

ORGANOSILANE POLYMERS: OXIDATION-CROSSLINKABLE CYCLOTETRAMETHYLENESILYLENE POLYMER AND COPOLYMERS

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ABSTRACT

Polysilane polymers containing cyclotetramethylenesilylene units were synthesized by sodium coupling of diorganodichlorosilanes in toluene. These polymers are soluble in common solvents, can be formed into a variety of shapes by molding, casting, coating or potting. They can be crosslinked by irradiation and oxidation at moderate or room temperature.

Recently we have reported on several polysilane polymers^[1-6] which are formable and photoactive. In this article, we describe cyclotetramethylenesilylene homopolymer **1**, cyclotetramethylenesilylene-dimethylsilylene copolymer **2** and cyclotetramethylenesilylene-methylphenylsilylene copolymer **3**. These polymers have the same useful properties as those organosilane polymers described earlier^[1-6], for example, high molecular weight, appreciable solubility in common solvents and good formability, but can be crosslinked easily by oxidation at moderate or room temperature.

EXPERIMENTAL

Synthesis

Dry toluene, 50 mL and 4.7 g (2% excess) of sodium metal were added to a 250 mL three-necked flask and degassed using a stream of argon. All subsequent reaction operations were carried out in argon and light was excluded from the reaction mixture. Over 5 min, 0.10 mol of diorganodichlorosilane was added dropwise to the stirred, refluxing mixture of toluene and sodium. (For copolymers **2** and **3**, a mixture of 0.05 mol of each of the two dichlorosilane precursors was used.) After refluxing for another 2h, the reaction mixture was cooled and quenched with 15 mL of ethanol and 250mL of water. The organic layer was then washed with 250mL of water to remove traces of sodium salts. The insoluble polymer fraction was removed by centrifugation. The soluble polymer was obtained by precipitation from the solution with methanol (8:1 ratio of methanol to toluene by volume), followed by drying in a vacuum oven (~1 Torr) at 50°C for 1.5h.

Samples of the resulting polymers should be stored in brown glass bottles and under argon.

Characterization

Molecular weights of the polymers were determined by GPC using four μ styragel columns of

the following pore sizes, in Å: 10^6 , 10^5 , 10^4 and 10^3 , with toluene as the eluant at a flow rate of 2 mL/min. The detection system was a Waters Associates Model 440 ultraviolet absorbance detector set at 254 nm. Data on molecular weights listed in Table 1 and Figure 1 are relative to polystyrene standards.

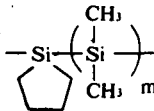
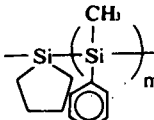
Proton and ^{13}C NMR spectra were examined with JEOL MH-100 and FX-60 spectrometers respectively, on polymer solutions in deuteriochloroform. Determination of m , the ratio of either dimethylsilylene or methylphenylsilylene to cyclotetramethylenesilylene units in the copolymers, was carried out by integration of the proton NMR signals for the different groups.

Infrared spectra were measured in the region from 4000 to 300 cm^{-1} on KBr pellets using a Perkin-Elmer 457 spectrometer. Ultraviolet spectra were obtained with a Cary Model 118 spectrophotometer in THF.

RESULTS AND DISCUSSION

Yields, molecular weights and compositions of these polymers are listed in Table 1. In earlier work, the yields of homopolymers have generally been lower than the yields of copolymers containing the same groups^[2-5], however the yield of homopolymer 1 is significantly greater than those of copolymers 2 and 3. Polymer 3 has both the lowest yield and molecular weight of these polymers. These soluble polymers, like the polymers reported earlier^[1-6], all exhibit a bimodal or trimodal molecular weight distribution, as shown in the typical GPC elution profile in Figure 1.

Table 1 Yields, molecular weights and compositions of polymers 1-3

Polymer No	Unit	Yield, Wt %		$\bar{M}_w \times 10^{-3}$	m
		Insol.	Sol.	Max ^a	
1		1.8	71	640 2.6	—
2		8.5	40	720 85 2.1	0.896
3		1.7	19	65 1.5	0.955

^aFrom GPC elution volume, relative to polystyrene.

Polymer 1 was obtained as a waxy solid, 2 a white powder and 3 a resinous solid. All three are soluble in benzene, toluene and chloroform, and 1 and 2 also dissolve in THF. The polymers can be drawn into fibers or formed into films by molding or casting; 1 and 2 have especially good film forming qualities, probably due to their high molecular weights.

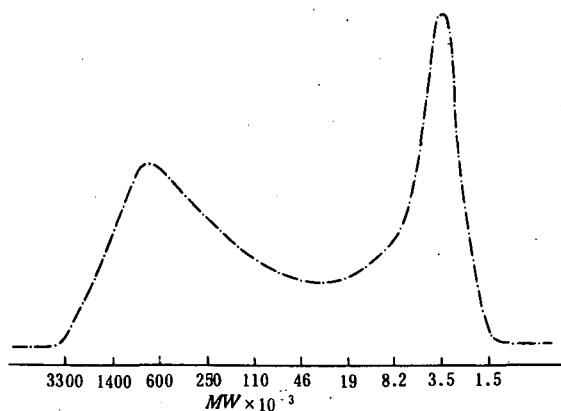


Fig. 1 GPC elution profile of polymer 1.

