

## Phenylene-Perfluoroalkylene Silicones

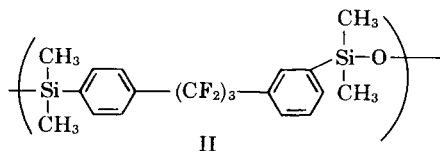
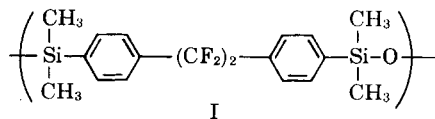
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### Synopsis

This paper described the preparation and properties of a new class of silicone polymers, the phenylene-perfluoroalkylene silicones. A direct measure of ratios of copolymer units in silicone copolymers was developed during this work.

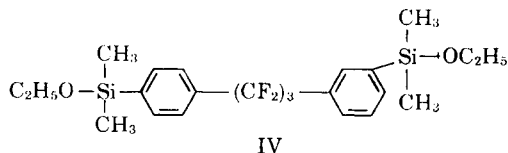
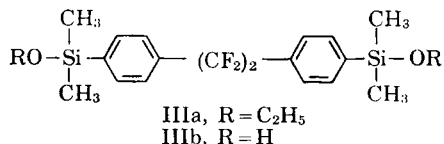
Silicone elastomers have found applicability because of the wide temperature range over which they are useful. Elastomers can be produced which are flexible below  $-100^{\circ}\text{F}$ . and yet retain useful properties—for a short period—at  $600^{\circ}\text{F}$ . This performance however has been achieved at some sacrifice of other properties. Compared with some elastomers that perform over a more limited temperature range, silicones are at a disadvantage with regard to tensile strength, compression set, solubility, creep, and resistance to radiation damage.

Thermal degradation of silicone elastomers containing the  $(-\text{Si}-\text{O}-)$  backbone occurs mainly by a process of depolymerization in which the chain reverts to small rings, mainly trimers and tetramers. In order to minimize this tendency, the  $(-\text{Si}-\text{O}-)$  repeating unit may be interrupted by rigid groups. This report is concerned with the preparation and properties of silicones I and II which contain phenylene groups separated by perfluoroalkylene groups. Improved radiation and solvent resistance in addition to increased thermal stability might be predicted for these structures. Copolymers VI containing dimethylsiloxane units were also prepared.

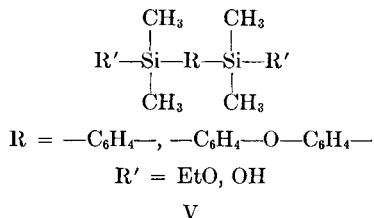


\* Deceased, September 2, 1963.

Polymer I was obtained by polymerization of 1,2-bis[*p*-(ethoxydimethylsilyl)phenyl]tetrafluoroethane(IIIa) and of 1,2-bis[*p*-(hydroxydimethylsilyl)phenyl]tetrafluoroethane(IIIb). Polymer II was obtained by polymerization of 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (IV). Synthesis of these monomers is described elsewhere.



Preliminary studies were carried out on the systems V described by Sveda<sup>1</sup> and by Omietanski and Reid.<sup>2</sup>



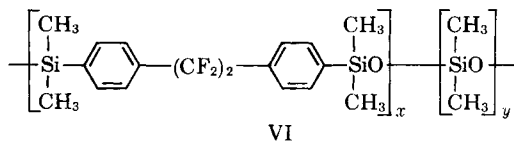
Satisfactory conversion to polymers (inherent viscosities of 0.7 to 1.0 in toluene, 0.5% at 25°C.) were obtained with the prescribed base catalysis.

Samples of 1,2-bis[*p*-(ethoxydimethylsilyl)phenyl]tetrafluoroethane (IIIa) left open to the air soon developed an odor of ethanol, indicating the ease with which they hydrolyzed and polymerized.

