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STATUS REPORT: DEVELOPMENT OF POLYMERIC MATERIALS FOR  
POTTING AND ENCAPSULATING ELECTRONIC ASSEMBLIES

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ABSTRACT

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The objective of this parallel in-house and contractual program has been to develop improved potting and conformal coating materials for protective electronic encapsulation. Urethane-siloxane and epoxy-siloxane copolymer systems were investigated. New epoxy-siloxane and epoxy-silane polymer precursors have been synthesized and characterized. Preliminary cure studies of the epoxy-silane material have indicated a definite polymerization to a solid polymer. Attractive mechanical strength and dielectric properties are apparent in silazane-cured, conventional epoxy resins. Urethane-siloxane polymers appear to have film or coating forming potential as well as some flexibility at temperatures below ambient. Analogous polymers have shown usable processing characteristics and promising dielectric properties.

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PROPULSION AND VEHICLE ENGINEERING LABORATORY  
RESEARCH AND DEVELOPMENT OPERATIONS

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## TECHNICAL MEMORANDUM X-53390

### STATUS REPORT: DEVELOPMENT OF POLYMERIC MATERIALS FOR POTTING AND ENCAPSULATING ELECTRONIC ASSEMBLIES

#### SUMMARY

A sustained program is in progress to develop polymeric materials with improved properties as encapsulating and coating compounds for electronic assemblies. The overall program is represented by three major divisions: (1) rigorous testing and evaluation of commercially available polymers to predict the material characteristics essential to fulfillment of the program goals; (2) application of these results to an intensive synthesis study of new polymer systems; and (3) integration of the new polymers into electronic hardware by establishing formulation and processing techniques as well as by carefully evaluating the critical parameters. This report covers the second phase of the investigation.

The general families of epoxy-siloxane and urethane-siloxane copolymers have been investigated in-house and under contract, the first being proposed as a candidate material for potting compounds and the second to be oriented toward conformal coatings. The internal program has yielded a series of urethane-siloxane copolymers which are characterizable to the extent that they reflect the validity of the synthetic approach. These materials form tough, flexible, transparent thin films or coatings. The increase in flexibility of these polymers is apparent as the degree of polymerization of the siloxane moiety is increased.

A series of epoxy-silane polymer precursors having a general structure designation of bis(alkenyldimethylsilyl)-benzenes has been synthesized and characterized in some detail. One compound, 1,4-bis(vinyldimethylsilyl)-benzene, has been epoxidized to the corresponding diepoxide and, subsequently, polymerized to a solid polymer which has reasonable mechanical strength.

The contractual program has paralleled the in-house effort and has resulted in the preparation of a series of urethane-siloxane copolymers utilizing bis(hydroxymethyl)-diphenylether-based siloxanes. A liquid siloxy-urethane prepolymer has been formulated which cures to clear, flexible elastomers that have dielectric constants as low as 3.38, measured at 1 kilocycle. A new epoxy-siloxane polymer precursor, 1,3-bis(m-allylphenyl)-tetramethyl disiloxane, has been synthesized and characterized during the contract investigation. This compound is to be epoxidized and, subsequently, polymerized with diamines to a solid polymer. The polymerization of a commercial monomeric bis-epoxide with bis(methylamino)-diphenylsilane has produced solid polymers with significantly lower dielectric constants than the conventionally-cured analogous epoxy resins.

## INTRODUCTION

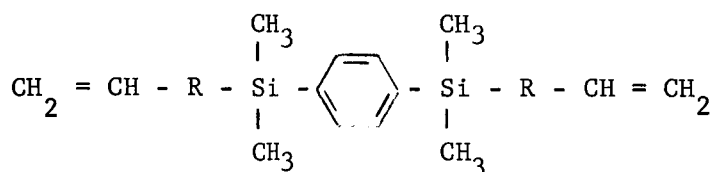
The development of improved polymeric materials for use as encapsulating compounds for service on electronic cordwood-type modules and as conformal coatings for service on printed circuit boards has been investigated as an internal research program and as a parallel contract program. This program was initiated as a materials evaluation and modification effort (ref. 1) to establish the target criteria and to determine the most fruitful area for a materials synthesis program. From the program, it was established that two materials, epoxy-siloxane copolymers for encapsulants and urethane-siloxane copolymers for conformal coatings, would be the most logical candidates for the synthesis effort.

The monomeric polymer precursors that are being synthesized in this program are designed molecularly to impart to the resulting polymer minimal values of dielectric constant and power factor. Formulation and filling techniques are being investigated which will allow polymer precursors to be filled to such a degree that the coefficient of thermal expansion of the cured encapsulant approaches that of the component, while also insuring that the consistency of the uncured resin-filler mix does not exceed a pourable viscosity. The expansion coefficient requirement of the encapsulating materials will preclude low temperature flexibility by virtue of the high proportion of filler. The conformal coating requirements include a low temperature flexibility that is inherent in elastomeric-type materials. It is evident that the two major areas of protective encapsulation must be approached, in one case, with a relatively rigid, fillable material that has a low differential thermal expansion between component and encapsulant and, in the other case, with a resilient, elastomeric material. The description of the synthesis program now in effect in-house and on contract is given below in detail; the theoretical basis is included in each section to elucidate the experimental approach. The dielectric properties were evaluated by the use of the Hartshorn flat dielectric specimens and the 4-rod embedded electrode configuration. Insulation resistance and volume resistivity measurements were taken from the 4-rod configuration. Unless otherwise specified, the values given for dielectric constant and dissipation factor were measured at one kilocycle.

## IN-HOUSE RESEARCH

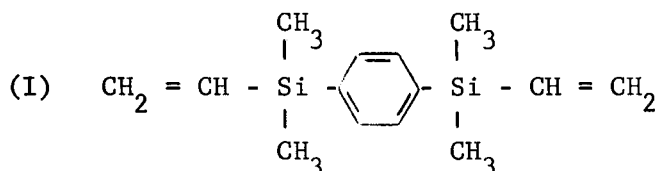
### Epoxy-Silane Copolymer Synthesis

Theoretical Basis. - A series of compounds has been investigated for encapsulating or embedment compounds, which is represented by the following basic silyphenylene olefin:

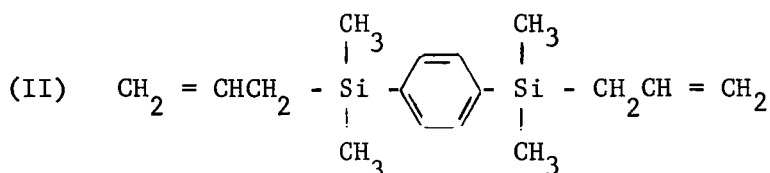


The terminal olefinic groups may be oxidized to the corresponding epoxide functionality. The scope of this synthetic approach has been to prepare difunctional copolymer precursors which polymerize only in the final curing or crosslinking reaction. The alternative procedure would involve a partial polymerization of the difunctional monomer to a liquid prepolymer which would then be crosslinked to a solid resin. This introduced problems of controlling the degree of polymerization of the prepolymer for reproducibility of the epoxide functionality. Purification in the prepolymer state also is much more difficult than in the difunctional monomeric form. Thus, in the interest of producing analytically controllable polymers, which appeared desirable to minimize dielectric breakdown, outgassing, and structural failure, the concept of the monomeric copolymer precursor has been utilized.

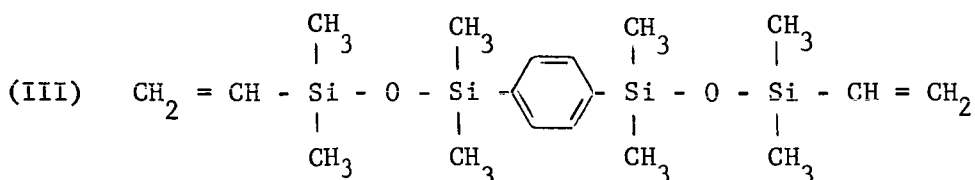
Three of these compounds have been investigated:



1,4-bis(vinyldimethylsilyl)-benzene



1,4-bis(allyldimethylsilyl)-benzene



1,4-bis(1,1-dimethyl-3-vinyl-3,3-dimethyl-disiloxanyl)-benzene

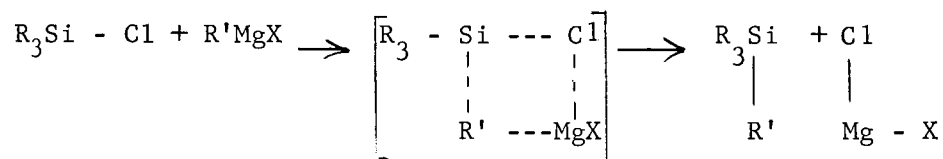


In earlier studies (ref. 1), a series of aliphatic epoxy-siloxane copolymers indicated a prohibitively low mechanical strength. Thus, compounds I, II, and III contain the phenyl bridge backbone to confer the requisite mechanical and thermal stability and also the silicon moieties, which appear to lend more favorable dielectric properties. Additionally, compound III contains the flexibilizing tetramethyl disiloxane group. Studies by the supporting contractor indicated that epoxidation of the terminal double bonds was accompanied by some phenyl-silicon bond cleavage. Thus, the structure of compound III was conceived partially to remove the aryl-silicon bonds from the immediate oxidation site.

One of the earlier synthesis objectives was to prepare a series of diphenols based on bis(hydroxyphenyl)-tetramethyldisiloxane and, thus, obtain the epoxy resin precursor through an addition reaction of the diphenol with epoxides. A rather exhaustive study of the reaction strongly indicated that, for a species containing the  $-O-Si-C_6H_4-OH$  linkage, the polarity of the Si-C bond is so enhanced that cleavage by nucleophilic attack at that site is inevitable under the hydrolysis conditions required to form the diphenol.

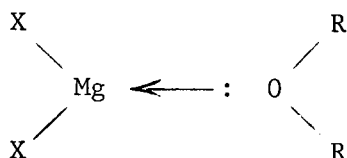
In view of this, the bis-alkenyl monomers were considered to be the more stable intermediates and also more practical because they have the potential of being epoxidated directly.

The synthesis mechanism involving compounds I and II employs a cleavage between an organomagnesium halide and a silane chloride. This may be viewed as a transition state coordination of the chloride of silicon with the magnesium (ref. 2) as follows:



The increased ionic character of the Si-Cl versus C-Cl bond partly is responsible for the occurrence of this reaction. The condensation would not be expected to occur solely on the basis of bond energy comparisons ( $Si - Cl = 91$ ,  $Si - C = 70$ ), but evidently the stability of the postulated cyclic transition allows the condensation to proceed with a lower activation energy contribution, thus overcoming the bond energy difference.

The magnesium dihalide, which formed as a condensation by-product in the reaction, was found to complex to some extent with the ether solvent



so that complications arose in the purification of the reaction product. An aqueous treatment to ionize the salt proved effective in destroying the complex and allowed uncontaminated recovery of the desired compound. A dilute sodium bicarbonate solution was used as the aqueous phase to neutralize any residual silane chloride functionality.

#### Experimental. -

Synthesis of 1,4-bis(chlorodimethylsilyl)-benzene (I) (ref. 3)--- A reaction vessel equipped with stirrer, equilibrating funnel, and reflux condenser was dried and equipped with a nitrogen inlet tube. Two mol-equivalents of dry magnesium metal turnings were introduced and activated by warming with a crystal of iodine. A solution of one mol-equivalent of p-dibromobenzene and four mol-equivalents of freshly distilled dimethyldichlorosilane in anhydrous diethyl ether was added dropwise to the stirred magnesium. The reaction started readily at 25°C, and its rate was controlled very efficiently by the addition rate of the ether solution. Approximately three hours were required to complete the addition; then the mixture was refluxed for an additional three hours. The condensation by-product, magnesium bromochloride, precipitated from the reaction mixture after approximately one hour of addition. The mixture then was chilled to precipitate MgBrCl and was filtered under nitrogen. The ether solvent was distilled, and the residue was vacuum-fractionated. The fraction boiling at 90-95°C/0.2 torr was collected. This boiling range agreed closely with several other literature values. (I) crystallized to a white solid at 25°C with a melting point of 87-90°C. (I) is extremely susceptible to hydrolysis; therefore, analytical data would be subject to large error. Based on p-dibromobenzene, a 41 percent yield of the fractionated material was recovered.

