

ORGANOSILANE POLYMERS: SYNTHESIS AND CROSSLINKING OF FORMABLE POLYMERS CONTAINING PHENYLSILYLENE UNITS

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ABSTRACT

Polysilane polymers which contain silicon hydride units in the chain were synthesized by sodium coupling of PhHSiCl_2 with $\text{R}^1\text{R}^2\text{SiCl}_2$ in toluene (R^1 and R^2 alkyl, aryl or aralkyl), followed by termination with a monochlorosilane and neutralization with sodium bicarbonate solution. These polymers are soluble in common solvents and can be formed into a variety of shapes by molding, casting, coating or potting. This class of polymers can be crosslinked by oxidation and irradiation, or by reaction with a multifunctional vinylsilane in the presence of platinum complexes.

INTRODUCTION

Recently, there has been considerable interest in organosilane polymers as precursors for β -SiC fibers^[1,2], as impregnating agents for strengthening ceramics^[3], and as dopable semiconductors^[4]. A series of tractable organosilane polymers have been prepared, and their photocrosslinking has been discovered.^[2,5-11] Crosslinking is very important to the applications mentioned above, both because the crosslinked polymers will retain their shapes in further processing to useful materials and because crosslinking is needed for successful conversion to silicon carbide. However, upon irradiation of the polymers with ultraviolet light degradation takes place along with, and usually predominates over, crosslinking. Although some organosilane polymers are easily crosslinked by oxidation^[12], their applications may be limited by the presence of oxygen atoms in the crosslinking bridges.

We have synthesized a new class of organosilane homopolymers, $\text{M}-(\text{PhHSi})_n\text{M}$ ($\text{M} = \text{MePh}_2\text{Si}$, MePhViSi or Ph_2ViSi), and copolymers, $\text{M}-(\text{PhHSi}-(\text{R}^1\text{R}^2\text{Si})_m)_n\text{M}$, in which R^1 and R^2 are alkyl, aryl or aralkyl groups. The resulting polymers have the same useful properties as polysilane polymers reported previously, but can be fully crosslinked by various reactions which establish a network of crosslinked polymer through Si-C or Si-Si bridges. Some of these polymers are flowable liquids, so that they can be formed into any desired shape by casting, coating or potting. In this article we describe a new method for the synthesis and workup of these polymers, which avoids the formation of Si-O groups. Their properties will be compared with those of a polymer prepared from PhSiHCl_2 by the earlier method, and containing Si-OH functions along the chain and in the terminating groups (Table 1). The characterization and crosslinking of phenylsilane polymers are also described.

EXPERIMENTAL

Syntheses of the polymers

A 500 mL three-necked, round-bottomed flask was set up with a motor driven stirrer, an efficient reflux condenser, and a pressure equalizing dropping funnel. This apparatus was thoroughly dried and a positive pressure of argon was introduced through the top of the condenser, so that all the air in the apparatus was displaced with argon. All subsequent operations were carried out under argon, and at all points, the reaction mixtures were protected from light.

Dry toluene, 60 mL, and 4.85 g of sodium metal were added to the flask carefully so as to avoid exposure to moisture and air as much as possible. The flask and contents were degassed using a stream of argon. Distilled phenyldichlorosilane (14.6 mL, 0.10 mol) was transferred to the dropping funnel using a syringe. The flask was heated until the sodium metal melted and the toluene refluxed gently, whereupon the stirrer was turned on at high speed to create a sodium dispersion. The heating mantle was then removed and the phenyldichlorosilane was added dropwise at a rate which maintained vigorous refluxing. Addition required about 5 min, during which time the reaction mixture turned from gray to dark purple.

Progress of the reaction was followed by taking small samples of the solution and of the solid suspension, washing them with water and checking the pH of the water with pH test paper. The mixture was refluxed for several days, until the solution no longer tested acidic, indicating that all the soluble Si-Cl had been consumed. (At this point the suspension tests alkaline.) Excess $R_2R'SiCl$ was then added and refluxing and stirring were continued until the solid suspension no longer tested alkaline, indicating that all Si-Na bonds in the solid had been used up in coupling. About 24 h was usually required. The mixture was then cooled and aqueous sodium hydrogen carbonate was added slowly with stirring, until the solution again tested neutral.

