal analysis system and an SSC-5670 thermomechanical analysis system (Seiko Electric Co., Ltd.). Tensile modulus was measured by Autograph AG-500A (Shimadzu Co., Ltd.) at a drawing rate of 5 mm min^{-1}. ^{1}H n.m.r. spectra were measured on a Joel GX-400 spectrometer (Joel, Tokyo, Japan) operating at 400 MHz at room temperature. Solid state ^{13}C and ^{29}Si n.m.r. spectra were also measured at room temperature on a Joel GX-400 spectrometer operating at 100 and 80 MHz, respectively. The conversion of the vinyl group in the crosslinking reaction was estimated under the measurement of solid state ^{13}C n.m.r. (c.p./m.a.s.), at a contact time of 2 ms, pulse delay of 5 s and m.a.s. rate of 4 kHz. I.r. spectra were measured on an infrared spectrometer of Type 260-50 (Hitachi Co., Ltd.).

Table 1 Solubility of vinyl-functionalized polysiloxane-*block*-polyimide before and after crosslinking reaction

	Polymer	Polysiloxane (wt%)	Hardener (mol%)	Solvent solubility[a]			
				NMP	THF	$CHCl_3$	$c\text{-}C_6H_4O$
Series of V1-PI	V1-PI-a	V1-PSX 30	–	S	S	S	S
	V1-PI-b	30	TMDS 1.0	S	SW	SW	SW
	V1-PI-c	30	TMDS 2.0	SW	SW	SW	SW
	V1-PI-d	30	TMDS 5.0	IS	IS	IS	IS
	V1-PI-e	30	H-PSX 2.0	IS	IS	IS	IS
	V1-PI-f	30	H-PSX 5.0	IS	IS	IS	IS
Series of V2-PI	V2-PI-a	V2-PSX 10	–	S	S	S	S
	V2-PI-b	10	H-PSX 2.0	SW	IS	IS	IS
	V2-PI-c	30	–	S	S	S	S
	V2-PI-d	30	H-PSX 2.0	IS	IS	IS	IS
	V2-PI-e	50	–	S	S	S	S
	V2-PI-f	50	H-PSX 2.0	IS	IS	IS	IS

[a] S, soluble; SW, swelling; IS, insoluble

RESULTS AND DISCUSSION

Structure analysis of copolyimides

The vinyl-functionalized polysiloxane-*block*-polyimides of V1-PI and V2-PI series (see *Table 1* for their compositions) were prepared by solution imidization of the polyamic acids formed from the reaction mixtures of BTDA/BAPSM/V1-PSX and BTDA/BAPSM/V2-PSX, respectively (*Scheme 1*). The typical ^1H and ^{13}C n.m.r. spectra of the copolyimide V2-PI-a and the starting diaminopolysiloxane V2-PSX in deuterated chloroform ($CDCl_3$) are compared in *Figure 3* and *Figure 4*, respectively. It is known that the proton signals of the vinyl groups of V2-PI-c are separated into two peaks at 5.6–6.0 ppm and 4.7 ppm while those of V2-PSX appear only in the lower magnetic field of 5.5–6.0 ppm. The carbon signals of the vinyl group of V2-PI-c appear at substantially similar magnetic field compared with those of V2-PSX (131.8 and 136.4 ppm). Three signals are detected due to the terminal trimethylene groups of V2-PSX and its repeating unit in the copolyimide in each of the ^1H and ^{13}C n.m.r. spectra. The downfield shift of the proton signal of $N\text{–}CH_2$ for V2-PI-c supports the copolymerization of the V2-PSX units. Similar results were obtained for the copolyimides of V1-PI series prepared from V1-PSX.