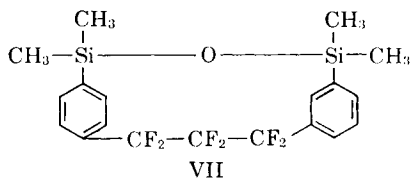
However, polymerization under a wide variety of conditions of both basic and acidic catalysis gave only low molecular weight solid polymers ( $\eta = 0.07$ – $0.2$ ). Basic polymerization of 1,2-bis[*p*-(hydroxydimethylsilyl)phenyl]tetrafluoroethane(IIIb) gave a low molecular weight solid polymer ( $\eta = 0.047$ ). Details for the procedures that gave optimum results are reported in the Experimental section.

Since all of the polymers from IIIa and IIIb were solids, too rigid for elastomeric utility, an investigation of the copolymers of IIIa and diethoxydimethylsilane was undertaken. Preliminary experiments were carried out by preparing copolymers (VI) and varying the monomer ratio ( $x/y$ ). In this way, suitable gums might be obtained with a fairly low concentration of Y units. A sample of 20 g of a copolymer (VI), containing 94.7 wt.-% (77.5 mole-%) of X, 5.0 wt.-% (21.3 mole %) of Y, and 0.3 wt.-% (1.2 mole %) of —OSi(CH<sub>3</sub>)<sub>2</sub>(CH=CH<sub>2</sub>)— units, was prepared. It

had an intrinsic viscosity of 0.3. The small amount of vinyl silane was added to furnish crosslinking sites.



A distilled sample of 1-*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (IV), on standing in the open air, soon developed an odor of ethanol, became more viscous, and gradually polymerized. After three weeks, the material was a sticky gum with an intrinsic viscosity of 0.2. Acid-catalyzed polymerization of a larger quantity (14 g.) of IV yielded a light amber gum which, upon heating to 150°C. in a vacuum, yielded a white sublimate. This sublimate (obtained in 12% yield) was identified<sup>3</sup> by its infrared spectrum, mass spectrum, elemental analysis, molecular weight, and NMR spectrum as a heterocyclic [3,3]-metaparacyclophane (VI).



It is not known whether formation of the metaparacyclophane VII represents depolymerization of polymer or cyclization of the monomer. No additional sublimate beyond the 12% yield could be obtained on further heating. No sublimate was formed on heating the polymer obtained without acid catalysis. Although the acid-catalyzed polymer was thoroughly washed, enough acid must have remained to catalyze formation of the metaparacyclophane VII.

In the course of our copolymerization studies, we developed a simple, direct procedure using nuclear magnetic resonance spectroscopy to determine ratios of copolymer units; this procedure should be widely applicable to silicone copolymer. In our case, the copolymer V was prepared so as to contain 77.5 mole-% of the aromatic fluorocarbon silane unit (i.e.,  $X = 77.5$  mole-%). The methylsilyl peak of the  $X$  fraction was at 9.63  $\tau$ , and the methylsilyl peak of the  $Y$  fraction was at 9.91  $\tau$ . Integration of the areas of these two peaks permitted calculation of the mole ratios of  $X$  and  $Y$ . The answer obtained was 77.7 mole-% for the  $X$  fraction, in excellent agreement with the calculated value.

Crosslinking of the polymers described in this report was attempted at Rock Island Arsenal by using peroxides, diisocyanates, and polyamines at temperatures of 250–320°F. All attempts were unsuccessful.

## EXPERIMENTAL

The proton NMR spectra were obtained with a Varian HR-60 spectrometer at 60 moles/sec. Solutions of polymers (5–15%) in carbon tetrachloride containing 1% cyclohexane were used. Shifts are reported in  $\tau$  values. A value of 8.56  $\tau$  was assigned to the cyclohexane resonance.

Infrared spectra were recorded on either a Perkin-Elmer 221 or a Beckman IR-5, the mass spectrum on a CEC21-103C spectrometer, and the isothermal distillation molecular weight on a Mechrolab osmometer 301.

