

SYNTHESIS AND CROSSLINKING OF LIQUID ORGANOSILANE POLYMERS

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ABSTRACT

Liquid organosilane polymers have been synthesized by sodium coupling of diorganodichlorosilanes with diphenylmethylchlorosilane in toluene. These polysilanes can be formed into desired shape by potting, casting or coating and crosslinked under ultraviolet irradiation in the presence of multifunctional vinylsilanes. The molecular weight distributions, infra-red, ultraviolet and nuclear magnetic resonance spectra for the organosilane polymers have been described.

Organosilane polymers possess unique sensitivity to irradiation and potential semiconductivity^[1], and can be used as precursors for β -SiC fibers^[2], impregnating agents for strengthening silicon nitride ceramics^[3], and dopable semiconductors^[1]. Recently, there has been considerable interest in this new class of polymers^[4-11].

Those organosilane polymers prepared previously by precipitation from the toluene solution with 2-propanol are solids (about 50% yield), therefore dissolution in an organic solvent to form desired shape by casting, coating or potting is necessary^[2, 7-11]. Although some organosilane polymers are easily crosslinked by oxidation, their applications may be limited by the presence of oxygen atoms in the crosslinking bridges^[12]. The crosslinked organosilane polymers through Si—C bridges can be obtained by UV photocrosslinking of the polymers mixed with multifunctional vinylsilanes^[13]. Some of the organosilane polymers containing Si—H groups are flowable liquids and can be vulcanized by reaction with a multifunctional vinylsilane in the presence of platinum complexes at room temperature. However, the procedure of synthesis for these polymers is fairly complicated^[14].

In this article, liquid organosilane polymers have been synthesized by sodium coupling of diorganodichlorosilanes with diphenylmethylchlorosilane in toluene. The process is much simpler than that for the flowable polymers having Si—H groups, and the yields of polymers are about 100%. The resulting polymers are very easy to form into a variety of shapes by potting, casting or coating, and fully crosslinked by UV irradiation in the presence of the crosslinkers.

EXPERIMENTAL

Materials

Dimethyldichlorosilane (b.p. 70°C), methylphenyldichlorosilane (205–6°C), methyl (β -phenethyl) dichlorosilane (99°C/6mm), cyclohexylmethyldichlorosilane (83°C/15 mm), *n*-hexylmethyldichlorosilane (204–6°C), diphenylmethylchlorosilane (295°C), trivinylmethylsilane (102°C) and tetravinylsilane (130–1°C) were produced by Petrarch Systems, Inc., USA, and purified by distillation under dry nitrogen, shortly before they were to be used. Toluene (CP) was dried by refluxing over sodium metal for 24 h, and then distilled into dry apparatus under an inert atmosphere.

Synthesis

A 250 mL three-necked, round-bottomed flask was set up with a motor driven stirrer, a reflux condenser, and a pressure equalizing dropping funnel. This apparatus was thoroughly dried and a positive pressure of nitrogen was introduced through the top of the condenser. All subsequent operations were carried out under nitrogen, and at all points, the reaction mixtures were protected from light.

Dry toluene, 80 mL, and 5.24 g of sodium metal were added to the flask carefully so as to avoid exposure to moisture and air as much as possible. Dimethyldichlorosilane, 6.45 g (0.05 mol), 9.56 g (0.05 mol) of methylphenyldichlorosilane and 4.66 g (0.02 mol) of diphenylmethylchlorosilane were 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 chlorosilanes were added dropwise quickly enough to maintain vigorous refluxing. The addition required about 5 min. After the addition was completed, the mixture was heated to reflux.