The i.r. spectra of the copolyimides showed the

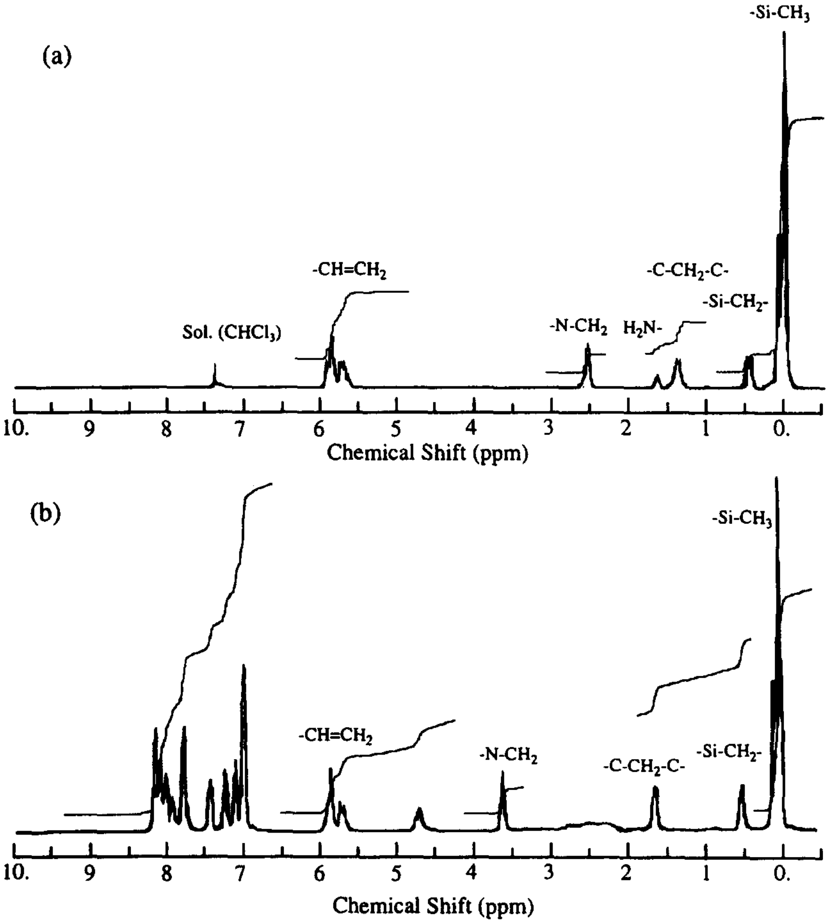


Figure 3 ^1H n.m.r. spectra of (a) V2-PSX and (b) V2-PI-c in $CDCl_3$

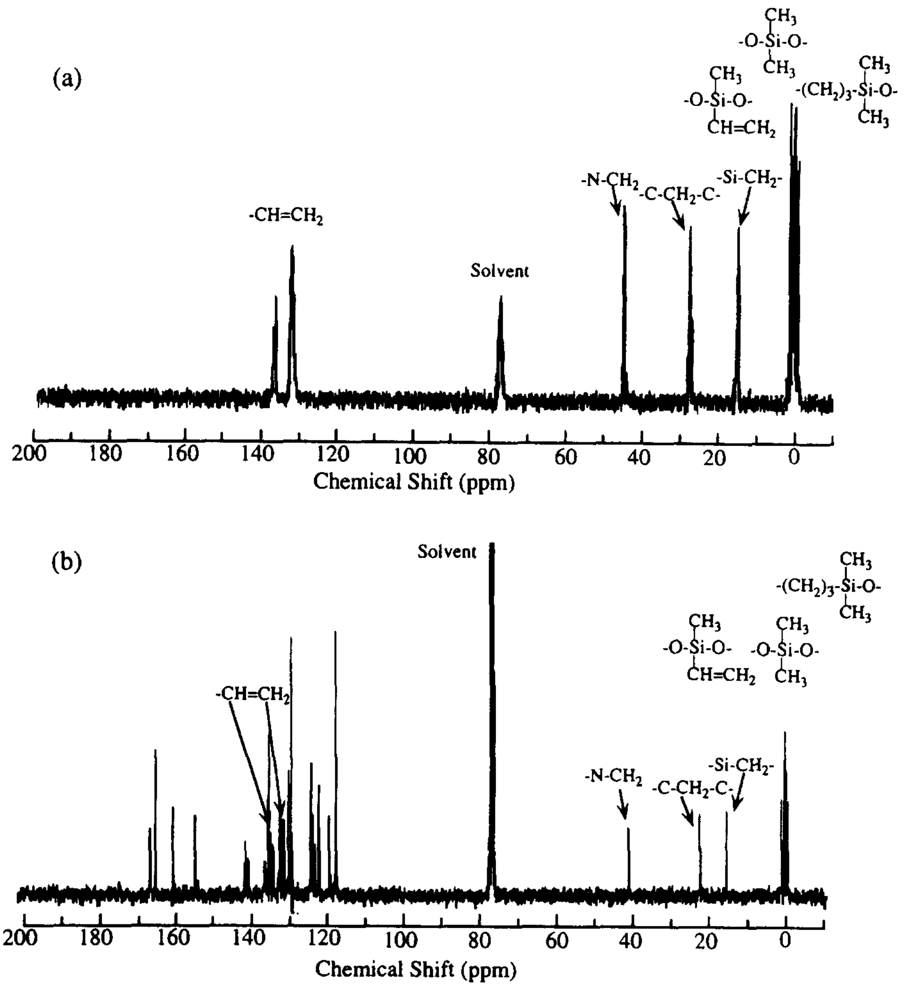


Figure 4 ^{13}C n.m.r. spectra of (a) V2-PSX and (b) V2-PI-c in $CDCl_3$

characteristic bands of the imide carbonyl groups at 1780 and 1725 cm^{-1} as well as those due to the Si–O–Si stretching and the symmetric and asymmetric Si–CH_3 deflections at 1100–1020, 1270–1250 and 900–750 cm^{-1}, respectively. The absorption bands due to the vinyl groups were also detected at 3050, 1600 and 1400 cm^{-1}, respectively[18]. These data also support the formation of the polysiloxane-*block*-polyimides.

Solubility and structure of the crosslinked copolyimides

Both series of copolyimides were reacted with two kinds of hydrosilanes for crosslinking. The crosslinking was accelerated enormously by addition of 0.1–0.2 wt% of H_2PtCl_6 relative to the weight of the hydrosilane compounds[18], because the hydrosilylation of the vinyl groups was accelerated. The solubilities of the copolyimides before and after the crosslinking reactions are summarized in *Table 1*. The original copolyimides showed good solubility in various organic solvents because the intermolecular interaction should be decreased in the presence of the polysiloxane segments[18]. The copolyimides crosslinked with TMDS showed swelling in most of the solvents examined, while those crosslinked with H-PSX lost affinity to the solvents. Therefore, H-PSX is more effective for crosslinking than TMDS