The reaction vessel was cooled to room temperature and the organic layer was washed quickly with two 250 ml portions of water, then separated and dried with anhydrous calcium chloride. The solvent was then stripped off on a rotary evaporator at 50°C under reduced pressure. After most of the toluene was removed, 50 ml of tetrahydrofuran (THF) was added. To precipitate the polymer, a mixture of 200 ml of 2-propanol and 400 ml of methanol was slowly added dropwise with stirring to the THF solution. The precipitate was separated and dried in a vacuum oven (ca. 1 Torr) at 50°C for 2 h. The polymer (2) was finally obtained as white powder and stored in a brown glass bottle.

Other polymers listed in Table 1 were prepared similarly. For polymer (4), it was necessary to centrifuge the toluene solution and decant before stripping, because an insoluble fraction was formed in this case.

Characterization

Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with four Microstyrigel columns of the following pore sizes, in Å: 10^6 , 10^5 , 10^4 , 10^3 and with a Waters Associates Model 440 ultraviolet (UV) absorbance detector set at 254 nm, using THF or toluene as the eluant. Data on molecular weights listed in Table 1 are relative to polysilastyrene standards for which preparation and molecular weight determination have been reported

recently^[2]. Infrared (IR) spectra were measured from 4000 to 300 cm^{-1} on KBr pellets with a Perkin-Elmer 457 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were examined in deuteriochloroform (CDCl_3) on a JEOL MH-100 spectrometer. The value of m , the ratio of $\text{R}^1 \text{R}^2 \text{Si}$ to PhHSi units in the copolymers, was determined by integration of the proton NMR signals for the different groups. A JEOL FX-60 Fourier transform NMR spectrometer was used to obtain ^{13}C NMR spectra. UV spectra were determined in spectrograde THF or cyclohexane using a Cary Model 118 spectrophotometer. The assignment of peak positions was assisted by taking the first derivative of those spectra that contained overlapping peaks.

Catalysts and crosslinkers

Distilled tetravinylsilane (20g) was placed in a round bottomed flask with a condenser, dried throughout with dry nitrogen. Chloroplatinic acid (0.1 g) was quickly added to the flask. The mixture was heated to 60°C for 0.5h, during which time some of the chloroplatinic acid reacted with the tetravinylsilane along with evolution of gas, while the rest of chloroplatinic acid deposited as platinum black. The reaction mixture was cooled to room temperature and washed with water to neutral. The organic layer was dried overnight with anhydrous calcium chloride, then filtered through a sintered glass funnel. The resulting solution of platinum complex in tetravinylsilane(A) served as both crosslinker and catalyst for the addition reaction of silicon hydrides in the polymer chain to vinyl groups of the crosslinker.

Solutions of platinum complex in trivinylmethylsilane (B), dimethyldivinylsilane (C) and 1,4-

Table 1 Syntheses and composition of these polymers

No.	Polymer $M-[\text{PhHSi}-(\text{R}^1\text{R}^2\text{Si})_m]_n\text{M}$			$\frac{\text{R}^1\text{R}^2\text{SiCl}_2}{\text{PhHSiCl}_2}$	Yield Wt. %	M_w max ^{a)}	m	Appearance
	R^1	R^2	M					
1	OH	Ph	OH or H	—	55	1,000	0.8596	white powder
2	—	—	MePh_2Si	—	56	1,000	—	white powder
3	—	—	MePhViSi	—	58	1,000	—	white powder
4	Me	Me	MePh_2Si	1.0	45	1,200	0.6250	white powder
5	Ph	Ph	MePh_2Si	1.0	48	900	— ^{b)}	white powder
6a	Me	Ph	MePh_2Si	1.0	53	1,000	0.6914	white powder
6b	Me	Ph	MePh_2Si	5.0	48	1,100	4.473	white powder
7a	Me	PhCH_2CH_2	MePh_2Si	1.0	34	1,000	1.149	resinous solid
7b	Me	PhCH_2CH_2	MePh_2Si	5.0	37	1,200	5.362	resinous solid
8a	Me	C_6H_{11}	MePh_2Si	1.0	36	1,100	0.7003	white powder
8b	Me	C_6H_{11}	MePh_2Si	5.0	38	1,300	5.260	white powder
9a	Me	$\text{CH}_3(\text{CH}_2)_5$	MePh_2Si	1.0	52	1,000	0.9132	grease
9b	Me	$\text{CH}_3(\text{CH}_2)_5$	MePh_2Si	5.0	46	1,400	4.831	fluid
9c	Me	$\text{CH}_3(\text{CH}_2)_5$	Ph_2ViSi	10.0	40	1,500	10.85	fluid

^{a)} From GPC elution volume, relative to polysilastyrene^[2].