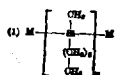
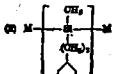
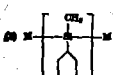
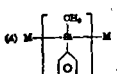
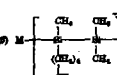
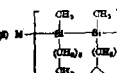
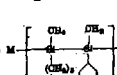
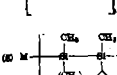
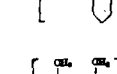
Progress of the reaction was followed by taking small samples of the solution, washing then with water and checking the pH of the water with pH test paper. After the solution no longer tested acidic, indicating that all the chlorosilanes had been consumed, the reaction vessel was cooled to room temperature. The reaction mixture was quenched with 25 mL of 2-propanol and washed with 250 mL of water until the solution tested neutral. The organic layer was separated and toluene was then stripped off on a rotary evaporator at 95°C under reduced pressure (10 torr). The residue was dried in a vacuum oven (10 torr) at 110°C for 2 h. The polymer, 1.28 g, was finally obtained as viscous liquid in 99.9% yield.

Other polymers listed in Table 1 were synthesized similarly. Fractionation of the polymers was accomplished by adding increments of 2-propanol to a dilute solution of the polymers in toluene⁽²⁾.

Determination of molecular weights

Molecular weights of the polymers were determined by GPC with four Microstygagel columns of the following pore sizes, in Å: 10⁶, 10⁵, 10⁴, 10³ and with a Waters Associates Model 440 UV absorbance detector set at 254 nm, using THF as the eluant at a flow rate of 2 mL/min.

Table 1 Molecular weights and viscosities of the polymers

Polymer*	Molecular weight			Viscosity, cp
	Calcd.**	GPC	$\overline{M}_w/\overline{M}_n$	
(1) 	1,674	1,400	1.04	510
(2) 	1,874	1,500	1.04	1,200***
(3) 	1,654	1,430	1.04	1,400***
(4) 	994	950	1.05	800***
(5) 	1,324	1,300	1.09	2,300
(6) 	1,774	1,460	1.08	4,200
(7) 	1,664	1,380	1.09	4,500
(8) 	1,634	1,320	1.10	9,800
(9) 	1,424	1,250	1.10	12,200
(10) 	1,314	1,230	1.08	13,500
(11) 	1,284	1,050	1.12	14,800

* M=MePh₂Si—

** From the ratios of diorganodichlorosilanes to diphenylmethylsilane

*** For the mixture of the polymer (5 g) with tetravinylsilane (1 g)

Data on molecular weights are relative to polysilastylene standards from which fractionation and molecular weight determination have been reported^[2]. Molecular weights of some polymers were also examined by H^1 NMR to compare with those from GPC.

Viscosity determination

Bulk viscosities for the polymers, as shown in Table 1, were measured with a Rheotest 2 viscosimeter at 25°C.

H^1 NMR

Proton NMR spectra were examined in $CDCl_3$ on JEOL MH-200 spectrometer. The content of end groups of the polymer was determined by integration of the proton NMR signals for the different groups, and the molecular weight was then calculated.

C^{13} NMR

A JEOL FX-100 Fourier transform spectrometer was employed to obtain C^{13} NMR spectra, using $CDCl_3$ as solvent.

UV spectroscopy

UV spectra of the polymers were determined in THF with a Cary Model 118 spectrophotometer. The assignment of peak positions was assisted by taking the first derivative of those spectra containing overlapping peaks.

IR spectroscopy

IR spectra were examined from 4000 to 300 cm^{-1} on KBr pellets with a Perkin-Elmer 457 spectrometer.

Crosslinking

Each sample of the liquid organosilane polymers, 2 g, was mixed with 0.4 g of trivinylmethylsilane or tetravinylsilane, followed by pouring the mixture on a glass plate to form a thin film (ca. 1 mm). The films were exposed under UV light at 254 or 300 nm for 4 h. The crosslinked films (2 g) were immersed in THF for 24 h, which was protected from light, and then dried in a vacuum oven (ca. 1 torr) at 100°C for 2 h. Thus the losses of weight after abstraction were measured.

