

SYNTHESES AND PROPERTIES OF SOME ORGANOSILANE POLYMERS*

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ABSTRACT

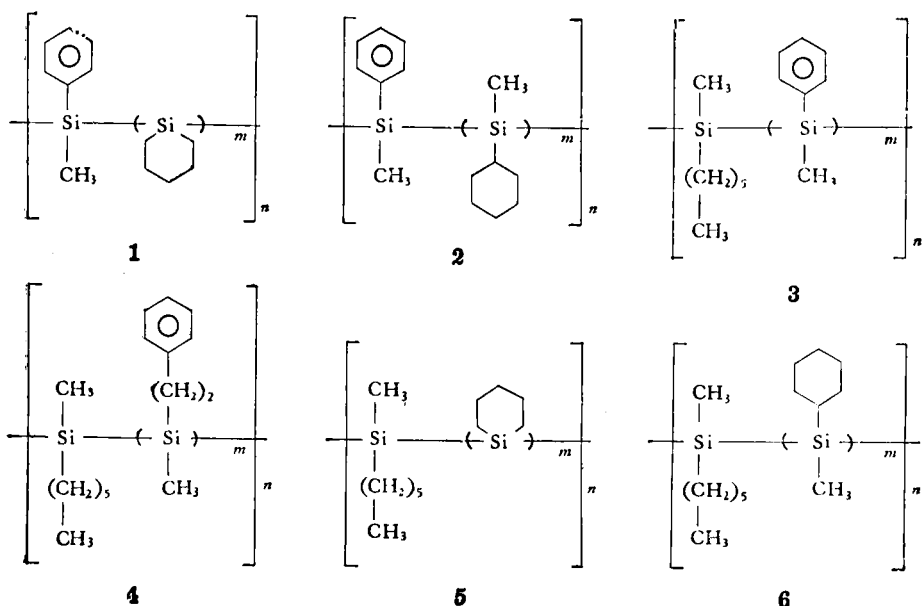
Some organosilane polymers with high molecular weights have been synthesized by cocondensation of organosilicon dihalide monomers with sodium metal in toluene. These polymers are both soluble in common solvents and meltable at lower temperatures, and can be molded, cast into films or drawn into fibers. Exposure of the solid polymers to ultraviolet light leads to degradation or crosslinking.

Although organosilane polymers were evidently obtained by Kipping more than 50 years ago^[1], and permethylpolysilane was prepared as early as 1949^[2], the chemistry of the polymeric polysilanes has been neglected until recently. Yajima and his coworkers demonstrated that permethylpolysilane can be converted in a two-step process to β -SiC fibers^[3-6], which has led to a resurgence of interest in these materials^[7-12].

Both permethylpolysilane^[2, 8] and perphenylpolysilane^[1] are highly crystalline, intractable, insoluble solids which have very high melting points and decompose before melting when heated. The introduction of larger substituent groups decreases the high crystallinity characteristic of permethylpolysilane^[7, 9-12]. These tractable organosilane polymers possess several unique properties, for example, sensitivity to radiation and potential semiconductivity^[12]. They have been used as impregnating agents for strengthening ceramics^[7], as precursors for β -SiC fibers^[13], and as dopable semiconductors^[12].

Among these soluble silane polymers which have been reported in the literature^[9, 11, 12], the methylphenylsilylene homopolymer has moderate molecular weight; the block copolymers of diphenylsilylene with dimethylsilylene, ethylmethylsilylene and diethylsilylene units have low molecular weights (5,000—10,000), and were produced by a more complex synthesis. The random dimethylsilylene-methylphenylsilylene copolymer, "Polysilastyrene", is of high molecular weight, but some insoluble polymer is simultaneously formed in the sodium condensation reaction, and removal of this undesirable byproduct complicates the workup. In an effort to overcome these problems, to improve film or fiber forming properties, and to study the effects of various bulky side groups on the properties of the polymers, we have developed a series of formable organosilane polymers^[14, 15]. In this paper we describe the syntheses and characteristics of the following silane copolymers:

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where $m=0.6-1.2$, $n=10-5,000$.

