

452. *The Synthesis and Irradiation of Polyborosiloxanes.*

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The preparation and properties of a series of condensation products of boric acid and organo-chlorosilanes are described. From the compositions and molecular-weight measurements a structure is proposed for the resulting polymers. Irradiation of the borosiloxanes induced a linking reaction, giving higher-melting materials with improved hydrolytic and heat stability.

THE work now described was initiated in an attempt to prepare high-temperature, stable, semi-inorganic polymers and to determine whether the cross-linking of polymer chains, containing hydrolysable atoms or groups, with ionising radiation would decrease the hydrolytic susceptibility of the polymers. The B-O-Si linkage has good thermal stability and therefore the preparation and properties of polyborosiloxanes were selected for this study.

Several methods have been reported for the synthesis of borosiloxanes. Henglein, Lang, and Scheinost¹ trans-esterified triethyl borate with diacetoxydimethylsilane which caused elimination of ethyl acetate to form a boron-oxygen-silicon bond. This reaction has been studied in more detail by Andrianov² *et al.*, using ¹⁸O-labelled esters.

Voronkov and Zgonnik³ studied the reaction between boric acid and alkylchlorosilanes and described their products as liquids of various viscosities, and also soluble or insoluble, plastic or brittle solids, but no molecular weights or structures were given.

In the present study the reaction between boric acid and dichlorodimethylsilane was investigated with and without solvent. The quantitative yields of hydrogen chloride were measured, and the effects of catalysts on the rate and extent of reaction determined. From a knowledge of the composition of the polymers and their molecular weights a possible structure was deduced. The effect of ionising radiation on the polymers was examined by subjecting samples to varying doses of electrons from a 4 Mev linear accelerator.

EXPERIMENTAL

Materials.—"AnalaR" boric acid was finely powdered and dried in a vacuum desiccator (CaCl₂). Commercial tetrahydrofuran was purified by distillation over sodium hydroxide, and then sodium wire, in an atmosphere of oxygen-free nitrogen. The distillate was stored over calcium hydride.

¹ Henglein, Lang, and Scheinost, *Makromol. Chem.*, 1955, **15**, 177.

² Andrianov, Kudriavtsev, and Kursanov, *Zhur. obshchei Khim.*, 1959, **29**, 1497.

³ Voronkov and Zgonnik, *Zhur. obshchei Khim.*, 1957, **27**, 1476.

Dichlorodimethylsilane was purified by fractional distillation through a column of 35 theoretical plates, and the fraction of b. p. 69.7°/754.5 mm. was used for all experiments.

Procedure.—Condensation polymerisation. Boric acid and dichlorodimethylsilane were mixed in the molar ratios 1 : 3, 2 : 3, 1 : 1, 3 : 2, or 3 : 1 and heated in a flask fitted with a calcium chloride tube at 90° until the evolution of hydrogen chloride ceased.

Solution polymerisation. Boric acid (5.804 g., 0.094 mole) was mixed with dichlorodimethylsilane (18.166 g., 0.141 mole) and various quantities of tetrahydrofuran (1—50 ml.). The reactants were magnetically stirred in a conical flask attached to a glass-spiral condenser, consisting of six 4 in. diam. turns and surrounded by solid carbon dioxide. The other end of the spiral was connected to two traps containing 1.0N-sodium hydroxide. The rate of evolution of hydrogen chloride at various temperatures was measured by titrating aliquot parts of alkali at selected time intervals. A continuous stream of dry nitrogen was passed into the mixture to ensure rapid removal of the hydrogen chloride. In a blank experiment in which the boric acid was omitted, no dichlorodimethylsilane was carried over by the nitrogen stream, even when the temperature of the reaction mixture was 60°. When the evolution of hydrogen chloride had ceased, tetrahydrofuran (50 ml.) was added, and the mixture shaken until a clear solution was obtained. The solvent and any unchanged silane were then removed by vacuum distillation. The residue was heated *in vacuo* (<1 mm.) at 80—100° for 3 hr., or until a constant weight of residue was obtained.