Synthesis of 1,4-bis(vinyldimethylsilyl)-benzene (II)---Two mol-equivalents of vinylmagnesium chloride\* were dissolved in tetrahydrofuran in a dry box and placed in a dried, stirred, nitrogen-swept reaction flask fitted with a reflux condenser and equilibrating funnel. One mol-equivalent of 1,4-bis(chlorodimethylsilyl)-benzene in THF was added dropwise to the flask while a gentle THF reflux was maintained. The addition was completed in one hour, and the mixture was refluxed an additional hour. The mixture was then chilled to precipitate the MgCl<sub>2</sub> condensation by-product. A quantity of MgCl<sub>2</sub> representing 90 percent of the theoretical yield was recovered. The salt was washed twice with ether and once with benzene, and the washings were combined with the original filtrate. As the solution was concentrated, more salt precipitated and was extracted by treatment with five percent aqueous sodium bicarbonate. The aqueous phase was washed twice with ether, and the ethereal layers were combined. Distillation of the solvent and subsequent fractionation of the residue

---

\* Produced by the Peninsular ChemResearch Corporation, Gainesville, Florida.

produced a 30 percent yield of the desired compound: boiling point = 108-110°C/0.8 torr.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>
<u>Analysis</u>	Theory	68.29	8.94	22.76
	Found	66.02	8.99	21.18

Synthesis of 1,4-bis(allyldimethylsilyl)-benzene (III)---The allyl magnesium chloride used in this reaction was prepared as follows:

One mol-equivalent of magnesium turnings was placed in a dried, nitrogen-swept flask fitted with a reflux condenser and equilibrating funnel; one mol-equivalent of freshly-distilled allyl chloride in anhydrous ether was added to the flask until approximately 10 ml were present. A crystal of iodine then was added, and the reaction started vigorously. The addition required approximately 1.5 hours per mol of halide employed. The reaction mixture then was refluxed three hours and filtered under nitrogen.

Two mol-equivalents of the allyl magnesium chloride in ether were placed in a dried nitrogen-swept reaction flask which was fitted with a reflux condenser and stirrer. The yield was calculated from the unreacted magnesium, and, from this, the required mol-equivalents of 1,4-bis(chlorodimethylsilyl)-benzene (I) were calculated.

One mol-equivalent of (I) in anhydrous ether was added dropwise to the contents of the flask under refluxing conditions. A time of addition corresponding to one hour per mol of (I) was used, followed by refluxing for three additional hours. Workup of the reaction mixture exactly as described for compound (II) produced a 30 percent yield of clear, colorless liquid boiling at 102-105°C/0.6 torr. The infrared spectrum indicated that the expected bonds were present.

		<u>% Si</u>
<u>Analysis</u>	Theory	20.44
	Found	20.4

Synthesis of 1,4-bis(1,1-dimethyl-3-vinyl-3,3-dimethyldisiloxanyl)-benzene (IV)---The synthesis of compound (IV) was attempted through reaction of 1,4-bis(hydroxydimethylsilyl)-benzene with chlorodimethylvinylsilane.

Synthesis of 1,4-bis(hydroxydimethylsilyl)benzene (ref. 4)---Ten grams of 1,4-bis(chlorodimethylsilyl)-benzene in 250 ml of ether were cooled to 0°C and added rapidly with vigorous shaking to a cooled solution of 250 ml of concentrated NH<sub>4</sub>OH, 250 ml of water, and 250 ml of ether. The mixture was allowed to stand 15 minutes; then the ether layer was recovered and concentrated until precipitation occurred. The solid was recovered and washed twice with n-hexane which had been chilled with dry ice-acetone. A 75 percent yield of the diol was recovered: Melting point = 135-136°C.

Synthesis of chlorodimethylvinylsilane---Freshly distilled ethoxydimethylvinylsilane was treated with a stream of anhydrous HCl for one hour at -5°C. The solution was distilled to give a 50 percent yield of the desired chloride: boiling point = 75°C/760 torr.

The synthesis of compound (IV) was carried out as follows: Two mol-equivalents of chlorodimethylvinylsilane in ether were placed in a stirred nitrogen-flushed flask which was cooled to 0°C. A solution containing one mol-equivalent of 1,4-bis(hydroxydimethylsilyl)-benzene and one mol-equivalent of anhydrous pyridine in ether was added dropwise to the reaction flask. After the addition was completed, the reaction mixture was refluxed for one hour and filtered to remove pyridine hydrochloride. A white, waxy solid was recovered, which melted at 40-50°C. Due to the polymeric nature of compound (IV), distillation could not be effected, nor could it be recrystallized.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>
<u>Analysis</u>	Theory	54.82	8.63	28.42
	Found	53.18	7.40	27.0

Synthesis of 1,4-bis(epoxyethyl dimethylsilyl)-benzene (V)---One mol-equivalent of compound (II) was dissolved in chloroform and placed in a stirred reaction flask. Two mol-equivalents of m-chloroperbenzoic acid in chloroform were added dropwise at 25°C at such a rate as to maintain the reaction temperature between 25-30°C. After the addition was completed, excess peracid was destroyed by the addition of 10 percent sodium sulfite until an aliquot which was tested with sodium iodide solution was colorless. The mixture was washed twice with 10 percent sodium bicarbonate and once with saturated sodium chloride solution. Extraction with ether yielded a pale yellow viscous liquid which was fractionated at 70-75°C/0.075 torr.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>
<u>Analysis</u>	Theory	60.43	7.91	20.14
	Found	60.92	7.97	17.0

Cure Studies. - Formulation and cure studies have been initiated on 1,4-bis(epoxyethyl dimethylsilyl)-benzene (II). Four curing agents are being evaluated to polymerize the material to a solid polymer:

1. bis(methylamino)-diphenylsilane
2. N,N'-dimethylethylenediamine
3. triethylenetetramine
4. methylene-bis(o-chloroaniline)

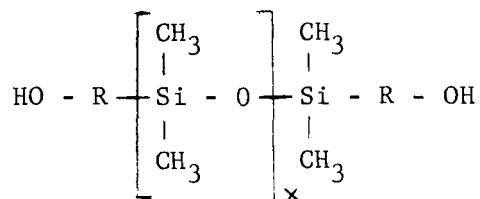
The cure studies were made under the conditions imposed in Table I.

Table I.- Cure Conditions for Polymerization of 1,4-bis(epoxyethyl-dimethyl-silyl)-benzene

Epoxy Monomer I Equivalents	Amine		Time (Hours)	Temperature (°C)	Degree of Cure
	Designation	Equivalents			
0.01	(1)	0.01	48	100	Gas evolution; no cure
0.01	(2)	0.01	48	100	No cure
0.01	(3)	0.0025	48	100	No cure
0.01	(4)	0.005	24	115	Stiff, solid resin

#### Urethane-Siloxane Copolymers Synthesis

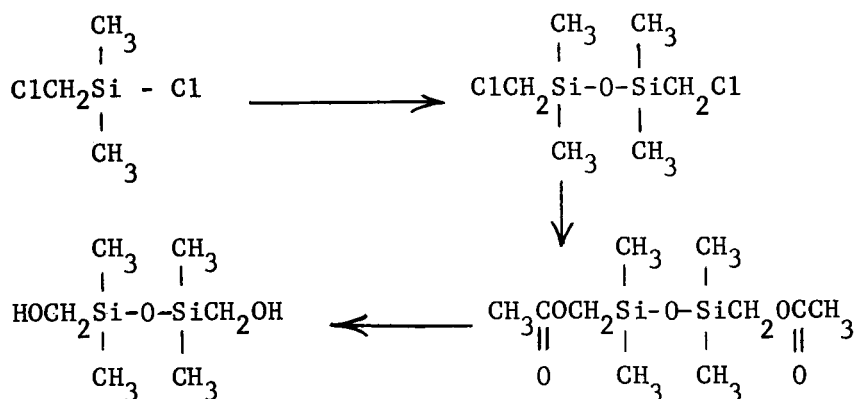
Theoretical Basis. - A series of urethane-siloxane copolymers has been synthesized toward fulfillment of the conformal coating program. The theory followed is that materials of improved low temperature flexibility and dielectric properties may be synthesized from polymerization of diisocyanates and siloxane diols. Previous investigations (ref. 1) have shown that characterizable polymeric materials form from this reaction and that they possess film and fiber-forming properties. A series of siloxane glycols based upon the following general structure



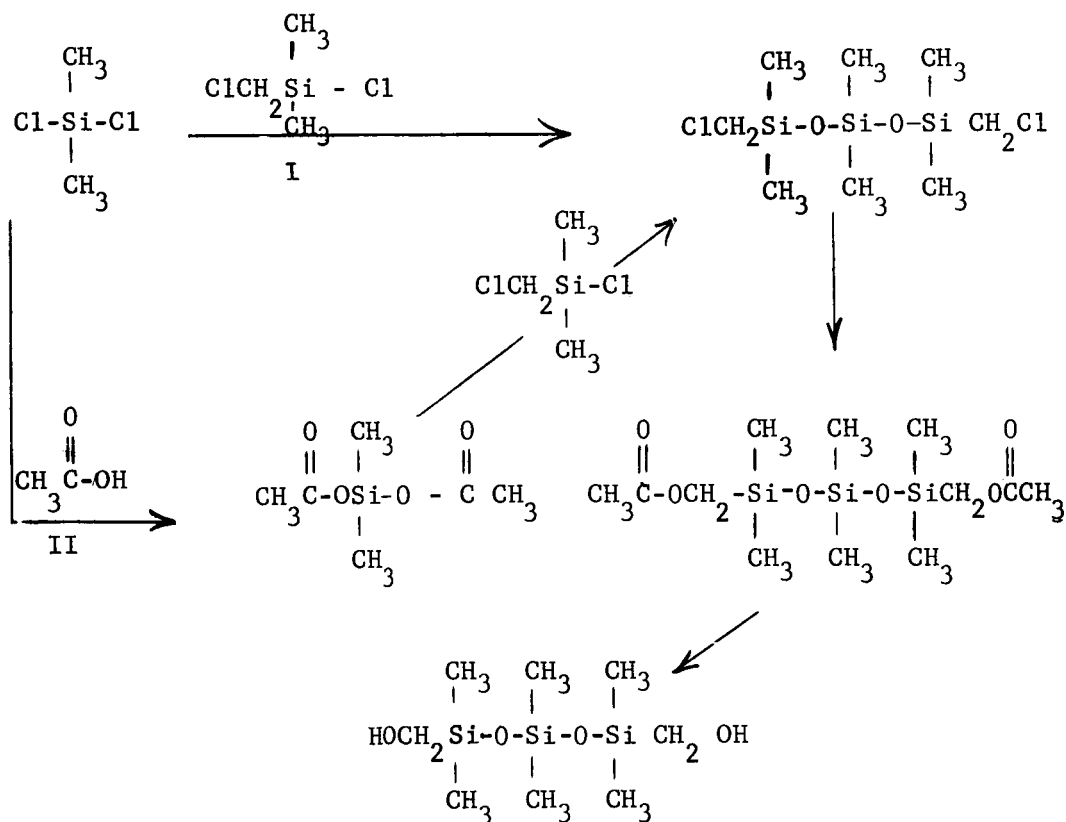
has been synthesized to incorporate the flexible Si-O-Si moiety into a urethane-type polymer.

Three diols were prepared during this study as shown below:

(1) bis(hydroxymethyl)-tetramethyldisiloxane



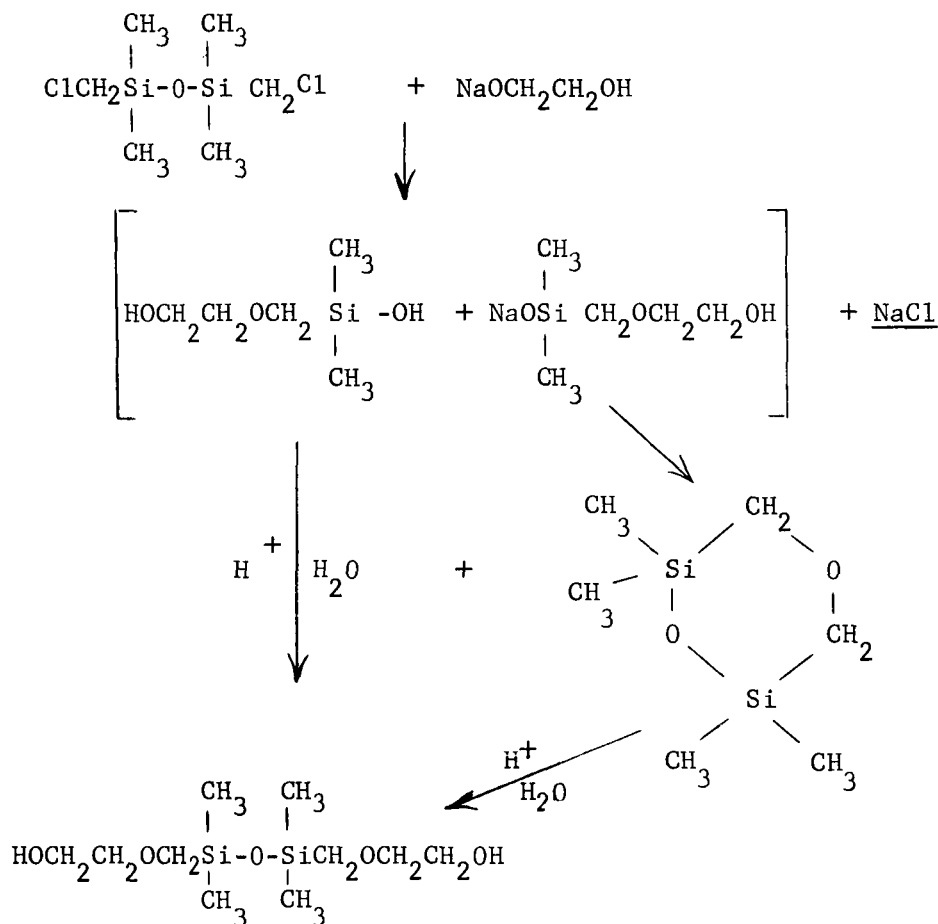
(2) bis(hydroxymethyl)-hexamethyltrisiloxane



