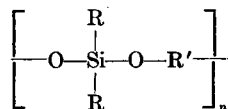


Silane Polymers of Diols

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Synopsis

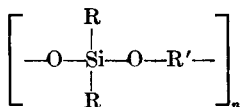
In an effort to develop new and improved polymeric materials for space application, a new series of polymers has been prepared. Some of these have shown outstanding thermal stability and good stability when exposed to ultraviolet radiation in a vacuum environment. High molecular weight polymers of the general type,



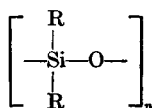
have been prepared by the reaction of a silyldiamine with various organic diols. Bis-(anilino)diphenylsilane has been reacted with such diols as hydroquinone, resorcinol, *p,p'*-biphenol, 2,7-naphthalenediol, 2,2-propane-bis(4-hydroxybenzene), 1,6-hexanediol, and 4,4'-dihydroxydiphenyl ether. Of these, the polymer containing the biphenyl linkage, polydiphenylsiloxylbiphenyl, has the more desirable properties. Polydiphenylsiloxylbiphenyl is stable to 600°C. for short periods of time. Fibers with fairly good tenacity, 0.5 g./den. may be drawn directly and continuously from the polymer melt. This polymer forms a hard protective coating on aluminum, remains stable after being heated at 500°C. for 60 min., and shows no change after 96 hr. at 270°C. (518°F.). It also forms good transparent semiflexible films and has good tensile strength as an ambient temperature adhesive.

INTRODUCTION

The need for new materials that will withstand the rigors of the space environment is evident in every phase of spacecraft development. One of the critical areas is the development of improved nonmetallic materials for use as coatings, plastics, adhesives, elastomers, etc. A research program has led to the development of new polymer systems which have shown a number of outstanding properties. These polymers have the general formula,

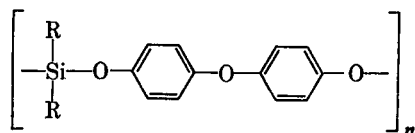


The silicone polymers having the general formula

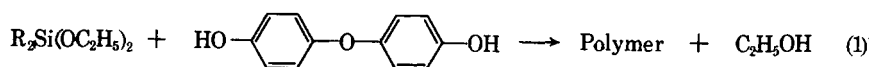


have many outstanding properties, although they do have some shortcomings for applications in extreme conditions. To improve these properties, the silicone polymer has been modified by incorporating the highly stable aromatic type groups into the "backbone" of the chain.

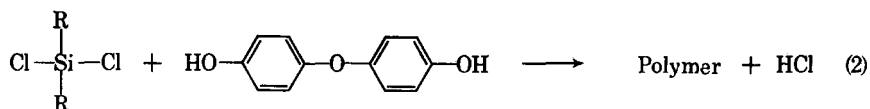
MacFarland and Yankura¹ reported the preparation of a polymer with the structure



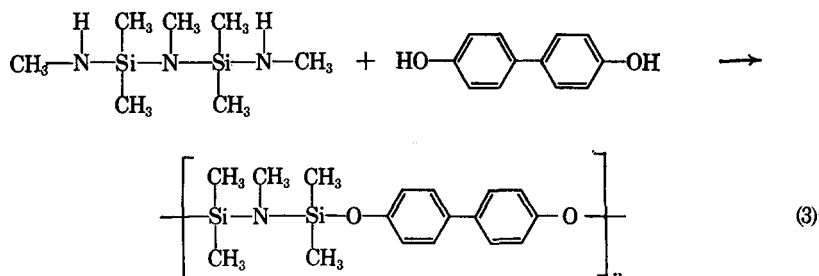
which can be prepared by two different methods. One method of preparation was by an alcoholysis type condensation reaction:



The other was a condensation between the chlorosilane and the dihydroxydiphenyl ethers.

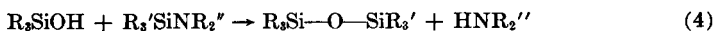


Breed and Elliott² have reported a polymer with good thermal stability which was prepared by the reaction:



Thermogravimetric analysis of this polymer showed a weight loss of 18% at 500°C. and 46% at 900°C.

The cleavage of Si—N bonds by nucleophilic reagents is discussed in numerous reports in the literature.³⁻⁷ Pike^{8,9} has studied the rate of condensation of monofunctional silylamines with monofunctional silanols.

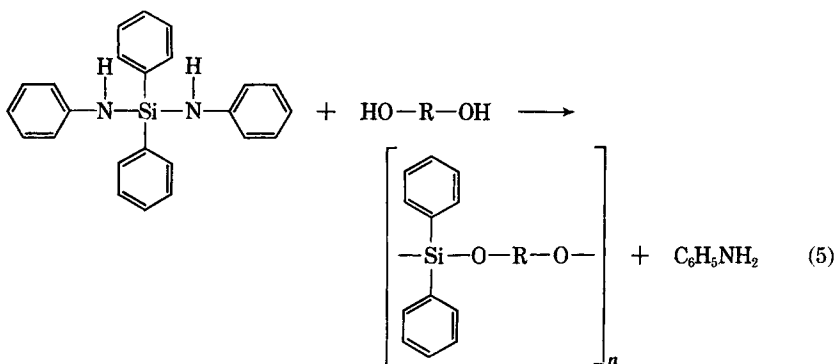


The extent and rate of reaction are dependent upon the steric hindrance around both the silicon-nitrogen bond and the hydroxyl group of the alcohol and the acidity of the attacking alcohol. The rate of reaction of silylamines toward a given silanediol decreased in the order, (CH₃)₃SiN-

$(C_2H_5)_2 > (CH_3)_3SiNH-C_4H_9-n > (CH_3)_2Si[N(C_6H_5)_2]_2$. However, our work has shown that the stable silylamine, bis(anilino)-diphenylsilane, $(C_6H_5)_2Si(NHC_6H_5)_2$, will react with a number of dihydroxy compounds at rates which are adequate to produce high molecular weights in relatively short periods of time. This silylamine appears to have enough steric hindrance so that there is no apparent tendency to cyclize.

