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Vinyl-substituted Polysilanes

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1-Vinylheptamethyltrisilane, 2-vinylheptamethyltrisilane and vinylpentamethyldisilane have been prepared from the corresponding chlorosilanes and vinylmagnesium chloride. In these compounds, intense absorption maxima were observed in the ultraviolet region, and both the λ_{max} and ε increased with an increase in the chain length. Nuclear magnetic resonance and infrared data are also recorded here. Free radical copolymerizations were carried out with styrene and with acrylonitrile, and the monomer reactivity ratios of vinylpentamethyldisilane and 2-vinylheptamethyltrisilane were determined. It has been concluded that the 3d orbital resonance is not important for the stabilization of an odd electron adjacent to the silicon atom in the free radical intermediate in copolymerization in spite of spectral and chemical evidence of enhanced conjugation between the vinyl group and the polysilanyl group.

In their studies of the copolymerization of vinyltriethoxysilane and vinyltrimethylsilane, Scott and Price reported a very low resonance stabilization factor, Q.[1] The low values of Q for both monomers (0.03—0.035) were further supported by the ultraviolet spectra of these compounds, which disclosed only a little conjugation between the vinyl group and the silicon atom. On the other hand, for vinyl sulfides[2] it was concluded, from the large Q values and the relatively intense ultraviolet absorption band, that a sulfide sulfur atom could conjugate with a p electron, either in the free radical intermediate or in the excited state, possibly through 2p-3p conjugation but *not through 2p-3d conjugation.*[1]

Recently, Hague and Prince[3] described an absorption at 246.5 mμ for hexaphenyldisilane and explained this absorption as due to an interaction between phenyl groups through the silicon-silicon bond. Subsequently, it was reported from this laboratory[4,4a] that polysilanes with phenyl or vinyl groups, unlike monosilanes, have a very intense absorption in the ultraviolet region, and it was proposed that the silicon-silicon bond itself is a chromophore, making an enhanced conjugation with pi-electron systems. This interesting ultraviolet property of polysilanes has also been studied independently by Gilman et al.[5,6] In relation to these findings our primary interest was to investigate if the enhanced conjugation of the disilanyl group with the ethylenic double bond influences the copolymerization characteristics and other properties of these vinylpolysilanes.

In the present paper we wish to describe the results of the preparation, spectral study and copolymerization study of vinyl-substituted polysilanes.

Results and Discussion

Vinylpentamethyldisilane (I), 1-vinylheptamethyltrisilane (II), and 2-vinylheptamethyltrisilane (III) were prepared from vinylmagnesium chloride and the corresponding chloropolysilanes in tetrahydrofuran. These three compounds were all colorless liquids and showed no tendency to spontaneous polymerization. Chernyshev et al.[7] reported on the preparation of vinylpentamethyldisilane, together with related disilanyl compounds.

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[3] D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 300 (1962).

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[6] H. Gilman, W. H. Atwell and G. L. Schwebke. *J. Organometal. Chem.*, **2**, 369 (1964).

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Table I. Ultraviolet spectra of some vinyl substituted silanes

Compound	Solvent	λ_{max}, mμ	ε_{max}	Ref.
$CH_2=CH-SiMe_3$ (IV)	Isooctane	202	1470	1
$CH_2=CH-Si(OEt)_3$ (V)	Isooctane	210	300	1
$CH_2=CH-SiMe_2SiMe_3$ (I)	*n*-Hexane	223.2	5200	4
$(CH_2=CH-SiMe_2-)_2$ (VI)	*n*-Hexane	227.0	9790	4
$CH_2=CH-SiMe_2SiMe_2SiMe_3$ (II)	*n*-Hexane	218.0 (sh)		This work
		237.0	6760	
$CH_2=CH-SiMe(SiMe_3)_2$ (III)	*n*-Hexane	221.0 (sh)		This work
		238.0	6090	
$(CH_2=CH-SiMe_2SiMe_2-)_2$ (VII)	Cyclohexane	243.5	14000	6

Table II. Infrared absorption associated with vinyl group (cm^{-1})

Mode of vibration	Compound		
	I	II	III
CH stretching	3055 (m)	3040 (m)	3060 (m)
	3010 (w)	2998 (w)	3005 (w)
C=C stretching	1587 (w)	1585 (w)	1580 (vw)
CH out-of-plane deformation	1009 (m)	1005 (m)	1003 (m)
CH_2 out-of-plane deformation	945 (s)	942 (s)	934 (s)

Table III. Nuclear magnetic resonance data[a]

Band	Compound (chemical shifts in τ)				
	IV	I	II	III	VI
$Si(CH_3)_3$	9.95	9.94	9.95	9.91	
$Si(CH_3)_2$		9.87	9.87		9.87
$Si(CH_3)$				9.87	
Vinyl group, multiplet centered at	4.14	4.09	4.02	4.01	4.05

a) Chemical shifts are expressed as τ values in p.p.m. relative to tetramethylsilane. When cyclohexane was used as internal standard, we have taken 1.43 p. p. m. as the signal difference between cyclohexane and tetramethylsilane to obtain τ values.