Both diols (1) and (2) are formed from the respective bis(chloromethyl) siloxanes by way of the acetoxy-derivatives. Diol (2) was prepared by two different methods. Method 1 utilized the cohydrolysis technique, which is accompanied by several competitive reactions. A more efficient mechanism involves the diacetoxydimethylsilane intermediate which condenses with the chlorosilane to split out acetyl chloride. Pyridine was found to facilitate the condensation by complexing the acetyl chloride as an insoluble precipitate. Method 2, in which all steps are non-aqueous, produced diol (2) in a significantly higher yield than does Method 1. In an attempt to lengthen the siloxane chain in this type of diol to the tetrasiloxane, bis(chloro)-tetramethyldisiloxane was substituted for dichlorodimethylsilane in Scheme II of the diol (2) mechanism. The product indicated a chemical reaction with diisocyanate but appeared to be incompatible since two liquid phases were present. This diol was not characterized since the silicon content appeared too high to produce a homogeneous product with the diisocyanate. Parallel investigations by the supporting contractor have supported this reasoning.

(3) bis(hydroxyethoxymethyl)-tetramethyldisiloxane

Synthesis of this diol probably proceeds through the following mechanism (ref. 5)







## Experimental.

Synthesis of bis(hydroxymethyl)-tetramethyldisiloxane---Chloromethyl dimethylchlorosilane (boiling point = 115°C/760 torr) was hydrolyzed by a dropwise addition to excess 10 percent aqueous sodium bicarbonate solution at 25°C over a period of one hour for each mole of silane used. Extraction of the mixture with ether and subsequent removal of the solvent produced a 90 percent yield of bis(chloromethyl)-tetramethyldisiloxane (I): boiling point = 204°C/760 torr,  $n_D^{20} = 1.4389$ . One mol-equivalent of (I) was reacted with two mol-equivalents of potassium acetate, two mol-equivalents of acetic acid, and 1 percent by weight acetic anhydride for six hours at acetic acid reflux to produce bis-(acetoxymethyl)-tetramethyldisiloxane (II) in 60 percent yield: boiling point 70°C/0.5 torr,  $n_D^{20} = 1.4240$ . Compound (II) was stirred with excess anhydrous methanol for two hours while anhydrous hydrogen chloride gas was bubbled through the reaction mixture. The mixture then was allowed to stand for 24 hours at 25°C. Subsequent distillation of the methyl acetate by-product and residual methanol at reduced pressure left the desired bis(hydroxymethyl)-tetramethyldisiloxane in 65 percent yield. The diol was fractionated, and the fraction boiling at 70-75°C/2 torr was collected. Infrared analysis of the diol supported the desired structure.

Synthesis of bis(hydroxymethyl)-hexamethyl trisiloxane---Two synthetic methods were employed to produce the desired diol.

Method 1: Method 1 involved cohydrolysis of one mol-equivalent dimethyldichlorosilane with two mol-equivalents chloromethyldimethylchlorosilane by dropwise addition of an ether solution of these reactants to an excess 10 percent aqueous sodium bicarbonate solution at 25°C at a rate necessary to maintain gentle ether reflux. Recovery and distillation of the ether layer produced a 30 percent yield of bis(chloromethyl)-hexamethyltrisiloxane (I): boiling point 57-60°C/0.6 torr,  $n_D^{20} = 1.4278$ . One mol-equivalent of compound (I) was refluxed with one mol-equivalent of glacial acetic acid, 1 mol-equivalent of potassium acetate, and one percent by weight of acetic anhydride for 6 hours. Workup and distillation of the reaction-mixture yielded bis(acetoxymethyl)-hexamethyltrisiloxane (II): boiling point = 158-162°C/0.1 torr. Compound (II) was treated with excess anhydrous methanol and anhydrous hydrogen chloride for two hours. The mixture was allowed to stand 24 hours, followed by distillation of the methyl acetate at reduced pressure. Fresh methanol then was added, and the solution was treated with hydrogen chloride again. After 24 hours, the solution was distilled under vacuum to remove methyl acetate and excess methanol. The resulting residue was determined to be bis(hydroxymethyl)-hexamethyl)trisiloxane. The product boiled at 105-108°C/0.6 torr and represented a 25 percent yield. The infrared analysis showed the presence of the expected absorption bands.

Method 2: A solution of one mol-equivalent of dimethyldichlorosilane and two mol-equivalents of anhydrous pyridine in ether was placed in a dried nitrogen-swept flask. Two mol-equivalents of glacial acetic acid in ether were added dropwise at such a rate that gentle ether reflux was maintained. Removal of the pyridine hydrochloride and ether left a

liquid residue which distilled at 160-163°C/760 torr. A yield of 56 percent of diacetoxydimethylsilane (I) was obtained. Infrared analysis supported the desired structure. One mol-equivalent of (I) in ether was added dropwise to a stirred solution of two mol-equivalents of chloromethyldimethylchlorosilane and two mol-equivalents of pyridine in ether while the mixture was heated at ether reflux. A pyridine-acetyl chloride complex precipitated from the reaction and subsequently was removed by filtration. The residual bis(chloromethyl)-hexamethyl-trisiloxane (II) was distilled at 50-53°C/0.5 torr. Synthesis of the corresponding diol from this step proceeded exactly as outlined in Method 1. The yield of diol from Method 2 was approximately 35 percent.

Method 2 offers a significantly higher yield of the diol than Method 1. The latter method involves several competitive reactions in the cohydrolysis step.

		<u>% C</u>	<u>% H</u>	<u>%Si</u>
<u>Analysis</u>	Theory	35.82	8.95	31.34
	Found	35.02	8.56	27.28

Synthesis of bis(hydroxyethoxymethyl)-tetramethyldisiloxane---  
Bis(chloromethyl)-tetramethyldisiloxane (I) was prepared by the method described on page twelve. One mol-equivalent of compound I was added dropwise with stirring to two mol-equivalents of ethylene glycol monosodium salt. The reaction temperature was held at 80°C, and a constant nitrogen flow was maintained through the reaction flask. Following the addition, the temperature was increased to 100°C for five hours. The mixture was extracted with ether several times and the extracts combined. The ethereal solution was concentrated and the residue hydrolyzed with an equal volume of water which had been acidified with hydrogen chloride to give a faint red reaction to Hydrion paper. The hydrolysis mixture was stirred at 60°C for three hours, then extracted with ether, dried, and concentrated under vacuum. Distillation produced a 30 percent yield of pure diol: boiling point = 130-133°C/2 torr,  $n_D^{20} = 1.4444$ .

Polymerization of diol (1) with toluene-2,4-diisocyanate---One mol-equivalent of toluene-2,4-diisocyanate and one mol-equivalent of diol (1) were placed in a dried, nitrogen-swept, stirred reaction flask. One drop of triethylamine was added, and the polymerization proceeded vigorously at 25°C to a solid glass. The polymer then was heated into a melt at 100°C for one-half hour, while vacuum was applied to remove entrapped air. This material softened at about 60°C.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>	<u>% O</u>
<u>Analysis</u>	Theory	48.91	6.52	15.22	7.61	21.74
	Found	51.06	6.44	14.20	7.96	20.50

Polymerization of diol (1) with methylene-bis(4-phenyl)-isocyanate---  
Equimolar quantities of diol (1) and methylene-bis(4-phenyl)-isocyanate were placed in a dried, nitrogen-swept, stirred reaction flask at 25°C with one drop of triethylamine. The oil-bath temperature was raised to

60°C for 15 minutes. At this point, the mixture polymerized to a viscosity which prevented further stirring. The temperature was increased to 100°C and a vacuum (3 torr) was applied for one-half hour. The polymer melt was cooled to 25°C where it became a brittle glass.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>
<u>Analysis</u>	Theory	56.76	6.31	12.61	6.31
	Found	57.12	6.51	12.81	6.82

Polymerization of diol (3) with hexamethylene diisocyanate---  
 Equimolar quantities of diol (3) and hexamethylene diisocyanate were added to a dried, nitrogen-swept, stirred reaction vessel. One drop of triethylamine was added, and the oil bath temperature was increased to 60°C. No apparent change in viscosity was observed, and the temperature again was increased to 100°C. After 15 minutes at this temperature, the melt viscosity increased significantly. The polymer was heated for an additional two hours, with a vacuum maintained during the last half hour. The cooled polymer melt was an extremely sticky viscous liquid:

		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>	<u>% O</u>
<u>Analysis</u>	Theory	48.00	8.44	12.44	6.22	24.89
	Found	46.93	8.44	13.70	6.91	23.20

Polymerization of diol (3) with methylene-bis(4-phenyl)-isocyanate---  
 Equimolar quantities of diol (3) and methylene-bis(4-phenyl)-isocyanate were added to a dried, stirred, nitrogen-swept reaction flask. One drop of triethylamine was added, and the oil-bath temperature was raised to 60°C. Polymerization was initiated after five minutes at this temperature. The melt temperature was increased slowly to 100°C and held for one hour, followed by application of vacuum for one-half hour. The cooled polymer melt was an amorphous glass at 25°C from which strong, flexible fibers could be pulled. The polymer was soluble in hot dimethylformamide, and transparent flexible films could be cast on aluminum from this solution.

		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>	<u>% O</u>
<u>Analysis</u>	Theory	56.37	6.77	10.53	5.26	21.05
	Found	57.52	6.77	9.90	7.04	21.00

Polymerization of diol (2) with hexamethylene diisocyanate---  
 Equimolar quantities of diol (2) and hexamethylene diisocyanate were added to a dried, stirred, nitrogen-swept reaction flask. One drop of triethylamine was added, and the oil-bath temperature was raised slowly to 60°C. The reaction was initiated after 15 minutes at this temperature, and the rapid increase in melt viscosity indicated a relatively high reaction rate. The polymerization was held at 60°C for 1-1/2 hours; then vacuum was applied for one-half hour. The cooled polymer was an extremely viscous liquid which remained tacky after being cast as a film from dimethylformamide.

<u>Analysis</u>		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>
		Theory	43.64	8.18	19.09
	Found	43.73	8.13	19.84	7.24

Polymerization of diol (2) with methylene-bis(4-phenyl)isocyanate--- Equimolar quantities of diol (2) and methylene-bis(4-phenylisocyanate) were placed in a dried, stirred, nitrogen-swept reaction vessel. One drop of triethylamine was added, and the oil-bath temperature was raised to 60°C. The reaction was initiated after five minutes, and the temperature was increased slowly to 100°C where it was held for two hours. Vacuum was applied during the last one-half hour. The cooled polymer melt was a glass at 25°C which could form tough, flexible films and fibers. The polymer was soluble in hot benzene and dimethylformamide.

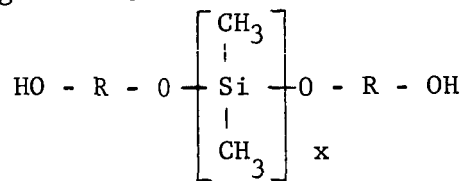
<u>Analysis</u>		<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>
		Theory	53.28	6.56	16.22
	Found	53.56	6.86	16.17	6.67

#### SUPPORTING CONTRACT RESEARCH

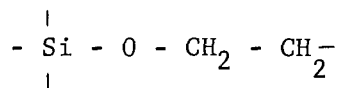
Parallel to the internal research effort discussed in the preceding section, the Non-Metallic Materials Branch has maintained a research contract with Hughes Aircraft Company, Culver City, California, to study related aspects of this problem area. This contract, NAS8-5499, entitled "Development of Improved Potting and Encapsulating Compounds for Space Applications," was initiated on June 29, 1963. The contracted program is oriented toward achieving essentially the same material properties with one added stipulation. The contract stipulates that the embedment and coating materials must be capable of withstanding the exigencies of biological sterilization by both thermal and chemical methods. The major contributors to this contracted program at Hughes Aircraft Company have been Mr. R. B. Feuchtbaum and Dr. N. Bilow. The following sections of this report summarize the synthetic aspects of the work accomplished to date by the Hughes Aircraft Company under contract. For more detailed information on this program the technical reports issued by the contractor should be consulted (ref. 7).