RESULTS AND DISCUSSION

Viscosities, molecular weights and compositions of the polymers

The results in Table 1 show that all the organosilane polymers made from sodium coupling of diorganodichlorosilanes with diphenylmethylchlorosilane in toluene are liquids. The bulk viscosities of these liquid polymers depend on their structures, among them, the polymers containing *n*-hexylmethylsilylene units exhibit lower viscosities. The molecular weights determined from GPC are consistent with those calculated from the ratios of diphenylmethylchlorosilane to the corresponding diorganodichlorosilanes employed as starting materials. The

liquid polymers display a monomodal, narrow molecular weight distribution, and markedly different from that for those solid polymers reported earlier, as shown in the typical GPC elution profile in Fig. 1.

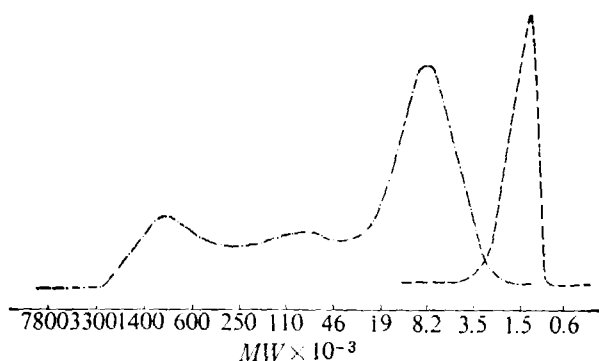


Fig. 1 GPC elution profiles of polymer 3 (---) and cyclohexylmethylsilylene high polymer (- · -)[6]

To verify the existence of MePh_2Si end groups on these polymer chains, the contents of the end groups for some fractions after fractionation of polymer 3 were analyzed with H^1 NMR, and molecular weights were calculated. As can be seen from Table 2, molecular weights from H^1 NMR are all in agreement with those from GPC.

The H^1 - and C^{13} -NMR spectral data and IR absorptions for these polymers, as shown in Tables 3 and 4, conform also to the expected polymeric structures^[15]. The absorption peaks, characteristic of the Si-H bonds, were observed in both IR and H^1 NMR for most of the polymers, probably due to reaction of 2-propanol with chain-terminal sodium.

Table 2 Fractionation of polymer 3

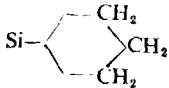
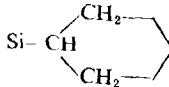
Fraction	GPC*		H^1 NMR	
	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\frac{\text{CH}_3\text{Si}-\text{C}_6\text{H}_{11}}{2 \text{ MePh}_2\text{Si}}$	$\overline{M}_n$
1	7,100	1.03	54.93	7,315
2	3,090	1.04	22.56	3,273
3	1,480	1.03	9.916	1,643
4	960	1.02	5.954**	1,040

* Use toluene as the eluant

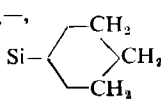
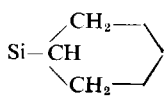
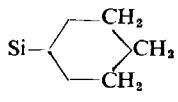
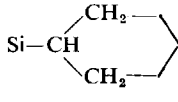