Table IV. Copolymerization characteristics of I and III

M_2	M_1	r_1	r_2	Q_2	e_2
I	Styrene	50±10	0	0.02	−0.6
	Acrylonitrile	3±1	0		
III	Styrene	38±5	0	0.02	−0.7
	Acrylonitrile	2±1	0		

They gave 120—121°C as the boiling point of vinylpentamethyldisilane, but our repeated preparation of this compound disclosed its boiling point to be 131°C.

Table I lists the ultraviolet spectral properties observed for I, II and III, together with vinyltrimethylsilane (IV), vinyltriethoxysilane (V), 1, 2-divinyltetramethyldisilane (VI) and 1, 4-divinyloctamethyltetrasilane (VII). With an increase in the number of silicon atoms, the position of the absorption maximum shifted to a longer wavelength and the molar extinction coefficient increased regularly. This is a tendency which was also observed with phenylsubstituted polysilanes[3,6] and with permethylated polysilanes.[6]

Recently West[8] illustrated the effect of metalloid substitution on the electronic spectra of simple chromophores using a qualitative molecular orbital theory. Since the electronic absorption of a simple olefin must be associated with only a transition from bonding pi-orbitals to antibonding pi-orbitals (π-π^* transitions) and since the resonant interaction of a vacant silicon d_π orbital is expected to be stronger with the antibonding orbital than with the bonding orbital,[8] the increasing bathochromic shift with an increase in the chain length of vinylpolysilanes may be a reflection of the lowering of the d_π level by the catenation of the silicon atom. As has been observed for 1-phenylheptamethyltrisilane,[3] it is interesting to note that vinylheptamethyltrisilanes possess two absorption maxima (or shoulders). All permethylated straight-chain polysilanes except hexamethyldisilane have been reported[6] to possess a characteristic absorption in

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[8] R. West, *J. Organometal. Chem.*, **3**, 314 (1965).

the normal ultraviolet region. Since octamethyltrisilane was found to have an absorption maximum at 215.0 mμ, the broad shoulder observed at 216—218 mμ for II and III may be attributed to the absorption of the trisilane chain itself, which originates in a different sort of transition, independent of the π-π^* transition.

The infrared absorption bands associated with the vinyl group are given in Table II. Significant shifts in CH_2 deformation and C=C stretching frequencies from normal positions in analogous carbon compounds were observed. Potts and Nyquist⁹⁾ pointed out that the out-of-plane CH_2 deformation frequencies in substituted ethylenes of the Y–CH=CH_2 type are sensitive to the nature of the substituent, Y. Thus, the CH_2 deformation band shifts to a higher frequency when the pi-electron-attracting power of Y becomes greater. As can be seen from Table II, the out-of-plane CH_2 deformation frequencies of the vinyl group for I, II and III shift from the normal frequency of the CH_2 deformation band to a frequency higher by 35 cm^{-1}. This abnormally high frequency of the CH_2 deformation may be explained by the interaction of silicon with an unsaturated system through a dative p_π-d_π overlap.¹⁰⁾ In a series of vinylsilanes of the $R_3SiCH=CH_2$ type, Eisch and Trainor¹⁰⁾ also found a correlation between the position of the CH_2 deformation frequency and the electron-withdrawing power of R as measured by σ_p or σ.* Although this interesting correlation may not be directly applicable to the vinylpolysilane system, it is likely that the electron-releasing inductive character of the pentamethyldisilanyl group is slightly greater than that of the trimethylsilyl group.