EXPERIMENTAL

Our investigation encompassed the melt polymerization of organic diols with bis(anilino)diphenylsilane.



This included such diols as hydroquinone, resorcinol, *p,p'*-biphenol, 2,7-naphthalenediol, 2,2-propanebis(4-hydroxybenzene) (bisphenol A), 1,6-hexanediol, and 4,4'-dihydroxydiphenyl ether. An alkyl-aryl copolymer was prepared also. All of these polymers showed elasticity at elevated temperatures, and fibers could be drawn from the elastic melt.

Monomers

Bis(anilino)diphenylsilane was prepared according to the procedure of Anderson¹⁰ by the reaction of diphenyldichlorosilane and aniline. Freshly distilled aniline (312 ml., 4.0 mole) and benzene (400 ml.) were placed in a round-bottomed flask. Diphenyldichlorosilane (208 ml., 1.0 mole) in 250 ml. of benzene was added dropwise with rapid stirring. After refluxing for 1 hr., the reaction products were allowed to stand overnight and were then filtered. The filter cake was slurred in 2.5 liters of boiling benzene, and the aniline hydrochloride was removed by filtration. The filtrate was evaporated to approximately one half of its volume to effect crystallization of the desired monomer. The bis(anilino)diphenylsilane was dried at room temperature under reduced pressure. The final product was a white crystalline material that melted at 156–161°C.

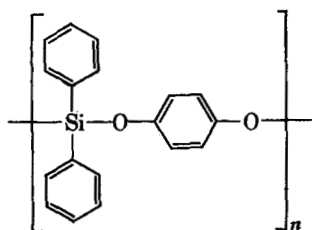
ANAL. Calc. C, 78.65%; H, 6.05%; N, 7.64%; Si, 7.66%. Found C, 78.00%; H, 5.73%; N, 7.20%; Si, 8.00%.

The organic diols were obtained from commercial sources, but, in each case, they were recrystallized before using. The Bisphenol-A was obtained from Dow Chemical, and all other diols were obtained from Eastman Organic Chemicals.

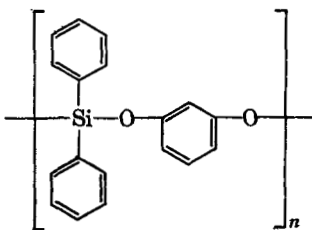
Polycondensations

Equimolar amounts of the monomers were placed in a thick-walled resin kettle which was equipped with liquid take-off condenser and a vacuum source. The kettle was heated, and the contents were stirred with a hot plate-magnetic stirrer combination. A heating mantle was used on the kettle to help remove the amine as it was evolved. The monomers were first mixed in the solid state and then heat was applied slowly. The monomers were thoroughly mixed after they melted. After about 30 min., vacuum was applied slowly. The final reaction conditions were about 1 mm. Hg vacuum at about 300–325°C. The heating time was generally 6 hr.

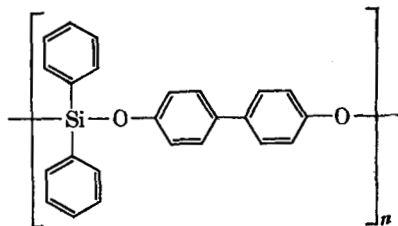
Polymers prepared by the above reaction, eq. (5), are shown as structures I–VIII.