As can be seen from Table 2, the ^1H and ^{13}C spectra of **1** are consistent with those for larger rings of the per(cyclotetramethylene)cyclopolsilane^[7], and a 1:1 ratio of integration of the two proton signals is observed. The proton and ^{13}C -NMR spectra of **2** and **3** are also in agreement with the structures proposed for these polymers. The ^1H and ^{13}C resonances are very broad^[9-12], probably reflecting the existence of regions of more than one stereoregular polymeric conformation. Hindered rotation in the polymer chains may also lead to nonequivalence of various nuclei^[8].

Polymers **1**, **2** and **3** display ultraviolet absorption maxima, λ_{max} at 281, 285 and 325 nm, with the molar absorptivity ϵ per average Si unit of 2,000, 3,400 and 3,700, respectively, as shown in Figure 2. These values are similar to those reported earlier for polymers containing cyclopentamethylenesilylene units^[3-5].

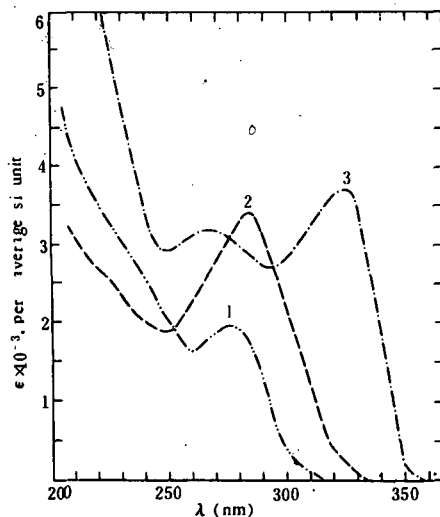
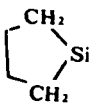
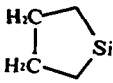
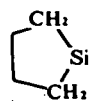
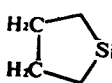
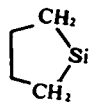
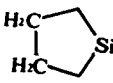
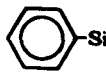


Fig.2 Ultraviolet absorption spectra for polymers 1-3, in THF solution

Table 2 ^1H and ^{13}C -NMR chemical shifts for polymers 1–3

Polymer	^1H (ppm)	^{13}C (ppm)	Assignments
1	0.89(b)	12.06(b)	
	1.61(b)	29.40(b)	
2	0.59 } (vb) 0.74 }	-3.65(vb)	$\text{CH}_3\text{—Si}$
	1.40(b)	12.01(b)	
	2.14(b)	29.24(b)	
3	0.38 } (vb) 0.70 }	-5.58(vb)	$\text{CH}_3\text{—Si}$
	1.14(b)	11.54(b)	
	1.36(b)	28.93(b)	
	7.04(vb)	127.6(b), 133.3(b)	
		134.8(b), 137.6(b)	

vb: very broad b: broad

These polymers are also photoreactive in ultraviolet light. Irradiation of the polymers at 254 nm in air, either as solids or dilute solutions, leads to rapid photolytic degradation, as shown by incremental decrease in the molecular weight determined by GPC. In argon, photocission also

takes place, but much more slowly.

All of the polymers investigated are susceptible to oxidation, like the cyclotetramethylenesilylene rotanes^[7]. When these polymers are heated in an oven in air at 70°C for 2 h, or exposed to air at room temperature for several months, full crosslinking takes place, as indicated by the formation of "gelled" particles. Under argon at 120°C for 2 h, no insoluble particles are formed and the molecular weight is essentially unchanged.

Table 3 Infrared absorptions of polymer 1

Absorption (cm^{-1})		Assignments ^[9-13]
original	gelled ^a	
3430(w,broad)		absorbed H_2O
	3450(s,broad)	OH and absorbed H_2O
	3038(w)	chelated OH
2930(vs)	2935(vs)	$-\text{CH}_2-$ stretch(a)
2860(s)	2860(s)	$-\text{CH}_2-$ stretch(s)
	1732(s)	$\text{C}=\text{O}$
	1605(m)	chelated ketone
	1495(m)	$-\text{CH}_2-$ deformation
1450(m)	1455(m)	
1408(m)	1408(w)	$\text{Si}-\text{CH}_2-$ deformation(a)
	1385(w)	CHO
1252(w)	1252(w)	$\text{Si}-\text{CH}_2-$ deformation (s)
	1200(sh)	$\text{C}-\text{O}-\text{C}$, $\text{Si}-\text{O}-\text{C}$, OH
	1150(m)	
1070(vs)	1070(m)	$-(\text{CH}_2)_4$ skeletal vibration
1020(vs)	1020(m)	
765(s)	765(s)	$\text{Si}-\text{CH}_2-$ rocking
700(m)	700(s)	$\text{Si}-\text{C}$ stretch (a)
648(s)	648(w)	$\text{Si}-\text{C}$ stretch (s)
	540(w)	$\text{Si}-\text{Si}$
495(w)	495(w)	

^aAfter exposure of the polymer 1 to air at room temperature for six months.

In comparison with polymer 1, the gelled particles show some new infrared absorption peaks (see Table 3) which are assigned to OH, $\text{C}=\text{O}$, CHO, $\text{C}-\text{O}-\text{C}$ or $\text{Si}-\text{O}-\text{C}$ groups respectively,^[13] while intensities of absorptions characteristic of $(\text{CH}_2)_4$ skeletal vibrations decline markedly. It is evident that the crosslinking results from oxidation. The oxidation reactions appear to be complicated, but it is clear that cyclotetramethylenesilylene rings are broken and yield one or two crosslinking bridges through oxygen atoms, resulting in the formation of an insoluble network polymer.

Keywords:

Polysilane polymers; Cyclotetramethylenesilylene polymer

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