because H-PSX contains a number of reactive Si–H functionalities. The affinity to solvent became poorer on increasing the content of the hardeners and the vinyl groups by which a more highly crosslinked structure can be formed. The i.r. spectroscopy of the crosslinked products revealed that the absorption bands due to =C–H and (Si)–CH=CH_2 vibrations were weaker. It was therefore assumed that the vinyl groups had reacted with the hydrosilanes.

This crosslinking reaction was further analysed by solid state ^{13}C and ^{29}Si n.m.r. spectroscopy. *Figure 5* shows the typical wide range solid state ^{13}C n.m.r. spectra of the copolyimides (V2-PI-b,d,f) crosslinked with H-PSX as compared with the spectrum of the original copolyimide V2-PI-a. In each spectrum, broad signals of the aromatic and carbonyl carbons are observed at 120–170 ppm together with many satellite bands which extend from 60–210 ppm. The signals due to the (N)–CH_2–(C) and (Si)–CH_2– carbons of the trimethylene derived from the terminal groups of V2-PSX are also observed around 45, 25 and 15 ppm, respectively. In the spectra of the crosslinked copolyimides, a new signal is detected around 10 ppm, which can be assigned to the carbons of the ethylene bridge formed by the hydrosilylation of the vinyl groups. In particular, the signal is stronger and clearer in the spectra of V2-PI-d and V2-PI-f for which the compositions of V2-PSX are higher. The conversion of the vinyl group by crosslinking was estimated from the integral ratio of the peak at 15 ppm and the methylene signal near 25 ppm.