** Contain a small amount of end group CH_3SiH (H^1 NMR 3.40 ppm, IR 2,080 cm^{-1})

Table 3 ^1H and ^{13}C NMR chemical shifts of the polymers

Polymer	^1H (ppm)	^{13}C (ppm)	Assignment
1	0.24, 0.68	-5.18, -4.13, -3.34	$\text{CH}_3\text{—Si}$
	0.87	14.26, 22.74	$\text{CH}_3\text{—CH}_2\text{—Si}$
	1.29	26.98, 31.71, 32.98, 33.64	$\text{—(—CH}_2\text{—)}_4\text{—}$
	7.23, 7.36	127.6, 128.7, 134.6	$\text{C}_6\text{H}_5\text{—Si}$
2	0.24, 0.75	-6.06, -3.36, -2.75	$\text{CH}_3\text{—Si}$
	1.26	18.67	$\text{—CH}_2\text{—Si}$
	2.56	32.32	$\text{—CH}_2\text{—}$
	3.64		H—Si
	7.12, 7.22, 7.46	125.3, 127.4, 128.1, 134.6, 137.2, 144.2	$\text{C}_6\text{H}_5\text{—Si}$, $\text{C}_6\text{H}_5\text{—(C)}$
3	0.23, 0.72	-7.76, -1.71	$\text{CH}_3\text{—Si}$
	1.18	26.81	
	1.68	28.63, 30.89	
	3.40		H—Si
	7.20, 7.40	127.6, 128.6, 134.8, 138.3	$\text{C}_6\text{H}_5\text{—Si}$
4	0.28	-6.61, -3.47	$\text{CH}_3\text{—Si}$
	3.68		H—Si
	7.10	127.5, 129.3, 133.0, 134.9, 135.7, 136.2	$\text{C}_6\text{H}_5\text{—Si}$
5	0.22, 0.61	-5.67, -4.40, -3.80, -3.03	$\text{CH}_3\text{—Si}$
	0.83	13.99, 22.46	$\text{CH}_3\text{—CH}_2\text{—Si}$
	1.26	26.76, 31.38, 33.42, 33.64	$\text{—(—CH}_2\text{—)}_4\text{—}$
	7.20, 7.37	127.5, 128.4, 134.3, 137.2	$\text{C}_6\text{H}_5\text{—Si}$
6	0.25, 0.70	-5.06, -3.80, -2.59	$\text{CH}_3\text{—Si}$
	0.88	14.32, 22.80	$\text{CH}_3\text{—CH}_2\text{—Si}$
	1.28	18.70, 26.26, 31.71, 32.98, 33.70	$\text{—CH}_2\text{—Si}$, $\text{—(—CH}_2\text{—)}_4\text{—}$
	2.56	32.41	$\text{—CH}_2\text{—}$
	3.58		H—Si
	7.06, 7.18, 7.39	125.4, 127.6, 128.1, 134.7, 137.7, 144.8	$\text{C}_6\text{H}_5\text{—Si}$, $\text{C}_6\text{H}_5\text{—(C)}$
7	0.24, 0.72	-8.75, -4.95, -2.53	$\text{CH}_3\text{—Si}$
	0.91	14.32, 22.80	$\text{CH}_3\text{—CH}_2\text{—Si}$

(continued)

Polymer	H ¹ (ppm)	C ¹³ (ppm)	Assignment
8	1.28, 1.34	26.98, 31.97, 32.99, 33.75	$-(\text{CH}_2-)_4-$, 
	1.72	28.96, 30.94	
	3.58		H—Si
	7.24, 7.42	127.6, 128.5, 134.7, 138.1	C ₆ H ₅ —Si
	0.24, 0.68	-5.94, -5.18, -2.86	CH ₃ —Si
	0.86	14.26, 22.69	CH ₃ —CH ₂ —Si
	1.19	26.32, 31.49, 32.80, 33.64	$-(\text{CH}_2-)_4-$
	3.64		H—Si
9	7.18, 7.36	127.5, 128.4, 133.1, 134.6, 136.7, 138.7	C ₆ H ₅ —Si
	0.35, 0.68	-3.41, -1.52	CH ₃ —Si
	1.47	18.72	—CH ₂ —Si
	2.60	32.71	—CH ₂ —
	3.80		H—Si
10	7.17, 7.29, 7.46	125.4, 127.6, 128.0, 134.6, 137.4, 144.5	C ₆ H ₅ —Si, C ₆ H ₅ —(C)
	0.24, 0.58	-4.57, -3.52	CH ₃ —Si
	1.17	26.98	
	1.66	28.63, 30.89	
11	3.57		H—Si
	7.18, 7.38	127.6, 128.5, 134.6, 137.4	C ₆ H ₅ —Si
	0.24, 0.60	-5.62, -4.68, -3.69	CH ₃ —Si
	3.62		H—Si
	7.24, 7.45	127.6, 128.5, 129.1, 133.7, 134.7, 136.7	C ₆ H ₅ —Si

UV absorption properties of the polymers

The UV absorption properties of the polymers are given in Table 5. Polymers 1—11 show strong UV absorption maxima between 280 and 329 nm. Among these polymers, polymers 4, 8 and 11, which contain phenyl side groups directly attached to Si in the polymeric

