NASA TECHNICAL
MEMORANDUM

NASA TM X-53536

November 14, 1966

NASA TM X-53536

FACILITY FORM 602

N67-16049	
(ACCESSION NUMBER)	(THRU)
54	/
(PAGES)	(CODE)
	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

EFFECT OF MOLECULAR STRUCTURE ON PHYSICAL CHARACTERISTICS OF POLYARYLOXYSILANES AND RELATED COMPOUNDS

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GPO PRICE $ ______

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Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

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ABSTRACT

In continuing studies of the thermal stability of polyaryloxysilanes, several new monomeric compounds of the structure,

$$(CH_3)_3SiOROSi(CH_3)_3$$

were prepared in which R was derived from 4,4'bis(hydroxymethyl)diphenylether, and the aromatic diols of diphenylsulfone, diphenylether, diphenyldimethylmethane, diphenylmethane, benzophenone, and 1,2-bis(p-phenyl)-1,2-diethylethylene. Fractional distillation of these compounds, followed by hydrolysis, provided a convenient means for purifying the starting aromatic diols. The purified diols were employed in reactions with bis(anilino)diphenylsilane yielding diphenylaryloxysilane polymers,

$$\left[Si(C_6H_5)_2ORO\right]_n$$

which possessed relatively high thermal resistance. Similar polymers were also prepared from the aromatic diols 4,4'-dihydroxyazobenzene and 3,4-bis(p-hydroxyphenyl)-2,4-hexadiene which were not purified by this technique. Each member of the group retained 48 percent or more of its original weight on heating at 4.1°C/min, in an atmosphere of nitrogen, to 900°C. The polymer containing the 4,4'-diphenylmethane linkage retained 90 percent of its original weight on heating under similar conditions to 566°C, and compared favorably in thermal resistance to the previously reported material containing the 4,4'-diphenylether linkage. These two products appear to be comparable in thermal stability to the polymer containing the 4,4'-diphenylene linkage which has the highest thermal stability of the materials studied previously in this polyaryloxysilane series.

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

TABLE OF CONTENTS

LIST OF TABLES

TECHNICAL MEMORANDUM X-53536

EFFECT OF MOLECULAR STRUCTURE ON PHYSICAL CHARACTERISTICS OF POLYARYLOXYSILANES AND RELATED COMPOUNDS

SUMMARY

A new group of monomeric compounds, conforming to the structure

$$(CH_3)_3SiOROSi(CH_3)_3,$$

has been prepared by the reaction of trimethylchlorosilane with 4,4'-bis(hydroxymethyl)diphenylether and the aromatic diols of diphenylsulfone, diphenylether, diphenyldimethylmethane, diphenylmethane, benzophenone and 1,2-bis(p-phenyl)-1,2-diethylethylene. These compounds were characterized by elemental, infrared, and molecular weight analyses and then hydrolyzed to yield the original diols in relatively pure form.

The purified diols were employed in reactions with bis(anilino)-diphenylsilane to yield aryloxy polymers,

$$\left[Si(C_6H_5)_2ORO \right]_n$$

which possessed relatively high thermal stability. The polymers were characterized by elemental analysis, infrared spectroscopy, and, in some cases, by determination of molecular weight. The thermal stability of the materials was measured by use of "thermogravimetric" and "differential scanning calorimetric" analyses. All of the polyaryloxysilanes exhibited a relatively high degree of thermal stability when compared with the heat resistance of organic polymers. The materials containing the 4,4'-diphenylmethane-, and 4,4'-diphenylether-, linkages exhibited the highest thermal stability and were judged to be nearly comparable in this property to polydiphenyldiphenyleneoxysilane, the material referred to as Polymer A which has been found to possess the highest thermal stability among the polymers previously studied in this polyaryloxysilane series.

INTRODUCTION

Polymers containing the -Si-O- linkage have been successfully used as coatings, lubricants, and elastomers for a number of years. Polyorganosiloxanes are noted especially for high thermal and oxidative stability, repellency of water, high dielectric strength, resistance to aqueous chemicals and corrosive gases, and unique rheological characteristics. The need for improved polymers for space application prompted a research program to develop a new series of polymers incorporating the -Si-O- linkage.