EXPERIMENTAL

Reagents

Methylphenyldichlorosilane (b.p. $205-6^{\circ}\text{C}$), *n*-hexylmethyldichlorosilane ($204-6^{\circ}\text{C}$), cyclohexylmethyldichlorosilane ($83^{\circ}\text{C}/15\text{ mm}$) and methyl (β -phenethyl) dichlorosilane ($99^{\circ}\text{C}/6\text{ mm}$) were produced by Petrarch Systems, Inc., USA, and purified by distillation in dry apparatus under an inert atmosphere shortly before use. Cyclopentamethylenedichlorosilane was prepared according to published directions^[16], b.p. $169-70^{\circ}\text{C}$, purity $\sim 99\%$, examined by GLC.

Solvents (toluene, decalin and THF) were dried by refluxing over sodium metal and a little benzophenone, until the blue color of the sodium ketyl appeared. The dry solvent was then distilled into dry apparatus under an inert atmosphere. Spectrograde THF was used for UV spectroscopic measurements.

Syntheses of the copolymers

Toluene was used as solvent in the syntheses of all copolymers, except 2, in which decalin was employed as solvent. Copolymer 6 is given as an example to illustrate the synthesis and isolation of these copolymers.

A 250 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 filled with nitrogen through the top of the condenser to displace air in it. All subsequent operations were carried out under nitrogen, and at all points, solutions of the reaction products were protected from light.

To the dry flask, 76 mL of toluene and 4.8 g ($\sim 0.209\text{ mol}$) of sodium metal were carefully placed keeping free from moist air. (The volume of toluene should be about four times as

large as the total volume of chlorosilanes to be used.) Cyclohexylmethyldichlorosilane (9.0 mL, 0.05 mol) and 10.0 mL (0.05 mol) of *n*-hexylmethyldichlorosilane were transferred into the dropping funnel, using a syringe. The flask was heated on a heating mantle until the sodium metal melted and the toluene refluxed gently. The stirrer was turned on at high speed to create a sodium dispersion. The heating mantle was then removed and the mixed chlorosilanes were 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. The mixture was refluxed with heating for another 3 hrs.

Isolation of the copolymers

The reaction vessel was cooled to near room temperature. Twenty-five mL of ethanol was added very slowly with stirring to the reaction mixture, to react with excess sodium. The reaction mixture was then washed twice with 250 mL of water. The organic layer was separated and stripped on a rotary evaporator at 95°C, ~10 Torr. (For copolymer 1, insoluble polymer was present and it was therefore necessary to centrifuge the solution and decant before stripping.) After most of the toluene was removed, 40 mL of THF was added to the flask. (The THF addition was necessary to remove traces of the toluene from the greasy product.) The solvents were evaporated under the same conditions until the weight of the residue was unchanged, yielding 12.6 g of polymer (98.5% yield). This product was dissolved in 50 mL of THF and a mixture of 200 mL of 2-propanol and 200 mL of methanol was slowly added dropwise with stirring to the THF solution to precipitate the polymer. The precipitate was dried in a vacuum oven (~1 Torr) at 110°C for 2 h. Copolymer 6 was finally obtained as sticky elastomer (7.52 g, 59% yield), leaving 39% of oligomeric products in solution after precipitation.

Fractionation of the copolymer was accomplished by dissolving it in THF and then reprecipitating by adding 2-propanol in small increments to the THF solution^[13]. All of the polymer samples should be stored in brown glass vials or bottles.

Molecular weight determination

Molecular weights of the copolymers were determined by GPC equipped with four μ -styragel columns (porosity ranges 10³, 10⁴, 10⁵ and 10⁶ Å) calibrated with polystyrene standards, using THF 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.