Analysis.—(i) Boron. The borosiloxane (ca. 0.2 g.) was dissolved in neutral methanol (20 ml.), and water (5 ml.) was added to hydrolyse the polymer. The resulting solution was titrated to the neutral point of Methyl Red, mannitol (2 g.) was then added, and the solution titrated to the phenolphthalein end-point. The first titre was equivalent to any acidity arising from hydrolysable chlorine in the polymer, and the second titre to the boric acid formed on hydrolysis of the boron-oxygen-silicon link.

(ii) *Silicon.* Polymer (ca. 0.1 g.) was digested, in a long tube fitted with a reflux condenser, with fuming sulphuric acid (0.5 g.) and fuming nitric acid (2.0 ml.). The mixture was heated carefully, and after 1 hr. the condenser was removed, and the solution evaporated to dryness. The tube was heated in a furnace at 700° to constant weight, giving the combined weights of boric oxide and silica.

Reverse Reaction.—A borosiloxane (1 g.) was dissolved in carbon tetrachloride (20 ml.) and dry hydrogen chloride was passed into the solution for 1 hr. at 0°, 20°, and 60° in three separate experiments. The flasks were fitted with reflux condensers surrounded with solid carbon dioxide. The solutions were later thoroughly flushed with nitrogen until free from unchanged hydrogen chloride, water (10 ml.) was added, and the mixture titrated with standard alkali with Methyl Red as indicator.

Molecular-weight Measurements.—Molecular weights of the polymeric products in solution in cyclohexane were determined ebullioscopically by means of a differential ebulliometer, using thermistors as the temperature-sensitive elements. Measurements were also made cryoscopically in dioxan solution. All measurements were made at several concentrations, and the results extrapolated to infinite dilution.

Irradiation.—Samples of borosiloxane were irradiated in sealed glass tubes *in vacuo* with 4 Mev electrons, from a linear accelerator. The dose rate was 5×10^8 rads/hr., and during the irradiation the temperature was kept below 60°.

Heat Stability Tests.—Samples were heated in a small desiccator containing phosphoric oxide at 210°.

RESULTS

In the bulk polymerisations, for which various molar ratios of boric acid to dichlorodimethylsilane were used, the products ranged from viscous liquids to white, opaque solids. A molar ratio of 2 : 3 gave clear, viscoelastic solids containing a small amount of trapped boric acid, and this ratio was used for all subsequent work. The polymers could be stored indefinitely in stoppered flasks but hydrolysed rapidly in the atmosphere to give white, opaque solids.

When the polymerisation was performed in certain solvents, *e.g.*, tetrahydrofuran, the rate of reaction, as determined by hydrogen chloride evolution, was greatly increased (see Fig. 1). The rate of condensation increased on dilution and passed through a maximum, decreasing at higher solvent concentrations. Very large quantities of solvent absorbed hydrogen chloride and apparently gave low rates and low conversions. This difficulty was overcome by using a

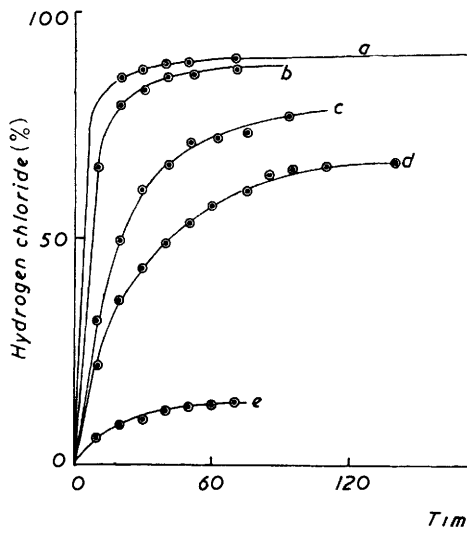
very high flow rate of nitrogen. Not all solvents had this marked catalytic effect, however; ethers and ketones appear to be specific. Benzene, carbon tetrachloride, and ethyl acetate, which are solvents for the borosiloxanes, have no effect on the rate of reaction. Organic bases, *e.g.*, pyridine and tertiary aliphatic amines, have a slight retarding effect. The rate of polymerisation is not greatly increased by a rise in temperature, and high conversions were obtained at 20–30° when using tetrahydrofuran as a solvent (Fig. 2).