#### Urethane-Siloxane Copolymer Synthesis

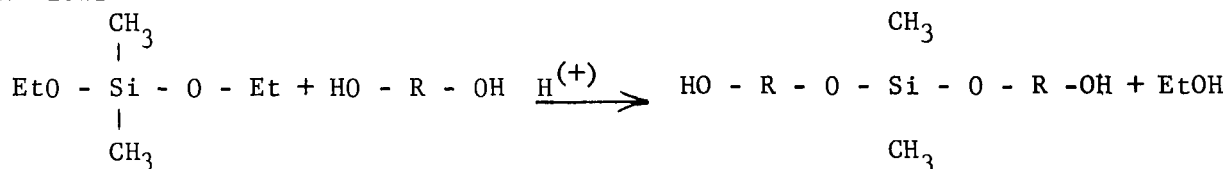
Theoretical Basis.- The synthesis of stable hydroxyl-terminated polysiloxanes of the general structure



has been investigated. The nature of the R group is considered critical to the stability of this type of compound. All materials of this type have been designed molecularly to avoid the sequence of a hydrogen atom in a beta position relative to the silyl-oxygen:



This linkage is particularly susceptible to acid- or base-catalyzed cleavage reactions which lead to degradation of the chain by splitting out olefinic fragments. Thus, the concept of placing a tertiary carbon in the beta position was introduced, effectively blocking the olefin pathway of degradation. These compounds, 1,1,1-tris(hydroxymethyl)propane, 2,2-bis(hydroxymethyl)propane, and bis(hydroxymethyl)-diphenyl-ether, were studied in a condensation with diethoxydimethylsilane derivatives. Polysiloxanes consisting of an equilibrium mixture containing the desired siloxane grouping were prepared by partial hydrolysis of diethoxydimethylsilane with stoichiometric quantities of water. Siloxanes whose degree of polymerization varied from one to five were produced by this method. An acid catalyzed exchange reaction was then carried out as follows



to yield the desired hydroxyl-terminated polysiloxanes. These monomers subsequently have been reacted with excess diisocyanate in an effort to produce liquid, isocyanate-terminated prepolymers. Considerable difficulty has been encountered at this step of the synthesis. The 1,1,1-tris(hydroxymethyl)-propane-based prepolymer tended to be glasses (melting point about 120°C) and were too highly crosslinked by the curing reactions to retain flexibility. This fact prompted the use of the 2,2-bis(hydroxymethyl)-propane-based prepolymers in an effort to achieve linearity. A considerable decrease in the prepolymers melting point was observed; however, as the siloxane bridge length was increased the heterogeneity of the siloxy polyol increased. The third hydroxyl compound, bis(hydroxymethyl)-diphenyl ether, then was studied to determine the degree of aromaticity necessary to promote compatibility.

The synthesis of discrete monomers of the polysiloxane type presupposes the concept of a stoichiometric reaction. Unfortunately, this does not usually occur where siloxanes are involved. These compounds have an inherent tendency to form a mixture of monomer, dimer, trimer, and higher polymers in addition to their tendency to cyclize to six- and eight-member rings. Thus, in any given acid-catalyzed transalkoxylation, the

driving force in the reaction is satisfied only by equilibration of the siloxanes into a particular molecular weight distribution of linear molecules accompanied by a small amount of cyclic impurities. It has been demonstrated during this contract investigation that, even though tedious separation techniques such as fractionation and phase separation have been employed, the siloxanes tend to re-equilibrate to a fairly predictable molecular weight distribution following fraction separation. However, it should be understood that the poly(alkylene) glycols from which normal polyurethanes are synthesized represent a molecular weight distribution, and they are not discrete, well-defined monomers.

Experimental.- The following experimental description using 1,1,1-tris(hydroxymethyl)-propane is typical of the general siloxy-urethane preparation. The 2,2-bis(hydroxymethyl)-propane and bis(hydroxymethyl)-diphenylether based-polymers were prepared by the same general procedure.

Synthesis of hydroxy-terminated polysiloxanes---A series of five ethoxy-terminated polysiloxanes were prepared by the following procedure under the conditions given in Table II:

Table II.- Reaction Conditions for Synthesis of Ethoxy-Terminated Polysiloxanes

$(\text{CH}_3)_2\text{Si}(\text{OEt})_2$ (mols)	$\text{H}_2\text{O}$ (mols)	Reaction Time (min.)	Reaction Temp. (°C)	Ethoxy-terminated Polysiloxane Degree of Polymerization
0.70	0.33	10	25	2
0.60	0.40	10	25	3
0.827	0.60	10	25	4
0.50	0.40	10	25	5

Freshly distilled diethoxydimethylsilane, water, and catalytic amounts of acetic acid were stirred under the above conditions to produce equilibrium polysiloxanes containing the desired degree of polymerization. Fractional distillation could not be effected without driving the mixtures toward cyclization. These materials then were reacted with 1,1,1-tris(hydroxymethyl)-propane by the procedure discussed below and under the conditions illustrated in Table III:

Table III.- Reaction Conditions for Synthesis of 1,1,1-tris(hydroxymethyl)-propane-based Polysiloxane Glycols

<u>Ethoxy-Terminated Polysiloxanes</u>			Reaction	EtOH	Analyzed
<u>Degree of Polymeri-</u>	<u>Mols</u>	<u>Glycol</u>	<u>Temp.</u>	<u>Recovered,</u>	<u>Hydroxyl</u>
<u>zation</u>		<u>(Mols)</u>	<u>(°C)</u>	<u>% of Theory</u>	<u>Equivalent</u>
1	0.90	0.90	150	89	121
2	0.35	0.50	150	99	102
3	0.23	0.40	150	94	98
4	0.175	0.45	150	96	121
5	0.14	0.20	150	98	---

Each of the ethoxy-terminated polysiloxanes was added dropwise to a mixture of molten 1,1,1-tris(hydroxymethyl)-propane and catalytic amounts of glacial acetic acid under the conditions stated in Table II. The ethanol generated by the condensation was removed continuously by distillation as the reaction mixture was heated to 150°C. The remainder of the volatiles was removed from the siloxypolyols by evaporation in a rotary film-type evaporator.

Synthesis of bis(hydroxymethyl)diphenyl-ether-terminated polysiloxanes--- Siloxypolyols composed of diphenyldiethoxysilane, phenyltriethoxysilane, bis(ethoxy)-tetraphenyldisiloxane, and bis(hydroxymethyl)-diphenyl ether were prepared from the procedure outlined in the preceding section. The pertinent reaction conditions are summarized in Table IV.

Synthesis of urethane-siloxane pre-polymers--- Each of the siloxypolyols described in Table IV was added dropwise to a stirred, nitrogen-swept flask containing a large excess of tolylene-2,4-diisocyanate and a drop of pyridine. The addition was initiated at 25°C and continued over a period of one hour; during this time, the temperature was increased gradually to approximately 100°C. The excess tolylene diisocyanate was removed by rotary evaporation at 150°C/2 torr.

Table IV. - Reaction Conditions for Synthesis of bis(hydroxymethyl)-diphenylether-based Polysiloxane Glycols

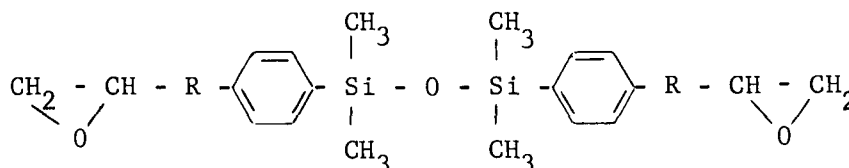
	Siloxypolyol		
	1	2	3
Diphenyldiethoxysilane (mols)	0.10	0.20	--
Phenyltriethoxysilane (mols)	--	0.033	0.018
Diethoxytetraphenyl-disiloxane (mols)	--	--	0.10
Bis(hydroxymethyl)-diphenylether (mols)	0.20	0.52	0.26
Reaction Temperature (°C)	160	120	110
EtOH Recovered (%)	--	100	100
Appearance	Viscous liquid	Viscous liquid	Viscous liquid



Polymer Cure and Evaluation.- The siloxypolyols prepared in this study were polymerized initially with a standard commercial isocyanate prepolymer.\* In this way, one standard coreactant was used to assess the relative reactivity of the experimental siloxypolyols. Following this, the best siloxypolyols were formulated with monomeric diisocyanates in an effort to produce liquid urethane-siloxane prepolymers containing an excess of free isocyanate groups. However, the prepolymer materials which were prepared proved to be glasses at room temperature. Formulation of these would require melting the prepolymer at some elevated temperature, which would lower the pot life of the blend to an impractical degree. Thus, the formulations employed represented an attempt to polymerize the siloxypolyol and the isocyanate directly to a cured solid. The materials which have shown the greatest promise to date are those derived from bis(hydroxymethyl)-diphenylether-terminated siloxypolyols. The pertinent data for cure and evaluation of the best of these materials are compiled in Table V.

### Epoxy-Siloxane Copolymer Synthesis

Theoretical Basis.- The supporting contract research has also been directed toward the development of an epoxy polymer precursor, 1,3-bis-(epoxypropylphenyl)-tetramethyldisiloxane, which contains the disiloxane linkage as illustrated below:



where R = -CH<sub>2</sub>-, -CH<sub>2</sub>-O-, etc.

The siloxane moiety is inherently thermally stable and extremely flexible; in addition, it exhibits favorable dielectric properties. Thus, an improved epoxy polymer would be potentially obtainable by this basic alteration of the polymer molecular configuration. As an analogy to the internal program, this material concept also is oriented toward a monomeric, difunctional polymer precursor which can be isolated, characterized, and polymerized stoichiometrically rather than dealing with partially polymerized prepolymers. This concept may be used when dealing with rigid rather than elastomeric materials. An advantage in the formulation and curing is achieved through the reduced viscosity of the precursor over that of the prepolymer. This allows higher filler/resin ratios and maintains a workable viscosity.

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\* Adiprene L-315, trade name of E. I. Dupont de Nemours and Company

Table V.- Reaction Conditions and Electrical Properties for Urethane-Siloxane Copolymers

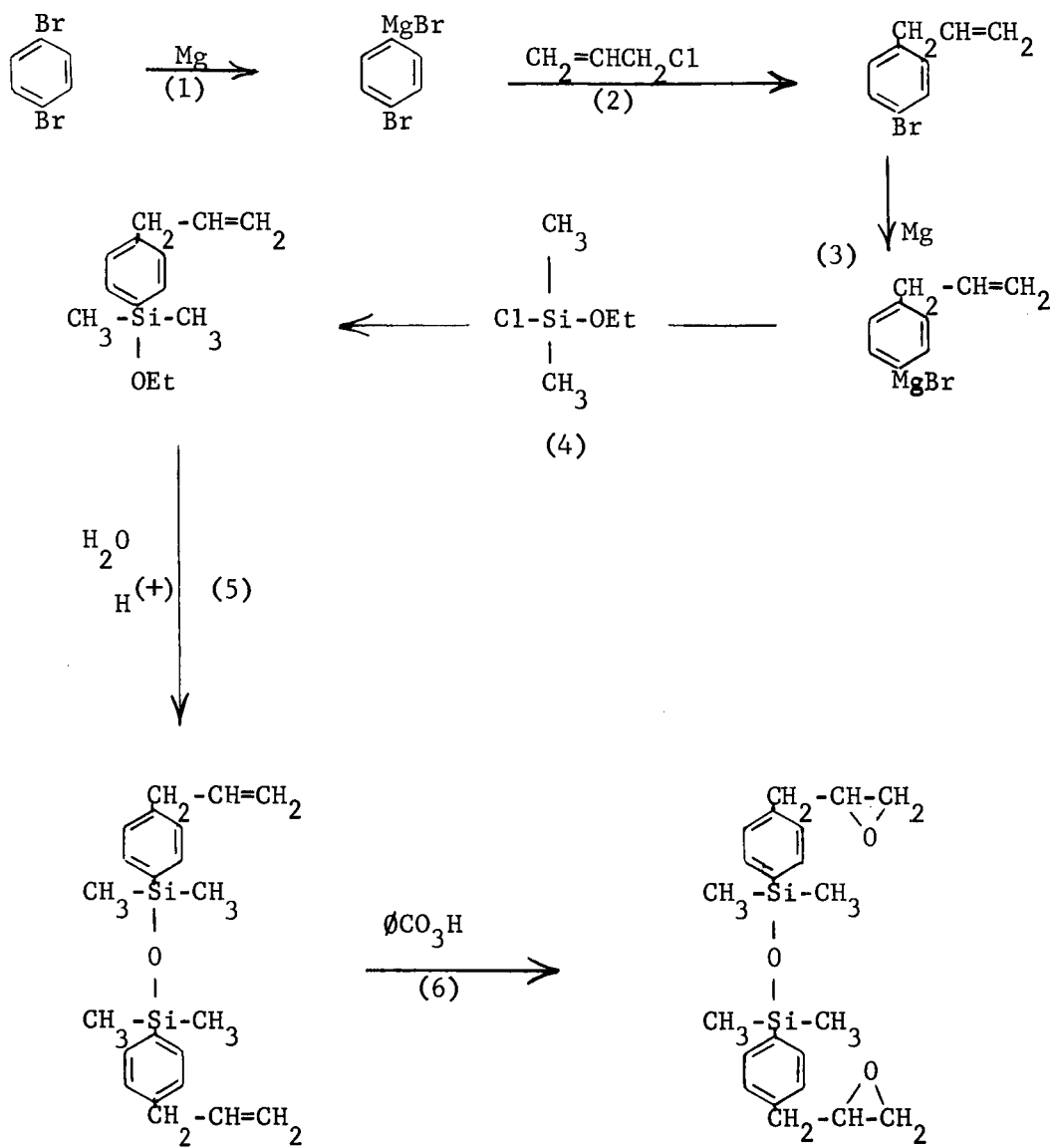
Formulation	Siloxypolyol*			Isocyanate Equivalents		Cure Time (hrs)	Temp. (°C)	Dielectric Constant	Dissipation Factor	Appearance
	A	B	C	Adiprene L-315**	Naccionate 200***					
1	-	0.033	0.015	0.05	-	16	74(N <sub>2</sub> ) 90(vac)	4.67	0.69	Very flexible, tough, clear
2	-	0.05	-	0.01	0.04	16	74(N <sub>2</sub> ) 90(vac)	3.38	0.012	Slightly flexible, tough, clear
3	0.04	-	-	0.016	0.035	16	68 100(vac)	3.86	0.011	Slightly flexible