Nuclear magnetic resonance spectroscopy

Proton NMR spectra were determined in CDCl₃ on a JEOL MH-100 spectrometer. Determination of *m*, the ratio of methylphenylsilyl or *n*-hexylmethylsilyl units to other units in the copolymers, was done by integration of the proton NMR signals for the different groups. ¹³C-NMR spectra were similarly obtained with a JEOL FX-60 Fourier transform NMR spectrometer, using CDCl₃ as solvent.

Ultraviolet spectroscopy

UV spectra were examined 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.

Infrared spectroscopy

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

Irradiation of the copolymers

Either dilute solutions or solid films of these copolymers were exposed to ultraviolet light at frequencies of 300 or 350 nm in air or argon for 30 min. Then it was carefully observed whether or not insoluble particles were produced, suspended in the solutions. The molecular weights of the soluble copolymers were finally determined by GPC, to compare with those before the irradiation.

RESULTS AND DISCUSSION

Molecular weights, yields and compositions of the copolymers

Sodium coupling of dichlorosilanes may lead both to long chain polysilanes and to cyclic polysilanes. The reaction rates for different chlorosilanes decrease in the order of $\text{Ph}_2\text{SiCl}_2 > \text{PhRSiCl}_2 > \text{XSiCl}_2 > \text{RR}'\text{SiCl}_2$, where R or R' represents alkyl or cycloalkyl, X cycloalkylene. In the case of "Polysilastyrene"^[13], a larger amount of insoluble polymer was formed along with soluble polymer because of a sizeable difference in the reaction rates of MePhSiCl_2 compared with Me_2SiCl_2 . A replacement of dimethyldichlorosilane with

Table 1 Yields, molecular weights and compositions of the copolymers

Copolymer	Yield (wt %)			$\bar{M}_w \times 10^{-3}$ max ^{a)}	$p^{b)}$	m
	Insol.	Olig.	Sol.			
1	2.2	59.0	36.0	60 2.6	0.47	0.8719
2	0	—	59.0	80 3.6	0.34	0.6257
3	0	48.4	50.0	400 3.0	1.5	1.159
4	0	40.5	56.5	990 110 3.1	1.8	1.047
5	0	38.9	58.4	330 40 2.5	2.0	0.700
6	0	39.5	59.0	1000 3.5	2.4	1.146

a) From GPC elution volume, relative to polystyrene.

b) The proportion of high molecular weight fraction to low molecular weight fraction in the bimodal distribution from GPC elution profile.

cyclopentamethylenedichlorosilane which has faster reaction rate than the former results in decrease of the insoluble polymer for copolymer 1, as shown in Table 1, but its molecular weight and yield are also apparently lower. An attempt to condense MePhSiCl_2 with Ph_2SiCl_2 led only to copolymer with very low molecular weight, probably due to preference of these silanes for cyclization rather than chain propagation.

High molecular weight homopolymers based on methylphenylsilylene or cyclohexylmethylsilylene units were easily synthesized by the condensation of methylphenyldichlorosilane or cyclohexylmethylsilylene with sodium in toluene^[14], however, it was unexpected that methylphenylsilylene-cyclohexylmethylsilylene copolymer with very low molecular weight (2×10^3) was exclusively produced by cocondensation of MePhSiCl_2 with cyclohexylmethylsilylene under the same conditions. When decalin (b.p. 194°C) was employed as solvent, instead of toluene, copolymer 2 with higher molecular weight was obtained, although P, the proportion of high molecular weight fraction to low molecular weight fraction in the bimodal distribution (as determined from the GPC elution profile, Fig. 1) was fairly small.