Table 4 IR absorptions of the polymers

Absorption (cm ⁻¹)						Assignment
1	2	3	4	5	6	
3078 (m)	3070 (m)	3080 (m)	3068 (m)	3080 (m)	3080 (m)	C ₆ H ₅ —
3060 (m)	3037 (m)	3037 (m)	3044 (m)	3060 (m)	3026 (m)	
2970 (s)	2960 (s)			2080 (s)	2960 (s)	CH ₃ —(C)
2925 (s)	2925 (s)	2925 (s)		2920 (s)	2920 (s)	—CH ₂ —
2890 (s)	2900 (s)			2900 (s)	2900 (s)	CH ₃ —(C)
2858 (s)	2860 (s)	2857 (s)		2858 (s)	2858 (s)	—CH ₂ —
2085 (w)	2090 (w)	2080 (w)	2085 (w)	2086 (w)	2080 (w)	H—Si
1980 (w)	1950 (w)	1950 (w)	1950 (w)	1950 (w)	1940 (w)	C ₆ H ₅ —Si
1878 (w)	1875 (w)	1880 (w)	1880 (w)	1877 (w)	1875 (w)	
1813 (w)	1800 (w)	1815 (w)	1814 (w)	1815 (w)	1810 (w)	C ₆ H ₅ —
	1603 (m)				1600 (m)	
	1496 (s)		1483 (w)	1490 (m)	1494 (m)	CH ₃ —(C)
1470 (s)				1470 (s)	1468 (m)	—CH ₂ —
1459 (m)	1453 (m)	1449 (m)			1450 (s)	C ₆ H ₅ —Si
1430 (m)	1430 (m)	1430 (m)	1427 (s)	1430 (s)	1427 (s)	—CH ₂ —
1410 (m)	1410 (w)	1410 (w)		1410 (m)	1410 (m)	CH ₃ —(C)
1380 (m)				1380 (m)	1378 (w)	CH ₃ —Si
1250 (s)	1250 (s)	1246 (s)	1245 (m)	1250 (s)	1245 (s)	—(—CH ₂ —) _n —
1175 (m)	1170 (w)	1170 (w)		1170 (m)	1168 (m)	C ₆ H ₅ —Si, CH ₂ (CH ₂) ₆ —Si
1100 (s)	1105 (s)	1100 (s)	1097 (s)	1100 (s)	1100 (s)	
1000 (s)	1000 (s)	996 (s)	996 (s)	1000 (s)	995 (s)	(CH ₃) ₃ —Si
				957 (m)		C ₆ H ₅ —Si, CH ₃ —Si
790 (s)	785 (s)	775 (s)	780 (s)	840 (s)	770 (s)	
690 (s)	697 (s)	697 (s)	692 (s)	685 (s)	695 (s)	Si—C
614 (s)	662 (m)	664 (m)	662 (m)	635 (s)	660 (m)	Si—Si
508 (w)	509 (w)	510 (w)		500 (w)	507 (w)	
470 (w)	470 (w)	470 (w)	464 (m)	464 (w)		
430 (w)	430 (w)	430 (w)		425 (w)	430 (w)	

(continued)