\* Refer to Materials described in Table IV, page 19.

\*\* Urethane prepolymer, trademark of E. I. duPont de Nemours and Company.

\*\*\* 3,3'-dimethylbiphenyldiisocyanate.

The synthetic scheme followed in preparation of this material involved the following steps:

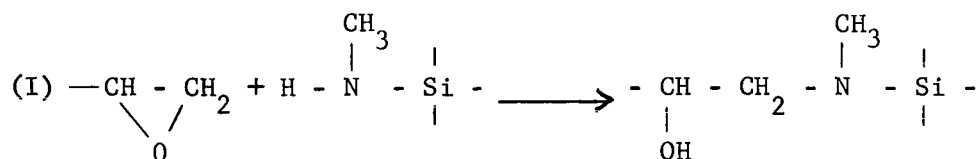


Step (2) of the reaction sequence utilized the efficient condensation between an activated halide and a Grignard reagent. This type of condensation was repeated in step (4), which demonstrates the preferential reactivity of a Grignard reagent for the silicon-halide bond over the silicon-alkoxy bond. Step (5) proved to be the most critical of the sequence. Several different approaches to insertion of the siloxane group had been investigated, both in house and on contract. This work leads to the conclusion that the formation of the sensitive disiloxane linkage must occur as near the end of the reaction sequence as possible. The oxidation of the terminal olefinic groups with a peracid proceeds fairly smoothly; however, with the particular compound illustrated, some Si-C bond cleavage occurred so the final bis-epoxide has not been isolated satisfactorily in pure form. A modification of the structure will be made to incorporate either one or two phenyl groups on the silicon atom, thus distributing the charge difference on the silicon-aryl bond among three benzene groups. It is believed that this modification will sufficiently stabilize the bond toward oxidative cleavage so that peroxidation of the terminal olefin groups will leave the molecule intact.

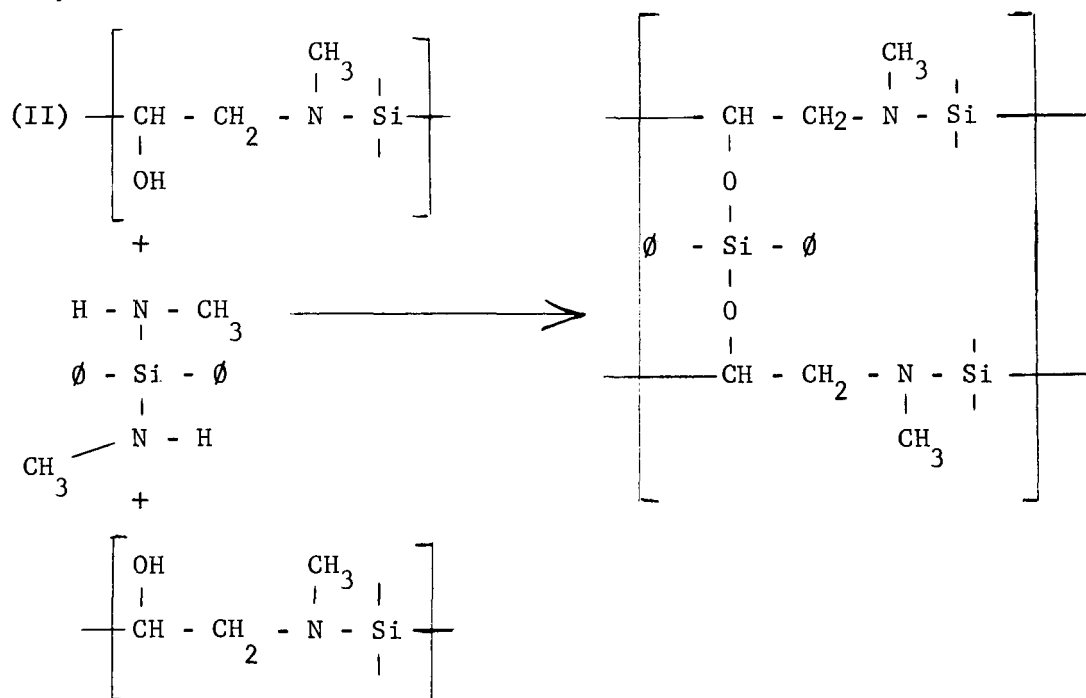
The attempted synthesis of an analogous compound, 1,3-bis(epoxypropoxyphenyl)-tetramethyldisiloxane, has not been achieved through the same general reaction sequence. One of the intermediates, p-bromophenylallyl ether, underwent preferential allylic rearrangement to 2-allyl-4-bromo-phenol, which inhibited the formation of a Grignard reagent from the ether. A subsequent attempt is being made presently to prepare the Grignard from 4-bromo-2,6-dimethylallyl ether. In this compound, the ring positions which previously promoted allylic rearrangement are blocked. The total reaction sequence has not been completed for this compound.

Alternate attempts to incorporate silicon into epoxy polymers have led to the use of bis(methylamino)-diphenylsilane to polymerize a standard epoxy polymer precursor, 2,2-bis(1,2-epoxypropoxyphenyl)-propane, to a solid resin exhibiting superior characteristics to those of conventional epoxies.

The diamine appears to polymerize the epoxide linearly to a high molecular weight by addition mechanism



and to effect some degree of crosslinking of the polymer chains by a secondary condensation mechanism:



Subsequent cure studies with analogous secondary organic diamines have produced epoxy polymers which exhibit the same favorable property trend. It is suggested that the secondary diamines having only one reactive site per amine group tend to extend the polymer chain linearly with a minimum of crosslinking. This would favor a higher molecular weight polymer capable of exhibiting improved properties.

#### Experimental.

Synthesis of 1,3-bis(m-allylphenyl)-tetramethyldisiloxane---One mol-equivalent of freshly distilled m-bromoallylbenzene in anhydrous tetrahydrofuran was added over a one-hour period to a slurry of one mol-equivalent of magnesium in tetrahydrofuran with constant stirring. After a total reflux period of two hours, the decanted THF solution was added dropwise to a solution of freshly distilled dimethylchloroethoxysilane in THF. The solution was refluxed for a total of 10 hours; then the THF was removed with a vacuum evaporator. The residue was hydrolyzed by treatment with equal volumes of 6N HCl, and the hydrolysis product was extracted with ether. Fractional distillation of the crude product gave a 37 percent yield of 1,3-bis(m-allylphenyl)-tetramethyldisiloxane (I).

		<u>% C</u>	<u>% H</u>	<u>% Si</u>
<u>Analysis</u>	Theory	72.20	8.26	15.35
	Found	71.14	8.14	15.22

Boiling point = 150°C/2 torr,  $n_D^{26} = 1.5196$ .

Attempted Synthesis of 1,3-bis(*m*-epoxypropylphenyl)-tetramethyl-disiloxane (II)---One mol-equivalent of (I) in chloroform was added slowly to a stirred solution of perbenzoic acid, *t*-butyl alcohol, and chloroform while the temperature of the reaction mixture was maintained at  $0 \pm 4^\circ\text{C}$ . Stirring was continued at  $0 \pm 4^\circ\text{C}$  until 95 percent of the perbenzoic acid was consumed. The benzoic acid was removed by extraction with 10 percent aqueous sodium hydroxide, and the organic phase was vacuum distilled. However, the two high boiling fractions recovered from the distillation did not have a silicon content which corresponded to that of the desired compound.

Epoxy-Silane Polymer Cure and Evaluation, - Shell X-24 difunctional epoxy polymer precursor, 2,2-bis(*p*-epoxypropoxyphenyl)-propane, was polymerized under the conditions outlined in Table VI to a cured material having several attractive features.

## RESULTS AND CONCLUSIONS

The internal study on urethane-siloxane copolymers has produced fiber and film-forming materials which have considerable potential for meeting the conformal coating requirements. Flexible, strongly-adhering transparent films or coatings of the copolymer formed from bis(hydroxymethyl)-hexamethyltrisiloxane and methylene-bis(4-phenylisocyanate) could be cast from benzene or dimethylformamide. The appendix contains infrared spectra of the diols employed in these polymerizations. The hydroxyl band is evident at  $3300\text{ cm}^{-1}$  (ref. 8). The impurity band at  $1720\text{ cm}^{-1}$  appears to be a carbonyl absorption from the acetate intermediate. The urethane-siloxane polymer spectra contained the characteristic carbamate bands at  $1700\text{-}1720\text{ cm}^{-1}$  and showed the secondary amide band at  $3270\text{ cm}^{-1}$ . The elemental analyses generally confirmed the assumed polymer structures. The increase in siloxane content from the disiloxane to the trisiloxane was manifested in the increased flexibility of the polymer formed from the latter. Films of the disiloxane-based polymer became brittle at  $20^\circ\text{C}$ , while the trisiloxane-based polymer had some flexibility at  $10^\circ\text{C}$ . The ultimate low-temperature requirement of  $-50^\circ\text{C}$  has not yet been attained; however, the inclusion of more highly polymerized siloxane units may be expected on the basis of these results to produce polymers which approach this behavior and also have correspondingly better dielectric properties. Attempts to prepare relatively low molecular weight liquid prepolymers using a six-fold excess of diisocyanate have resulted in glassy, low melting solids which could be liquified only through monomer or solvent dilution. This technique, although used commercially, results in more highly reactive materials with undesirably shorter pot lives. The greater outgassing potential of materials formed from such diluted prepolymers also would be unattractive.

Table VI.- Cure Conditions and Electrical Properties for Modified Epoxy Polymers

Formulation	Composition		Conditions of Cure		Dielectric Constant (1 Kc, 25°C)	Dissipation Factor (1 Kc)	Insulation Resistance (Megohms)	Volume Resistivity (ohm-cm)
	Amine Type	Equivalents	Time (hrs)	Temp (°C)				
1	A*	0.59	12 16	28 121	4.31	0.0157	1.0x10 <sup>7</sup>	5.0x10 <sup>14</sup>
2	B*	0.59	12 16	28 85	4.00	0.0066	1.0x10 <sup>7</sup>	4.5x10 <sup>14</sup>
3	C*	0.10	24 24	74 (N <sub>2</sub> ) 125 (vac)	3.36	0.0130	2.8x10 <sup>3</sup>	1.4x10 <sup>11</sup>
4	C* D*	0.05 0.10	24 24	74 (N <sub>2</sub> ) 125 (vac)	3.70	0.0155	3.6x10 <sup>4</sup>	2.0x10 <sup>11</sup>
5	E*	0.20	16 6 4	74 (N <sub>2</sub> ) 110 (vac) 70 (N <sub>2</sub> )	4.39	0.0090	--	7.3x10 <sup>13</sup>
6	E* F*	0.034 0.066	17 48	80 (N <sub>2</sub> ) 90 (N <sub>2</sub> )	3.71	0.0047	1.0x10 <sup>7</sup>	7.4x10 <sup>13</sup>

A\* m-phenylenediamine adduct of 2,2-bis(epoxypropoxyphenyl)-propane

B\* m-aminothiophenol adduct of 2,2-bis(epoxypropoxyphenyl)-propane

C\* Bis(methylamino)-diphenylsilane

D\* m-phenylenediamine

E\* 4,4'-diaminodiphenylmethane

F\* N,N'-diphenylethylenediamine

X-24: Trade name, Shell Chemical Company epoxy polymer intermediate

Efforts are being intensified toward development of a formulating technique which will yield a prepolymer either as a liquid or as a reasonably low melting glass. The contractual program has shown considerable promise for the bis(hydroxymethyl)-diphenylether-based urethane-siloxane copolymers. Flexible elastomers of this type were formed in the case of the disiloxane glycol from a processible liquid prepolymer. Materials of this type exhibit a dielectric constant as low as 3.38, which compared favorably with a value of approximately 4.0 for Adiprene L-100\* based-polymers.