^{b)} No proton NMR signal for Si-H groups appeared (see Fig. 2 and Table 5), therefore it was not possible to determine m .

divinyl-1,1,4,4-tetramethyl-disilylethylene (D) were prepared similarly.

Crosslinking of the polymers

Photocrosslinking The solid polymers (1 g) were dissolved in approximately two times the amount of THF. Tetravinylsilane (0.15 g) or 0.20 g of trivinylsilane was added into the solution, and the THF was evaporated thoroughly on a glass plate which was protected from light. A thin film of the mixture was obtained. For flowable polymers (9a)–(9c) (Table 1), the mixing was accomplished by stirring them along with the requisite amount of the crosslinker, followed by pouring the mixture on a glass plate to form a thin film. The films were exposed on UV light at 254 or 300 nm under argon for 2 h. The crosslinked films so produced were immersed in THF for two days, then dried in a vacuum oven (ca. 1 Torr) at 50°C for 2 h.

Oxidative crosslinking The polymers as fine powder were heated in air at 120°C for 2 h, during which time the polymers turned from white to yellow. These crosslinked polymers were immersed in THF for two days and weight losses were measured.

Room temperature vulcanization (RTV) The polymers (1 g) were mixed with 0.1 g of component (A) or 0.12 g of (B) by the procedure described in the photocrosslinking. The mixture obtained stood in air at room temperature for 24 to 72 h. The soluble fraction was abstracted by immersion of the crosslinked polymer in THF for two days.

RESULTS AND DISCUSSION

Syntheses and structures

According to IR and proton NMR analysis, as shown in Tables 1, 2, 5 and Figures 1 and 2, polymer (1) made from PhHSiCl_2 by the usual coupling procedure reported previously^[2,7], had not only hydroxyl end groups, but also Si–OH groups on the chain. The ratio of PhSiOH to PhSiH units, m , was as high as 0.8596. These Si–OH groups in the chain presumably resulted from hydrolysis of Si–H groups. When the reaction mixture was washed with water, sodium hydroxide was formed from both unreacted and chain-terminal sodium. The silicon hydride interacted with water in the presence of alkali and produced the silanol and hydrogen^[13]. This is in agreement with finding that a large amount of gas was evolved during washing of the polymer.

In the modified synthesis used for polymers (2)–(9c) after dichlorosilanes and chlorine end groups of the polymer were all reacted, Ph_2RSiCl (R = methyl or vinyl) or MePhViSiCl was added to the flask. The additional monochlorosilane reacted with any excess sodium metal and with silyl anions at the termini of the polymer chains. The excess monochlorosilane was finally neutralized with sodium bicarbonate. As a result the Si–H bonds in the polymer did not hydrolyze during the water washing in the workup. The polymers so obtained, (2)–(9c), showed only a sharp IR absorption peak at about 2100 cm^{-1} , characteristic of the Si–H group, and no detectable hydroxyl group (see Figure 1 and Tables 2–4).

The methyl proton resonances (Table 5) and IR absorptions (Tables 2 and 3) for polymers (2), (3) and (5) verified the existence of MePh_2Si or MePhViSi end groups on these polymer chains, as reported in Table 1. However, molecular weights that were calculated with contents of the end groups from ^1H NMR analysis always were approximately two times as high as those from GPC for