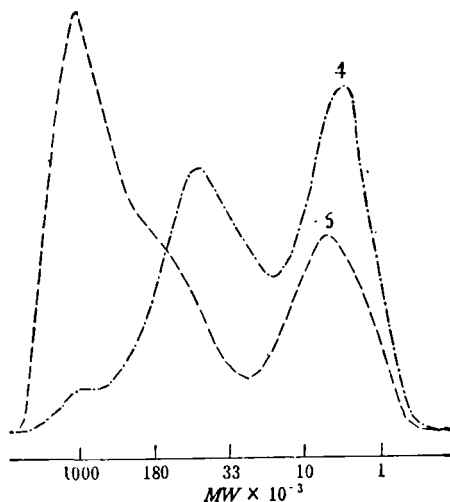


Fig. 1 GPC elution profiles of copolymers 4 and 6

Copolymer 3 has high molecular weight and larger P proportion, while the various fractions show considerably different compositions, for example, when $\bar{M}_w = 450 \times 10^3$ ($\bar{M}_w/\bar{M}_n = 1.19$), $m = 1.485$; $\bar{M}_w = 2.9 \times 10^3$ ($\bar{M}_w/\bar{M}_n = 1.04$), $m = 0.579$. Copolymers 4–6, obtained by the cocondensation of *n*-hexylmethylsilylene with those dichlorosilanes which have close reaction rates to the former, not only have very high molecular weights, appreciable yields and P proportions, but also exhibit no apparent difference in the compositions for various individual fractions; for instance in 6, when $\bar{M}_w = 800 \times 10^3$ ($\bar{M}_w/\bar{M}_n = 1.16$), $m = 1.208$; $\bar{M}_w = 4.0 \times 10^3$ ($\bar{M}_w/\bar{M}_n = 1.05$), $m = 0.845$. These m data evidently indicate that the polymers have the copolymerization structure from two precursors. In addition, no insoluble fraction was produced in the syntheses for copolymers 3–6. As a result, separation of the toluene solutions from water is easy to be carried out, and no centrifugation to remove

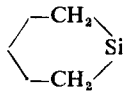
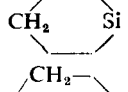
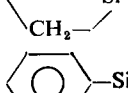
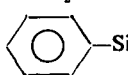
insoluble byproduct is necessary. The workup is much simpler than that for the dimethylsilylene-containing copolymers^[13, 15].

All of the copolymers display a bimodal or trimodal molecular weight distribution, as shown in the typical GPC elution profile in Fig. 1. The yield and molecular weight distribution was unchanged when reaction was carried out for longer than 3 h. No visible effect of amount of solvent used on the molecular weight and yield of the copolymer was found. If the volume of toluene is decreased to about two times as large as the total volume of chlorosilanes employed, the viscosity of the polymer solution is too high to facilitate washing with water. Either a deficiency or an excess of more than 15% of the required amount of sodium led to a decrease in both molecular weight and yield of the copolymer. Thus the optimal amount of sodium is 2–5% excess.

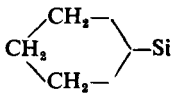
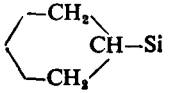
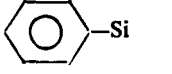
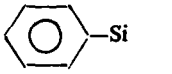
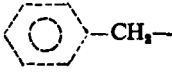
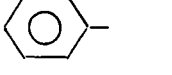
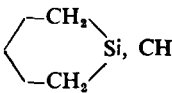
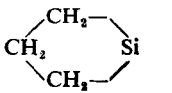
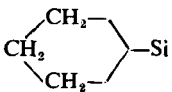
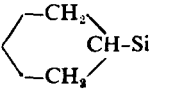
Characteristics of the copolymers

The ¹H and ¹³C-NMR spectral data and assignments for copolymers 1–6, as shown in Table 2, are all consistent with the expected structures^[9, 13–15]. Typical proton and ¹³C-NMR spectra are given in Figs. 2 and 3. For copolymers 1–3 containing phenyl groups directly attached to silicon, all ¹H resonance peaks (except those of *n*-hexyl groups) are exceptionally broad, and all of ¹³C spectra, except those in *n*-hexyl groups, are also broad. The ¹H and ¹³C-signals in the methyl regions for 1–3 lie upfield compared with those of 4–6. These results conform with those reported in previous papers^[9, 13–15], and indicate that the phenyl groups directly attached to silicon in the polymer backbone have a significant effect on the shielding of nearby protons and carbons. Copolymer 4 with phenyl groups separated from the silicon by two CH₂ groups, like 5 and 6 without phenyl groups, does not display the extreme broadening of proton and ¹³C-signals found for 1–3, although proton and ¹³C resonance peaks in methyl region still appear to consist of three or more overlapping peaks. The broad and multiple signals observed for these copolymers may show the existence of regions of more than one stereoregular polymeric conformation. Hindered rotation in the polymer chains may also lead to non-equivalence of various nuclei^[17].