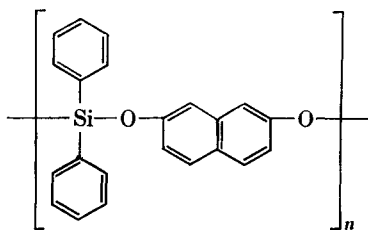
I



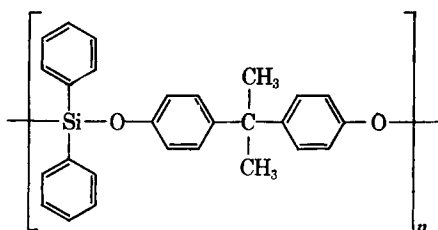
II



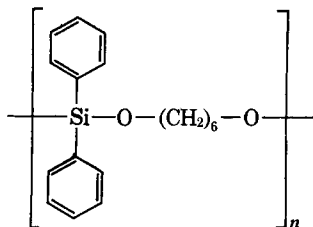
III



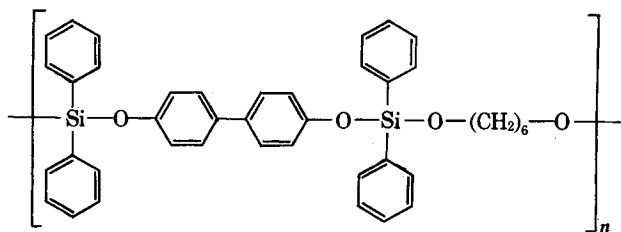
IV



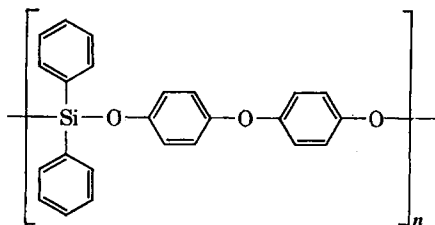
V



VI



VII



VIII

TABLE I
 Silicon Polymers of Aryl Diols

Polymer	Polymer repeating unit	Description of polymer ^a	Melting point, °C.	Yield, %
I	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si} - \text{O} - \text{C}_6\text{H}_4 - \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, slightly brittle amber solid	>300	
II	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si} - \text{O} - \text{C}_6\text{H}_5 - \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, slightly brittle amber solid	240-245	96.7
III	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si} - \text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, tough, semiflexible amber light solid	>300	98.4
IV	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si} - \text{O} - \text{C}_{10}\text{H}_7 - \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, brittle brown solid dark	123-125	
V	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, brittle, amber solid	99-100	

^a All polymers were soluble in DMF, THF, and DMSO.

The properties of the polymers prepared are given in Tables I and II. Results of analyses are shown in Table III.

A study has been made of the infrared spectra obtained on the polymers presented in this report, and the correlation of data from these similar compounds gives credence to their assigned structures (Figs. 1-4). It is possible to give assignments to aromatic substitution patterns, hydrocarbon groups, and silicon-to-oxygen bonds, etc. In polymers I, III, V, VII, and VIII, there is a common absorption band between 824 and 835 cm^{-1} wave numbers. This band can be attributed to the C-H out-of-plane deformation by the 1,4-disubstituted aromatic rings. In addition, all of the polymer spectra show two distinct absorption bands at 720 and 690 cm^{-1} . These absorption bands arise from the monosubstituted aromatic rings attached to the silicon. In the case of polymers II and IV, identification of the aromatic structures, other than the monosubstituted system, is

TABLE II
Silicon Polymers of Alkyl Diols, Alkyl-Aryl Diols, and Dihydroxyphenyl Ether

Polymer	Polymer repeating unit	Description of polymer ^a	Melting point, °C.	Yield, %
VI	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{—Si—O—(CH}_2\text{)}_6\text{—O—} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Light, amber, soft, tacky gum	253–257	96.0
VII	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{—Si—O—} \\ \\ \text{C}_6\text{H}_5 \end{array} \right] \text{—} \text{C}_6\text{H}_4 \text{—} \text{O—} \left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{—Si—O—(CH}_2\text{)}_6\text{—O—} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, tough, semi-flexible, light amber solid	>300	
VIII	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{—Si—O—} \\ \\ \text{C}_6\text{H}_5 \end{array} \right] \text{—} \text{C}_6\text{H}_4 \text{—} \text{O—} \text{C}_6\text{H}_4 \text{—} \text{O—} \left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{—Si—O—} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Hard, tough, semi-flexible, fiber-forming polymer	127–130	

^a All polymers with the exception of VII were soluble in DMF, THF, and DMSO.

difficult. It may be possible that the very strong absorption bands at 768 cm.^{-1} in polymer II is caused by the three adjacent hydrogen atoms in the 1,3-disubstituted aromatic ring. Polymer IV does not show any specific bands in the $900\text{--}650\text{ cm.}^{-1}$ region that would enable one to assign aromatic substitution. However, the shifting of the 1600 and 1590 cm.^{-1} bands may be an indication of the naphthalene structure. Therefore, additional data on similar polymer structures would be required before positive assignments can be made.

Based on the correlation of data from these polymers and other organo-silicon structures, the sharp medium absorption bands at 1429 cm.^{-1} and the strong broad system at 1125 cm.^{-1} can be attributed to the $\text{Si-C}_6\text{H}_5$ linkage. The Si-O linkage gives rise to the rather broad band system observed just below 1100 cm.^{-1} . The absorption band observed between 1200 to 1300 cm.^{-1} is apparently due to the phenoxysilicon portion of

TABLE III
Analyses of Silicon Polymers of Diols

Polymer	Empirical formula	Calculated			Found		
		C, %	H, %	Si, %	C, %	H, %	Si, %
I	$(\text{C}_{18}\text{H}_{14}\text{O}_2\text{Si})_n$	74.45	4.86	9.67	73.43	4.54	10.49
II	$(\text{C}_{18}\text{H}_{14}\text{O}_2\text{Si})_n$	74.45	4.86	9.67	74.45	4.86	10.56
III	$(\text{C}_{24}\text{H}_{18}\text{O}_2\text{Si})_n$	78.65	4.95	7.66	78.13	4.94	8.7
IV	$(\text{C}_{22}\text{H}_{16}\text{O}_2\text{Si})_n$	77.75	4.71	8.20	77.67	4.74	8.92
V	$(\text{C}_{27}\text{H}_{24}\text{O}_2\text{Si})_n$	79.37	5.92	6.88	78.41	5.94	7.10
VI	$(\text{C}_{18}\text{H}_{22}\text{O}_2\text{Si})_n$	72.44	7.43	9.41	71.13	7.11	9.86
VII	$(\text{C}_{21}\text{H}_{20}\text{O}_2\text{Si})_n$	75.86	6.06	8.45	74.78	5.08	10.7
VIII	$(\text{C}_{24}\text{H}_{18}\text{O}_2\text{Si})_n$	75.33	4.74	7.34	75.46	4.67	7.96

these polymer structures. This phenoxysilicon assignment is indicated by the appearance of the very strong band in all of the spectra, except in the case of polymer VI, where this structure does not occur. The structural arrangement of the propyl group in polymer V should give rise to a vibrational pattern similar to that of an isopropyl radical. This pattern is confirmed by the strong peak at 1429 cm.^{-1} and the two weak peaks at 1385 and 1363 cm.^{-1} .