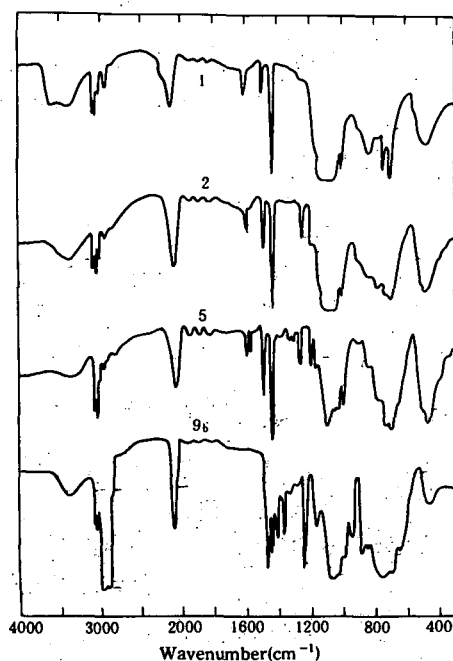
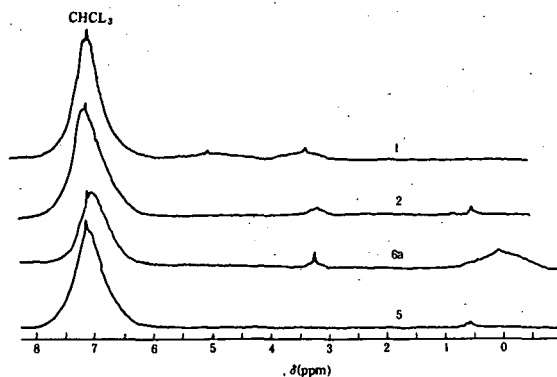
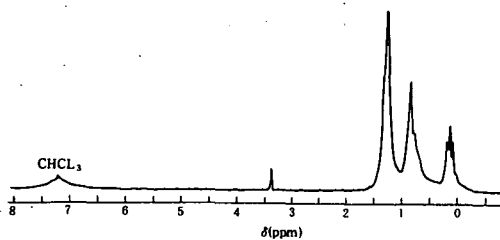


Fig. 1 Typical IR spectra of the polymers

the polymers, indicating that these polymers in fact were a mixture of the $R_2R'Si$ -ended polysilanes with large cyclopolysilanes. In addition, the IR (Tables 2–4), ^1H and ^{13}C NMR (Table 5) spectra for these polymers all were consistent with the structures proposed^[5,6,14–17]. In polymers (3) and (9c), very small amounts of products resulting from addition reaction of unsaturated groups of the terminators in the presence of sodium were also observed.

Fig. 2 ^1H NMR spectra of polymers (1), (2), (6a) and (5) in $CDCl_3$ Fig. 3 ^1H NMR spectrum for polymer (9a) in $CDCl_3$

These polymers were synthesized in appreciable yields, and except (4), for which 4% insoluble polymer was produced, no insoluble fraction was formed. All of the polymers have low molecular weights, and in contrast to those copolymers containing diphenylsilylene units^[11], in

which molecular weights increased markedly with increment of the ratios of corresponding organodichlorosilanes to diphenyldichlorosilane, molecular weights for these polymers were generally unchanged as the ratios of $R^1R^2SiCl_2$ to $PhHSiCl_2$ increased. Like polymer (1), polymers (2)–(9c) also displayed a monomodal, narrow molecular weight distribution. The ratios ($\bar{m}$) of R^1R^2Si to $PhHSi$ units in these polymers were generally close to the ratios of $R^1R^2SiCl_2$ to $PhHSiCl_2$ employed in the cocondensation that led to their formation.

Table 2 Infrared absorptions of polymers (1)–(3)

Absorption (cm^{-1})			Assignment
(1)	(2)	(3)	
3630(w)			HO-Si stretch
(3445)	(3440)	(3440)	(absorbed H_2O)
3080(w)	3080(w)	3075(m)	CH (phenyl) stretch
3062(w)	3060(w)	3058(m)	
3040(w)	3030(w)	3020(w)	
		2962(w)	CH_3 -Si stretch
2938(w)			chelated OH
		2920(w)	CH_2 stretch
2120(w)	2110(m)	2095(m)	H-Si stretch
1960(w)	1958(w)	1955(w)	phenyl-Si
1890(w)	1890(w)	1885(w)	
1820(w)	1820(w)	1820(w)	
1600(w)	1595(w)	1590(w)	phenyl skeletal ring breathing
1490(w)	1487(w)	1485(w)	
1435(s)	1433(s)	1430(s)	
		1407(w)	CH_2 = in-plane deformation
	1265(w)	1255(m)	CH_3 -Si deformation
1140	1130	1130	CH (phenyl) in-plane deformation
(s)	(s)	(s)	
1030	1030	1020	
1000(m)	1000(m)	1000(m)	or Si-O stretch
		900(w)	$CH_2 = CH$ -Si
850(m)	850(m)	850(sh)	H-Si deformation
795(m)	790(m)	780(s)	CH (phenyl) out-of-plane deformation
740(s)	740(s)	738(s)	
700(s)	700(s)	690(s)	
485(m)	490(s)	475(s)	Si-C stretch
			Si-Si stretch

Table 3 Infrared absorptions for polymers (4)–(6)