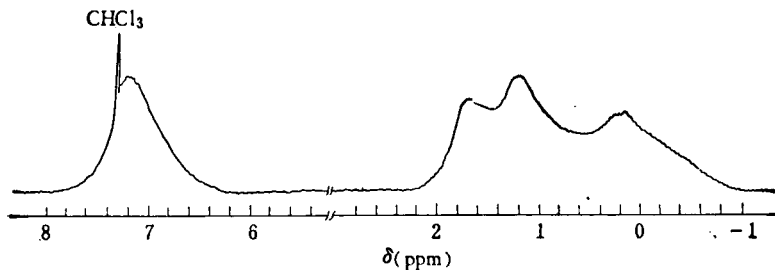
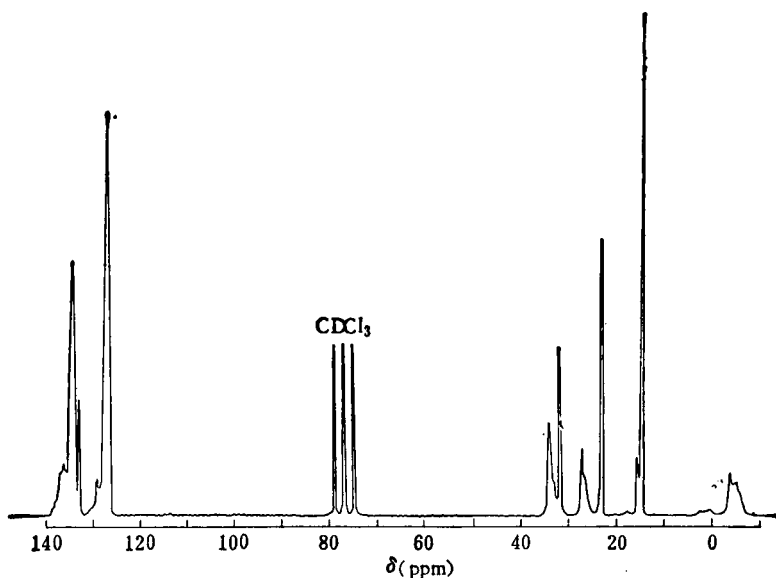
Table 2 ¹H and ¹³C-NMR chemical shifts for the copolymers

Copolymer	¹ H (ppm)	¹³ C (ppm)	Assignment
1	0.17(vb)	–6.00(b)	CH ₃ –Si
	1.03(vb)	11.95(b)	
	1.56(vb)	26.92(b)	
	1.85(vb)	29.73(b)	
	7.21(vb)	127.3(b), 133.0(b), 134.7(b), 136.4(b)	

(Table 2 cont'd)