The solid state ^{29}Si n.m.r. spectra of V2-PI-c and V2-PI-d are shown in *Figure 6*. Three major signals are observed in both spectra. They can reasonably be assigned to the silicon atoms of the methylvinylsiloxane unit (− 35 ppm), dimethylsiloxane unit (− 20 ppm), and alkylene(dimethylsiloxyl) unit (0–12 ppm). Comparison of the spectra reveals that the contents of methylvinylsiloxane units have

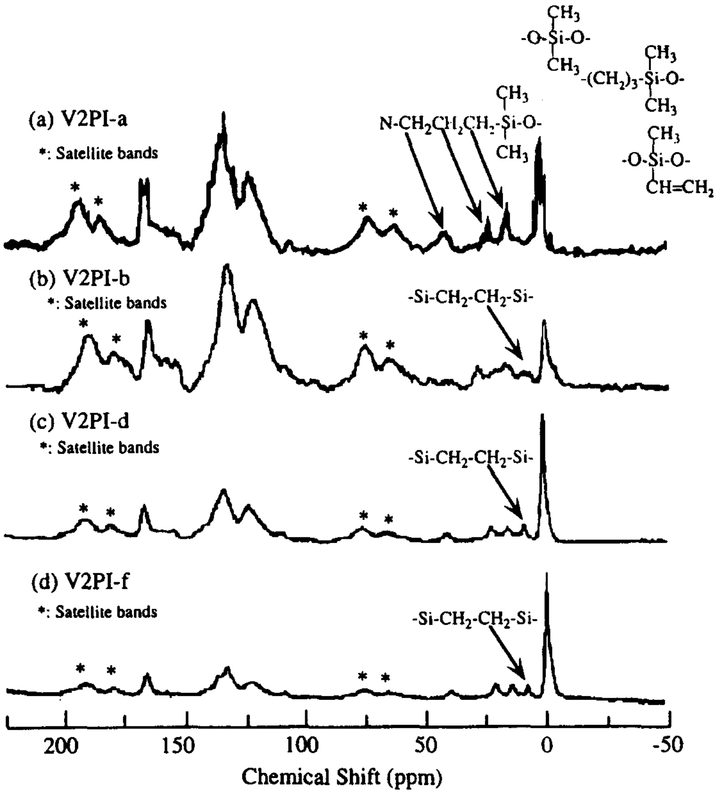


Figure 5 Solid state ^{13}C n.m.r. spectra of the copolyimides of V2-PI series

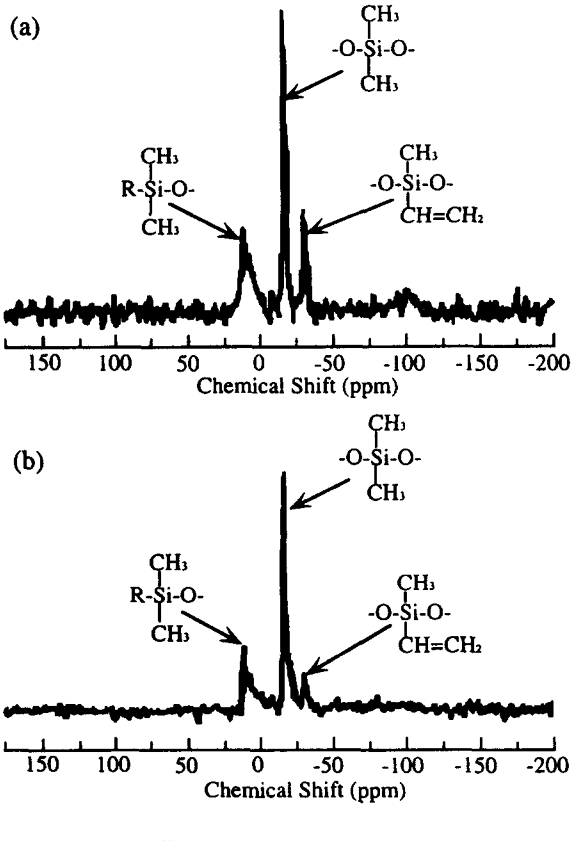


Figure 6 Solid state ^{29}Si n.m.r. of vinyl-functionalized copolyimides (a) V2-PI-c and (b) V2-PI-d

decreased with their hydrosilylation and that the intensity of the signal at -20 ppm has increased relatively. These results support the crosslinking reactions postulated in *2 2*.