Abel and Singh⁴ found that tristrimethylsilyl borate, $B(O\cdot SiMe_3)_3$, reacts rapidly and completely with hydrogen chloride at 0° to produce boric acid and trimethylchlorosilane. In the borosiloxane synthesis this would represent a reverse reaction leading to the following equilibrium:



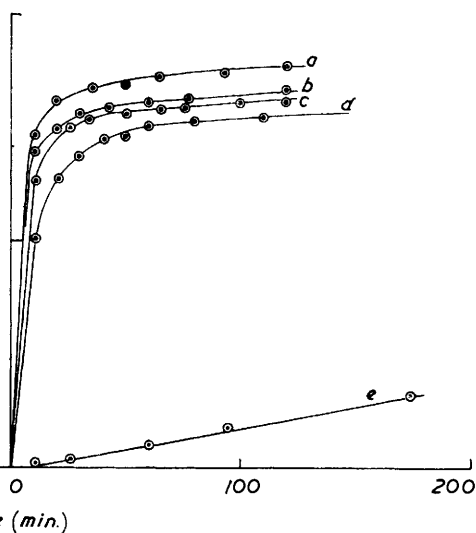
The solutions of the borosiloxanes in carbon tetrachloride contained no dichlorodimethylsilane after hydrogen chloride had been passed in for 1 hr. at 0°, 20°, and 60°, and no hydrolysable

FIG. 1. Effect of increasing solvent (tetrahydrofuran) concentration.



$a = 5, b = 10, c = 30, d = 50$ ml., $e =$ no solvent. $B(OH)_3 : SiMe_2Cl_2 = 2 : 3$.

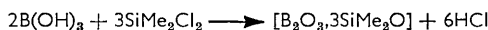
FIG. 2. Effect of temperature on the rate of condensation.



$a = 60^\circ, b = 50^\circ, c = 40^\circ, d = 30^\circ, e = 60^\circ$ (no solvent). $B(OH)_3 : SiMe_2Cl_2 = 2 : 3$. Tetrahydrofuran = 8 ml.

chlorine was detected in the samples. Carbon tetrachloride was chosen in preference to tetrahydrofuran for the reverse reaction as it was easier to remove excess of hydrogen chloride from this solvent.

Extent of reaction. With a molar ratio $B(OH)_3 : SiCl_2Me_2 = 2 : 3$, the complete reaction of all the hydroxyl groups may be represented by



The maximum yields of hydrogen chloride observed ($6HCl \equiv 100\%$) were 90–95% and the difference could be accounted for as unchanged dichlorodimethylsilane. The reaction products were isolated by adding solvent to the mixture and distilling under *vacuo*. Unchanged dichlorodimethylsilane was determined by titrating the distillate, after the addition of water, with standard alkali. Chlorine could not be detected in the polymeric residues, whereas free hydroxyl groups were detected by infrared analysis. In two experiments (K33 and K37) a large excess (20 ml.) of dichlorodimethylsilane was added to the mixture when the evolution of hydrogen chloride had ceased, *i.e.*, 95% conversion. This addition caused a further evolution of hydrogen chloride and a yield of 100% was obtained. The products from these two

⁴ Abel and Singh, *J.*, 1959, 690.

experiments were viscous liquids containing chlorine end groups, and furthermore, no hydroxyl groups could be detected by infrared analysis.

Composition. The boron and silicon contents of several polymers of varying degrees of condensation are shown in Table 1. The weight of polymer residue per chlorine atom for

TABLE 1.

Sample No.	B (%)	Si (%)	HCl yield (%)	Wt. per Cl atom	<i>M</i> (f. p.)	<i>M</i> (b. p.)
K37, viscous liquid	6.35	28.5	100	335	750	813
K33, viscous liquid	6.17	—	100	284	620	—
K42, solid	7.92	26.6	89.9	—	—	940
K18, solid	8.63	24.9	68.2	—	477	—
K37, hydrolysed and heated	7.37	—	—	—	—	1040
K25, solid	7.88	27.1	92	—	760	—

K33 and K37 is the experimentally determined value. Two chlorine end groups being assumed per molecule, the corresponding molecular weights are 670 and 568.