Copolymer	^1H (ppm)	^{13}C (ppm)	Assignment
2	0.16(vb)	-4.90(vb)	$\text{CH}_3\text{-Si}$
	1.17(vb)	26.81(b)	
	1.64(vb)	28.52(b), 30.61(b)	
	7.14(vb)	127.3(b), 133.1(b), 134.7(b), 136.5(b)	
3	0.27(vb)	-3.96(b)	$\text{CH}_3\text{-Si}$
	0.90(b)	14.26, 15.31	$\text{CH}_3\cdots\text{CH}_2\text{-Si}$
	1.31(b)	22.80, 27.14, 31.77, 34.14	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
	7.06(vb)	127.5(b), 133.1(b), 134.7(b), 136.3(b)	
4	0.45(b)	-3.63(b)	$\text{CH}_3\text{-Si}$
	0.95(b)	14.26, 15.31	$\text{CH}_3\cdots\text{CH}_2\text{-Si}$
	1.33(b)	17.18, 22.85, 27.14, 31.71, 34.08	$\text{-CH}_2\text{-Si}$, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
	2.73(b)	32.98	
	7.15(b)	125.4, 127.4, 128.2, 144.6	
5	0.33(b)	-2.97(b)	$\text{CH}_3\text{-Si}$
	0.86(b)	13.38, 14.32, 15.31	
	1.28(b)	22.91, 26.98, 31.77, 34.14	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
	1.73(b)	26.54, 30.06	
6	0.30(b)	-2.81(b)	$\text{CH}_3\text{-Si}$
	0.91(b)	14.32, 15.58	$\text{CH}_3\cdots\text{CH}_2\text{-Si}$
		22.91, 27.09, 31.77, 34.19	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
	1.32(b)	27.97	
	1.78(b)	28.69, 31.05	

b: broad; vb: very broad.

Fig. 2 ^1H -NMR spectrum of copolymer 2 (in CDCl_3)Fig. 3 ^{13}C -NMR spectrum for copolymer 3 (in CDCl_3)

As can be seen from Table 3 and Fig. 4, the copolymers 1–6 all show strong ultra-violet absorption maxima between 280 and 334 nm. Polymers 1–3 with phenylsilyl groups have very intense UV absorptions at wavelengths longer than 324 nm, similar to polysilastyrene (330 nm)^[12]. The bathochromic shift is probably related to increased conjugative interactions between phenyl substituents and the silicon spinal chain acting as a σ - σ^* or σ - π chromophore and to the increased chain length of the copolymers^[18–25]. Thus copolymer 4, unlike 1–3, displays both shorter λ_{max} and weaker absorptivity. Copolymer 5 exhibits λ_{max} at unusually high energy, much shorter than that of *n*-hexylmethylsilylene homopolymer (306 nm)^[14]. However, in comparison with the *n*-hexylmethylsilylene homopolymer

Table 3 UV absorption properties for the copolymers

Copolymer	$\lambda_{\max}$ (nm)	$\epsilon \times 10^{-3a}$
1	324	4.0
	269	3.5
	227	5.6
2	334	7.8
	273	4.0
	227	6.6
3	333	7.4
	275	3.5
	226	5.5
4	301	3.9
	269	2.4
	238	3.3
	220	5.9
5	280	2.8
	231	2.4
6	310	4.3
	237	2.0

a) Per average Si unit.

or copolymer 4, 6 has both longer $\lambda_{\max}$ and stronger absorptivity. These are in agreement with earlier findings that an insertion of cyclopentamethylenesilylene units in the silane polymer chain shifts the absorption maximum to shorter wavelength, and that cyclohexylsilyl groups in silane polymer behave somewhat as arylsilyl groups which are very intense chromophore. Certainly the side groups directly attached to silicon have marked effect on the properties of the silane polymers.

Infrared spectral absorptions for these copolymers are listed in Tables 4 and 5, and tentative assignments for the vibrational bands are also given in the tables^[8, 10, 11, 26-28]. Sample spectra are shown in Figs. 4 and 5. The IR spectra are also in agreement with the structures proposed for these copolymers.

The appearances and softening temperatures (at which the polymers can be molded or cast into films, or drawn into fibers) are summarized in Table 6. Copolymers 1-3 with lower molecular weights exhibit higher softening temperatures, in comparison with 4-6, possibly an effect of steric hindrance to chain rotation due to the phenyl substituents. Copolymers 4-6 have both high molecular weights and large proportions of the high molecular weight fractions, but can be shaped at lower temperatures (even at room temperature), and the tenacious fibers or films so obtained are not easily breakable. This is perhaps due to chain