Thermal and mechanical properties

The thermal and mechanical properties of the copolyimides before and after the crosslinking reactions were characterized by t.g.a., t.m.a. and d.m.a. Comparison of the t.g.a. curves of V2-PI-c and V2-PI-d (*Figure 7*) suggests that the thermal stability of the copolyimides can be improved significantly with the progress of the crosslinking reaction. The crosslinked structure through bridging (*Scheme 2*) is effective for resisting mass diffusion at high temperature. The heat distortion temperature (T_{hd}) and the thermal expansion coefficients below and above T_{hd} (shown by α_1 and α_2, respectively) of the copolyimides measured by t.m.a. are summarized in *Table 2*. The crosslinked copolyimides (V2-PI-b, V2-PI-d and V2-PI-f) had slightly higher T_{hd} than their original copolyimides (V2-PI-a, V2-PI-c and V2-PI-e) because crosslinking between the soft segments could have little effect on the glass transition of the hard-and-soft segment copolymers of this type. However, the α_1 and α_2 values of the crosslinked copolyimides decreased with increasing crosslinked structure. In particular, the decrease in α_2 was large. The pronounced decrease in α_1 of V2-PI-f relative to that of V2-PI-e may probably be attributed to other factors such as difference in morphological structure[19].

Typical d.m.a. curves of the copolyimides before and after crosslinking reaction are shown in *Figure 8*. The original copolyimide V2-PI-c exhibited the typical behaviour of thermoplastics to lose its modulus above the softening point, whereas the crosslinked copolyimide V2-PI-d retained elastic modulus at a level of 0.03 GPa even

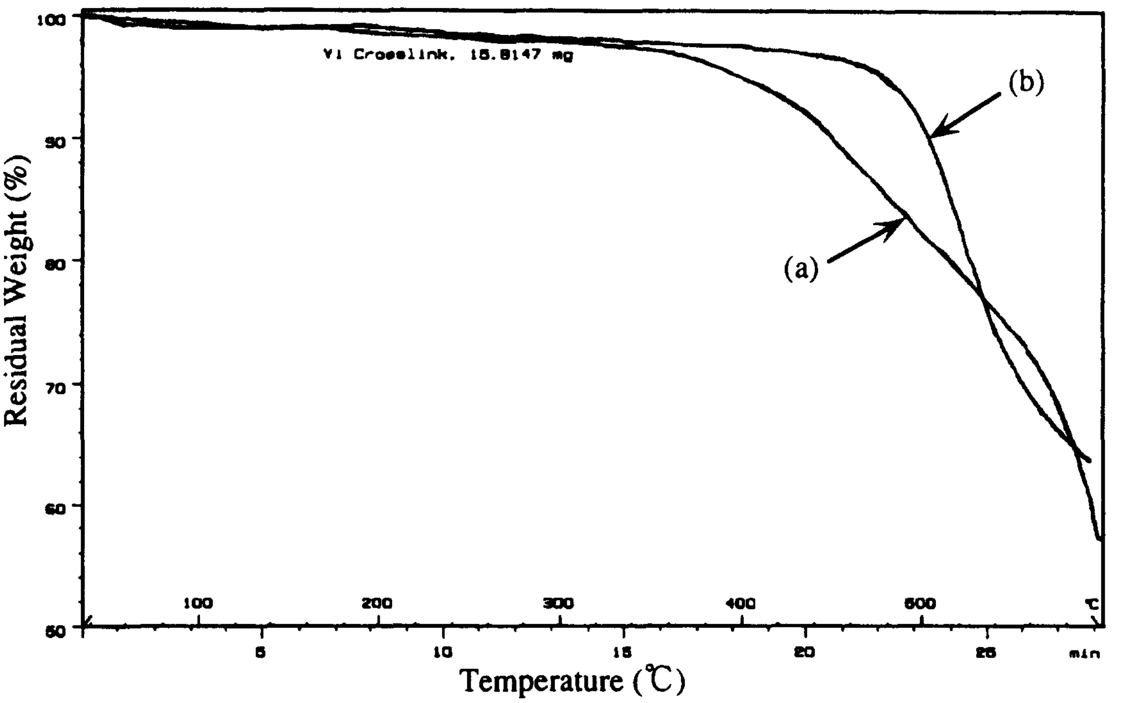


Figure 7 Thermogravimetric analyses of (a) V2-PI-c and (b) V2-PI-d

Table 2 Thermal properties of copolyimides of V2-PI series before and after crosslinking

Polymer	T_{hd}^{a} (°C)	α_1^{b} (ppm °C^{-1})	α_2^{c} (ppm °C^{-1})
V2PI-a	192	182	12900
V2PI-b	192	175	8062
V2PI-c	148	271	7623
V2PI-d	152	123	457
V2PI-e	98	3350	38610
V2PI-f	100	111	342

