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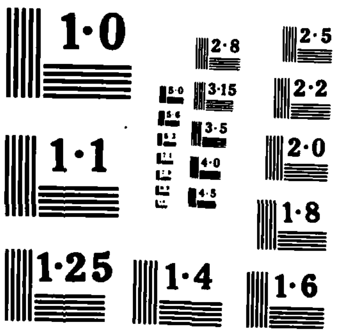
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Thermally Stable Elastomers: Review of Silarylene-Siloxane Polymers and Polysilmethylenes

by
Robert A. Rhein
Advanced Technology Division
Ordnance Systems Department

OCTOBER 1984

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001

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FOREWORD

This is a review of the literature of thermally stable elastomers, consisting of either silarylene-siloxane copolymers or polysilmethylenes, that were described in the unclassified literature during the period 1950-1982. This effort was conducted during FY 1983 and was supported by Independent Research funding under Work Order No. 132890.

This report was reviewed for technical accuracy by Dr. J. C. Baldwin.

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~~(U)~~This technical report is a review of the literature that pertains to two types of thermally stable elastomers: silarylene-siloxane polymers and polysilmethylenes.

(U) The silarylene-siloxane copolymers were generally prepared from the reaction of a bis(hydroxydialkylsilyl)arylene with a dialkylsilane containing two active groups, such as dichloro or bis(dimethylamino). These copolymers are thermally stable, decomposing at temperatures 50-100°C higher than that of the silicone polymers.

(U) The preparation and properties of the polydialkylsilmethylenes are discussed, with emphasis placed on polydimethylsilmethylene. These polymers are typically prepared from the ring-opening polymerization of 1,3-disilabutadienes; the preparation and physical properties of the polymers and the monomers are presented. → cont keywords include: see 1473

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INTRODUCTION

This report is a review of the literature pertaining to two types of thermally stable elastomers: (1) alternating copolymers of siloxane units and silylarylene bulky groups and (2) polysilmethylenes. This effort is an expansion and continuation of NWC TP 6372.[1] Although a number of types of thermally stable elastomers were described in that review, two promising areas for further investigation appeared to be in the areas of copolymers of siloxane and bulky groups, such as silarylene, and in the investigation of polysilmethylenes. The need for cost-effective preparation of the precursors required for making these elastomers was indicated in that review.

This report describes the preparation of these two classes of elastomers. The first type of elastomer considered here, silarylene-siloxane polymers, is prepared by condensation polymerization of a siloxane (or di- or trisiloxane), such as dichlorodimethylsilane or bis(dimethylamino)dimethylsilane, with a bis-silanol, such as *p*-bis(hydroxydimethylsilyl)benzene. In the next section of this report the preparation and physical properties of the known types of bis-silanols are described. Most of these were made by Grignard methods, but there are a few examples of other methods of preparation that could conceivably be used in large-scale production. The various types of alternating copolymers of bis-silanols with siloxanes are described in the third section.

The other class of thermally stable elastomers described in this report is the polysilmethylenes. The polysilmethylene most frequently described in the literature, polydimethylsilmethylene, was generally prepared by the ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Other types of polysilmethylenes have been described; these were prepared by substituting another group for methyl. The fourth section of this report describes the literature methods for preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and other 1,3-disilacyclobutane derivatives. The fifth section describes the literature methods for the polymerization of the cyclic monomers to the polysilmethylenes and describes the physical properties of these polymers.

BIS(HYDROXYDIALKYLSILYL)ARYLENES

PHENYL DERIVATIVES

p-Phenyl Derivatives

The type of bis(hydroxydialkylsilyl)arylenes most frequently described in the literature are those in which the arylene group is *p*-phenyl. Most of the examples of the preparation of *p*-bis(hydroxysilyl)benzene compounds were those that use the Grignard reaction of *p*-dibromobenzene, magnesium, and a silane to form a bis(silyl)benzene, followed by hydrolysis to make the corresponding bis-silanol. Other methods were used to produce *p*-bis(silyl)benzene compounds, and these are also described here.

p-Bis(dimethylhydrogensilyl)benzene was prepared from the reaction of dimethylchlorosilane, magnesium, and *p*-dibromobenzene in tetrahydrofuran (THF)[2-5] or in ether.[2,6] Another method of preparation of bis(dimethylhydrogensilyl)benzene was the reaction of *p*-dichlorobenzene with dimethylchlorosilane in the presence of dispersed sodium in octane/ether in the presence of ethyl acetate.[7] *p*-Bis(dimethylhydrogensilyl)benzene is a liquid with a boiling point (bp) of 60-61°C/1.5mm[6] and 112-113°C/29mm; n_D^{20}=1.5007, and d_{25}=0.8832.[2,3]

The Grignard preparation of *p*-bis(hydrogenmethylphenylsilyl)benzene by the reaction of *p*-dibromobenzene with methylphenylchlorosilane and magnesium in THF was described;[3,8] the physical properties of the liquid were bp=60-61°C/1.5mm[6] and 112-113°C/29mm, and n_D^{25}=1.5892.[8]

p-Bis(diphenylhydrogensilyl)benzene was prepared from the reaction of *p*-dibromobenzene, magnesium, and diphenylchlorosilane;[3,8,9,10,11] it is a solid with a melting point (mp) of 105-108°C;[3,8] the infrared spectrum (IR) was described.[12]

These bis-silanes were converted to the bis-silanols by ethanolysis, followed by NaOH hydrolysis;[2,3,6,8] for example, the bis(dimethylsilyl)benzene was reacted with ethanol containing sodium, then NaOH, and neutralized with potassium dihydrogen phosphate to make bis(dimethylhydroxysilyl)benzene.[2]

Another method of preparing *p*-bis(hydroxydialkylsilyl)benzene was the Grignard reaction of *p*-dihalobenzene, magnesium, and dichlorodialkylsilane, to make the *p*-bis(chlorodialkylsilyl)benzene, followed by hydrolysis. In the Grignard preparation of bis(chlorodimethylsilyl)benzene with magnesium and dichlorodimethylsilane, it was found that ether was an effective solvent when *p*-dibromobenzene was used;[4,12,13,14,15] however, when ether was used as the solvent with *p*-dichlorobenzene, then only a mono-reaction took place with magnesium and dichlorodimethylsilane to form *p*-chlorophenyl dimethylchlorosilane. However, if THF was used as the solvent in this reaction rather than ether, then *p*-bis(chlorodimethylsilyl) benzene was formed.[16,17] Bis(chlorodimethylsilyl)benzene is a solid; mp=85-86°C, bp=101-102°C/1.0mm[4] and 150-155°C/19mm. In addition, the Grignard preparation of *p*-bis(chlorodiphenylsilyl)benzene was described, using diphenyldichlorosilane in THF; it is a solid, mp=195-198°C.[13]

Another method described for the preparation of *p*-bis(chlorodimethylsilyl) benzene was the reaction between a disilane and a dihalobenzene. Halophenyl and *p*-halotoluene were converted to the trimethylsilyl derivatives by the reaction of the haloaryl compound with hexamethyldisilane and potassium methoxide in hexamethylphoric triamide at 25°C in good yields; the reactivity increases in the order $Cl<Br<I$.[18] *p*-Dichlorobenzene (10 m-mole), hexamethyldisilane (20 m-mole), and 1% $Pd(PPh_3)_2Cl_2$, autoclaved 40 hours at 200°C, yielded a 48% yield of *p*-bis(trimethylsilyl)benzene.[19] Under the same reaction conditions the use of 1,2-dichlorotetramethyldisilane resulted in a 53% yield of *p*-bis(chlorodimethylsilyl) benzene.[20,21]

Chlorobenzenes and hydrosilane reacted to produce HCl and silylbenzene. *p*-Dichlorobenzene and chlorodimethylsilane (mole ratio of 1:3), upon irradiation with 1.5-2.0 MeV electrons in sealed ampoules at 300°C, reacted to produce bis(chlorodimethylsilyl)benzene in a maximum yield of 13%.[22] Chlorophenylchlorodimethylsilane and chlorodimethylsilane reacted at 640°C for 60 seconds to produce a 3.8% yield of bis(chlorodimethylsilyl)benzene.[23] However, heating *p*-dichlorobenzene with methylphenylchlorosilane or *p*-chlorophenylmethylchlorosilane at 650°C in a quartz tube yielded up to 25% *p*-bis(phenylmethylchlorosilyl)benzene, a liquid, bp=187-196°C/1-2mm, density 1.1815 g/cm^3, $n_D^{20}=1.6072$.[24]

p-Bis(chlorodimethylsilyl)benzene was converted to *p*-bis(hydroxydimethylsilyl) benzene by NaOH hydrolysis;[12] by the reaction with ammonium hydroxide in ether;[17] by reaction with ethanol and then NaOH;[4,6] and by reacting with aqueous NaOH in ether.[14,15,25,26] For example, the ether solution of the bis-chloro compound reacted with an aqueous solution of alkali at -12°C for 1.5 hours; the aqueous solution of sodium silanolate was neutralized with dilute acetic acid, forming a pure product.[27]