### Homopolymerization of 1,2-Bis-*[p*-(ethoxydimethylsilyl)phenyl]-tetrafluoroethane(IIIa)

(a) **Acid-catalyzed Polymerization.** A mixture of 600 mg. of 1,2-bis-*[p*-(ethoxydimethylsilyl) phenyl]tetrafluoroethane (IIIa) in 5 ml. of benzene and 5 ml. of 80% sulfuric acid was refluxed for 16 hr. Water and benzene were added and the benzene layer washed twice with water. After removal of the solvent at reduced pressure and heating the residue *in vacuo* to 125°C., there was obtained a colorless resin with reduced specific viscosity of 0.05. The product was then heated at 260°C. under vacuum for 5 min. The material became slightly colored but the viscosity was unchanged.

In another preparation, 498 mg. (1.09 mmoles; 99.7 wt.-%; 99.3 mole-%) of the aromatic fluorocarbon silane and 1.5  $\mu$ l. (0.008 mmole; 0.3 wt.-%; 0.7 mole-%) of methylvinyl-diethoxysilane in 2 ml. of benzene was stirred for 11 hr. with 2 ml. of 80% sulfuric acid at room temperature. Addition of water and benzene, separation of the benzene layer, thorough washing with water, and evaporation of the solvent under vacuum yielded 402 mg. (theoretical: 417 mg.) of solid white polymer. The product had a reduced specific viscosity of 0.07.

(b) **Base-Catalyzed Polymerization.** A mixture of 600 mg. of 1,2-bis-*[p*-(ethoxydimethylsilyl)phenyl]tetrafluoroethane (IIIa) in 5 ml. of benzene and 5 ml. of 50% sodium hydroxide was refluxed for 16 hr. After addition of more benzene, the organic layer was separated, washed with water, and evaporated up to 125°C. *in vacuo*. The product was a white solid with a reduced specific viscosity of 0.2. In an attempt to raise the molecular weight, the product was dissolved in 8 ml. of benzene, and 8 ml. of 0.02% sodium hydroxide solution was added. The mixture was distilled to dryness under a nitrogen atmosphere. It was then heated at 250°C. and 1 mm. pressure for 10 min. The product was a light brown glassy resin. Its reduced specific viscosity, however, was still 0.2.

### Polymer from 1,2-Bis-*[p*-(hydroxydimethylsilyl)phenyl]-tetrafluoroethane(IIIb)

A solution of 111 mg. (0.28 mmoles) of 1,2-bis-*[p*-(hydroxydimethylsilyl)phenyl]tetrafluoroethane (m.p. 171–172°C.) in 1 ml. of benzene was treated with 1 ml. of 0.03*N* sodium hydroxide solution. The mixture was swirled and taken to dryness at reduced pressure. Upon heating the

residue at 205–230°C. for 2 hr., it became a sticky solid, only partially soluble in benzene. After several extractions with benzene and removal of residual benzene under vacuum at 160°C., there was obtained 64 mg. (61%) of solid polymer. The inherent viscosity in dimethylformamide solution (0.43 g./100 ml.) was 0.047.

### Copolymerization of 1,2-Bis-*[p*-(ethoxydimethylsilyl)phenyl]-tetrafluoroethane with Diethoxydimethylsilane

A mixture of 22.51 g. (49.1 mmoles; 91.4 wt.-%; 77.5 mole-%) of 1,2-bis-*[p*-(ethoxydimethylsilyl)phenyl]tetrafluoroethane(IIIa) (99+ % by vapor phase chromatography), 1.997 g. (13.5 mmoles; 8.1 wt.-%; 21.3 mole-%) of diethoxydimethylsilane, and 140  $\mu$ l. (0.75 mmole; 0.5 wt.-%; 1.2 mole-%) of methylvinyl-diethoxysilane was dissolved in 70 ml. of benzene. Water (3 ml.) was added, and the mixture was stirred and refluxed for 3 days. Removal of the solvents at reduced pressure gave a colorless oil that partially crystallized. The viscosity was obviously very low. The material was redissolved in 50 ml. of benzene and refluxed with 9 ml. of 50% sulfuric acid for 6 hr. Water and benzene were added. The aqueous layer was separated and extracted with benzene. After the benzene solution was washed and extracted with water (3 times) until neutral to pH paper, the combined solution was evaporated. Heating *in vacuo* for 2 hr. at 95–100°C. gave 19.86 g. (theoretical: 19.94 g.) of clear, light-amber gum, with an inherent viscosity in benzene (2.75 g./100 ml.) of 0.31. After continued heating at 145–155°C. and 2 mm. pressure for 3 hr., the polymer VI weighed 19.21 g. An infrared spectrum showed no trace of hydroxyl or ethoxy groups. The NMR spectrum consisted of three sharp peaks: an aromatic singlet, arising from a broad base, of 2.49  $\tau$ , a methylsilyl singlet at 9.63  $\tau$ , and another small methylsilyl singlet at 9.91  $\tau$  due to the dimethylsilane copolymer units. By integration of the spectrum and comparison of the area ratios of the two methylsilyl peaks, the percentage of the two copolymer units could be calculated. Values for the mole per cent of the aromatic-fluorocarbonsilane unit were determined by two integrations to be 77.9% and 77.4% (theoretical: 77.5 mole-%).