Polymer VII is a copolymer of the structures suggested for polymers III and VI. It is evident when comparing the spectra of III and VII that there is little difference between these spectra to suggest a new structure with the exception of the weak aliphatic CH doublet between 2850 and 2940 cm.^{-1} . Thus, the infrared spectrum of polymer VII does not indicate whether the suggested structure is correct. At this time, it is not understood why the absorption intensity of this CH doublet between 2850 and 2940 cm.^{-1} is weak, nor does the structure for polymer VII suggest why the normal aliphatic stretching mode should be attenuated to the degree observed in the spectrum. Correlation assignments for the diphenoxy linkage in polymer VIII could not be made from the infrared spectra.

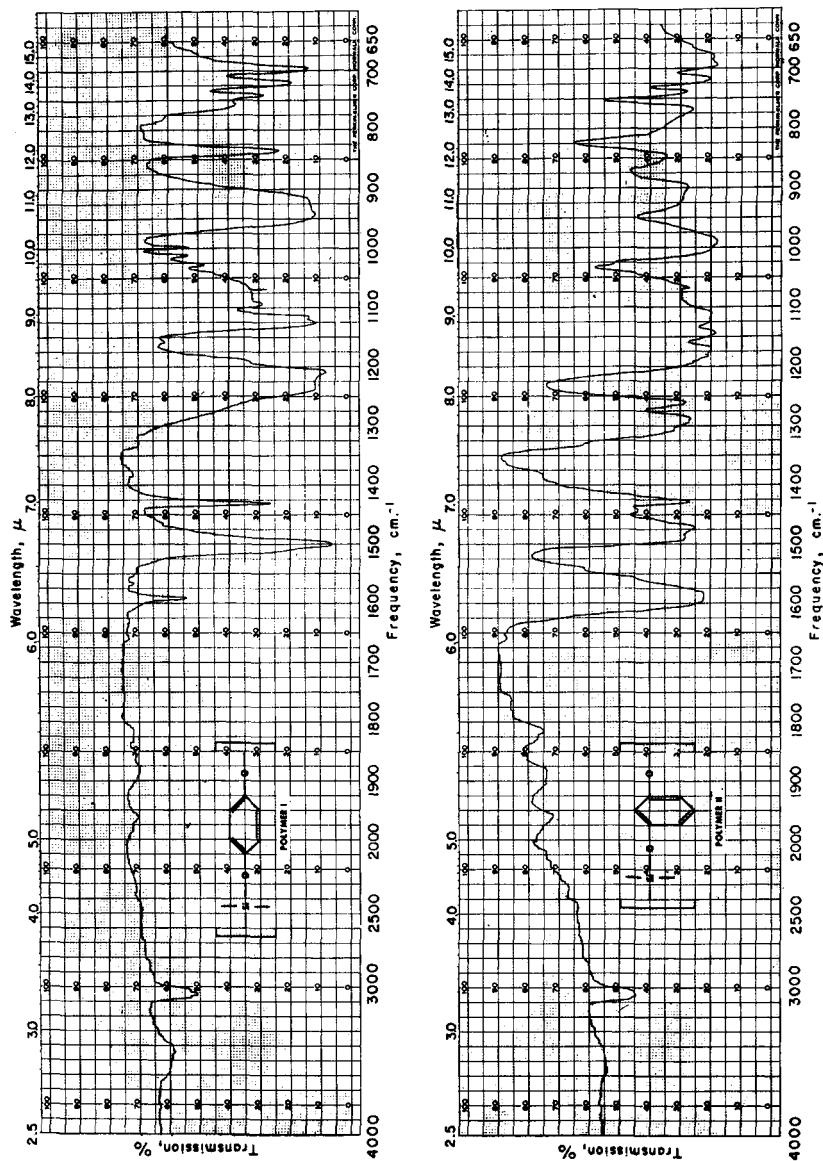


Fig. 1. Infrared spectra of polymers I and II. Each silicon atom has two attached phenyl substituents.