Another method for the preparation of *p*-phenylenedisilanes was by the Grignard method, using *p*-dibromobenzene, magnesium, and dialkoxydialkylsilanes in ether. Using this method the preparation of bis(ethoxydimethylsilyl)benzene and the corresponding methylvinyl compound was described.[12] THF was found to be the preferred solvent in the Grignard preparation of bis(propoxydimethylsilyl)benzene or the ethoxy compound, from the reaction of *p*-dichlorobenzene, magnesium, and dimethyldipropoxysilane or dimethyldiethoxysilane.[28,29] Bis(ethoxydimethylsilyl) benzene was hydrolyzed with NaOH to give the bis-silanol.[29] Bis(alkoxydimethylsilyl)benzene was also converted to the corresponding disilanol by reacting with a water-miscible solvent and a small amount of water and refluxing.[30] Another method to convert bis(ethoxydimethylsilyl)benzene to the bis-silanol was to react with BF_3-etherate to form the bis(dimethylfluorosilyl)benzene, followed by reaction with ammonium hydroxide.[31]

The physical properties of a number of the *p*-bis(hydroxysilyl)benzene compounds were presented.[32] These materials are solids. For *p*-bis(dimethylhydroxysilyl) benzene, the melting point is 136-137°C.[33] The IR spectra were described.[4,27,32] and the nuclear magnetic resonance spectra (NMR) in CCl_4[4] and deuterated DMSO[6] were presented. For *p*-bis(methylphenylhydroxysilyl)benzene, the IR was presented;[12,34] the melting point is 128-140°C,[12,33] and the H^1 NMR was described.[12] For *p*-bis(diphenylhydroxysilyl)benzene, the melting point is 224-226°C,[12,33] or 226-228°C;[6] the IR and H^1 NMR were described.[33] For *p*-bis(hydroxymethylvinylsilyl)benzene, the melting point is 95-96°C.[29]

m-Phenyl Derivatives

m-Bis(dimethylhydrogensilyl)benzene was prepared from the reaction of *m*-dibromobenzene, magnesium, and dimethylchlorosilane in THF; it is a liquid, with a boiling point of 58-59°C/1.1mm, n_D^{25}=1.4974, d_{25}=0.8703.[8] The properties of *m*-bis(ethoxydimethylsilyl)benzene were presented.[33] Hydrolysis of this produced *m*-bis(dimethylhydroxysilyl)benzene, a solid, with a melting point of 81.5-83°C.[8] *m*-Bis(chlorophenylmethylsilyl)benzene was likewise made; it is a liquid, with a boiling point of 179-185°C/.07mm. The corresponding disilanol is a solid, with a melting point of 101-102°C; the H^1 NMR was described.[33]

The reaction between *m*-dibromobenzene with magnesium and 3,3,3-trifluoropropyldimethylchlorosilane in THF to prepare *m*-bis(3,3,3-trifluoropropylmethylchlorosilyl)benzene[35] and the reaction between *m*-dibromobenzene with magnesium and 3,3,3-trifluoropropylmethylchlorosilane in THF to make *m*-bis(3,3,3-trifluoropropylmethylhydrogensilyl)benzene[35,36] were described, along with the procedure for hydrolysis of these (using $NaOH/NaH_2PO_4$ solution, with Pd/C) to make the bis-silanol.[36] Another preparation of the bis-silanol was the in-situ Grignard reaction of *m*-dibromobenzene, magnesium, and diethoxymethyl-(3,3,3-trifluoropropyl)silane, followed by hydrolysis; for the bis-silanol, the boiling point is 140-142°C/0.1mm.[37]

Other Bis-Silyl Benzenes

A number of other bis(silyl)benzene derivatives have been prepared by reactions other than the Grignard method. The reaction between chlorophenyl and hydrosilane groups was found to produce HCl and the phenylsilyl group under certain conditions. The reaction between *p*-dichlorobenzene and trichlorosilane at 300°C and 60 atmospheres under cobalt-60 irradiation produced a 50% yield of *p*-bis(trichlorosilyl)benzene; under similar conditions, dimethylchlorosilane produced a monosilylbenzene.[38,39] Dichlorobenzenes reacted with hydrochlorosilanes (mole ratio 1:3) in sealed ampoules under irradiation with 1.5-2.0 MeV electrons at

300°C. Under these conditions, the reaction between trichlorosilane and either *m*- or *p*-dichlorobenzene produced the corresponding bis(trichlorosilyl)benzene in a yield of around 60%. In the reaction between dichloromethylsilane and dichlorobenzene, the yield of bis(methyldichlorosilyl)benzene was around 50% for the para isomer, 38% for the meta isomer, and 18% for the ortho isomer.[22]

Heating *p*-dichlorobenzene and methyldichlorosilane produced bis(methyldichlorosilyl)benzene, along with other products.[40,41] *p*-Dichlorobenzene/benzene mixture reacted with methyldichlorosilane at 640°C for 30 seconds to produce *p*-bis(methyldichlorosilyl)benzene in a yield of 8%.[42] *p*-Dichlorobenzene/benzene mixture reacted with trichlorosilane at 640°C and 30 seconds to produce a 15% yield of *p*-bis(trichlorosilyl)benzene;[42] *p*-dichlorobenzene and trichlorosilane reacted at 620-640°C to form a 21.4% yield of *p*-bis(trichlorosilyl)benzene. Under these same conditions, a mixture of trichlorosilane and (*p*-chlorophenyl)trifluorosilane reacted to produce a 40% yield of 1-trifluorosilyl-4-trichlorosilyl benzene; chlorophenyltrifluorosilane and dichloromethylsilane reacted to produce a 33.3% yield of methyldichlorosilyl trifluorosilyl benzene; trichlorosilane reacted with *p*-chlorophenyltrichlorosilane to produce a 65% yield of *p*-bis(trichlorosilyl)benzene; and chlorophenyltrichlorosilane and dichloromethylsilane reacted to produce a 52% yield of methyldichlorosilyl trichlorosilyl benzene.[43]

A number of reactions between equimolar mixtures of chlorohydrosilanes and chloroarylalkylchlorosilanes were conducted at 640°C for 60 seconds. The reaction between trichlorosilane and chlorophenyltrichlorosilane produced a 48% yield of bis(trichlorosilyl)benzene.[23] dichloro(chlorophenyl)methylsilane and trichlorosilane produced a 40.2% yield of 1-(dichloromethylsilyl)-4-(trichlorosilyl)benzene; chlorophenylchlorodimethylsilane and trichlorosilane produced a 15% yield of 1-trichlorosilylbenzene; chlorophenylmethyldichlorosilane and chlorodimethylsilane produced a 3.8% yield of 1-dichloromethylsilyl-4-chlorodimethylsilylbenzene; chlorophenyltrimethylsilane and trichlorosilane produced a 6.5% yield of 1-trimethylsilyl-4-chlorosilylbenzene and a 4.3% yield of 1-chlorodimethylsilyl-4-trichlorosilylbenzene; chlorophenyltrimethylsilane and methyldichlorosilane produced a 5.6% yield of (trimethylsilyl)-dichloromethylsilylbenzene and an 8% yield of (chlorodimethylsilyl)-methyldichlorosilylbenzene.[23]

Heating dichlorodiphenylsilane to 500°C resulted in a 10.6% yield of *p*-(chlorodiphenylsilyl)-phenyldichlorosilyl benzene.[44] Heating phenyltrichlorosilane to 720°C resulted in a 25.25% yield of higher boiling materials that consisted of bis(chlorophenyl)silyl benzenes,[45] and heating phenyldichlorosilane to 450-550°C for 8 hours resulted in dichlorophenylsilyl dichlorosilyl benzene and higher-boiling derivatives. Heating a 1:1 molar mixture of phenyldichlorosilane and methyldichlorosilane resulted in a residue containing (methyldichlorosilyl)dichlorosilylbenzene.[46]