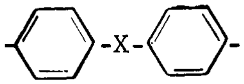
In continuing the general studies of Curry and Byrd (ref. 1) on polyaryloxysilanes, a series of seven monomeric compounds of the structure,

$$(CH_3)_3SiOROSi(CH_3)_3$$

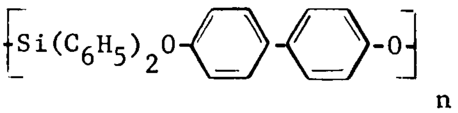
has been prepared by the reaction of trimethylchlorosilane with various aromatic diols. The products are of interest because their chemical structures are somewhat similar to those of the polyaryloxysilanes which possess high thermal stability. These monomeric or model compounds are of further interest because they can be purified by fractional distillation at reduced pressure and then hydrolyzed to yield the original aromatic diols in relatively pure form. In extending the specific studies of Curry and Byrd (ref. 1) on polyaryloxysilanes, these purified diols were used in reactions with bis(anilino)diphenylsilane to yield polymers of the structure,

$$\left[Si(C_6H_5)_2ORO \right]_n$$

where R is derived from an aromatic diol possessing a "bridging" group, X, between two phenylene units,



Polymers were prepared from the aromatic diols containing $-SO_2-$, $-O-$, $-C(CH_3)_2-$, $-CH_2-$, $-C(C_2H_5):C(C_2H_5)-$, $-N=N-$, $-CO-$, and $-C(:CHCH_3)-C(:CHCH_2)-$ as the bridging groups. The product, poly(diphenyldiphenyleneoxysilane),



possessed the highest thermal stability in the series of polyaryloxysilanes described by Curry and Byrd. The present study provides the opportunity to observe the thermal stabilities of materials of similar structure which contain various groups between the two phenylene units.

EXPERIMENTAL RESULTS

Monomeric Compounds

The model compounds listed in Table I were prepared by the reaction of trimethylchlorosilane with the aromatic diol in benzene solution with pyridine as the acid acceptor,

$$2(CH_3)_3SiCl + HOROH + 2\ C_5H_5N \longrightarrow (CH_3)_3SiOROSi(CH_3)_3 + 2\ C_5H_5NH^+Cl^-$$

The organic diols were obtained from commercial sources and were used without further purification. 4,4'-Dihydroxybenzophenone and diethylstilbestrol (1,2-bis-(p-hydroxyphenyl)-1,2-diethylethylene) were obtained from K and K Laboratories. Bisphenol A and 4,4'-bis(hydroxymethyl)diphenylether were obtained from Dow Chemical Company; 4,4'-sulfonyldiphenol and 4,4'-oxydiphenol from Distillation Products Division, Eastman Kodak Company, and 4,4'-dihydroxydiphenylmethane from Aldrich Chemicals. The trimethylchlorosilane was used as supplied by Peninsular ChemResearch, Incorporated. In each reaction, one mol-equivalent of the diol, two mol-equivalents of pyridine and benzene were placed in a round-bottom flask and agitated while two mol-equivalents of the silane were added dropwise. The reaction was exothermic. In several cases the reaction temperature was held at 50°C. In others, the temperature was maintained by the refluxing benzene solution. At the end of the reaction period of three to six hours the mixture was cooled and the solid pyridine hydrochloride was removed by filtration. After evaporation of the major part of the benzene by heating to 135°C at atmospheric pressure, the desired product was obtained by distillation at reduced pressure.

The reaction conditions and the boiling points of the products are summarized in Table I. The results of elemental analyses and molecular weight measurements are presented in Table II. Compound IV has been described by Martin (ref. 2). The others are believed to be new to the literature (compare ref. 3 and 4).

Infrared Spectra of Monomeric Compounds.- The infrared spectra of the several monomeric compounds are presented in FIG 1-7. Analyses of the spectra by the conventional assignment of absorption bands gave strong support for the structures of the materials shown in Table I.