Absorption (cm ⁻¹)			Assignment
(4)	(5)	(6a)	
(3450)	(3445)	(3440)	(absorbed H ₂ O)
3080(w)	3080(m)	3078(m)	CH (phenyl) stretch
3060(w)	3062(m)	3058(m)	
3030(w)	3020(w)	3025(w)	
2968(w)		2960(m)	CH ₃ -Si stretch
2100(m)	2104(w)	2092(m)	H-Si stretch
1960(w)	1960(w)	1950(w)	phenyl-Si
1890(w)	1890(w)	1885(w)	
1820(w)	1820(w)	1815(w)	
1597(w)	1590(w)	1588(w)	phenyl skeletal ring breathing
	1570(w)	1570(w)	
1490(w)	1490(m)	1486(m)	
1434(s)	1435(s)	1430(s)	
		1410(m)	
1267(m)	1265(w)	1260(sh)	CH ₃ -Si deformation
1250(m)		1250(s)	
1140	1103(s)	1100(s)	CH(phenyl) in-plane deformation
(s)	1072(s)	1070(s)	
1030	1035(s)	1030(s)	
1003(m)	1005(s)	1000(s)	
840(m)	854(w)	850(w)	H-Si deformation
805(m)	795(m)	780(s)	CH(phenyl) out-of-plane deformation
740(m)	738(s)	730(s)	
700(s)	700(s)	695(s)	Si-C stretch
		660(s)	
	521(m)		Si-Si stretch
485(m)	475(s)	473(s)	

Table 4 Infrared absorptions of polymers (7)–(9)

Absorption (cm ⁻¹)			Assignment
(7a)	(8b)	(9b)	
3445	(3450)	(3450)	(absorbed H ₂ O)
3080(m)	3080(w)	3080(w)	CH (phenyl) stretch
3065(m)		3065(w)	
3042(m)	3043(w)	3040(sh)	
2972(s)		2975(vs)	CH ₃ -Si stretch
2940(s)	2935(vs)	2928(vs)	CH ₂ stretch(a)
2880(sh)	2860(s)	2868(vs)	CH ₂ stretch(s)
2100(m)	2095(m)	2096(m)	H-Si stretch
1958(w)	1950(w)	1960(w)	phenyl-Si
1890(w)	1880(w)	1890(w)	
1820(w)	1810(w)	1820(w)	
1608(m)	1607(w)	1473(s) 1435(m) 1417(m) 1386(m)	skeletal ring breathing
1500(m)	1500(m)		
1460(m)	1452(m)		
1437(s)	1435(w)		
			CH ₃ (-C) deformation(a)
			CH ₃ (-C) deformation(s)
1267(m)	1250(m)	1252(s)	CH ₃ -Si deformation
	1175(w)	1185(m)	(CH ₂) _{n>4} deformation
1140	1100(m)	1100(s)	CH (phenyl) in-plane deformation cyclohexyl-Si n-hexyl-si
	1075(m)	1030(s) 1000(s) 960(m) 880(m)	
(s)	1040(m)		
	1000(m)		
1000			
	890(w)		
850(m)	850(w)	850(m)	H-Si deformation
790(m)	775(m)	770(s)	CH (phenyl) out-of-plane deformation
	750(m)	700(s)	Si-C stretch
690(m)	700(s)	670(m)	
480(m)	545(w)	475(w)	Si-Si stretch