One striking confirmation of the effect of the siloxane moiety in the electrical performance of urethane-siloxane copolymers was illustrated by the variation of dissipation factor with siloxane content. The dissipation factor was observed to drop approximately 10 percent for each increasing degree of polymerization of the siloxane moiety. This supports the original concept that optimization of properties might be achieved in copolymers whose molecular structure had been oriented carefully toward these properties.

The synthesis effort has reached the point where it appears feasible to evaluate the best urethane-siloxane copolymers as conformal coatings on printed circuit boards. Emphasis will now be placed on coating formulations and cure cycles which will allow practical application.

The in-house program concerned with epoxy-silane polymers has demonstrated a feasible synthetic route to several new polymer intermediates. 1,4-bis(vinyldimethylsilyl)-benzene has been synthesized and characterized. The infrared spectrum of this compound indicates a C-H overtone of the terminal vinyl group at  $1810\text{ cm}^{-1}$  (ref. 9). A band consistent with the p-silyl-phenyl linkage is observed at  $1135\text{ cm}^{-1}$ . A sharp absorption is observed at  $1260\text{ cm}^{-1}$ , which is generally assigned to Si-CH<sub>3</sub>. Three other reference values of the -Si-CH=CH<sub>2</sub> linkage are  $1590\text{-}1610\text{ cm}^{-1}$ ,  $1000\text{-}1010\text{ cm}^{-1}$ , and  $943\text{-}980\text{ cm}^{-1}$ . The spectrum shows bands at  $1590\text{ cm}^{-1}$ ,  $1010\text{ cm}^{-1}$ , and  $955\text{ cm}^{-1}$ .

This compound has been epoxidized to yield a monomeric epoxy-silane polymer precursor. Elemental analysis of the epoxidation product was low in silicon, which indicates that some oxidative cleavage of the silicon-phenyl bond had occurred. Additionally, some opening of the epoxide ring to yield a secondary hydroxyl had occurred, as evidenced by condensation with bis(methylamino)-diphenylsilane with the concomitant evolution of methylamine. However, the confirmation of a preponderance of reactive epoxy groups in the molecule was established by its polymerization with an organic diamine to form a solid resin since the structural nature of the latter amine precluded its reaction with hydroxyl groups.

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\* L-100, trade name, urethane prepolymer, E. I. DuPont de Nemours and Company



The synthesis of two analogous monomers, 1,4-bis(allyldimethylsilyl)benzene and 1,4-bis(3-vinyl-1,1,3,3-tetramethyldisiloxanyl)-benzene, has been investigated to the point that the confirmation of these structures by elemental and infrared analysis is fairly well established.

The allyl compound (II) has an IR spectrum similar to its vinyl analog (I) with shifts of the vinyl absorption which are possibly due to complication by the saturated methylene group. The third monomer (III) contains, in addition, the disiloxane linkage and has a spectrum which again bears similarity to (I). The very strong absorption at  $1080\text{ cm}^{-1}$  in the spectrum of (III) supports the presence of the siloxane moiety.

A larger scale quantity of these three monomers is being prepared presently for epoxidation and polymerization reactions. Since 1,4-bis-(epoxyethyl dimethylsilyl)-benzene is a pourable liquid at  $25^{\circ}\text{C}$ , it should be readily processible as an encapsulating compound.

The epoxy-siloxane copolymer studies within the contractual program have led to the synthesis of a new monomer, 1,3-bis(m-allylphenyl)-tetramethyldisiloxane, which is a viscous liquid. This compound is being epoxidized to yield the corresponding 1,3-bis(m-epoxypropylphenyl)-tetramethyldisiloxane. This procedure by analogy with the internal program utilized the concept of a difunctional, monomeric polymer precursor whose lower viscosity makes it much more amenable to processing and filling.

Monomeric silazanes as well as polymeric amine adducts have been investigated as curing agents for the conventional epoxy resins. X-24\* epichlorohydrin-bisphenol-A adduct was polymerized with these materials to a solid compound exhibiting attractive electrical properties. The silazane-cured polymer gave a dielectric constant of 3.36 at 1 kilocycle. The polymer prepared with an N-methylaniline-formaldehyde adduct gave a somewhat higher value of 3.86 at  $25^{\circ}\text{C}$  but only increased to 3.90 at  $100^{\circ}\text{C}$ . This fact may indicate an application of the polymeric amine adducts in cases where dielectric properties must not vary significantly with temperature. An interesting observation concerning the epoxy curing agents was that every amine which presented a secondary group as the reactive site produced polymers having more attractive dielectric properties than their primary amine-cured counterparts.

Pending successful completion of the synthetic phase of the overall program, the most promising candidate materials will be directed toward the formulation of processible encapsulants and coatings and subsequently evaluated on electronic hardware under simulated working conditions. It is indicated from the results of the synthesis program to date that a suitable encapsulating system and conformal coating system will be evolved.

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\* Trade name, epoxy polymer intermediate, Shell Chemical Company.

Several of the property and processing characteristics required of these materials have been met, and it is hoped that improvements will be made in reaching the remaining property criteria.