Polyaryloxysilanes

Purification of Diols.- While the melting ranges of the aromatic diols from commercial sources were increased on crystallization from solvent, some color remained in a few of the materials even after repeated recrystallizations. Martin (ref. 2) found that 4,4'-dihydroxydiphenylmethane could be purified by preparation and fractional distillation of the bis(trimethylsilyl) derivative (Compound IV, Table I), followed

TABLE I.- PREPARATION AND PROPERTIES OF ARYLOXYSILANE MODEL COMPOUNDS

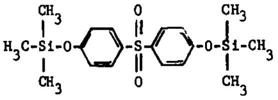
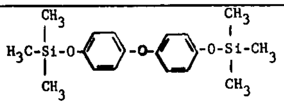
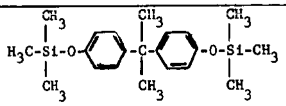
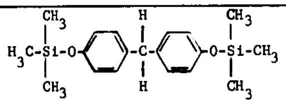
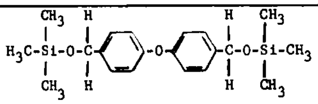
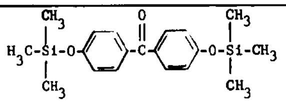
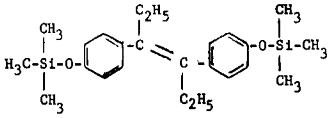
Compound Number	Structure	Reaction Time Hrs.	Reaction Temp. °C	Yield of pure Compound %	Physical Properties
I	 4,4'-Bis(trimethylsiloxy)diphenylsulfone	5	50	51	White crystalline (waxy) M.P. 61.5-66°C B.P. 195-207°C (0.14 mm Hg) hydrolyzes rapidly
II	 4,4'-Bis(trimethylsiloxy)diphenylether	4	50	82	White crystalline, B. P. 130°C (0.22 mm Hg)
III	 4,4'-Bis(trimethylsiloxy)diphenylisopropane	4-1/2	50	80	Clear, pale yellow liquid, B.P. 171°C (0.71 mm Hg)
IV	 4,4'-Bis(trimethylsiloxy)diphenylmethane	3	80	78	Clear yellow oil, B.P. 157°C (0.4 mm Hg)
V	 4,4'-Bis(trimethylsiloxymethyl)diphenylether	5	80	82	Clear, almost colorless liquid, B.P. 182°C (0.58 mm Hg)
VI	 4,4'-Bis(trimethylsiloxy)diphenylketone	6	81	69	Clear, bright yellow liquid, B.P. 205°C (1.0 mm Hg); viscous
VII	 1,2-Bis(p-trimethylsiloxyphenyl)-1,2-diethylethylene	6-1/2	81	85	Off-white waxy crystals, B.P. 200-203°C (1.6 mm Hg)

TABLE II.- ELEMENTAL ANALYSIS OF MODEL COMPOUNDS

Compound	Calculated						Found					
	$\overline{M}_n$	%C	%H	%Si	%N	%S	$\overline{M}_n$	%C	%H	%Si	%N	%S
I	394.6	54.78	6.64	14.24	0	8.12	376	49.25	5.63	12.50	-	8.99
II	346.6	62.38	7.56	16.21	0	0	332	60.60	6.40	15.55	-	-
III	372.7	67.68	8.65	15.08	0	0	343	66.58	7.72	14.39	-	-
IV	344.6	66.22	8.19	16.30	0	0	344	65.13	7.25	15.65	-	-
V	374.6	64.12	8.07	15.00	0	0	374	62.35	7.11	13.69	-	-
VI	358.6	63.64	7.31	15.66	0	0	336	61.84	6.56	15.06	-	-
VII	412.7	69.85	8.79	13.61	0	0	403	69.45	7.50	12.70	-	-

by hydrolysis and recovery of the diol. Martin's procedure was employed in this study.

The bis(trimethylsilyl) derivative of each diol was hydrolyzed in refluxing 1:1 methanol-water solution for a period, usually of several hours, until the mixture became cloudy. The diol crystallized upon cooling the mixture. The recovered diols were colorless with the exception of 4,4'-dihydroxydiphenylmethane. The colored materials were removed by one recrystallization from isopropyl alcohol. The melting points of the diols as received from the commercial sources and after purification, are listed in Table III.