Table III lists the proton magnetic resonance data for carbon tetrachloride solutions of some vinyl-substituted silanes. The deshielding effect of the vinyl group on the proton of the methyl groups bound to silicon was observed to be transmitted along the polysilane chain. As the same trend was also observed for phenyl-substituted polysilanes,¹¹⁾ these results suggest some d_π-d_π double-bond character of the polysilane chain. As one can see from Table III, only two kinds of methyl peaks were observed for II. It had been found¹¹⁾ that internal Si-CH_3 groups were more shielded than terminal Si-CH_3 groups* in octamethyltrisilane, although inner Si-CH_3 groups were generally more deshielded than outer Si-CH_3 groups in homologous permethylated straight polysilanes.¹¹·¹²⁾ Therefore, the peak of the internal $Si(CH_3)_2$, rather than of the $Si(CH_3)_2$ attached to the vinyl group, was supposed to fall at the position for the terminal $Si(CH_3)_3$.

The copolymerizations of both I (M_2) and III (M'_2) with styrene (M_1) and with acrylonitrile (M'_1) were carried out at 60°C. From the composition analyses of the resulting copolymers, the monomer reactivity ratios were determined. These copolymerization characteristics are summarized in Table IV.

The values of Q for both monomers are low and in the same range of magnitude as for many other vinyl-substituted monosilanes.¹³⁾ This fact suggests that the 3d orbital resonance is not important for the stabilization of an odd electron adjacent to the silicon atom in the free radical intermediate in the copolymerization in spite of spectral and chemical evidence of enhanced conjugation between the vinyl group and the polysilanyl group. The more negative e values of both monomers than the value for trimethylvinylsilane could be ascribed to a slightly greater electron-releasing character of the disilanyl group and of the 2-trisilanyl group. This observation is compatible with the infrared spectral evidence.

Experimental

Boiling points are uncorrected. NMR spectra were obtained in carbon tetrachloride solution with a Varian A-60 spectrometer. Tetramethylsliane or cyclohexane was used as an internal standard. The infrared spectra were obtained with a Nippon Bunko DS-402G Grating Infrared Spectrophotometer. The ultraviolet spectra were obtained with a Shimadzu SV-50A Automatic Recording Spectrophotometer.

1-Chloroheptamethyltrisilane,¹⁴⁾ 2-chloroheptamethyltrisilane¹⁴⁾ and chloropentamethyldisilane¹⁵⁾ were prepared as reported previously. Styrene was distilled under reduced pressure in a stream of nitrogen after steam distillation. Acrylonitrile was redistilled through a 30-cm. column packed with glass helicoils under nitrogen.

Vinylpentamethyldisilane. — In a 2-l. flask equipped with a stirrer, a reflux condenser filled with dry-ice and a gas inlet tube, 32 g. (1.32 g.-atoms) of magnesium turnings and 700 ml. of tetrahydrofuran freshly distilled from lithium aluminum hydride were placed. A few drops of ethyl iodide, together with a crystal of iodine, was added to initiate the reaction. To the stirred solution there was then added through a gas inlet vinyl chloride, which had been previously passed through a saturated solution of sodium hydroxide, a Drielite tube and a phosphorus pentoxide tube. When the Grignard preparation was complete, the condenser was replaced with a water condenser and chloropentamethyldisilane (171.5 g., 1.03 mol.), dissolved in an equal volume of tetrahydrofuran, was added at such a rate that a gentle reflux was maintained. After this addition was complete (after one hour), the reaction

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9) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **15**, 679 (1959).

10) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963).

11) Unpublished results in this Laboratory.

* The τ values of terminal Si-CH_3 and internal Si-CH_3 are 9.93 and 9.95 respectively.¹¹⁾

12) U. G. Stolberg, *Angew. Chem.*, **75**, 206 (1963).

13) L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).

14) M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, **2**, 478 (1964).

15) M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina *J. Org. Chem.*, **21**, 1264 (1956).

mixture was refluxed for further 20 hr. It was subsequently cooled and hydrolyzed by the addition of a saturated aqueous solution of ammonium chloride. The organic layer was separated, washed, and distilled to remove the solvent. The residue was then fractionally distilled through a 30-cm. column packed with glass helices to give 99 g. (60.8%) of vinylpentamethyldisilane, b. p. 131—132°C, n_D^{20} 1.4497, d_4^{20} 0.7673 (lit.,7) b, p. 120—121°C, n_D^{20}, 1.4441, d_4^{20} 0.7621).