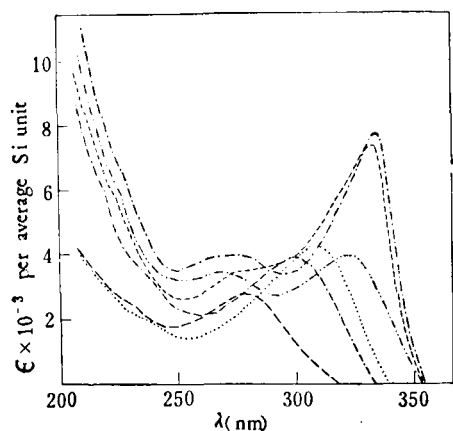


Fig. 4 Ultraviolet spectra for copolymers 1—6 in THF solution
— · · 1; — · 2; - - - 3; — — · 4;
— — 5; · · · 6.

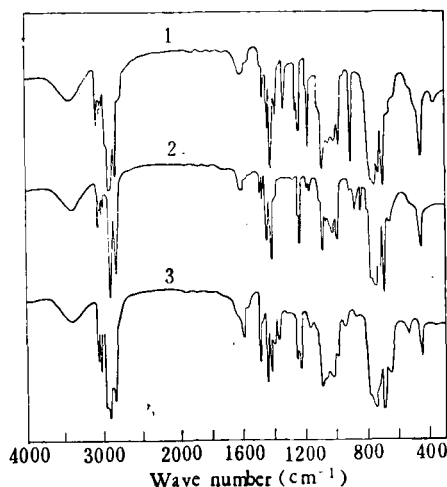
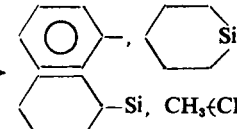


Fig. 5 Infrared spectra of copolymers 1—3

Table 4 Infrared absorptions of copolymers 1—3

Absorption (cm ⁻¹)			Assignment
1	2	3	
(3440)	(3440)	(3440)	(adsorbed H ₂ O)
3070(m), 3050(m)	3072(m), 3057(w)	3070(m), 3030(m)	CH (phenyl) stretch
2960(sh)		2960(s)	CH ₃ —C stretch (a)
2920(vs)	2922(vs)	2924(vs)	—CH ₂ —stretch (a)
		2880(s)	CH ₃ —C stretch (s)
2854(s)	2857(s)	2860(s)	—CH ₂ — stretch (s)
1494(w), 1485(w)	1495(w), 1486(w)	1493(m)	phenyl skeletal breathing
		1470(m)	CH ₃ —C deformation (a)
1446(m)	1448(m)	1453(m)	—CH ₂ — in-plane bending
1429(s)	1429(m)	1429(m)	phenyl—Si bending
1405(m)	1410(w)	1410(w)	—CH ₂ — out-of-plane bending
		1380(w)	CH ₃ —C deformation (s)
1260(m)	1260(sh)	1260(m)	CH ₃ —Si deformation
1246(m), 1178(m)	1246(m)	1246(m)	—CH ₂ —Si, —CH—Si deformation
1094(s), 1062(s)	1098(m), 1070(m)	1098(m), 1066(m) }	phenyl—Si
1022(s), 980(s)	1028(m), 997(m)	1029(m), 1000(m) }	
903(s), 756(vs)	750(vs)	749(s)	—CH ₂ —Si, CH ₃ —Si rocking
733(s)	730(vs)	730(sh)	{CH ₂ } _n (n ≥ 4) in-plane bending
710(s)	696(s)	695(s)	phenyl—Si, out-of-plane bending
670(w), 630(b, w)	663(w)	662(m)	Si—C stretch
463(m)	465(m)	540(w), 463(w)	Si—Si stretch