Table 5 ^1H - and ^{13}C -NMR chemical shifts for the polymers^a

Polymer	^1H (ppm)	^{13}C (ppm)	Assignment
(1)	3.39(vb)		Si-H
	5.13(vb)		Si-OH
	7.11(vb, m)	127.7, 129.9, 134.0(b), 135.9(b) 136.6(b) }	Si-C ₆ H ₅
(2)	0.51(vb, m)		Si-CH ₃
	3.24(b)		Si-H
	7.16(vb, m)	127.7, 129.7, 133.4(b), 134.6(b) 136.2(b) }	Si-C ₆ H ₅
(3) ^b	0.05(vb, m)	- 0.11(b), - 1.54(b, m)	Si-CH ₃
	3.22(b)		Si-H
	7.23(vb, m)	127.5, 128.9(b), 133.1(b), 135.8(b) 136.3(b) }	Si-C ₆ H ₅
(4)	0.36(vb, m)	- 3.58(b), 1.21(b, m)	Si-CH ₃
	3.24(b)		Si-H
	7.24(vb, m)	127.8(b), 134.2(b), 136.4(b)	Si-C ₆ H ₅
(5)	0.54(vb, m)		Si-CH ₃
	7.10(vb, m)	124.5(b), 127.5(b), 133.7(b), 136.8(b) }	Si-C ₆ H ₅
(6a)	0.02(vb, m)	- 6.44(vb, m)	Si-CH ₃
	3.26(b)		Si-H
	7.07(vb, m)	127.4, 128.1(b), 133.2(b), 134.9(b) 136.3(b) }	Si-C ₆ H ₅
(7a) ^c	0.17(b) }	- 3.69(b), - 0.61(b), 1.04(b)	Si-CH ₃
	0.45(b) }		
	1.37(b)	17.01(b)	Si-CH ₂ -
	2.75(b)	32.38(b)	-CH ₂ -
	3.80(b)		Si-H
	7.21(vb, m)	125.4(b), 127.5, 133.5(b), 134.3(b) 136.2(b), 144.3(b) }	Si-C ₆ H ₅ , (C)-C ₆ H ₅
(8b)	0.26(vb) }	1.98(b)	Si-CH ₃
	0.44(vb) }		
	1.32(b)	27.20(b)	Si-C ₆ H ₁₁
	1.82(b)	28.96(b), 31.49(b) }	
	3.46(b)		Si-H
	7.25(vb, m)	127.5(b), 133.9(b), 136.8(b)	Si-C ₆ H ₅
(9b)	0.17(b) }	- 6.99(b), - 3.80(b)	Si-CH ₃
	0.23(b) }		
	0.28(b) }		

Table 5 (Continued)

Polymer	^1H (ppm)	^{13}C (ppm)	Assignment
(9b)	0.94(b)	14.21, 15.30	$\text{Si}-\text{CH}_2 \cdots \text{CH}_3$
	1.39(b)	22.80, 26.98, 31.77, 33.69(b)	$(-\text{CH}_2)-_4$
	3.46		Si-H
	7.29(vb, m)	127.5(b), 133.0(b), 134.1(b), } 136.6(b)	Si-C ₆ H ₅

^a (b) broad; (vb) very broad; (m) multiplet.

^b A second set of detectable resonances was shown as follows:

^1H -NMR δ 0.95, 1.73; ^{13}C -NMR δ 13.54, 25.49 and 50.66. These peaks were assigned to $\text{Si}-\text{CH}_2$, $-\text{CH}_2-$ and $-\text{CH}-$ as a result of addition reactions of unsaturated groups from MePhViSiCl .

^c Two smaller ^{13}C -NMR peaks at 19.33 and 29.02 ppm almost always appeared for the polymers containing methyl (β -phenethyl) silylene units^[8].

Characteristics

As can be seen from Figures 1 and 2, in comparison to polymer (2) without hydroxyl group, polymer (1) showed a broader IR absorption for Si-H group at 2120 cm^{-1} along with Si-OH peak at 3630 cm^{-1} and very broad ^1H NMR peaks for Si-H and Si-OH, perhaps due to an interaction between Si-H and Si-OH groups. All of the polymers which had no hydroxyl groups invariably exhibited sharp IR absorptions for Si-H at about 2100 cm^{-1} . In the ^1H NMR spectra, on the other hand, homopolymer (2), (3) and copolymer (6a) which contained high content of the Si-H and phenyl groups attached to silicon atoms displayed a broad Si-H signal at about 3.24 ppm. No visible Si-H proton resonance peak was observed for the diphenylsilylene-contained copolymer (5). However for the rest of the copolymers, especially those copolymers that contained dialkylsilylene units, for instance (9b), the Si-H proton resonance was very sharp, as shown in Fig. 3. This may be related to an effect of the phenyl groups attached to silicon atoms on the shielding of nearby Si-H groups.

In consistent with those of other high molecular weight organosilane polymers that were described earlier^[2,7-11], all ^1H (except some Si-H) and ^{13}C (except for *n*-hexyl groups) resonance peaks were broad (Table 5), and both phenyl and methyl proton resonances were exceptionally broad and appeared to consist of three or more overlapping peaks (Figures 2 and 3). The broad and multiple resonances observed for these polymers may indicate the existence of regions of more than one stereoregular polymer conformation. Hindered rotation in the polymeric chains may also lead to nonequivalence of various nuclei^[18].