Infrared analyses. Solid samples prepared in solution were analysed both in dioxan solution

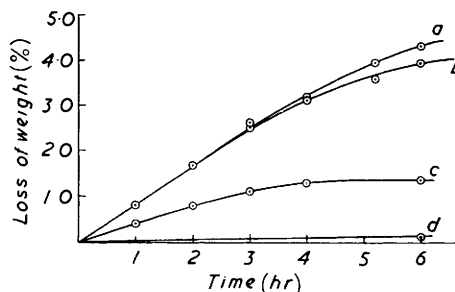


FIG. 3. Loss of weight on heating irradiated polyborosiloxanes at 210° in air.

a = control, *b* = 4×10^7 rads., *c* = 5×10^8 rads., *d* = 1.2×10^9 rads.

and also as films cast from dry dioxan. The solutions gave a series of absorption peaks at 3400, 3350, 3300, and 3240 cm^{-1} , in which the 3400 absorption band was the strongest. The films gave a strong diffuse band at 3235 cm^{-1} .

Molecular weights. The measurement of the molecular weights was difficult owing to the ease of hydrolysis of the borosiloxanes and their association in solution. Anomalous results were obtained by ebulliometry in acetone and isopropyl ether, but cyclohexane solutions were more satisfactory. Table 1 gives a selection of values obtained by two independent methods.

Effects of radiation. Sample K42 was irradiated with a 4 Mev electron beam from a linear accelerator and received doses of 10^7 , 5×10^7 , 10^8 , 5×10^8 , 10^9 , and 5×10^9 rads. The samples showed an increased rigidity with increasing dose and became brittle with doses $> 5 \times 10^8$. On irradiation, the m. p. increased from 105° to 145° at 10^9 rads, and at higher doses became infusible. Samples left in the laboratory atmosphere were compared with non-irradiated samples, and there was no apparent difference in hydrolytic susceptibility for samples receiving doses up to 5×10^7 rads. At higher doses, however, the samples showed a progressive inertness to water, and the sample at 5×10^9 rads was infusible, insoluble, and could be kept in contact with water without significant hydrolysis.

In Table 2 the analyses (in volume %) of the gaseous products of irradiation are compared

TABLE 2.

Component	Borosiloxane	Charlesby (irradiated siloxane)	St. Pierre <i>et al.</i> (irradiated siloxane)
H ₂	34.1	41.0	31.0
CH ₄	54.2	47.0	47.0
C ₂ H ₆	11.7	12.0	22.0

with those obtained by Charlesby⁵ and St. Pierre *et al.*⁶ for irradiated polydimethylsiloxanes. The two systems have in common the $\cdot\text{SiMe}_2\cdot$ grouping.

Thermal stability. The thermal stability of these polymers has not been thoroughly investigated. The results at 210° are shown in Fig. 3. It can be seen that the irradiated

⁵ Charlesby, *Proc. Roy. Soc.*, 1955, *A*, **230**, 120.

⁶ St. Pierre, Dewhurst, and Bueche, *J. Polymer Sci.*, 1959, **36**, 105.

sample showed a smaller loss when heated, probably owing to bonding together of the more volatile low-molecular-weight species in the polymers. It was not possible to follow the molecular-weight changes as the polymers became insoluble in cyclohexane after irradiation. The sample which had received a dose of 5×10^9 rads. lost 4.6% in weight at 420° after 3 hours' heating in air.

The loss in weight may be accounted for largely on the basis of dehydration of unchanged hydroxyl groups on the polymers. On heating, the intensity of the hydroxyl absorption in the infrared region falls, and traces of water can be recovered. On the basis of the structures proposed in the Discussion, the maximum calculated losses on dehydration are given in Table 3.

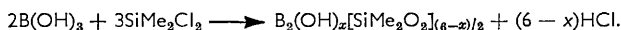
TABLE 3.