In the reaction between an arylsilane and a chlorohydrosilane catalyzed by BCl_3, a hydrogen in the phenyl group is replaced by the chlorosilyl group, forming a silicon-phenyl bond.[47,48,49] In the direct synthesis preparation of phenyl trichlorosilane and diphenyldichlorosilane from the BCl_3-catalyzed reaction of benzene and trichlorosilane, there were stillpot residues containing, among other substances, bis(trichlorosilyl)benzene and phenyldichlorosilyl trichlorosilyl benzene resulting from further reaction of the desired product with $HSiCl_3$;[50] this residue constituted 5-10% of the products of this reaction.[51] If an excess of trichlorosilane was used in this reaction, there was a greater yield of bis(trichlorosilyl)benzene.[52,53] The reaction between phenyltrichlorosilane and trichlorosilane produced primarily bis(trichlorosilyl)benzene, some phenyldichlorosilyl trichlorosilyl benzene, and a smaller amount of bis(trichlorosilylphenyl)dichlorosilane.[47,48,49]

For the reaction between hydrochlorosilanes and aryl materials, BCl_3 was found to be the best catalyst, compared to $AlCl_3$ and others. The reaction between benzene and methyldichlorosilane with BCl_3 catalyst produced the expected phenylmethyldichlorosilane; but, at temperatures above 240°C, further reactions between the phenyl and the silane took place, producing substantial stillpot residues.[48,49] Heating diphenyldichlorosilane with $AlCl_3$ at 210 to 250°C for 4 hours resulted in a reaction between the phenyl and the chlorosilyl group producing bis(dichlorophenylsilyl)benzene and polydichlorosilphenylenes.[54] Heating chlorobenzene with trichlorosilane in the presence of BCl_3 or $AlCl_3$ produced some chlorophenyl trichlorosilane and also some distillation residue containing bis(trichlorosilyl)chlorobenzene.[55]

XYLYL DERIVATIVES

p-Xylyl Derivatives

The preparation of *p*-bis(hydrogendimethylsilyl)xylene by the Grignard reaction of xylene dibromide with dimethylchlorosilane and magnesium in THF was described; it is a liquid, with a boiling point of 81°C/0.8mm, $n_D^{25}=1.5002$, $d_{25}=0.8203$.[3,8] This was converted to the bis-silanol by basic hydrolysis; the bis-silanol is a solid, with a melting point of 121-122°C.[8]

m-Xylyl Derivatives

To prepare *m*-bis(dimethylhydroxysilyl)xylene, *m*-xylene was first brominated with N-bromosuccinimide in CCl_4 under UV irradiation to make dibromo-*m*-xylene. This reacted with dimethyldichlorosilane and magnesium in THF to make *m*-bis(dimethylhydrogensilyl)xylene; this reacted with sodium ethoxide and then NaOH to make the desired bis-silanol. Physical properties of these, including IR, NMR, boiling point, etc., were presented. The bis(methylphenylhydrogenatosilyl) derivative was made similarly from *m*-xylene and methylphenylchlorosilane. The IR, NMR, and physical properties of these materials were presented.[56]

Other Xylyl Derivatives

The reaction between chloromethyltrichlorosilane and benzene, at reflux in the presence of $AlCl_3$, produced a 75% yield of *o*-, *m*-, and *p*-bis(trichlorosilylmethyl)benzene.[57]

TOLUENE DERIVATIVES

2,4-Bis(dimethylchlorosilyl)toluene was made in a Grignard reaction, consisting of the reaction of 2,4-dibromotoluene and dimethyldichlorosilane and magnesium in ether. It is a liquid, with a boiling point of 105-107°C/1.5mm.[58]

p-DIPHENYL DERIVATIVES

The Grignard preparation of *p*-bis(hydrogendimethylsilyl)diphenyl by the reaction of the diphenyldibromide with dimethylchlorosilane and magnesium in THF was described; it is a liquid, with a boiling point of 140-141°C/.85mm, d_{25}=0.963, n_D^{25}=1.4724.[3,8] This was converted to the corresponding bis-silanol by ethanolysis, followed by NaOH hydrolysis. The bis-silanol is a solid, with a melting point of 176-180°C.[8] The Grignard preparation of *4,4-bis(ethoxydiphenylsilyl)biphenyl and* 4,4-bis(methoxydiphenylsilyl)biphenyl and the properties of these materials were described.[59] 4,4′-Dibromodiphenyl or -diphenyl ether reacted with butyllithium to form the dilithio derivative. This reacted with dichlorodimethylsilane to produce 4,4′-bis(chlorodimethylsilyl)diphenyl or -diphenyl ether.[60] 4,4′-Biphenyl dilithium was used in the preparation of *4,4′-bis(methoxydiphenylsilyl)biphenyl*; the properties were described.[59]

Biphenyl and trichlorosilane (1:4 mole ratio, 300°C, BCl_3 catalyst) reacted to produce a 31.2% yield of monosilyl adduct and a 20.7% yield of disilyl adduct.[53]

p-DIPHENYL ETHER DERIVATIVES

p-Bis(hydrogendimethylsilyl)diphenyl ether was prepared by the Grignard reaction of *p*-dibromodiphenyl ether with dimethylchlorosilane and magnesium in THF; it is a liquid, with a boiling point of 132°C/.5mm, n_D^{25}=1.5478, d_{25}=0.976.[3,8] This was converted to the corresponding bis-silanol by ethanolysis, followed by NaOH hydrolysis.[8] *p*-Bis(ethoxydimethylsilyl)diphenyl ether was prepared from *p*-dibromodiphenyl ether, followed by ethanolysis and NaOH reaction to form the bis-silanol.[6,29] The IR was presented.[34] This bis-silanol is a solid, with a melting point of 103-104°C; the H^1 NMR was presented.[33]

p-Bis(bromophenyl)ether reacted with chlorodimethylethoxysilane in sodium to produce bis(*p*-dimethylethoxysilylphenyl) ether. This was hydrolyzed with NaOH solution to form the bis-silanol.[33,34]

materials. Dichlorodimethylsilane reacted with this complex to make polydimethylsilmethylenes.[147] The reaction between silicon, containing 10% copper, with methylene chloride in a nitrogen stream at 300°C, produced a small fraction of residue consisting of polydichlorosilmethylene, along with trichlorosilyl dichlorosilylmethane, bis(trichlorosilyl)methane, dichlorosilmethylene trimer.[148]

PHYSICAL PROPERTIES OF POLYSILMETHYLENES

Polydimethylsilmethylenes of molecular weight 6,000,000 were announced; they were described as elastomers.[149] Various physical properties of polydimethylsilmethylene were presented.[98] The polymer physics of polydimethylsilmethylene were described.[150] The gums produced from the polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, using cyclohexene platinous chloride complex, were cured with dicumyl peroxide; they were compounded with ground quartz and fume silica; the procedure was described. Rubber samples with an ultimate tensile strength of 650 psi and a corresponding elongation of 320% were made. This rubber maintained satisfactory properties after heating at 150°C for 20 hours.[151] In another study, the elastomer was formulated with fume silica and ground quartz, cured with dicumyl peroxide to give sheets of rubber that possessed nearly uniform tensile properties between -78°C and 150°C. For these rubber samples, the ultimate elongation was in the range of 200-350%, and the hardness was in the range of 40-45 BS.[127] Polymethylphenylsilmethylene varied in properties from a clear, tough rubber to a glassy resin, depending upon DP. Copolymers of dimethyl and methylphenyl silmethylene were generally rubbery.[125]

The thermal depolymerization of polydimethylsilmethylene requires a substantially higher activation energy than does polydimethylsiloxane, as it does not have the same low-energy path for decomposition; however, the depolymerization of silmethylene-siloxane silethylene-siloxane polymers was found similar to that of polydimethylsiloxane.[152] Polydimethylsilmethylene is more thermally stable, and more resistant to alkalis and acids than the corresponding polysiloxane.[140] The thermal stability in helium is good, with 10% weight loss at 600°C for a sample precipitated from hexane solution.[126] For a polydimethylsilmethylene of molecular weight 500,000, the TGA in nitrogen indicated substantial thermal stability; the weight loss in 30 minutes was 1.1% at 400°C and 2.0% at 450°C.[127] This polymer can withstand 420°C, and has been recommended for use as a gas chromatography stationary phase.[153]