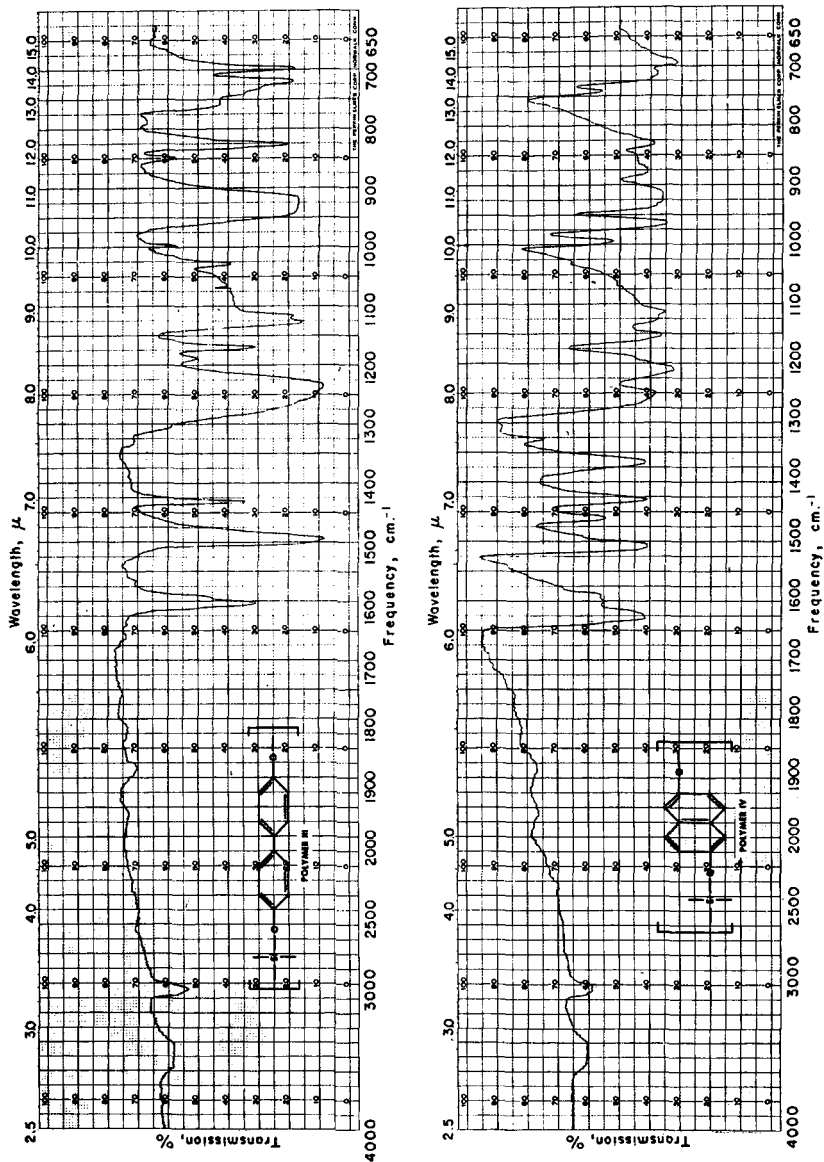


Fig. 2. Infrared spectra of polymers III and IV. Each silicone atom has two attached phenyl substituents.

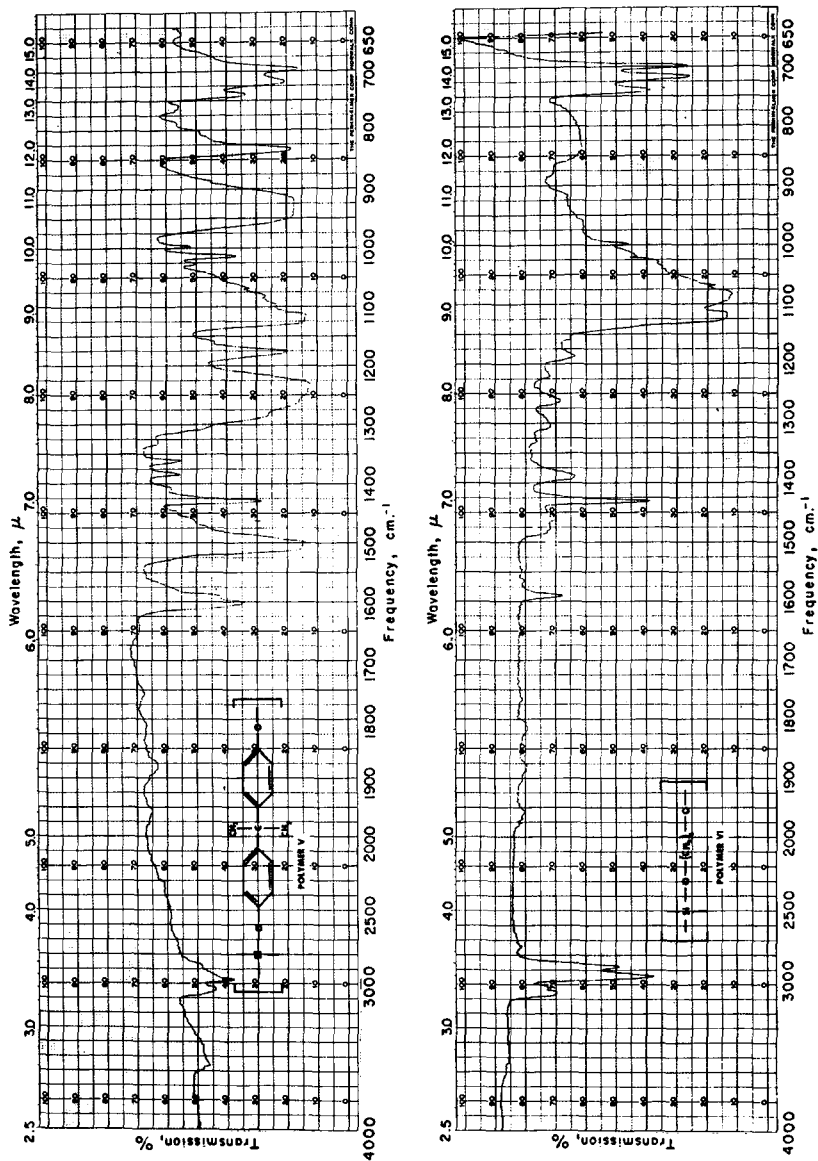


Fig. 3. Infrared spectra of polymers V and VI. Each silicon atom has two attached phenyl substituents.