Absorption (cm ⁻¹)					Assignment
7	8	9	10	11	
3080 (w)	3070 (w)	3078 (w)	3070 (w)	3078 (w)	C ₆ H ₅ —
3060 (w)	3050 (w)	3038 (w)	3050 (w)	3060 (w)	
2969 (s)	2960 (s)	2960 (s)	2960 (s)	2960 (s)	CH ₃ —(C)
2940 (s)	2920 (s)	2930 (s)	2920 (s)		—CH ₂ —
2900 (sh)	2900 (sh)	2900 (s)	2890 (s)	2903 (s)	CH ₃ —(C)
2860 (s)	2857 (m)	2860 (sh)	2843 (s)		—CH ₂ —
2080 (w)	2080 (w)	2085 (w)	2080 (w)	2090 (w)	H—Si
1950 (w)	1950 (w)	1950 (w)	1950 (w)	1952 (w)	C ₆ H ₅ —Si
1880 (w)	1880 (w)	1880 (w)	1878 (w)	1880 (w)	
1810 (w)	1812 (w)	1815 (w)	1812 (w)	1816 (w)	C ₆ H ₅ —
		1604 (m)		1588 (w)	
		1497 (m)		1488 (m)	CH ₃ —(C)
1465 (m)	1467 (m)				—CH ₂ —
1450 (s)		1456 (m)	1446 (m)		C ₆ H ₅ —Si
1430 (s)	1426 (s)	1430 (m)	1427 (m)	1430 (s)	CH ₃ —Si
1410 (w)	1410 (w)	1410 (m)	1405 (m)	1410 (m)	CH ₃ —(C)
1380 (w)	1378 (w)				CH ₃ —Si
1250 (s)	1245 (s)	1250 (s)	1245 (s)	1250 (s)	—(CH ₂) _n —
1170 (w)	1180 (w)				C ₆ H ₅ —Si, CH ₃ (CH ₂) ₅ —Si, Si— 
1100 (s)	1100 (s)	1105 (s)	1100 (s)	1100 (s)	
1000 (s)	960 (s)	1000 (s)	940 (s)	1000 (s)	C ₆ H ₅ —Si, CH ₃ —Si
770 (s)	780 (s)	840 (s)	838 (s)	840 (s)	
702 (s)	694 (s)	660 (s)	700 (s)	690 (s)	Si—C
665 (w)	660 (m)	630 (m)		660 (m)	
		565 (w)	565 (m)		Si—Si
502 (m)	507 (s)	508 (m)	507 (m)	505 (m)	
470 (w)	470 (m)	470 (w)	470 (w)	470 (m)	430 (w)
430 (w)	435 (m)	435 (w)	430 (w)	430 (w)	

chains, have strong absorptions at longer wavelengths. The bathochromic shift is perhaps related to increased conjugative interaction between phenyl substituents and the silicon spinal chain acting as a σ - σ^* or σ - π chromophore^[16,17]. Thus polymers 2,6 and 9 with phenyl groups separated from the silicon by $-\text{CH}_2\text{CH}_2-$ display UV absorption bands similar to those of the

polymers containing *n*-hexyl side groups. However, polymer 3, like the polymers with phenyl side groups, exhibits longer λ_{max} . This is in agreement with earlier finding that cyclohexylsilyl groups in silane high polymer behave somewhat as arylsilyl groups which are a very intense chromophore^[7, 8].

Table 5 UV absorption properties of the polymers

Polymer	λ_{max} (nm)	ϵ^*
1	306	800
2	310	600
3	329**	300
4	328	1,200
5	296	2,200
6	280	2,600
7	315	400
8	326	1,600
9	294	2,000
10	295**	2,200
11	328	800

* Per average Si unit

** Determined in toluene

Shaping and crosslinking of the polymers

All of polymers investigated are flowable liquids, so that they can be formed into any desired shape by casting, coating or potting, and no any solvent is necessary.

These liquid polymers, unlike the organosilane high polymers, are very easy to be mixed with the crosslinkers (trivinylmethylsilane or tetravinylsilane) because of their complete miscibility with the latter. The liquid mixture can be crosslinked with UV irradiation, and soluble fraction for the cures is only about 3%. The soluble fraction was detected by both NMR and IR, no unreacted crosslinker was found. It may be presumed that this crosslinking results from the addition reaction of vinyl groups, initiated by organosilyl free radicals generated from scission of the organosilane polymers under UV radiation^[1a].

Polymerization of multifunctional vinyl silanes can be initiated by these radicals, for instance, mixing 1.0 g of trivinylmethylsilane or tetravinylsilane with 0.1 g any one of the above-mentioned liquid polymers, followed by UV irradiation, produces the crosslinked polymer based on Si—C chain.

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