[a] Heat distortion temperature determined by t.m.a. measurement (10°C min^{-1}, under N_2)
[b] Coefficient of thermal expansion below T_{hd} (range 50–100°C)
[c] Coefficient of thermal expansion above T_{hd} (range T_g–T_g + 50°C)

Table 3 Annealing effect on the progress of crosslinking of V2-PI-b

Temperature[a] (°C)	Heating time[a] (h)	T_g^{b} (°C)	α_1 (ppm °C^{-1})
200	1	201	124
200	5	208	132
300	1	215	133

[a] Heating was carried out under nitrogen atmosphere
[b] Value of glass transition temperature was determined by t.m.a. measurement

above the softening point. The annealing effect on the T_{hd} and α_1 of the copolyimide (V2-PI-b) is summarized in *Table 3*. It is known that T_{hd} increased with increasing annealing time and temperature owing to the progress of crosslinking reaction. However, α_1 also increased slightly. This increase should be attributed to the local structure change which would be induced during the annealing.

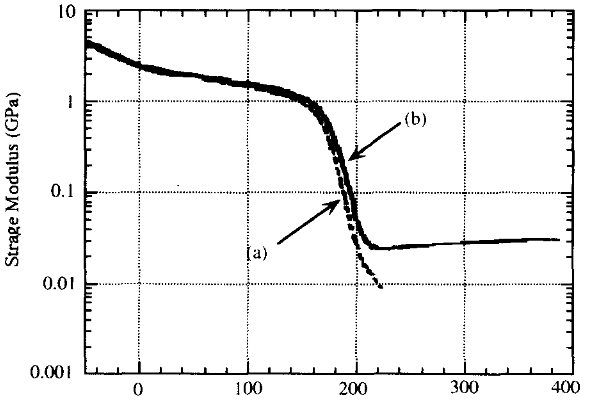


Figure 8 Dynamic mechanical analysis of (a) V2-PI-c and (b) V2-PI-d

The mechanical properties of the copolyimides before and after the crosslinking are summarized in *Table 4*. The tensile modulus and strength of V2-PI-b crosslinked with 10 wt% of V2-PSX were slightly lower than those of the original V2-PI-a. In this case the crosslinking effect by H-PSX cannot have surpassed its plasticizing effect in the copolyimide. On the contrary, both V2-PI-d and V2-PI-f exhibited higher tensile modulus and strength than the original copolyimides. In particular, the increase was very large for V2-PI-f relative to V2-PI-e. If the soft segments are phase-separated and dispersed in particle form in the polyimide matrix, their crosslinking would bring little increase in mechanical properties. If the opposite matrix-dispersion structure is realized with formation of the continuous phase of the soft segments, the crosslinking effect would be significantly larger with progress of crosslinking and exceed the plasticizing effect of the soft segment. The relation between the mechanical properties of V2-PI-f and V2-PI-e, having a polysiloxane composition of 50 wt%, should be due to this different morphological structure, while the relation between V2-PI-d and V2-PI-c, having a polysiloxane composition of 30 wt%, should be explained by the crosslinking of the phase-separated particles[19]. The copolyimides possessed two different glass transition temperatures (see *Figure 8*). One was attributed to the polysiloxane phase in the lower temperature

Table 4 Mechanical properties, conversion of vinyl groups, and crosslinking density of the copolyimides of V2-PI series before and after crosslinking

Polymer number	Hardener (mol%)	Tensile modulus (GPa)	Tensile strength (MPa)	Conversion of vinyl groups[a] (mol%)	Crosslinking density[b] ($\times 10^{-3}$ mol cm^{-3})
V2PI-a	H-PSX 0	2.73	79.4	–	–
V2PI-b	H-PSX 1.0	2.67	68.7	16	0.42
V2PI-c	H-PSX 0	1.37	41.2	–	–
V2PI-d	H-PSX 2.0	1.47	44.1	44	0.70
V2PI-e	H-PSX 0	0.35	11.8	–	–
V2PI-f	H-PSX 2.0	0.77	19.6	72	1.01

[a] Calculated from the results of ^{13}C n.m.r. measurement

[b] Calculated from the results of d.m.a. measurement by the Mooney–Rivlin equation: $E = 3dRT/Mc = 3\rho RT$, $\rho = d/Mc$