### Polymer from 1-*[m*-(Ethoxydimethylsilyl)phenyl]-3-*(p*-(ethoxydimethylsilyl)phenyl)hexafluoropropane

(a) **Polymerization without Catalyst.** When flasks containing samples of 1-*[m*-(ethoxydimethylsilyl)phenyl]-3-*(p*-(ethoxydimethylsilyl)phenyl)hexafluoropropane (IV) were allowed to stand, first open to the air and then loosely cork-stoppered, the samples gradually became viscous over a period of several days. The odor of ethanol was discernible in the flask. After three weeks, the materials were clear, colorless gums that flowed with difficulty. The NMR of the sample (in carbon tetrachloride containing 1% tetramethylsilane) showed a strong aromatic singlet at 2.48  $\tau$  arising from a broadly based multiplet, and a CH<sub>3</sub>-Si single at 9.67  $\tau$ . with only a

trace of a methyl triplet at  $8.83 \tau$  from residual ethoxy groups and ethanol. The inherent viscosity, taken after two months, as a solution of 1.77 g./100 ml. of benzene was found to be 0.23. To a solution of 1.72 g. of this material in 10 ml. of benzene was added 1 ml. of water. The benzene was removed at reduced pressure and the residue heated *in vacuo*. The polymer foamed as the water evaporated. Heating was continued up to  $170^{\circ}\text{C}$ ., where it was maintained for 30 min. The sample now appeared very viscous even at  $170^{\circ}\text{C}$ .; the inherent viscosity (1.77 g./100 ml. benzene) was found to be 0.21. Continued heating of the sample at  $165\text{--}170^{\circ}\text{C}$ . for 9 hr. gave a product with unchanged inherent viscosity (0.22 at 2.18 g./100 ml. of benzene). The infrared spectrum was very similar to that of the starting monomer. However, there were a few major differences. The polymer had no absorption at 3.48 and  $10.55 \mu$  due to the ethoxy group. In addition the  $9.3 \mu$  peak of the monomer was considerably broadened up to  $9.6 \mu$  (Si-O-Si stretching). The  $12\text{--}13 \mu$  region was also significantly different. The polymer exhibited less absorption at  $12.1\text{--}12.2 \mu$  and had a band at  $12.65 \mu$ , shifted from  $12.75 \mu$  in the monomer.