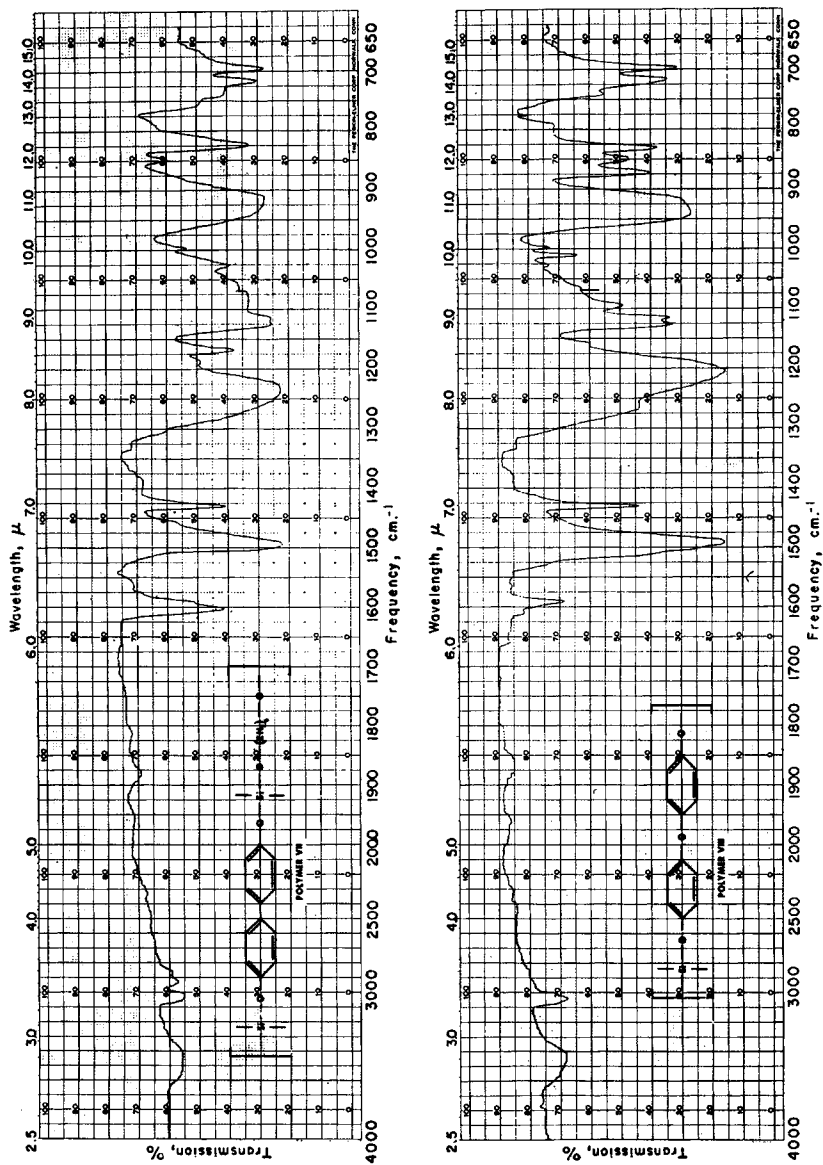


Fig. 4. Infrared spectra of polymers VII and VIII. Each silicon atom has two attached phenyl substituents.

The N-H vibration band of aminosilanes between 3320 and 3340 cm.^{-1} is absent in each case, indicating that there is no bis(anilino)-diphenylsilane present.

Discussion

With the exception of polymer VII, all products are soluble in tetrahydrofuran (THF), dimethylformamide (DMF), or dimethylsulfoxide (DMSO). Protective coatings from THF solutions upon ceramic-coated metal plates have considerable ultraviolet stability (see Table IV). The change in per cent reflectance with wavelength for irradiation time* for 48 hr. at a pressure of 2×10^{-5} mm. Hg was determined.

TABLE IV
Ultraviolet Irradiation^a

Wavelength, m μ	Reflectance of polymer III, %		Reflectance of control sample, % ^b	
	Initial	Final	Initial	Final
400	69.0	42.5	64.0	25.0
425	79.0	53.0	78.5	35.0
450	82.0	60.5	81.5	46.0
475	84.0	68.0	84.5	57.0
500	85.0	72.5	85.5	65.0
525	87.0	76.0	87.5	72.0
550	87.0	78.0	87.0	76.5
575	87.0	78.5	87.5	79.0
600	85.0	79.0	87.0	81.0
625	85.0	81.0	85.0	82.0
650	85.0	81.5	85.5	82.5
675	85.0	81.5	85.5	82.0
700	85.0	82.0	85.0	82.0

* Irradiation conditions: time: 48 hr., pressure: 2.0×10^{-5} mm. Hg, ultraviolet source: Hanovia Quartz mercury vapor lamp, Type 54A-10.

^b A commercial high temperature coating material.