Polydimethylsilmethylene is not very stable to oxidation;[127] oxidative thermal degradation was found to take place at temperatures less than 300°C.[126] For polysilmethylenes containing both methyl and phenyl groups, the oxidative thermal stability increased with the phenyl content, for example, the TGA onset temperature in air for polydimethylsilmethylene was 260°C, for a polysilmethylene containing one phenyl group for every three methyl groups, the corresponding temperature was 290°C. For polymethylphenylsilmethylene, a stiff material, the Tg was 18°C and the ranging from 400,000 to 4,000,000.[132,133] The thermal polymerization was studied, and a kinetic equation was derived. It was found that the molecular weight of the resulting polymer increased with reaction temperature in the range 140-240°C, and time in the range 1.5 to 5 hours. When the temperature was held at 160°C, the conversion of monomer to polymer increased, not only with time, but with monomer concentration in toluene solution.[134] At 320°C, the monomer polymerized to a white, elastomeric substance. When heated to 380-400°C for 3.5 hours, the cyclic trimer, hexamethyltrisilacyclohexane, polymerized to a rubbery material.[135] 1,1,3,3-Tetramethyl-1,3-disilacyclobutane polymerized at 300°C (1.5 hours, 400 psi) to a polymer of degree of polymerization (DP) of around 200;[119] in another effort, using the same experimental conditions, a viscous oil of molecular weight 15,000 was produced, and other 1,3-disilacyclobutanes were also polymerized.[103,104]

1,1,3,3-Tetraphenyl-1,3-disilacyclobutane polymerized upon heating to 180-200°C, 2-4 hours, to make a white powder with a crystalline melting point of 340°C.[136]

METAL COUPLING REACTIONS

Low-molecular-weight polydimethylsilmethylene was made by reacting a mixture of dichlorodimethylsilane and chloromethyldimethylchlorosilane with sodium in refluxing toluene. This reaction also took place if ethoxy groups were substituted for chlorine.[137] The reaction of chloromethyldimethylchlorosilane with magnesium produced chloride-terminated dimethylsilmethylene oligomers; the lower homologs, DP 1-4, could be distilled out, leaving higher molecular-weight residue. Zinc or sodium could be substituted for magnesium in this reaction.[138] Chloromethyldimethylchlorosilane, containing minor amounts of bis(chloromethyl)methylchlorosilane, reacted with sodium in toluene to make viscous polydimethylsilmethylene oligomers.[139] Bis(chloromethyl)dimethylsilane and bis(chlorodimethylsilyl)methane reacted with sodium in toluene, under reflux, to form polydimethylsilmethylene macrocycles;[140] it was stated that the polydimethylsilmethylenes produced were cyclic compounds.[141]

Chloromethyldialkylchloro- (or ethoxy-) silanes react with molten sodium to make carbosilane polymers. For example, sodium, added to chloromethyldimethylethoxysilane under reflux, produced a variety of products, including a residue that was an oil of molecular weight 562. Chloromethyldimethylchlorosilane reacted with sodium in xylene at 110°C to produce a viscous oil. This oil was distiliable above 350°C, indicating the high thermal stability. Likewise prepared were methylphenyl- and methylbutyl-carbosilane polymers.[142,143] This process was modified by adding trimethylsilyl chloride or ethoxide; physical properties of a number of these materials were presented.[144,145,146]

Aluminum containing 3 copper reacted with methylene chloride to form a viscous complex. This complex reacted with trimethylchlorosilane to form various products, including the dimer and trimer of dimethylsilmethylene and high-boiling bulk compared to solution polymerization. Other disilacyclobutanes were also polymerized; under these conditions, methoxymethyl- and chloromethylsilmethylene polymers were generally viscous liquids.[125] These were polymerized with chloroplatinic acid catalyst under several conditions. In the presence of 10% water, only a low-molecular weight polymer was formed in poor yield, but in the presence of 17-23 ppm platinum catalyst, bulk polymerization produced polymers rather rapidly at 100°C, of molecular weight greater than 100,000; a mechanism for the polymerization was discussed.[126] When Pt/C was used as catalyst at 90°C, the polymerization proceeded exothermally, raising the reaction vessel temperature to 150°C. The polydimethylsilmethylene was clear and pliant, resembling polyisobutylene.[126] Other types of disilacyclobutanes were also polymerized under these conditions.[124]

Using di-μ-chlorodichlorobis(cyclohexene)diplatinum (II) catalyst, copolymers can be produced from 1,1,3,3-tetramethyl-1,3-disilacyclobutane and other 1,3-disilacyclobutanes. Other disilacyclobutanes that polymerized to high molecular weight were 1,3-diethoxy-1,3-dimethyl-1,3-disilacylcobutane and 1,3-diphenyl-1,3-dimethyl-1,3-disilacylcobutane. Under the same reaction conditions, 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane and 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasilicacyclooctane did not polymerize.[127] 1,1,3-Trimethyl-3-(3,3,3-trifluoropropyl)-1,3-disilacyclobutane was polymerized by heating to 100°C in the presence of 28 ppm chloroplatinic acid to a polymer of Mw=150,000; this polymer was peroxide-cured to an elastomer that had superior solvent swelling resistance, compared to polydimethylsilmethylene.[126]

Catalysts containing platinum or other transition metal compounds were used in concentrations 1 part catalyst to 500 parts monomer. For example, the use of chloroplatinic acid at 70°C for 2 minutes resulted in a liquid polydimethylsilmethylene of viscosity 300 cS; the use of di-μ-chloro-dichlorobis(cyclohexene) diplatinum as catalyst at 70°C and 5 minutes resulted in a gum. The use as catalysts of $PtBr_2$ (70°C, 2 minutes), $PdBr_2$, $RuCl_3$, and others produced gums. 1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane was also polymerized.[128]

π-Crotyl nickel chloride was used as a catalyst for this polymerization, in concentrations less than 1%, at temperatures of 35-50°C, in toluene solvent. Polymers of intrinsic viscosity greater than 1 dl/g were produced in some cases.[129] The salts of a number of transition elements were also studied as polymerization catalysts; found effective were $AuCl_3$, $CuCl_2$, and CuCl, in concentrations around 1%; the conditions were 90°C, time 1-12 hours. Polydimethylsilmethylenes with instrinsic viscosities as high as 3.2 dl/g were prepared.[130] $AlCl_3$ also polymerized the ring-opening polymerization of silacylcobutanes.[131]

THERMAL RING-OPENING POLYMERIZATION

Under very dry conditions, at temperatures to 250°C for 6 hours, 1,1,3,3-tetramethyl-1,3-disilacyclobutane polymerized to elastomers with molecular weights

1,1-dimethyl-1-silacyclobutane, passed through a quartz tube heated to 600°C produced 1,1,3,3-tetramethyl-1,3-disilacyclobutane in 55% yield, with ethylene as by-product. Likewise, 1,1-dichloro-1-silacyclobutane, when heated to 680°C, produced 1,1,3,3-tetrachloro-1,3-disilacyclobutane in high yield.[110,111] In the former reaction, $(CH_3)_2Si{=}CH_2$ is believed to be the intermediate.[112,113] Heating 1,1,3-trimethyl-1-silacyclobutane resulted in propene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Literature methods to prepare 1,1-dimethyl-1-silacyclobutane by ring closure to allyldimethylsilane have been unsuccessful; catalysts tried were Pt/C[114] and chloroplatinic acid.[115]

The gas-phase flow pyrolysis at 700°C and pressures less than 700 microns of 1,2-dimethoxy-tetramethyldisilane gave, as major products, 1,1- and 1,3-dimethyl-1,3-disilacyclobutanes in yields of 10% and 17%.[116]

Pyrolysis of tetramethylsilane at 700°C produced 1,1,3,3-tetramethyl-1,3-disilacyclobutane in 3.2% yield.[117,118,119]

PHOTOLYSIS METHODS

1,1,3,3-tetramethyl-1,3-disilacyclobutane was produced in the mercury sensitized photolysis of tetramethylsilane; theorized was the formation of $(CH_3)_2Si{=}CH_2$, which dimerized.[120] It was produced in 30% yield by liquid-phase photolysis of tetramethylsilane.[121]

ALKALI METAL METHODS

Bis(chloromethyl)dimethylsilane reacted with lithium in ether to form the dilithio derivative; dimethyldichlorosilane was added to the ether mixture and left overnight at room temperature. Distillation of the products indicated a 24% yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.[122] The reaction between t-butyllithium and vinyldimethylchlorosilane produced 46% of 1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane; yields of 80% can be obtained by warming the reactants from -78°C.[123]