The UV spectral absorptions and typical spectra for these polymers were reported in Table 6 and Figure 4. Homopolymers (2) and (3) only showed the usual phenyl absorption at about 258 nm, similar to that of (1). The introduction of $\text{R}^1\text{R}^2\text{Si}$ units shifts the absorption maxima (λ_{max}) to longer wavelengths. The bathochromic shift, in general, is related to increased conjugative interreactions between aryl and alkyl substituents and the silicon spiral chain which acts as a $\sigma-\sigma^*$ or $\sigma-\pi$ chromophore.^[19-23] Therefore, copolymer (5) with diphenylsilylene units displayed the

longest wavelength λ_{max} . For copolymer (7) containing phenyl groups separated from the silicon by two CH_2 groups, this shift was small, rather similar to those of the copolymers with alkyl groups. Those copolymers which had different m ratio of some $\text{R}^1\text{R}^2\text{Si}$ to PhHSi units, for example copolymers (8a) and (8b), showed quite different UV spectra. Like other cyclohexylsilane polymers, (8a) and (8b) also showed unusually low energy UV absorptions.

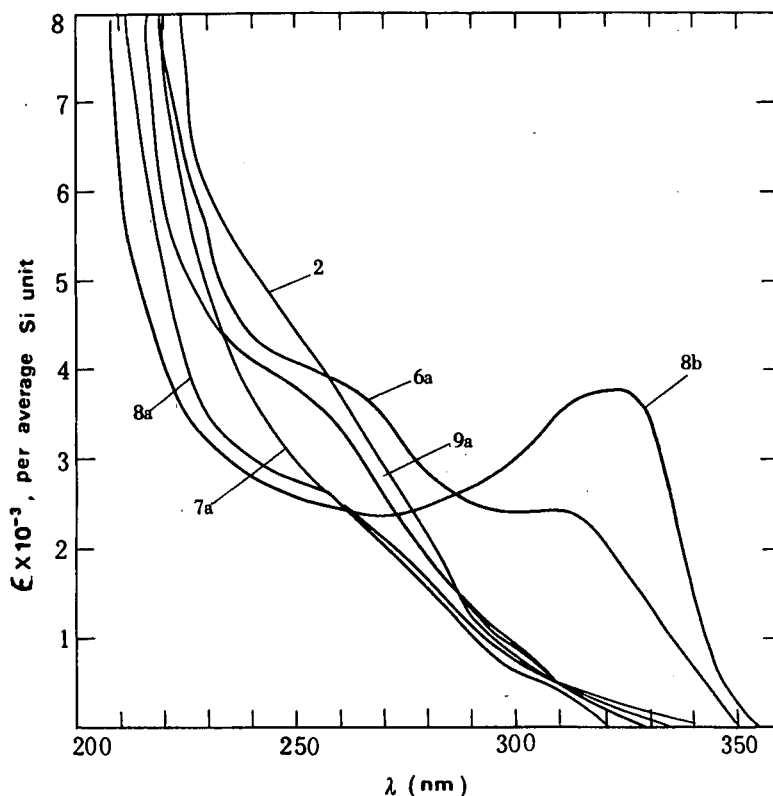


Fig. 4 UV spectra for polymers

Among these polymers, (9a)–(9c) are flowable liquids, and the rest all are solids (Table 1). They are readily soluble in common solvents, for instance benzene, toluene, THF and chloroform (polymer (8b) is not soluble in THF, but is soluble in cyclohexane). They can be formed into a variety of shapes by molding, casting, coating or potting.

Table 6 UV Absorption properties for polymers

Polymer	λ_{max}	$\epsilon \times 10^{-3}^a$
(1)	258	3.3
(2)	258	3.9
(3)	260	2.8
(4)	299	1.4
	258	3.3
(5)	325	— ^b
	259	— ^b
(6a)	316	2.3
	263	3.8
(7a)	305	0.5
	258	1.3
	265	2.3
(8a)	309(sh)	0.5
	260	2.5
(8b)	323	3.8
	258	2.5
(9a)	300(sh)	0.9
	255	3.6
(9b)	300	0.9
	270	1.7
	240	2.4

^a) per average Si unit.

^b) It was not possible to calculate ϵ value for lack of m datum (see Table 1).