The thermal stabilities of all the polymers are given in Figures 5-7. These were obtained by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 4.1 $^{\circ}\text{C.}/\text{min.}$

Figure 5 presents the TGA data of the four polymers which are true aromatic types. It may be observed from this data that polymer III has the best thermal stability, losing 10% of its weight at 600 $^{\circ}\text{C.}$ Figure 6 shows the effect of using a propyl group or oxygen between the two phenyl groups in this polymer. Again, polymer III is the most stable. Figure 7 shows the relative stabilities of aromatic and aliphatic polymers and a copolymer which contains both types at groups. It may be seen that the aliphatic polymer lost most of its weight at 500 $^{\circ}\text{C.}$, while a 50/50 copolymer is only slightly less stable than the totally aromatic polymer.

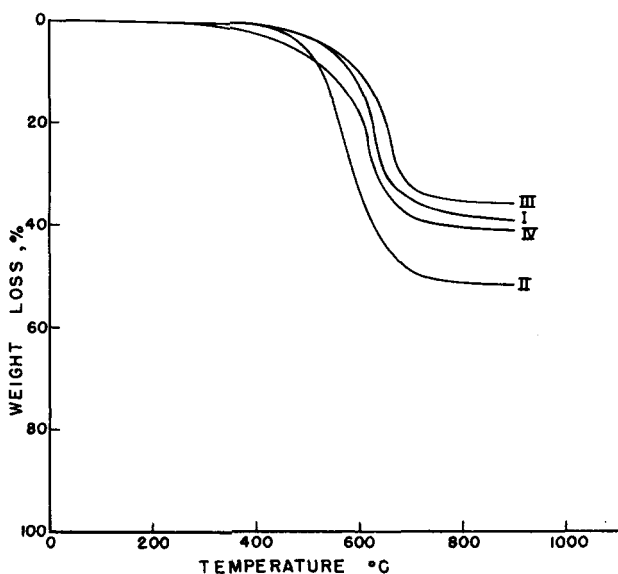


Fig. 5. Thermogravimetric analysis of polymers I, II, III, and IV.

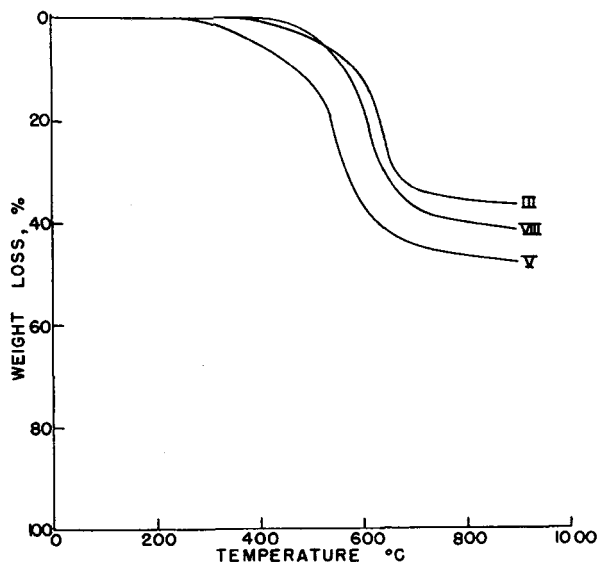


Fig. 6. Thermogravimetric analysis of polymers III, V, and VIII.

When polymer III was prepared with starting materials which were re-crystallized three times, fairly strong fibers could be drawn continuously from its melt. These fibers showed an initial tenacity of 0.5 g./den. Since they may be hot or cold drawn, their strength should be greatly increased if proper spinning methods are used. Brittle fibers could be drawn from the

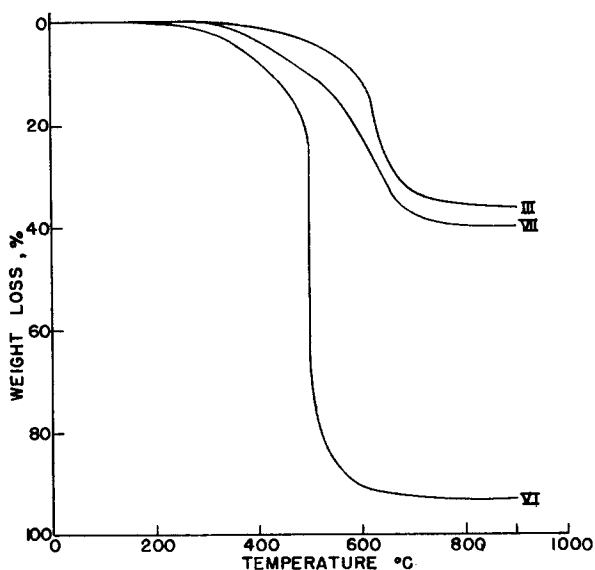
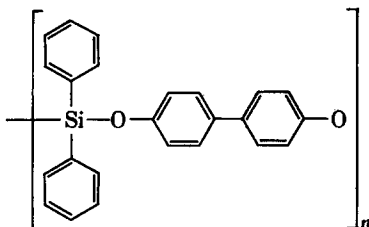


Fig. 7. Thermogravimetric analysis of polymers III, VI, and VII.

melt of all other polymers. Polymer VIII gave a semiflexible, fairly weak fiber which showed improved strength after drawing over a hot plate.