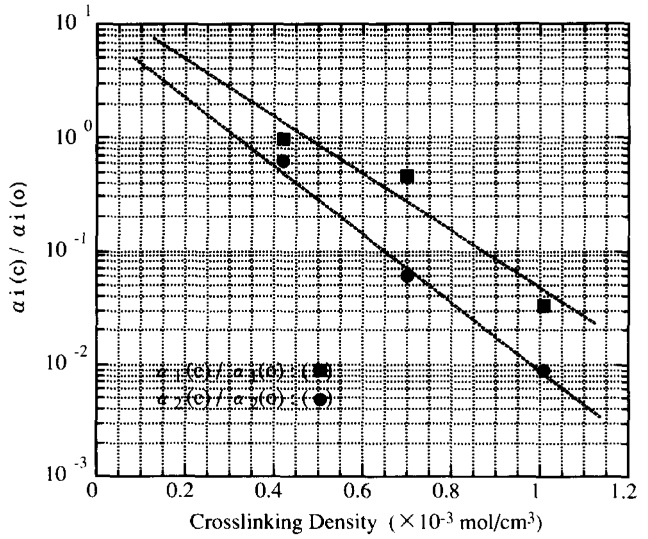


Figure 9 Relationship between crosslinking density and ratio of coefficients of thermal expansion of crosslinked (α_i(c)) and original (α_i(o)) copolyimides

range (T_{g1}) and the other was for the aromatic component in the higher temperature range (T_{g2}). It is suggested that the shift of T_{g1} and T_{g2} is dependent on the compatibility between the polysiloxane and aromatic components. The storage modulus of the copolyimides with a polysiloxane composition less than 30 wt% was of the order of 1 GPa, while that of the copolyimides with a polysiloxane composition of 50 wt% was significantly lower. The copolyimides showed two drops of storage modulus corresponding with two peaks of loss modulus, while the polysiloxane-free PI showed a very small drop at the lower temperature region of − 100°C. As reported before[19], the change of peak height in loss modulus are related to the morphological differences of the copolyimides. It should be noted here that the morphological changes were further supported by scanning electron microscopy (s.e.m.), atomic force microscopy (a.f.m.) and d.m.a. measurements as previously reported[1,2,6,7,19]. The aforementioned increase in α_1 should also be related to this phase separation in which the crosslinking effect was compensated by the increased phase separation of the soft segment during the annealing.

Crosslinking density

As mentioned above, the conversion of the vinyl groups was estimated by the solid state ^{13}C n.m.r. spectra, and the crosslinking density was calculated by applying the d.m.a. data to the Mooney–Rivlin equation (see *Table 4*)[20]. The crosslinking density increased with increasing concentration of the vinyl groups which was in accordance with the composition of V2-PSX in the copolyimides. *Figure 9* shows the relations between the crosslinking density and the ratios of the thermal expansion coefficients, $\alpha_1(c)/\alpha_1(o)$ and $\alpha_2(c)/\alpha_2(o)$, where $\alpha_i(c)$ and $\alpha_i(o)$ denote the thermal expansion coefficients of the crosslinked copolyimides and the original copolyimides below ($i = 1$) or above ($i = 2$) T_{hd}, respectively. The ratios of the thermal expansion coefficients are exponentially decreased with increasing crosslinking density. This fact should strongly support the proposal that the inferior effect arising from the introduction of soft segment should be compensated by the crosslinking.

CONCLUSIONS

The novel polysiloxane-*block*-polyimides containing vinyl-functionalized polysiloxane segments were successfully synthesized, and their crosslinking was carried out with hydrosilane compounds. The structures of the original crosslinked copolyimides were analysed by solid state ^{13}C and ^{29}Si n.m.r. spectroscopy. The solubility and thermal and mechanical properties of the copolyimides before and after the crosslinking reactions were also characterized by t.g.a., t.m.a. and d.m.a. The properties of the copolyimides after the crosslinking were well explained both by the phase separation structure and the crosslinking density.

ACKNOWLEDGEMENTS

The authors would like to thank Dr K. Saito and Mr M. Shinohara of The Advanced Technology Research Laboratories, Nippon Steel Corporation, for their help in the analysis of the solid state ^{13}C and ^{29}Si n.m.r. spectra.

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