POLYSILMETHYLENES

CATALYZED RING-OPENING POLYMERIZATION

1,1,3,3-tetramethyl-1,3-disilacyclobutane was polymerized with chloroplatinic acid catalyst.[98,124] It polymerized in bulk with chloroplatinic acid solution, 0.01% mole ratio, 25°C, to a rubber with Mw of 200,000. Other catalysts of platinum were also effective. It was found that higher polymer molecular weight resulted in

In another preparation, a solution of chloromethyldimethylchlorosilane in THF was slowly added to magnesium in THF; the mixture was refluxed 12 hours, decanted, and added to HCl solution; ether was added, and the organic layer was dried and distilled. In this procedure, 1,1,3,3-tetramethyl-1,3-disilacyclobutane was produced in 20% yield, it is a liquid, bp=115-117°C, n_D^{20}=1.4412.[101] Another preparation involved the reaction of 1-chloromethyl-3-chlorodisilmethylene in THF with magnesium in THF, refluxing 5 hours; 1,1,3,3-tetramethyl-1,3-disilacyclobutane was produced in 65% yield.[102] Other Grignard methods for the preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were also described.[103,104,105]

Other disilacyclobutanes were prepared, and their physical properties listed: 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane and others.[99] The Grignard method of reacting chloromethylmethyldichlorosilane with magnesium to make 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane was described; this reacted with $LiAlH_4$ to make 1,3-dimethyl-1,3-disilacyclobutane, and reacted with phenylmagnesium bromide to make 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane.[100] The preparation of chloromethylmethylethoxychlorosilane was described; using the above-described Grignard method, 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane was made, and the properties were described.[99,100]

Reacting chloromethyldimethylchlorosilane with magnesium produced 1,1,3,3-tetramethyl-1,3-disilacyclobutane; reacting chloromethyldiphenylchlorosilane or chloromethylmethylphenylchlorosilane with magnesium resulted in 1,1,3,3-tetraphenyl-1,3-disilacyclobutane or 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane; likewise, chloromethyltrichlorosilane produced 1,1,3,3-tetrachloro-1,3-disilacyclobutane; the propoxy analog was also prepared.[106] Reacting chloromethylmethylphenylchlorosilane with magnesium resulted in 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane; reacting chloromethyldimethylchlorosilane mixed with chloromethylmethyldichlorosilane with magnesium produced 1,1,3-trimethyl-3-chloro-1,3-disilacyclobutane; reacting this with phenylmagnesium bromide or allylmagnesium bromide resulted in the corresponding monophenyl or monoallyl disilacyclobutane; physical properties of these monomers were presented.[107]

To make fluoroalkyl-substituted silacyclobutane and polyfluoroalkylsilmethylenes, the method of preparation of the silacyclobutanes is to add a mixture of chloromethyldimethylchlorosilane and chloromethylmethyldichlorosilane to magnesium, to make the chloromethylsilacyclobutane, and to treat this with bromofluorocarbon, such as 1,1,1-trifluoro-3-bromopropane, and magnesium; in that case, 3-(3,3,3-trifluoropropyl)-1,1,3-trimethyl-1,3-disilacyclobutane was produced. Likewise, the dimethyldi(3,3,3-trifluoropropyl) analog was made, along with the corresponding polymer.[108]

THERMOLYSIS METHODS

Several studies have shown that 1,1-dimethyl-1-silacyclobutane, when heated, produced 1,1,3,3-tetramethyl-1,3-disilacyclobutane.[109,110] For example, A number of the trifluoropropyl-containing copolymers were prepared. These were shown to be superior in solvent resistance, compared to the all-methyl polymers; however, the Tgs were higher, and the TGA decomposition temperatures were substantially lower than the all-methyl polymers.[93,94]

BIS(*p*-DIMETHYLHYDROXYSILYLPHENYL)DIMETHYLSILANE DERIVATIVES

Bis-(*p*-dimethylhydroxysilylphenyl)dimethylsilane was prepared from the Grignard reaction of dichlorodimethylsilane and bis(*p*-bromophenyl)dimethylsilane to form the bis-chloro analog; this was converted to the bis-hydroxy derivative and then polymerized in the presence of KOH to the homopolymer, a clear elastic solid that could be mixed with fillers and peroxide-cured.[78,96]

POLYSILPHENYLENES

The di-Grignard reaction of 1,4-dibromobenzene with diphenyldichlorosilane in THF/benzene at -80°C to produce polydiphenylsilphenylene was described.[78] Polydiphenylsilphenylene was made also from the reaction of *p*-dibromobenzene, diphenyldichlorosilane with sodium in refluxing xylene, and from the reaction of diphenyldichlorosilane with *p*-phenylenedimagnesium dibromide, in ether. The polymer is a brown resin.[97] Polydimethylsilphenylene and polydiphenylsilphenylene were made from the reaction of sodium and either *p*-chlorophenylchlorodimethylsilane or *p*-chlorophenylchlorodiphenylsilane. Properties, including TGA, of these polymers were described; decomposition temperatures (onset) above 400°C were noted; thermal stability increased with molecular weight. However, none of these were elastomeric.[13]

DISILACYCLOBUTANES

GRIGNARD PREPARATIONS

To prepare 1,1,3,3-tetramethyl-1,3-disilacyclobutane, a solution of chloromethyldimethylchlorosilane in THF was slowly added to a small amount of magnesium in THF, and more magnesium was gradually added, with temperature held to 30-50°C; a yield of 35% was reported.[98] Using the same procedure, a yield of 49.9% and physical properties were reported.[99] Also reported in using this procedure was a 35% yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and some of the cyclic trimer as by-product.[100] In addition, there was reported as by-product some viscous residue consisting of higher cyclic and linear polydimethylsilmethylenes.[99]

alternating copolymers of the bis-silanol and tetramethyldisiloxane; intrinsic viscosities to 3.5 dl/g were found. The polymers were cured with *t*-butylperoxybenzoate, and milled with silica and ferric oxide. For some of these cured elastomers, ultimate stress to 600-800 psi, with corresponding strain to 50-150%, was found. TGA measurements of these polymers showed thermal stability above 300°C.[29,91]

TGA studies of alternating copolymers of the bis-silanol and dimethylsiloxane, tetramethyldisiloxane, and the corresponding tri- and tetrasiloxanes have shown that there is greater thermal stability for fewer dimethylsiloxane units; although, even with the tetrasiloxane copolymer, the thermal stability is substantially greater than that of polydimethylsiloxane. In comparing the thermal stability of aryl moieties, for copolymers containing hexamethyltrisiloxane units, the diphenyl ether moiety was found to be the most stable, followed by the *p*- and then *m*-phenylene. All of these were found to have TGA onset temperature of thermal degradation greater than 400°C.[34,92]

m-XYLYL DERIVATIVES

α,α′-Bis(dimethylhydroxysilyl)-*m*-xylene was homopolymerized, using as catalysts either *n*-hexylamine-2-ethylhexanoate or 1,1,3,3-tetramethylguanidine. Molecular weight for the homopolymer obtained from the former catalyst was 38,800; for the latter catalyst, 3400. For the former polymer, TGA measurements showed 10% weight loss at around 530°C in nitrogen and around 300°C in air.[56] In using 1,1,3,3-tetramethylguanidine-2-ethylhexanoate as homopolymerization catalyst, the resulting homopolymer had an intrinsic viscosity in toluene of 0.51 dl/g and a molecular weight of 41,700. If ferric chloride was used as catalyst, rather low molecular weights of polymer were obtained.