1-Vinylheptamethyltrisilane.—To a stirred solution of vinylmagnesium chloride prepared from 5 g. (0.2 g.-atom) of magnesium and vinyl chloride in 200 ml. of tetrahydrofuran in the same manner as described above there was added, drop by drop, 31 g. (0.14 mol.) of 1-chloroheptamethyltrisilane over a 40-min. period. After the addition was complete, the reaction mixture was refluxed for 5 hr.; then the solvent was distilled off through a short column to ensure a complete reaction and the residual mass was hydrolyzed with an aqueous solution of ammonium chloride. After the usual treatment simple distillation gave 26 g. of a practically pure liquid (on v. p. c.) boiling over the range of 70—79°C (16 mmHg). Fractional distillation gave 18 g. (59%) of 1-vinylheptamethyltrisilane, b. p. 79°C (16 mmHg), n_D^{20} 1.4741, d_4^{20} 0.7972. (Found: C, 49.32; H, 10.83; MR_D, 76.35. Calcd. for $C_9H_{24}Si_3$: C, 49.92; H, 11.17%; MR_D, 76.32.)

2-Vinylheptamethyltrisilane. — Vinylmagnesium chloride was prepared from 15 g. (0.62 g.-atom) of magnesium and vinyl chloride in 300 ml. of tetrahydrofuran. 2-Chloroheptamethyltrisilane (37 g., 0.16 mol.) was added drop by drop to the Grignard reagent over a period of 40 min. After the treatment in virtually the same manner as with 1-vinylheptamethyltrisilane, 21 g. (61%) of 2-vinylheptamethyltrisilane was obtained as a colorless liquid, b. p. 75°C (17 mmHg), n_D^{20}, 1.4761, d_4^{20}, 0.7945. (Found: C, 50.04; H, 10.99; MR_D, 76.89. Calcd. for $C_9H_{24}Si_3$: C, 49.92; H, 11.17%; MR_D, 76.32.)

Copolymerization Procedure. — The copolymerizations of pairs of monomers were carried out at 60±0.1°C in sealed glass tubes which had been degassed three times on a vacuum line. Benzene and dimethylformamide were used as the solvent for the copolymerization with styrene and with acrylonitrile respectively, while azobisisobutyronitrile (0.5 mol. per cent to the total of monomers) was used as the initiator. Polymerization was interrupted when it was estimated that 5—10% of the copolymer had been formed. The copolymers were then precipitated by pouring the reaction mixture into 200 ml. of cold methanol. The resultant copolymers were further purified by repeated reprecipitations and were subjected analysis; the results are listed in Tables V, VI, VII and VIII.

TABLE V. COPOLYMERIZATION OF STYRENE (M_1) WITH VINYLPENTAMETHYLDISILANE (M_2)

M_2	Reaction time, hr.	Conversion, %	C, %	m_2
0.400	4.5	4.89	91.12	0.0194
0.500	7	5.25	91.04	0.0207
0.600	12	5.84	90.64	0.0276
0.800	24	2.72	88.27	0.0694
0.850	35	2.16	86.51	0.101

TABLE VI. COPOLYMERIZATION OF ACRYLONITRILE (M'_1) WITH VINYLPENTAMETHYLDISILANE (M_2)

M_2	Reaction time, hr.	Conversion, %	N, %	m_2
0.200	2	7.36	21.07	0.078
0.400	5	5.81	18.53	0.125
0.500	8	6.21	17.65	0.143
0.600	15	5.84	17.13	0.154

TABLE VII. COPOLYMERIZATION OF STYRENE (M_1) WITH 2-VINYLHEPTAMETHYLTRISILANE (M'_2)

M'_2	Reaction time, hr.	Conversion, %	C, %	m'_2
0.400	3	1.20	89.84	0.0283
0.500	7	4.22	90.31	0.0227
0.600	22	6.54	89.33	0.0345
0.800	29	2.09	87.43	0.0583

TABLE VIII. COPOLYMERIZATION OF ACRYLONITRILE (M'_1) WITH 2-VINYLHEPTAMETHYLTRISILANE (M'_2)

M'_2	Reaction time, hr.	Conversion, %	N, %	m'_2
0.200	2	5.21	19.41	0.081
0.400	4	1.51	16.94	0.120
0.500	13	5.56	15.77	0.135
0.600	22	3.31	14.57	0.166

From the data of analysis the monomer reactivity ratios, r_1 and r_2, were estimated by the intersection method using Eq. 1. The r_2 values in each case were virtually zero, so the Q and e values were calculated by solving Eqs. 2 and 3:

$$r_2 = \frac{M_1}{M_2}\left[\frac{dM_2}{dM_1}\left(1+\frac{M_1}{M_2}r_1\right)-1\right] \tag{1}$$

$$r_1 = \frac{Q_1}{Q_2}\exp\left[-e_1(e_1-e_2)\right] \tag{2}$$

$$r'_1 = \frac{Q'_1}{Q_2}\exp\left[-e'_1(e'_1-e_2)\right] \tag{3}$$

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