Crosslinking

Photocrosslinking Irradiation of these polymers with UV light of wavelength 254 or 300 nm in air led rapidly to photoscission, as shown by a decrease in the molecular weight determined by GPC, but in argon or vacuum some insoluble particles were formed along with degradation. Polymers of this type appeared to undergo more photocrosslinking than those without silicon hydride groups which were described previously. Among these polymers greater crosslinking was observed for homopolymers (2) and (3) than for any of the others. Among sets of copolymers containing the same R^1R^2Si units, the copolymers with high PhHSi content afforded more crosslinked product than those with low PhHSi, and for copolymers containing different R^1R^2Si units the phenyl-containing polymers underwent more crosslinking than the alkyl-containing polymers. The mechanism of photocrosslinking is still obscure, but these results suggest that the crosslinking arises from initial scission of the polymer to silyl radicals upon UV irradiation, followed by abstraction of hydrogen atoms either from Si-H groups or from aromatic rings^[24-26]. A disadvantage of photocrosslinking is that some degradation always occurs along with the

crosslinking (soluble fraction was as high as 40–60% after immersion of the crosslinked polymers in THF for two days).

However, when the polymers which were mixed with tetravinylsilane or trivinylmethylsilane were irradiated on UV light under argon, they were almost entirely converted to insoluble films (soluble fraction after immersion was only 5%, and no appreciable difference was observed for all of the polymers investigated.) The flexibility of the film depended both on the nature of the polymer and on the proportion of crosslinker to polymer. Polymers (9b) and (9c) can form flexible films, perhaps due to chain flexibility contributed by *n*-hexyl groups. The proportion of crosslinker to polymer may be broadly changed, but must be at least 1:10 in order for the crosslinking to take place.

When excess, for example, an equal weight of 1,4-divinyl 1,1,4,4-tetramethyldisylethylene was employed as crosslinker, vulcanization also proceeded. An advantage of this crosslinker is that evaporation losses are low. The photocrosslinking in the presence of a vulcanizing agent was highly suitable for fluid polymers (9a)–(9c) because of their good miscibility with these crosslinkers.

Oxidative crosslinking Any one of these polymers can transform into fully insoluble particles, (the soluble fraction is only about 3%), when heated in air. The degree and rate of crosslinking increased with increase in content of the silicon hydrides, for instance, for the polymers containing high Si–H content, after heated for 2 h, their increases in weight were about 2%, but for those polymers containing low Si–H only 1%. When the Si–H content was as low as $m = 10$, only partial crosslinking took place. On the other hand, all crosslinked polymers, including that of $m = 10$, remained IR absorption peak at about 2100 cm^{-1} , although their intensities decreased relatively to those before crosslinking, respectively. The results about the increase in weight also indicated that all the Si–H groups of the polymers had not been used up in crosslinking. In a control experiment, when the polymers were heated in high vacuum at 120°C for 4 h, no insoluble material was formed and the molecular weight was basically unchanged. It may be presumed that this crosslinking results from oxidation of the silicon hydrides in the polymer chain, followed by the condensation of the resulting hydroxyl groups. The crosslinking bridges so formed through oxygen atoms between the polymer chains may however be undesirable for some applications.

RTV Mixing each of these polymers with a specified amount of component (A), (B), (C) or (D) for 24 to 72 h produced cures at room temperature. The cures from (A) or (B) contained soluble fraction of 3%, but 6% from (C) or (D). The degree and rate of crosslinking also depended both on the content of Si–H and on the proportion of Si–H to vinyl groups. Homopolymer (2), (3) and the copolymers containing high Si–H content were very easy to yield crosslinking, even in the presence of (A) or (B) of less than 8%. Molar ratio of vinyl to silicon hydride groups of more than 1.5 was necessary for the copolymers with low contents ($m = 5$) of Si–H. When the content of silicon hydride in the polymer was as low as $m = 10$, for example (9c), a termination agent that contained vinyl group had to be used, otherwise a part of polymer was not cured, possibly for lack of silicon hydride. These catalysts based on platinum complexes with multivinylsilanes in forms soluble in the crosslinkers were very effective to the addition reaction, so that amount of the catalyst used was only a few millionths of these two precursors.

Because this vulcanization reaction is relatively free of side reactions, flexibility and toughness of these crosslinked materials so obtained can be easily controlled by using different variety or amount of the crosslinkers. As discussed on photocrosslinking, flexible films can be produced

from polymers (9b) – (9c). This crosslinking method is sepecially convenient for polymers (9a) – (9c), which are liquids and can be formed into a variety of shapes by casting, coating or potting. Another considerable advantage of RTV is that the cure proceeds both in the deep inside of the sample and to high conversion. In fact, the fractions left in solution after the precipitation also can be vulcanized by RTV method. RTV cures also do not require additional energy during fabrication.

Keywords:

Organosilane; Polymer; crosslinking; phenylsilylene

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