To prepare alternating copolymers containing dimethylsiloxane or tetramethyldisiloxane groups, either bis(dimethylamino)dimethylsilane or bis(dimethylamino) tetramethyldisiloxane was reacted with the bis-silanol, either neat or in solution.[93,94] These alternating copolymers were also prepared by the condensation of the bis-silanol with diacetoxysilanes, resulting in dimethylsiloxane and tetramethyldisiloxane copolymers of intrinsic viscosities between 0.5 and 1.0 dl/g.[83]

TGA data indicated that the homopolymer, dimethylsiloxane copolymer, and hexamethyldisiloxane copolymer were all substantially more stable than polydimethylsiloxane, with the dimethylsiloxane copolymer the most stable. The homopolymer is elastomeric, and is more thermally stable than the *p*- or *m*-bis(dimethylhydroxysilyl) benzene homopolymers. For the homopolymer, the Tg was -41°C; for the tetramethyldisiloxane copolymer, the Tg was -81°C. These polymers were cured with di-*t*-butyl peroxide or with dicumyl peroxide.[93,94] For the copolymer with dimethylsiloxane, the polymer of intrinsic viscosity 0.355 dl/g in benzene, the Mn was 14,500 the Tg was -62°C, and from TGA measurements, the decomposition temperature at 10% weight loss was 537°C. For the tetramethyldisiloxane copolymer, TGA measurements indicated the temperature of 10% weight loss at 598°C.[93,95]

Another method of making the fluorine-containing copolymer was the reaction of *m*-bis(3,3,3-trifluoropropylmethylhydroxysilyl)benzene and 1,3-diacetoxy-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane (prepared from acetic anhydride and the corresponding cyclotrisiloxane), catalyzed by tetramethylenediamine, and subjected to further heating with tetramethylguanidine trifluoroacetate; polymers of Mn=15,659 and Mw=106,000 were made. The reverse reaction, using bis(acetoxy)-*m*-silphenylene was also conducted. Copolymer of lower molecular weight was made from the *m*-bis-silanol and the corresponding dichlorodisiloxane. The reaction of *m*-bis(3,3,3-trifluoropropylmethylhydroxysilyl)benzene and trifluoropropylmethylchlorosilane produced *m*-bis(1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxanyl)benzene, the properties were presented. This reacted with NaOH/NaH_2PO_4 in dioxane, in the presence of lead and carbon, to give the corresponding bis-silanol; this bis-silanol was homopolymerized. Properties of these materials, including the IR spectrum, were presented.[35] The Grignard reaction of *m*-dibromobenzene and trichloro(trifluoropropyl)silane to make bis(trifluoropropyldichlorosilyl)benzene was described; this reacted with chlorodimethylsilane in the presence of water to make *m*-bis((dimethylsiloxy)trifluoropropylhydrogenatosilyl)benzene, hence called "crosslinker".[35] Further studies were conducted on the *homopolymerization* of *m*-bis(1,3-dimethyl-1,3-bis(3,3,3trifluoropropyl)-disiloxanyl)benzene to form the hydroxy-terminated polymers. These polymers were vinyl-terminated by reacting with vinyldimethylsilylisocyanate, and cured, using "crosslinker" and platinum catalyst. Various formulations were described, where silica, ferric oxide, and other materials were added; tensile and other properties were presented.[90]

p-DIPHENYL ETHER DERIVATIVES

The preparation of exactly alternating copolymers from bis(hydroxydimethylsilyl)diphenyl ether and dimethylsiloxane, methylvinylsiloxane, and mixtures was done by reacting the bis-silanol with bis(1,1-tetramethylene-3-phenylureido)dimethylsilane and bis(1,1-tetramethylene-3-phenylureido)methylvinylsilane; various polymers of Mw over 100,000 were made.[6,80,84] For these polymers, the H^1 and C^{13} NMR, the IR spectra, the Tg and TGA were determined. The Tg was -42°C and the onset of thermal degradation by TGA was 335°C in air and 470°C in nitrogen for dimethylsiloxane copolymer; for the methylvinylsiloxane copolymer, the Tg was -51°C, and the onset temperature of thermal degradation by TGA was 425°C in air and 490°C in nitrogen, pyrolysis studies showed gas evolution above 400°C.[6]

These alternating copolymers were also prepared from the reaction of *p*-bis(dimethylhydrogensilyl)diphenyl ether with diacetoxysilanes, including dimethyldiacetoxysilane and tetramethyl-1,3-diacetoxydisiloxane, and these polymers had intrinsic viscosities between 0.5 and 1.0 dl/g.[83] A large number of copolymers were made, using *p*-bis(dimethylsilyl)diphenyl ether, with small amounts of *p*-bis(methylvinylhydroxysilyl)benzene, reacting with either heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane to make alternating copolymers of the bis-silanol and hexamethyltrisiloxane, or decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane to make rubber materials, using silica, partially hydrolyzed ethyl silicate, and dibutyltin diacetate were described.[25]

Copolymers With *p*-Bis(methylphenylhydroxysilyl)benzene

1,2-Dimethyl-1,2-diphenyldisiloxane copolymer was prepared by reaction of the bis-silanol and $(SiMePh\text{-}O\text{-}SiMePhNMe)_2$ in xylene reflux. The polymer was a tacky gum: inherent viscosities (toluene, 30°C) of 0.07 to 0.13 dl/g were obtained.[12]

Copolymers With *p*-Bis(diphenylhydroxysilyl)benzene

The hexamethyltrisiloxane copolymer was prepared from the bis-silanol and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane; it was an elastomer. The 1,2-diphenyl-1,2-dimethyltetrasiloxane copolymer, a hard and brittle polymer, was prepared from the reaction of the bis-silanol with $(SiMePh\text{-}O\text{-}SiMePhNMe)_2$ in toluene and in xylene reflux.[12] The diphenylsiloxane copolymer, a brittle solid, was prepared from the reaction of the bis-silanol and diphenylbis(methylamino)-silane,[12] or from the reaction of the bis-silanol with diphenyldichlorosilane in THF in the presence of pyridine.[88]

m-PHENYLENE DERIVATIVES

m-Bis(dimethylhydroxysilyl)benzene and *m*-bis(methylphenylhydroxysilyl)benzene were both reacted with heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane at 160°C for 8 hours to make the corresponding hexamethyltrisiloxane copolymers. For the dimethyl copolymer, the inherent viscosity was 1.60 dl/g (toluene, 30°C) and the Tg was -75°C; for the methylphenylsiloxane copolymer, the inherent viscosity was 1.62 dl/g, and the Tg was -42°C.[34]

In the search for thermally stable, fuel-resistant elastomers for aircraft tank sealants, silphenylene-siloxanes containing the 1,1,1-trifluoropropyl group, called FASIL polymers, were developed. The ethoxy precursor, *m*-bis(3,3,3-trifluoropropylmethylethoxysilyl)benzene, was homopolymerized by hydrolysis. This polymer had a Tg of -23°C and a Mw of 17,457. In making FASIL polymers, the condensation polymerization reaction between *m*-bis(3,3,3-trifluoropropylmethylethoxysilyl)benzene and bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, catalyzed by tetramethyl guanidine trifluoroacetate, was described.[35] In a similar effort, 12.8 m-moles of 1,3-bis(hydroxymethyl-3,3,3-trifluoropropyl silyl)benzene, 11.16 m-moles of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino) disiloxane and .36 m-moles of methylvinylbis-(dimethylamino)silane were refluxed in toluene, producing a copolymer of Mw = 3700.[37,89]

presented; the inherent viscosity (toluene, 30°C) was 0.73 dl/g and the Tg was -62°C. The TGA was presented;[34] the inflection temperature was 510°C.[6]

Hexamethyltrisiloxane Copolymer. The hexamethyltrisiloxane copolymer was prepared by the reaction of the bis-silanol with heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclobutane at 160°C for 8 hours. The IR was presented; the inherent viscosity (toluene, 30°C) was 2.77 dl/g and the Tg was -72°C.[34]

Octamethyltetrasiloxane Copolymer. The octamethyltetrasiloxane copolymer was prepared from the reaction of the bis-silanol with nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane at 160°C for 8 hours. The inherent viscosity (toluene, 30°C) was 2.48 dl/g and the Tg was -80°C; the IR was presented.[34]

Methylphenylsiloxane Copolymer. The methylphenylsiloxane copolymer was prepared from the reaction of the bis-silanol with diacetoxymethylphenylsilane, using triethylamine catalyst; inherent viscosity (THF, 25°C) was 0.38.[83] The relationship between intrinsic viscosity and molecular weight in THF is given as $\eta = 5.34 \times 10^{-5}$ Mw$^{0.799}$; Tg = -25°C.[6] Also made by this acetoxy-hydroxyl condensation was the copolymer of the disilanol with 1,2-dimethyl-1,2-diphenyldisiloxane; intrinsic viscosity was 0.41 dl/g.[83]

Copolymers containing methylphenyl, dimethyl, and methylvinylsiloxane, where the mole ratio of the sum of these is equal to the mole ratio of bis-silanol in an alternating copolymer were obtained. These mixed alternating copolymers were prepared from bis-silanol and mixtures of dichlorodialkylsilane in THF at 25°C with nitrogen flowing through to remove HCl.