A thermally pressed film of 15 mil thickness of polymer III had a tensile strength of 3560 psi with an 11% elongation. When tested as a hot melt

TABLE V
Molecular Weights of Polymer III



Experi- ment number	Reac- tion time, hr.	M.W. ^a	Physical description		Melting point, °C.	Film- forming quality ^b
			Color	Flexibility		
1	3	38,000	Light gray	Brittle	135-137	None
2	6	75,000	Light amber	Semiflexible	300	Good
3	6	180,000	Light amber	Semiflexible	300	Fair ^c

^a Determined by light-scattering technique by Southern Research Institute, Birmingham, Alabama.

^b Thermally pressed film.

^c Sample of M.W. 180,000 did not melt sufficiently to form uniform film.

adhesive on 1020 mild steel, the average tensile shear strength of the polymer was 3920 psi.

Polymer I formed a good hot melt adhesive and had tensile shear strength of 2950 psi. When the shear tensile strengths of polymers I and III were compared, an increase of about 33% was observed due to the replacement of a benzene ring by diphenyl.

The thermal stability of copolymer VII was remarkably improved when compared with the aliphatic polymer VI and only slightly deteriorated when compared with polymer III, which contained only diphenyl units in the chain. Unfortunately, polymer VII could not be tested as a hot melt adhesive because of insufficient melting at 400°C. A number of average molecular weights ranging up to 180,000 have been obtained with polymer III. Table V shows the range of molecular weights obtained in various reactions. No attempts were made to define conditions for obtaining maximum or optimum molecular weights. However, it may be noted in Table V that reaction time affects molecular weights.

Polymer III produces a flexible coating on aluminum which may be cured by heating at 270°C. for 16 hr. This film remained stable after being heated to 400°C. for 4 hr. and showed no decomposition after 96 hr. at 270°C.

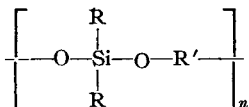
Appreciation is expressed to Mr. J. K. Davis and Miss Barbara Mrazek for their assistance in the preparation and study of these polymers and to Messrs. Albert C. Krupnick, John W. Barnes, Thomas H. Arnold, and Forrest T. Wells, and all of the Analytical Chemistry Section for their assistance in the analysis and characterization of these materials. Appreciation also is expressed to Dr. Robert E. Burks of Southern Research Institute for his assistance in this study.

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Résumé

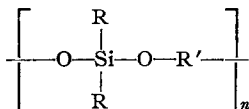
Une nouvelle série de polymères a été préparée pour essayer d'augmenter le nombre de substances polymériques à des fins spatiales. Certains polymères présentent une stabilité thermique remarquable et une bonne stabilité aux radiations ultraviolettes sous vide. Des polymères de haut poids moléculaire du type général



ont été préparés par la réaction d'une silyldiamine avec différents diols organiques. Le bis(anilino)diphénylsilane réagit avec des diols tels que l'hydroquinone, le résorcinol, le *p,p*,-bisphénol, le 2,7-naphthalènediol, le 2,2-propane-bis(4-hydroxybenzène), le 1,6-hexanediol, et le 4,4,-dihydrodiphényl éther. Parmi ceux-ci le polymère contenant la liaison biphenyle, le polydiphénylsiloxybiphényle, a des propriétés plus intéressantes. Le polydiphénylsiloxybiphényle est stable à 600°C pendant une période assez courte. Des fibres, possédant une bonne ténacité, 0,5 grammes par denier, peuvent être étirées directement et en continu à partir du polymère fondu. Ce polymère forme une couche protectrice dure sur l'aluminium et reste stable après avoir été chauffé à 500°C pendant 60 minutes, et ne montre pas de changement après 96 heures à 250°C (518°F). Il forme aussi des films transparents et semiflexibles et a une bonne résistance à la traction sous forme d'adhésif à température ambiante.

Zusammenfassung

Bei einem Versuch zur Entwicklung neuer und verbesserter Polymermaterialien zur Raumfahrt wurde eine neue Reihe von Polymeren hergestellt. Einige davon zeigten besondere thermische Stabilität und gute Stabilität bei UV-Bestrahlung im Vakuum. Polymere mit hohem Molekulargewicht des allgemeinen Typs



wurden durch Reaktion eines Silyldiamins mit verschiedenen organischen Diolen hergestellt. Bis(anilin)diphenylsilan wurde mit Diolen wie Hydrochinon, Resorcin, *p,p*,-Biphenol, 2,7-Naphthalindiol, 2,2-Propan-bis(4-hydroxybenzol), 1,6-Hexandiol und 4,4,-Dihydroxydiphenyläther zur Reaktion gebracht. Von diesen hatte das Polymere mit Biphenylbindung, Polydiphenylsiloxydiphenyl, die besten Eigenschaften. Polydiphenylsiloxybiphenyl ist bis zu 600°C für kurze Zeitdauer stabil. Fasern mit recht guter Festigkeit, 0,5 Gram pro Denier, können direkt und kontinuierlich aus der Polymerschmelze gezogen werden. Dieses Polymere bildet um Aluminium eine harte Schutzhülle, bleibt nach Erhitzen bis zu 500°C durch 60 Minuten stabil und zeigt nach 96 Stunden bei 270°C (518°F) keine Veränderungen. Es bildet auch gut transparente halbwegs Filme und hat als Adhäsiv bei Raumtemperatur gut Zugfestigkeit.

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