	<i>M</i>	Loss on dehydration (%)		<i>M</i>	Loss on dehydration (%)
Monomer ...	236	7.6	Trimer	820	2.2
Dimer	528	3.4	Tetramer ...	1112	1.6

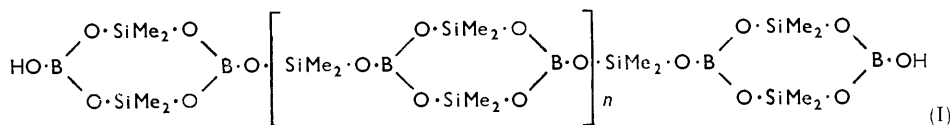
DISCUSSION

The solid polymers show remarkable viscoelasticity (80% rebound) and behave like "bouncing putty," the substance formed on mixing polydimethylsiloxane and boric acid. This is a property normally associated with substances of high molecular weight and it is surprising that materials of such low molecular weight behave in this manner. The explanation probably lies in the extensive hydrogen bonding between terminal hydroxyl groups in the solid polymer, as shown by infrared absorption spectra. The characteristic absorption frequency usually found at 3600 cm^{-1} for non-associated hydroxyl groups is shifted to a broad maximum in the solid polymer at 3235 cm^{-1} , whereas in solution a band at 3400 cm^{-1} is found, and also smaller bands at 3350, 3450, 3330, and 3240 cm^{-1} , representing varying degrees of association. When the hydroxyl groups are removed by reaction with an excess of dichlorodimethylsilane, as in samples K33 and K37, hydrogen bonding is no longer possible and the polymers are viscous liquids. Controlled hydrolysis of these liquids reconverts them into viscoelastic solids.

The reaction of boric acid with dichlorodimethylsilane in the mole ratio of 2 : 3 may be generalised as



This includes intermediate condensation products having unchanged hydroxyl groups but no chlorine, *e.g.*, $(\text{HO})_2\text{B}\cdot\text{O}\cdot\text{SiMe}_2\cdot\text{O}\cdot\text{B}(\text{OH})_2$. Since in all the polymerisations the yields of hydrogen chloride were greater than 4 mols. (66⅔% of theory) the linear structure $\cdot\text{B}(\text{OH})\cdot\text{O}\cdot\text{SiMe}_2\cdot\text{O}\cdot\text{B}(\text{OH})\cdot$ must be excluded. The cyclic structure (I) is postulated on the basis of the molecular weights, composition, and end-group analysis of the polymers.



As chlorine groups were not detected in the solid polymers, the chains must be terminated by hydroxyl groups, measured by infrared analysis. The liquid samples, K33 and K37, did possess chlorine end-groups.

Table 4 gives the calculated boron contents, molecular weights, and hydrogen chloride yields for compounds (I) of various degrees of polymerisation. The ring size is not known,

TABLE 4.

Structure	B, calc. (%)	<i>M</i>	Yield of HCl (%), calc.	$\cdot\text{SiMe}_2\text{Cl}$ end groups	B, calc. (%)	<i>M</i>
Monocyclic	9.34	235.9	66.6	Monocyclic	5.14	421
Dicyclic (<i>n</i> = 0) ...	8.20	527.9	80.0	Dicyclic	6.07	713.09
Tricyclic (<i>n</i> = 1) ...	7.92	819.9	88.8	Tricyclic	6.46	1005.1
Tetracyclic (<i>n</i> = 2)	7.80	1112.0	91.7			

but larger rings containing more than two boron atoms would not be consistent with the analytical data. On comparison of these values with the experimentally determined values for K42 and K25 it can be seen that the solid polymers correspond to a mixture of tri- and di-cyclic polymers, and K18 to a mixture of mono- and di-cyclic.

Conclusions.—Although the polyborosiloxanes have desirable thermal and elastic properties, yet the low molecular weights obtained give inferior mechanical properties and also make the radiation cross-linking an inefficient process. The increase in hydrolytic stability following irradiation could be applied to other inorganic polymeric systems which are too easily hydrolysed.

The author is grateful to Miss S. Miller for experimental assistance and Mr. P. J. Fydeler for the infrared measurements.

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