For 99% methylphenyl/1% methylvinylsiloxane copolymer, the Mw was 51,000 and the Tg was -32°C; the H^1 NMR was presented, and TGA data showed an onset of thermal degradation at 400°C, with leveling off at 650°C, and 52% residue. For 66% methylphenyl/33% dimethyl/1% methylvinyl copolymer, the Tg was -44°C, the Mw was 71,000 and the H^1 NMR was presented; TGA data indicated an onset of thermal degradation at 410°C and a 50% residue at temperatures equal or greater than 660°C. For 33% methylphenyl/66% dimethyl/1% methylvinylsiloxane copolymer, the Tg was -60°C, the Mw was 33,000 and the H^1 and C^{13} NMR were presented, and TGA data showed an onset at 400°C and 37% residue at and above 660°C. For 99% dimethyl/1% methylvinylsiloxane copolymer, the Tg was -65°C. Copolymers containing 98% methylphenyl/2% methylvinylsiloxane were cured with 30 phr hydrophobic silica, 0.5 phr dicumyl peroxide, and 3 phr ferric oxide; mechanical properties were given.[5,87]

Diphenylsiloxane Copolymer. The diphenylsiloxane copolymer was prepared from the reaction of the bis-silanol with diphenylbis(methylamino)silane either neat[12] or in toluene reflux.[25] This copolymer is an elastic gum. The equation between intrinsic viscosity and Mw is $\eta = 5.7 \times 10^{-5}$ Mw$^{0.75}$; for this polymer, the Tg was 0°C, and TGA showed a 10% weight loss at 460°C. Formulations to make methylvinyl, Mn = 69,000, and Mw = 125,000; and for 100% methylvinyl copolymer, Mn = 103,500 and Mw = 199,000.[6,80] The TGA onset temperature in air and weight-percent remaining after 737°C were: 5% methylvinyl copolymer, 370°C, 46%; 7.5% methylvinyl, 375°C and 49.5%; for 100% methylvinyl, 420°C, 58.5%. For TGA tests in nitrogen, the onset temperature, the temperature at which further degradation ceases, and the weight-percent residue were: 5% methylvinyl, 360 and 670°C and 41%; for 7.5% methylvinyl, 420 and 680°C and 51%; for 100% methylvinyl, 450 and 690°C and 75%. After degradation in air, the residue consisted of SiO_2, but the residue after decomposition in nitrogen was an intractable black substance essentially stripped of hydrogen, but otherwise containing a similar composition of silicon, carbon, and oxygen, compared to the starting material.[6,84,85]

Mass spectra were obtained from the pyrolysis products of a 1% methylvinyl-99% dimethylsiloxane copolymer, and a 100% vinylmethylsiloxane copolymer. It was concluded not only that the methylvinyl copolymer was more thermally stable than the dimethylsiloxane copolymer, but also that there was less silicon in the degradation products of the latter.[81,82]

The copolymers containing 5% methylvinyl/95% dimethylsiloxane, 7.5% methylvinyl/92.5% dimethylsiloxane, and 100% methylvinylsiloxane were cured with dicumyl peroxide, and a hydrophobic silica was added as filler. Either Fe_2O_3 or $Fe(CO)_5$ were added as antioxidants. Tensile strength, elongation, stress-relaxation, heat aging, and other properties were determined. The Tg for the cured elastomer was very close to the Tg for the uncured materials.[86]

A number of polymer samples were prepared from the bis-silanol and methylvinyldichlorosilane or its mixtures with dimethyldichlorosilane (so that the bis-silanol and the mixed dichlorosilane had 1:1 mole ratio) in ether or in THF solvent; Mw values above 100,000 were obtained in many cases. It was found that Tg was -76°C for 100% methylvinyl copolymer and -69°C for 98% dimethyl/2% methylvinylsiloxane copolymer; these polymers were cured with dicumyl peroxide, with hydrophobic silica filler, and 3 phr ferric oxide; mechanical properties were given.[5] Other copolymers were made from these reactants in THF solvent at 25°C, with nitrogen flowing through to remove HCl product. For the copolymer of 99% dimethyl/1% methylvinylsiloxane, the Tg was -65°C, the Mw was 27,000, and the H^1 NMR was presented. The TGA data indicated an onset of thermal degradation (subsequently referred to as "onset") at 420°C and end of degradation at 670°C, with 33% residue. For the copolymer of 99% dimethyl and 3% methylvinylsiloxane, the Tg was -69°C, and the Mw was 28,000; the H^1 NMR was presented. For the 100% methylvinylsiloxane polymer, the Mw was 97,000, the Tg was -76°C, and the H^1 and C^{13} NMR were presented.[87]

Tetramethyldisiloxane Copolymer. The alternating tetramethyldisiloxane copolymer was prepared from the reaction of the bis-silanol with decamethyl-1,5-diaza-3,7-dioxo-2,4,6,8-tetrasilacyclooctane, at 160°C for 8 hours. The IR was

The homopolymer is not elastomeric; it is a strong fiber-forming polymer; it is more stable to thermal and oxidative degradation than polydimethylsiloxane in the temperature range 200-305°C. The relationship between the weight-average molecular weight (Mw) and intrinsic viscosity (η) was expressed by the equation: $\eta = 1.12 \times 10^{-4} Mw^{0.75}$.[2] The glass transition temperature (Tg) was -25°C.[77] The IR of this homopolymer was described;[27] other properties were presented.[78]

Dimethylsiloxane Copolymer. A method for preparing a very high molecular weight alternating copolymer of the bis-silanol and dimethylsiloxane was from the condensation of the disilanol with bis(1,1-tetramethylene-3-phenylureido(dimethylsilane).[79] For molecular weights exceeding 100,000 the reaction was monitored by either H^1 NMR or by gel permeation chromatography (GPC). The IR, H^1 NMR, and the C^{13} NMR of this polymer were presented. The number-average molecular weight (Mn) was 71,500 and the Mw was 132,000 by GPC for this polymer.[80] Tg was -62°C for this very viscous polymer. The onset of thermal degradation as determined by thermogravimetric analysis (TGA) was 345°C in air and 400°C in nitrogen; there was 39.5% residue at temperatures above 735°C. The degradation products from the pyrolysis were identified.[81,82] The intrinsic viscosity versus molecular weight relationship in THF was given as $\eta = 7.86 \times 10^{-5} Mw^{0.757}$.[6]

This polymer was also prepared from the reaction of the bis-silanol and bis(dimethylamino)dimethylsilane in toluene under reflux conditions. Polymer with intrinsic viscosity 0.98 dl/g in THF was obtained. Polymer was prepared of intrinsic viscosity (in THF) of 0.71 by the reaction of the disilanol with bis(acetoxy)dimethylsilane in refluxing toluene,[83] or by the reaction of bis-silanol and dimethyldichlorosilane; Mw above 100,000 were obtained.[5] The temperature corresponding to 10% weight loss by TGA was 440°C. In an isothermal TGA test at 316°C, the polymer lost 5% in 2 hours and 31% in 11 hours.[77] Upon completion of the TGA decomposition in air, the residue was found to consist of SiO_2. However, upon completion of this test in nitrogen, the residue was found to be an intractable Si-O-C material. During pyrolysis in helium, volatile products began to be emitted around 400°C, with maximum gas evolution around 500°C. Further volatiles were not evolved above 630°C.[6]

Films were prepared from toluene solution, adding partially hydrolyzed ethyl silicate and dibutyltin diacetate, with or without colloidal silica. Elastomers of ultimate tensile strength 16,000 psi and elongation 1130% were obtained.[77]

Copolymer with Dimethylsiloxane and Methylvinylsiloxane. Polymers were prepared with a 1:1 mole ratio of *p*-bis(dimethylhydroxysilyl)benzene and with a mixture of bis(1,1-tetramethylene-3-phenylureido)methylvinylsilane and -dimethylsilane. For copolymers containing 95% dimethyl- and 5% methylvinylsiloxane and for copolymers containing 92.5% dimethyl- and 7.5% vinylmethyl, and for polymer containing 100% vinylmethylsiloxane, the H^1 NMR, the IR, the C^{13} NMR were presented and discussed. After reprecipitation from THF into methanol, the molecular weights were: 5% methylvinylsiloxane, Mn = 67,000, Mw = 119,000; for 7.5%

1,4-Disila-2,5-Cyclohexadiene Derivatives

These compounds can be considered similar to the bis(silyl)arylenes in that such compounds would constitute a bulky disilyl group if homopolymerized or copolymerized with other groups, such as siloxanes.