APPENDIX A  
INFRARED SPECTRA

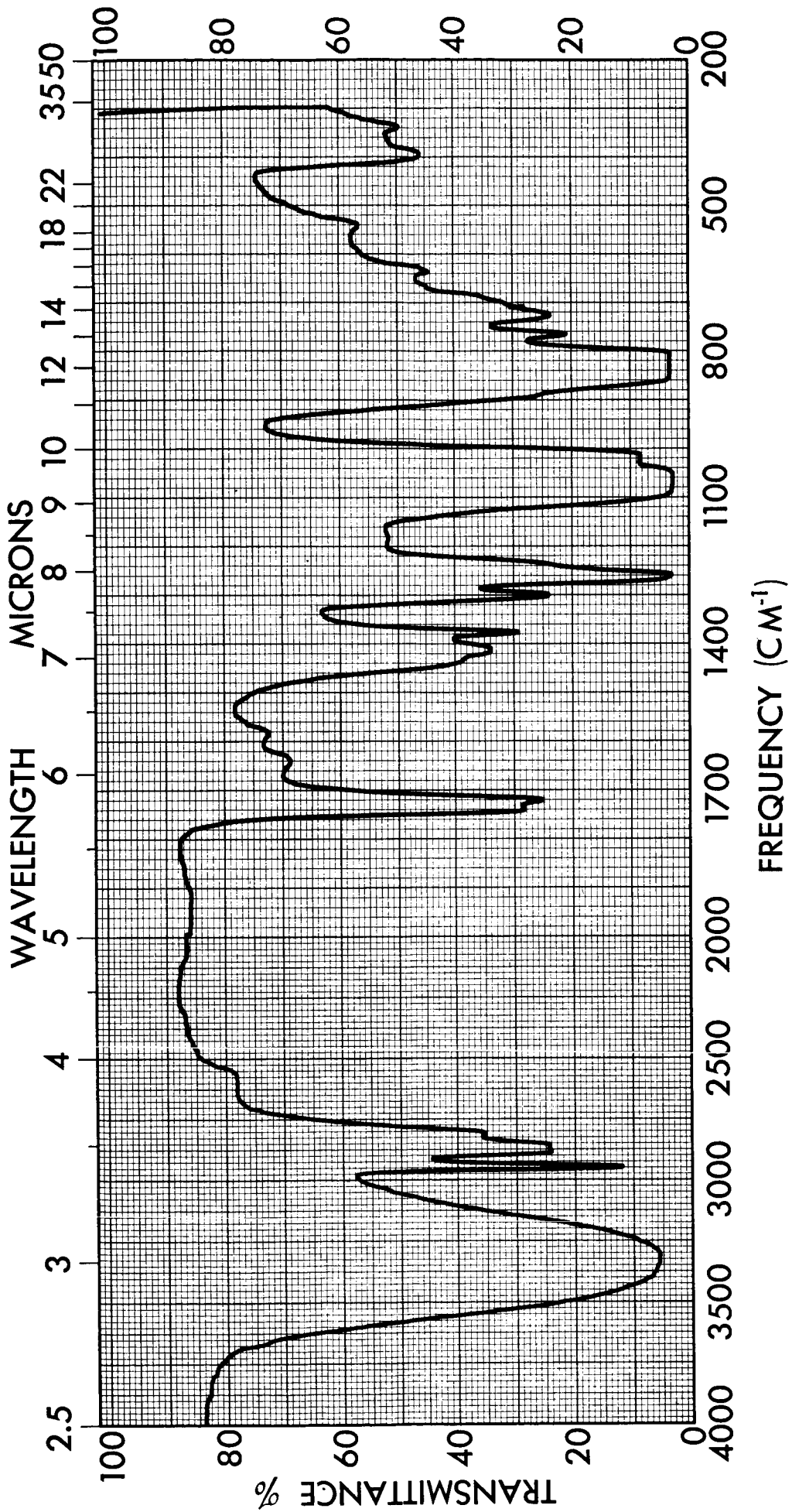


FIGURE 1.- INFRARED SPECTRUM OF BIS(HYDROXYMETHYL)-TETRAMETHYLDISILOXANE

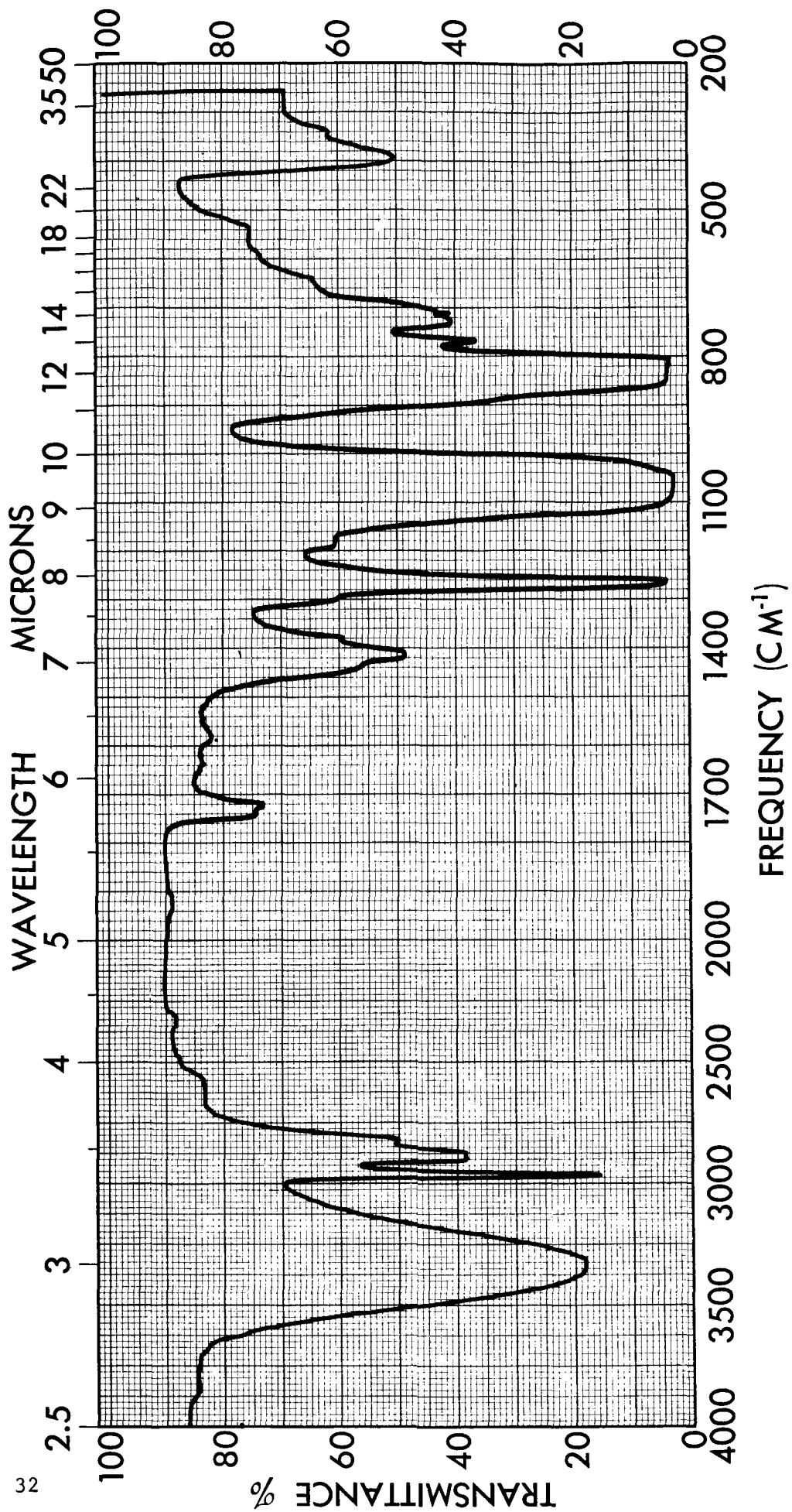


FIGURE 2.- INFRARED SPECTRUM OF BIS (HYDROXYMETHYL) - HEXAMETHYLTRISILOXANE

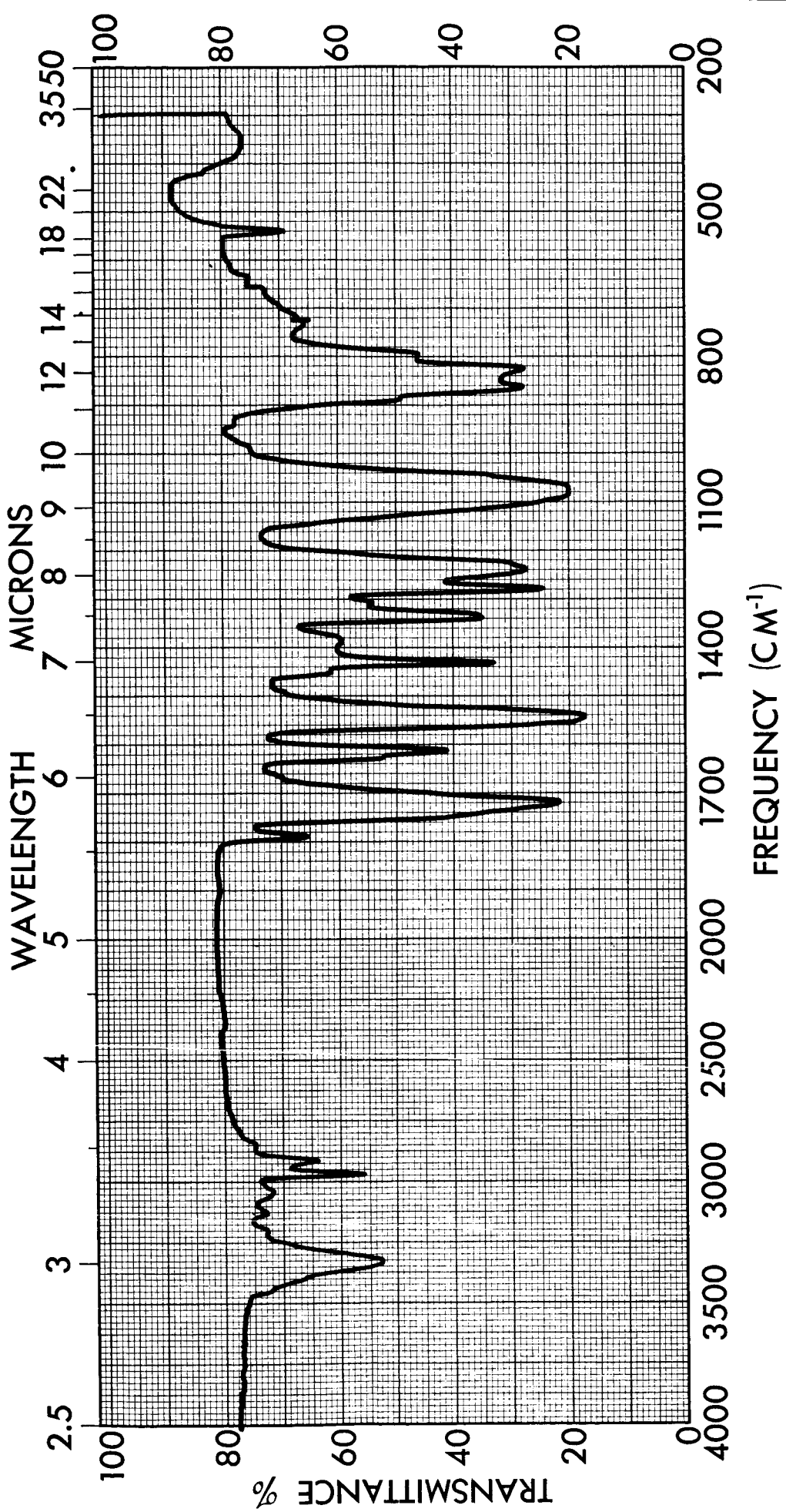


FIGURE 3.- INFRARED SPECTRUM OF COPOLYMER FROM BIS (HYDROXYMETHYL) - HEXAMETHYLTRISILOXANE AND METHYLENE - BIS (4 - PHENYLISOCYANATE)

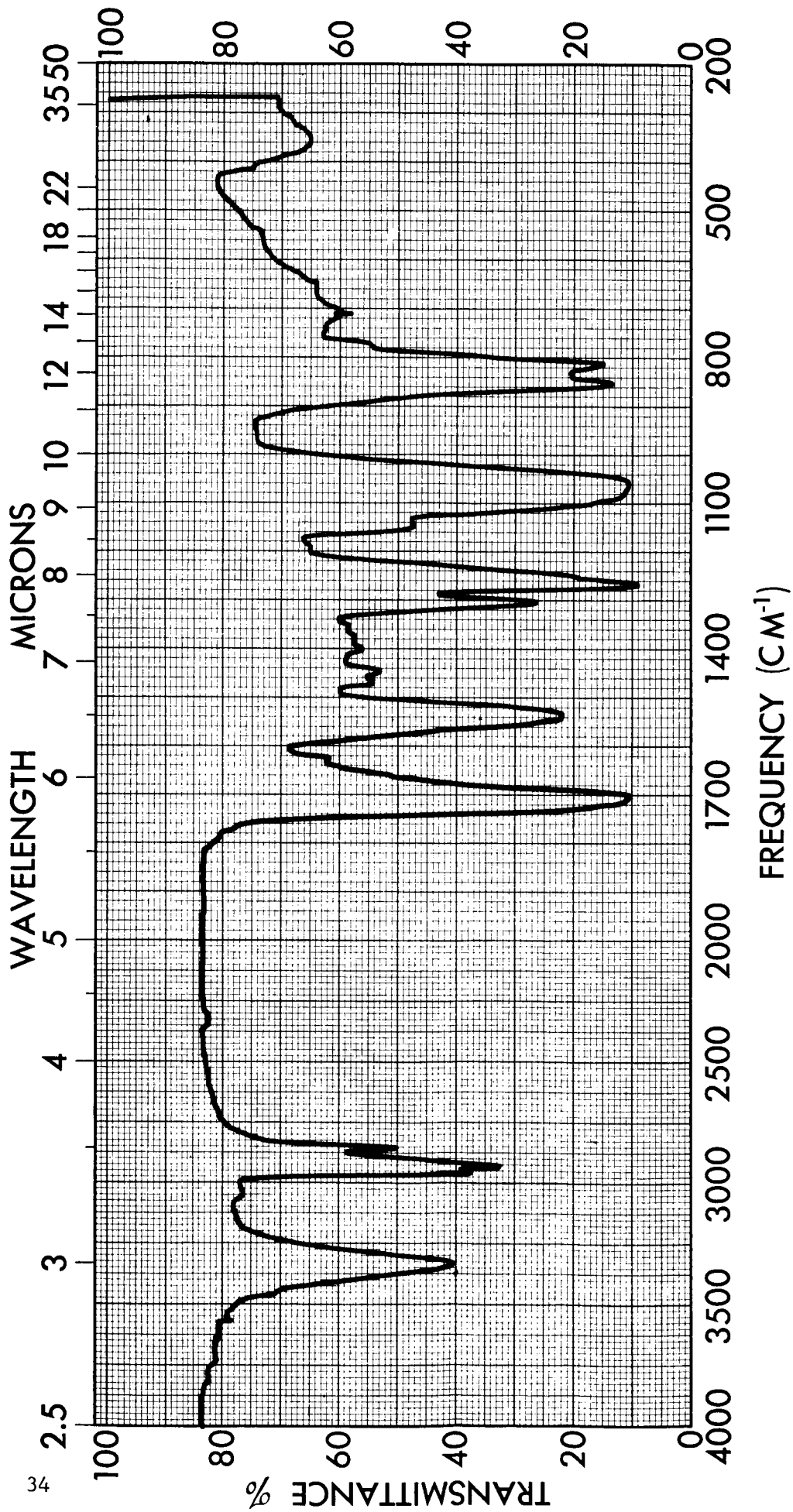


FIGURE 4.- INFRARED SPECTRUM OF COPOLYMER FROM BIS(HYDROXYMETHYL)-HEXAMETHYLTRISILOXANE AND HEXAMETHYLENE DIISOCYANATE

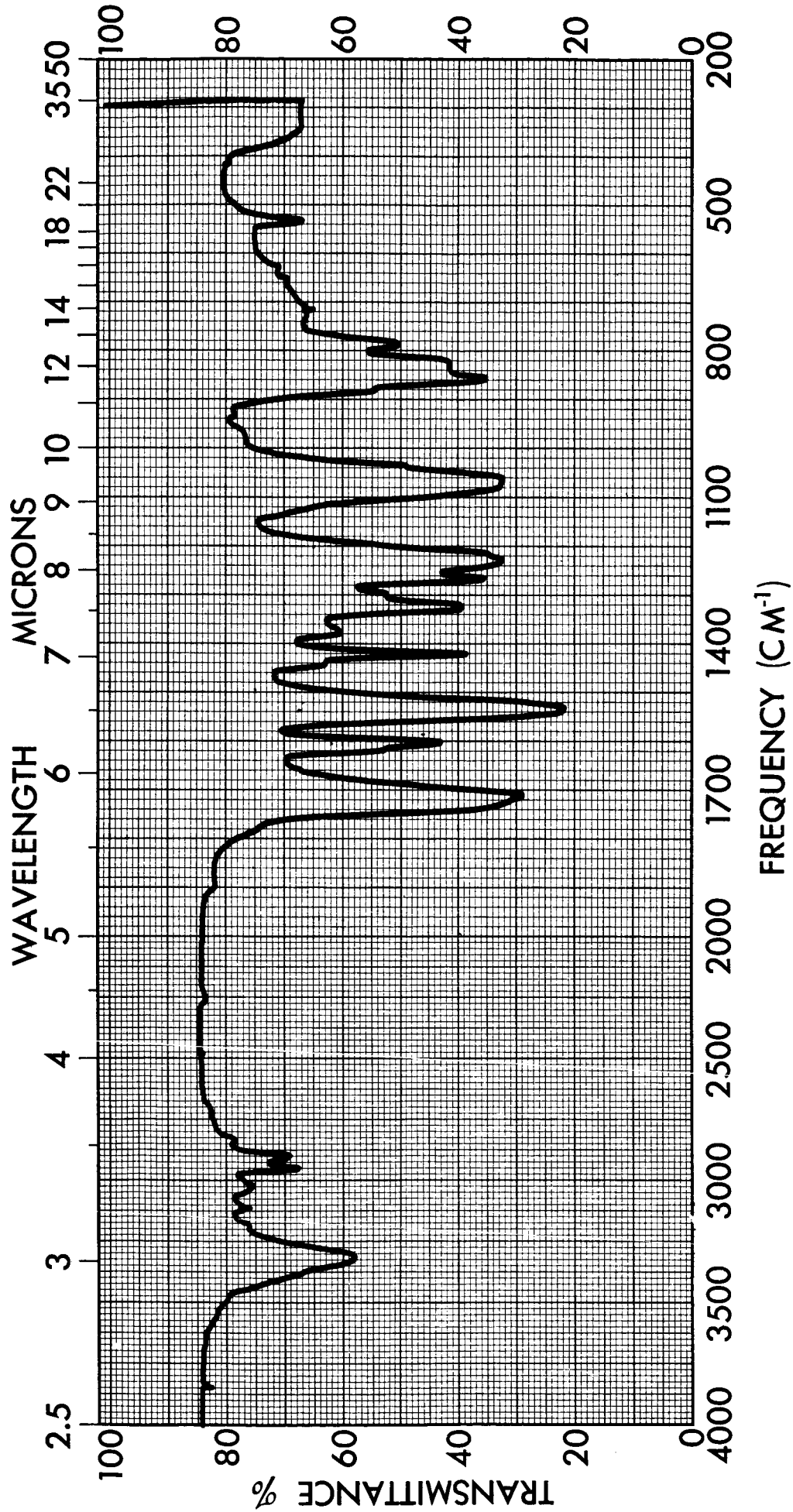


FIGURE 5.- INFRARED SPECTRUM OF COPOLYMER FROM BIS (HYDROXYMETHYL)-TETRAMETHYLDISILOXANE AND METHYLENE-BIS(4-PHENYLISOCYANATE)