**(b) Acid-Catalyzed Polymerization.** A solution of 4.312 g. (28.14 mmoles; 99.5 wt.-%; 98.5 mole-%) of 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (IV) (99 + mole-% by vapor phase chromatography and  $80.0 \mu\text{l}$ . (0.43 mmole; 0.5 wt.-%; 1.5 mole-%) of methylvinyl-diethoxysilane in 50 ml. of benzene was prepared. To this solution was added a solution of 5 ml. of concentrated sulfuric acid and 10 ml. of water. The mixture was stirred and refluxed for 12 hrs. Additional water and benzene were added, and the benzene layer was separated. The acid layer was extracted with benzene, and the two benzene layers were consecutively washed three times with water. The combined solvent was removed at reduced pressure and then *in vacuo*. The residue weighed 12.33 g. (theoretical polymer; 12.26 g.). It was heated at  $150^{\circ}\text{C}$ . and 1 mm. pressure for 1 hr., during which time the viscosity increased and considerable bubbling was evident. The mixture was dissolved in benzene and transferred to another flask. The benzene was removed, and the residue was heated at  $145\text{--}155^{\circ}\text{C}$ . and 1 mm. pressure for 4 hr. During this time, white crystals sublimed out into the neck of the flask. The residue in the flask was still a viscous, light-amber oil. Upon removal of the sublimate and continued vacuum heating, white sublimate formation continued. A total of 1.12 g. of crystalline white sublimate (m.p.  $80\text{--}83^{\circ}\text{C}$ .) was collected. The polymer residue weighed 11.07 g. The residue was again heated in vacuum and the sublimate was again formed. After removal of the sublimate, the polymer residue now weighed 10.99 g. It had an inherent viscosity (0.05 g./100 ml. benzene) of 0.07. Resublimation gave an analytical sample (m.p.  $80.0\text{--}81.5^{\circ}\text{C}$ .). Further heating of the polymer produced no additional sublimate.

ANAL. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{F}_6\text{O}_2\text{Si}_2$ : C, 52.51%; H, 4.64%. Found: C, 52.55, 52.62%; H, 4.64, 4.75%.

The molecular weight was taken in benzene solution, using an isothermal distillation apparatus. The original reading showed a molecular weight value of 436 (calcd.: 435). However, on two subsequent readings the value climbed to 449 and then to 496, indicating that repolymerization was occurring.

All of the bands of the infrared spectrum of the sublimate were also present in the polymer. However, the polymer absorptions at 8.95, 11.40, 11.65, 13.7, 14.1, and 15.1  $\mu$  were absent. Also, the 9.5  $\mu$  region of the sublimate spectrum showed considerably more resolution. It is important to note that the spectrum of the sublimate still had the  $\text{CH}_3\text{-Si-CH}_3$  symmetrical deformation band at 7.95  $\mu$ , the phenyl-Si band at 8.74  $\mu$ , and the Si—O stretching band at 12.6  $\mu$ , but lacked the ethoxy C—O—Si band at 10.55  $\mu$ .

The NMR spectrum corroborated the cyclic monomer structure for the sublimate. It consisted of an aromatic multiplet with the largest peak at 2.84  $\tau$ , a singlet at 3.73  $\tau$ , and two equal intensity methylsilane singlets at 9.59 and 9.69  $\tau$ . Integration of these three regions gave an area ratio of 7.13:1.00:12.05. The 3.73  $\tau$  singlet arose from the *meta* proton resonance shielded by the adjacent ring to give a high shift position.

From these results, the sublimate was identified as 10,10,11,11,12,12-hexafluoro-1,1,3,3-tetramethyl-1,3,2-disiloxa-(3,3)-metaparacyclophane (VI).

Mr. Robert Parkhurst, Mr. Philip Stevenson, and Mr. Fred Dreier assisted in portions of the experimental work reported here. The NMR spectra were obtained by Mr. W. R. Anderson, Jr., the mass spectrum by Mrs. L. Peters, and the isothermal distillation molecular weight by Mr. D. Tieszen.

The work was supported by Rock Island Arsenal under Contract No. DA-11-070-508-ORD-906. Mr. Z. T. Ossefort and Mr. R. F. Shaw were project monitors for Rock Island Arsenal.

### References

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2. Omietanski, G. M., and W. G. Reid, *Proceedings of the Sixth Joint Army-Navy-Air Force Conference on Elastomers, Boston, Mass., Oct. 18-20, 1960*, p. 603.
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### Résumé

Ce papier décrit la préparation et des propriétés d'une classe nouvelle de silicones à savoir les silicones de phénylène et de perfluoroalcoylène. On a mis au point une méthode de mesure directe de la composition des copolymères des silicones.

### Zusammenfassung

In der vorliegenden Arbeit werden Herstellung und Eigenschaften einer neuen Art von Silikonpolymeren, der Phenylperfluoralkylen-Silikone, beschrieben und ein direktes Mass für das Verhältnis der Copolymereinheiten in Silikoncopolymeren angegeben.

Received July 15, 1963

Revised September 16, 1963