Hexachlorodisilane reacts with acetylene at 450-550°C in a quartz tube to produce 1,1,4,4-tetrachloro-1,4-disila-2,5-cyclohexadiene in a 30% yield.[69,70] The reaction between 1,1,2,2-tetramethoxy-1,2-dimethyldisilane with acetylene at 400°C produced, 1,4-dimethoxy-1,4-dimethyl-1,4-disila-2,5-cyclohexadiene in a 60% yield; this is a liquid, with a boiling point of 100°C/40mm; the H^1 NMR and the IR were described.[71]

1,1,2,2-Tetramethoxy-1,2-dimethyldisilane reacted with dimethyl-acetylene to produce 1,4-dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disila-2,5-cyclohexadiene;[72,73] and the reaction between 1,1,2,2-tetramethoxy-1,2-dimethyldisilane and 1,2-diphenylacetylene produced 1,2,5,6-tetraphenyl-1,4-disila-2,5-hexadiene.[72]

OTHER DERIVATIVES

Bis(chloro-*t*-butyl)benzene (the preparation is described) reacted, in THF solvent, with magnesium and dimethylchlorosilane to form bis(dimethylsilyl-*t*-butyl) benzene. The diethoxy analog was made. By NaOH hydrolysis, *p*-bis(1,1-dimethyl-2-dimethylhydroxysilyl)ethyl benzene was made. This was polymerized in the presence of KOH.[74]

Benzylphenyltrichlorosilane reacted with trichlorosilane, 300°C, in the presence of BCl_3 to produce a 17% yield of bis(trichlorosilylphenyl)methane, and benzyltrichlorosilane reacted with trichlorosilane in the presence of BCl_3 at 300°C to form a 16% yield of (trichlorosilyl)trichlorosilylmethylbenzene; trimethylphenylsilane reacted with trichlorosilane under the same reaction conditions to form a 37.7% yield of a mixture of compounds of formula $((CH_3)_nCl_{3-n}Si)_2C_6H_4$.[75]

POLY(ARYLENE-SILOXANES)

p-BIS(SILYLBENZENE) DERIVATIVES

p-Bis(dimethylhydroxysilyl)benzene Polymers

Homopolymers. Bis(dimethylhydroxysilyl)benzene was homopolymerized, using as catalyst *n*-hexylamine-2-ethylhexanoate,[2] or by heating the disilanol with 0.02% NaOH in N_2 to 250°C for 47.5 hours.[15] Tetracyanoethylene is an excellent catalyst, effectively homopolymerizing the disilanol.[76]

NAPHTHALENE AND ANTHRACENE DERIVATIVES

The Grignard preparation in THF of 1,4-bis(dimethylhydrogensilyl)naphthalene was described. This was converted to the corresponding bis-silanol by ethanolysis, followed by NaOH hydrolysis. Some physical properties were listed.[8] The reaction between 2,7-dibromo-naphthalene, dimethyldichlorosilane, and magnesium in ether produced 2,7-bis(dimethylchlorosilyl)naphthalene and polymeric materials.[61]

9,10-Dilithio-9,10-dihydroanthracene reacted with dimethylchlorosilane to produce a 59% yield of 9,10-bis(dimethylsilyl)-9,10-dihydroanthracene.[62]

Naphthalene reacted (BCl_3 catalyst, 300°C) with an excess of trichlorosilane to produce bis(trichlorosilyl)naphthalene (in a yield of 16%) and hydrogenated naphthalene derivatives. When this reaction was conducted with methyldichlorosilane, the products consisted of around 10% bis(methyldichlorosilyl)naphthalene, along with hydrogenated naphthalene derivatives.[63]

1,4-Dimethylnaphthalenes and 1,5-dimethylnaphthalenes were heated with trichlorosilane at 660°C and produced 1,1-dichloro-5- and -6-methyl-1-silaacenaphthenes in approximately 30% yield. If these products were passed through the tube with trichlorosilane, then tetrachloro-1,5- and 1,6-disilapyracenes were formed in a yield of 85%.[64] The pyrolysis of dichloro-1-naphthylsilane under these conditions produced 1,1,2,2-tetrachloro-1,2-disilaacenaphthene, along with 1,2-dichloro-1,2:1,2-di-1,8-naphthalenedisilane.[65] 2-Biphenyl trichlorosilane and trichlorosilane reacted under these conditions to produce 9,9-dichloro-4-trichlorosilyl-9-silafluorene in a yield of 15%.[66]

In a direct synthesis reaction, passing dichlorophenyl-*o*-chlorophenylsilane over a contact mass containing 25% copper, 4%$CdCl_2$, 3%Co_3O_4, and 68% silicon at 540°C resulted in a yield as high as 60% of 9,9,10,10-tretrachloro-9,10-dihydro-9,10-disilaanthracene.[67] In an extension of this effort, it was found that *o*-dichlorobenzene reacted with a contact mass of silicon, copper, and small amounts of zinz, cadmium, and cobalt compounds to produce 9,9,10,10-tetrachloro-9,10-dihydro-9,10-disilaanthracene.[68]

DURYLENE DERIVATIVES

The Grignard preparation in THF of bis(dimethylhydrogensilyl)-durylene was described. This was converted to the corresponding bis-silanol by ethanolysis, followed by NaOH hydrolysis. Some physical properties were listed.[8]

temperature from TGA corresponding to 10% weight loss was 350°C. For polydiphenylsilmethylene (mp=340°C), the temperature from TGA corresponding to 10% weight loss was 390°C.[107]

A low-molecular weight sample of polydimethylsilmethylene, when pyrolyzed to 585°C, left only 1% residue, and was not regarded as an effective SiC precursor.[154] In another study, TGA results indicated that one high-molecular-weight sample left a 10% residue at 670°C and another sample left a 5% residue at 660°C.[126] However, the thermal decomposition of polydimethylsilane produced polymethylsilmethylene, $(SiH(CH_3)CH_2)_n$; this decomposed upon further heating to form SiC.[155,156,157,158,159]

CONCLUSIONS

Of the various types of thermally stable elastomers, two types are worth further investigation: silarylene-siloxane polymers and polysilmethylenes. The silarylene-siloxane polymers and the polysilmethylenes are more thermally stable than the corresponding polysiloxanes.

The preparation and properties of alternating copolymers that were prepared from the condensation polymerization of arylenedisilanols with silanes, disiloxanes, and other silicon compounds were described. The preparation and properties of the known arylenedisilanols have been presented in this report. The bis-silanols were generally prepared by the Grignard addition of halosilane to dihalobenzene, a process that would be expensive if conducted in a large-scale operation. In this report, reactions are described that may potentially yield a bis-silanol at reasonable cost. For example, the reaction of 1,2-dichlorotetramethyldisilane with *p*-dichlorobenzene reportedly yielded *p*-bis(chlorodimethylsilyl)benzene. Likewise, the reaction of 1,1,2,2-tetramethoxydimethyldisilane with acetylene to form 1,4-dimethoxy-1,4-dimethyl-1,4-disila-2,5-cyclohexadiene is worth examining. It should be possible to hydrolyze this to the bis-silanol and produce alternating copolymers, via condensation, that are thermally stable. Hence, there are several possible approaches to the cost-effective preparation of thermally stable silarylene-siloxane polymers.

There is a substantial literature regarding polysilmethylenes, generally prepared by the ring-opening polymerization of 1,3-disilacyclobutanes to produce the polymer; discussed most frequently is polydimethylsilmethylene, prepared from 1,1,3,3-tetramethyl-1,3-disilacyclobutane. A Grignard method was used for the preparation of the disilacyclobutane, although it can also be made by the thermolysis of 1,1-dimethyl-1-silabutane. Polydimethylsilmethylene is quite thermally stable, although it did not yield SiC upon thermal decomposition.

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NOMENCLATURE

bp	Boiling point
C^{13}	Carbon-13
DMSO	Dimethylsulfoxide
DP	Degree of polymerization
d_{25}	Density at 25°C
GPC	Gel permeation chromatography
IR	Infrared
Mn	Number average molecular weight of a polymer
mp	Melting point
Mw	Weight average molecular weight of a polymer
NMR	Nuclear magnetic resonance
n_D	Index of refraction
n_D^{25}	Index of refraction at 25°C
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
η	Intrinsic viscosity
π	Pi

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