Table 5 Infrared absorptions for copolymers 4-6

Absorption (cm ⁻¹)			Assignment
4	5	6	
(3440)	(3440)	(3440)	(adsorbed H ₂ O)
3065(m), 3032(m)	3047(m)	3032(m)	CH stretch
2960(s)	2980(sh)	2960(sh)	CH ₃ ⟨C⟩ stretch (a)
2925(vs)	2940(vs)	2920(vs)	-CH ₂ - stretch (a)
	2870(s)		CH ₃ ⟨C⟩ stretch (s)
2860(s)	2850(sh)	2854(2)	-CH ₂ - stretch (s)
1494(s)			phenyl skeletal breathing
1494(s)	1492(m)	1493(m)	CH ₃ ⟨C⟩ deformation (a)
1452(s), 1410(w)	1452(s), 1408(m)	1452(s), 1410(w)	-CH ₂ - out-of-plane bending
1378(w)	1380(w), 1340(m)	1380(w)	CH ₃ ⟨C⟩ deformation (s)
1260(sh)	1260(m)	1263(w)	CH ₃ -Si deformation
1246(m)	1245(m)	1250(w)	-CH ₂ -Si deformation
1175(b, w)	1197(sh), 1180(s)	1187(w), 1170(w)	⟨CH ₂ ⟩ _n (n ≥ 4) in-plane bending
1100(sh), 1070(m)	1100(s), 1070(s)	1100(m), 1070(m)	
1030(m), 995(m)	1030(s), 985(s)	1030(m), 996(m)	
900(b, w)	910(s)	910(w), 890(w)	
780(sh), 750(b, s)	752(b, s)	750(b, s)	⟨CH ₂ ⟩ _n (n ≥ 4) out-of-plane bending
696(s), 660(sh)	696(s), 660(sh)	696(s), 660(sh)	Si-C stretch
560(w), 540(w)	540(b, w), 515(b, w)	540(w)	Si-Si

flexibility contributed by the *n*-hexyl groups. These factors mentioned above, namely, high molecular weight, freedom from volatile fractions, and lower shaping temperature for the polymer, may be important in further processing to high strength silicon carbide fiber, because such a polymer will retain its physical shape during shaping^[3-6].

All copolymers investigated are readily soluble in common solvents, for example, benzene, toluene, THF and chloroform, and have good film-forming properties. Especially, copolymers 4 and 6 can easily be formed into transparent, tough and flexible thin films. This is probably due to their high molecular weights and large proportions of the high molecular weight fractions, as well as their excellent solubilities in common solvents, besides the flexible *n*-hexyl groups.

These copolymers all are also photosensitive. Irradiation of the polymers with ultraviolet light leads to photolytic degradation, more rapid in dilute solutions than as solids, as shown by incremental decrease in the molecular weights. In argon, some crosslinking takes place along with degradation, as indicated by the formation of particles which are

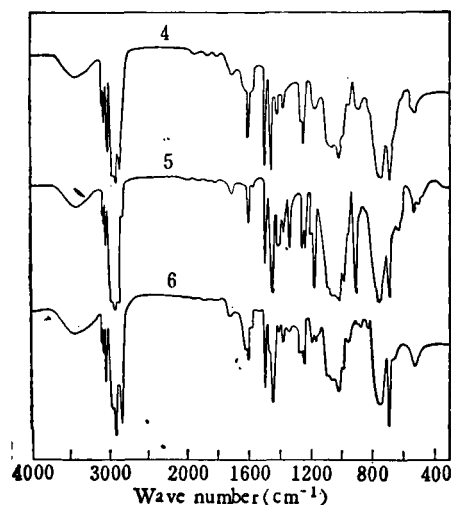


Fig. 6 Infrared spectra for copolymers 4—6

Table 6 Appearances and softening temperatures for the copolymers

Copolymer	Appearance	Softening temp. (°C)
1	Resinous solid	90—120
2	Resinous solid	125—160
3	Waxy solid	110—140
4	Sticky elastomer	30—60
5	Sticky elastomer	30—60
6	Sticky elastomer	40—80

somewhat less soluble. The mechanism of photocission or photocrosslinking is not known, but it is surely related to organosilyl free radicals generated from scission of the polymers under radiation^[29, 30].

Further studies on the sensitivity to radiation and potential semiconductivity for these polymers are in progress.

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