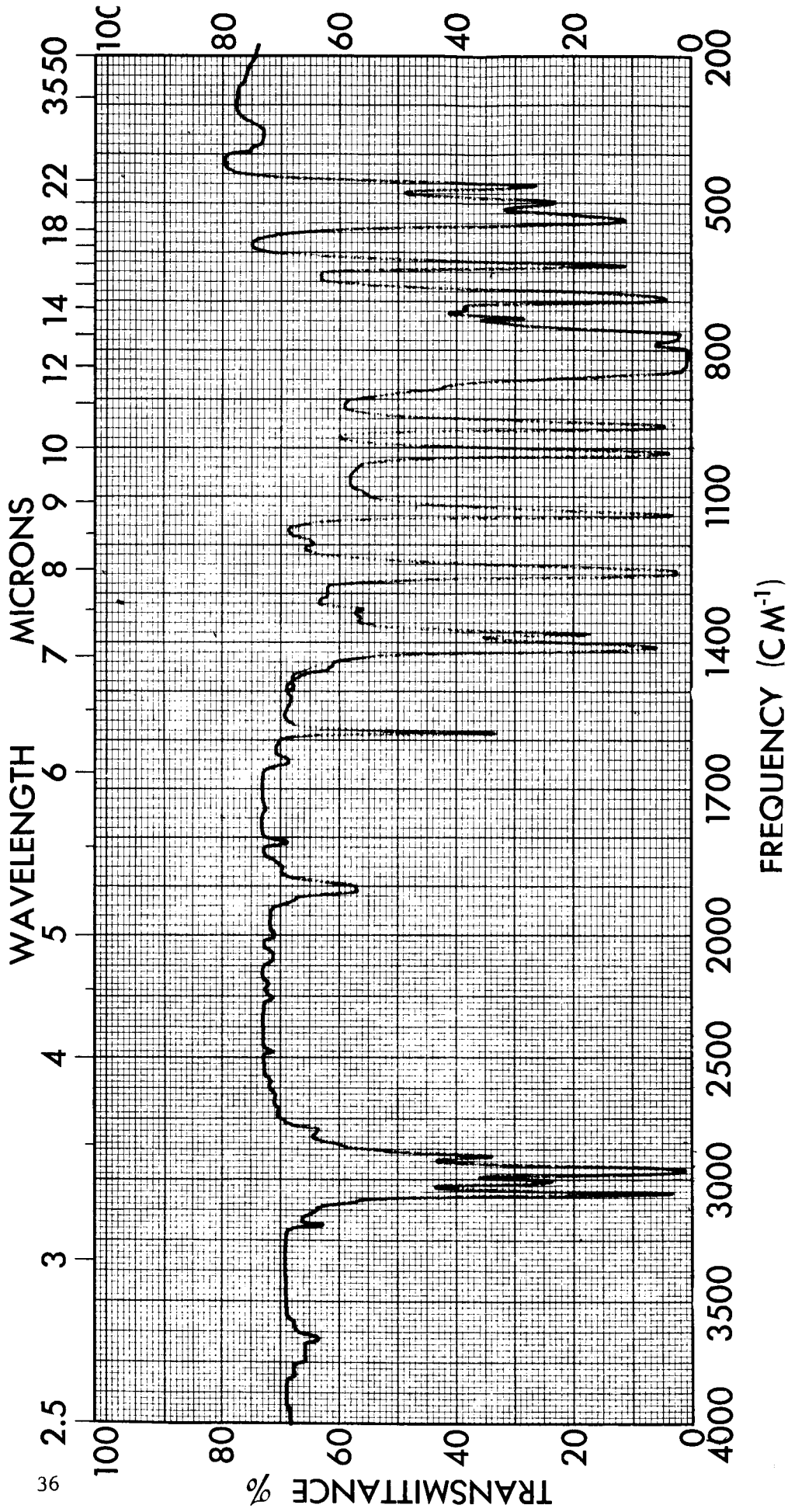


FIGURE 6.- INFRARED SPECTRUM OF 1,4-BIS(VINYLDIMETHYLSILYL)-BENZENE

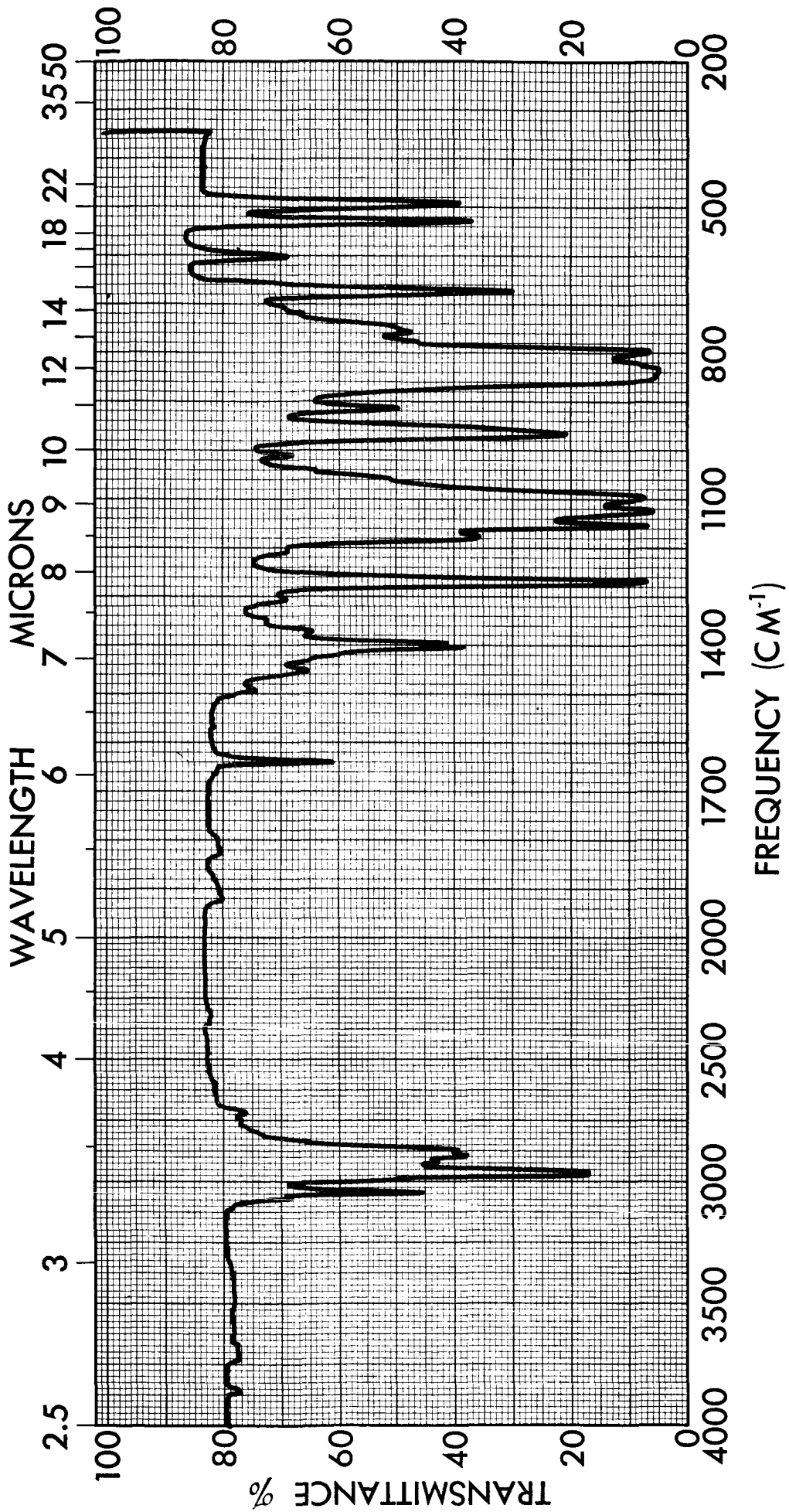


FIGURE 7.- INFRARED SPECTRUM OF 1,4-BIS(ALLYLDIMETHYLSILYL)-BENZENE

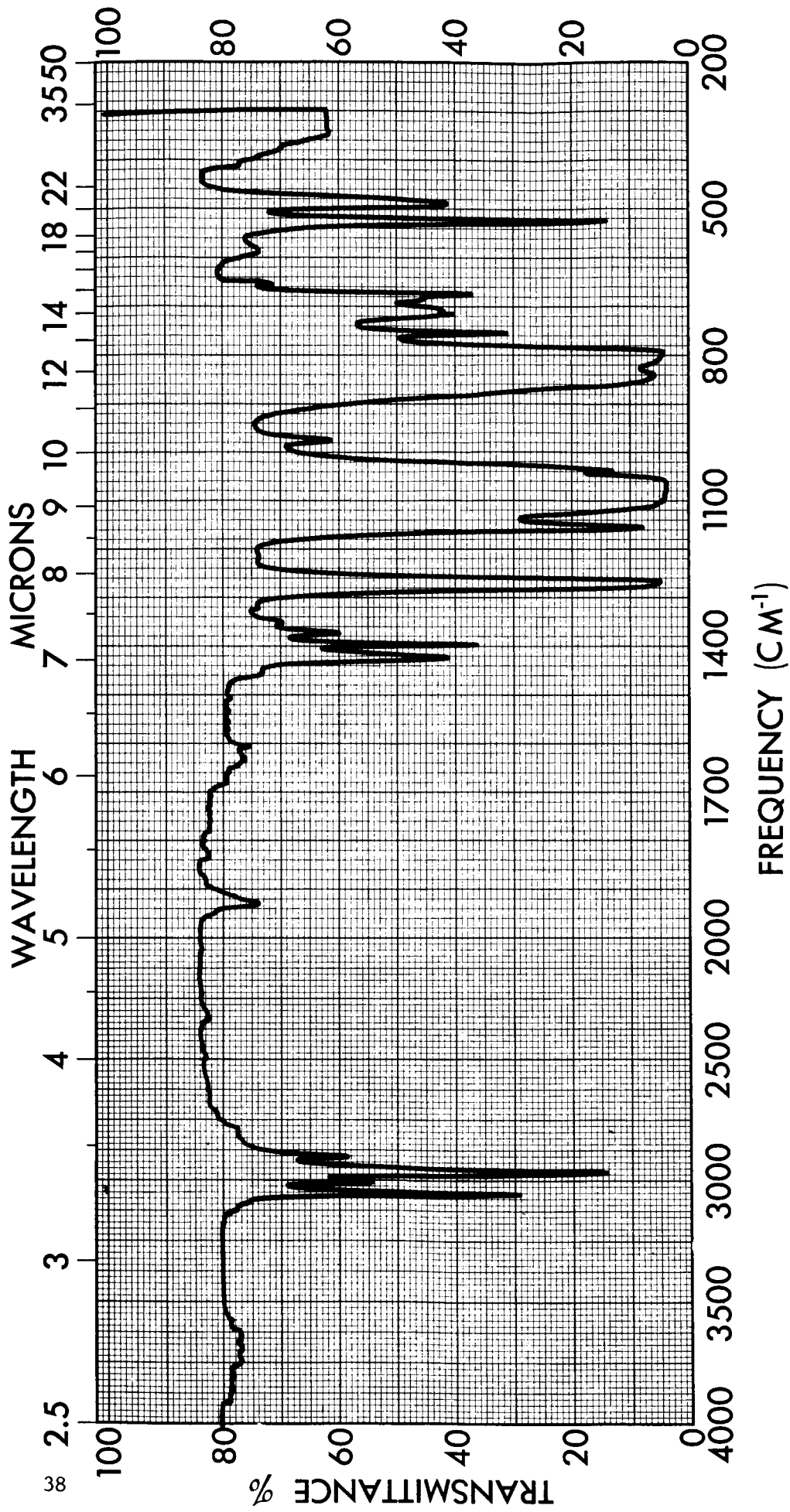


FIGURE 8.- INFRARED SPECTRUM OF 1,4-BIS(3-VINYL-1,1,3,3-TETRAMETHYLDISILOXYL)-BENZENE

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February 9, 1966

APPROVAL

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STATUS REPORT: DEVELOPMENT OF POLYMERIC MATERIALS FOR  
POTTING AND ENCAPSULATING ELECTRONIC ASSEMBLIES

by William J. Patterson

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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