Preparation of Bis(anilino)diphenylsilane.- The Curry and Byrd (ref. 1) modification of the original Anderson procedure (ref. 5) for the preparation of this compound has been further altered by Battelle Memorial Institute (ref. 6) to include the use of γ-collidine as the acid acceptor,

$$(C_6H_5)_2SiCl_2 + 2\ C_6H_5NH_2 + 2\ (CH_3)_3C_5H_2N \longrightarrow$$

$$(C_6H_5)_2Si(NH\ C_6H_5)_2 \ + \ 2\ (CH_3)_3C_5H_2NH\ ^{+}Cl^{-}$$

The Battelle modification has been employed in this study.

To a stirred refluxing benzene solution of two molar equivalents each of aniline and γ-collidine, one molar equivalent of diphenyldichlorosilane (Dow Corning Corporation) was added dropwise. The temperature of about 80°C was maintained for four to six hours. The mixture was chilled overnight and the insoluble γ-collidine hydrochloride was removed by filtration. After evaporation of a large portion of the benzene, the bis(anilino)diphenylsilane was precipitated from the benzene solution by the addition of an equal volume of "SuperNaphtholite" (AMSCO Solvents and Chemical Company). After allowing the mixture to stand for several hours the solid was separated, slurried with cold chloroform, again separated from solvent and dried under vacuum at 100°C in a Rinco Evaporating Apparatus. The product, in the form of snow-white powdery crystals, contained, as indicated by gas chromatographic analysis, a small amount of aniline. Since aniline is the by-product in the polycondensation reaction described below, it was not considered a detrimental impurity. In carrying out the polycondensations with the material, the stoichiometry was adjusted to account for the aniline content.

Preparation of Polyaryloxysilanes.- The purified diols listed in Table III were used in polycondensation reactions with bis(anilino)-diphenylsilane. Two additional diols, 4,4'-dihydroxyazobenzene from the K and K Laboratories, Incorporated, and "Dienestrol" (3,4-bis(p-hydroxyphenyl)-2,4-hexadiene) from the City Chemical Corporation, did not react with trimethylchlorosilane and were recrystallized before they were used in the polymerization.

TABLE III.- PURIFICATION OF DIOLS

	Diols	Before Purification		After Purification	
		Melting Range (°C) *	Appearance	Melting Range (°C) *	Appearance
I.	4,4'-Dihydroxydiphenylsulfone	244-247.5	Off-white fluffy powder	245.5-250	Snow-white crystals
II.	4,4'-Dihydroxydiphenylether	165-170	Tan powder	167.5-170	Snow-white crystals
III.	2,2-Bis(4-hydroxybenzene)propane	152-158	Waxy, off-white flakes	157.5-160.5	White crystals
IV.	4,4'-Dihydroxydiphenylmethane	156-162	Bright orange crystals	161-165.5	Off-white crystals
V.	4,4'-Bis-(hydroxymethyl)diphenylether	128.5-133	Fluffy tan powder	131-133	White crystals
VI.	4,4'-Dihydroxybenzophenone	209-215	Bright orange powder	215-218	Off-white powder
VII.	1,2-Bis(p-hydroxyphenyl)-1,2-diethylethylene	171.5-174	White powder	171-173	White powder

* Melting points are uncorrected.

Equimolar quantities of bis(anilino)diphenylsilane and the aromatic diol were mixed thoroughly in a thick wall resin pot. The pot, equipped with a nitrogen inlet, vacuum connection, and stirring mechanism, was placed in an oil bath at 220°C. Gaseous nitrogen was passed through the system until the mixture was completely fused; then the mixture was stirred and the the pressure reduced to about 0.1 mm Hg. These conditions, with the temperature of the bath held between 220 and 260°C, were maintained for about 6 hours. The conditions of preparation and some of the properties of the products are summarized in Table IV.

Infrared Spectra of Polymers.- The infrared spectra of the several polymers are reproduced in FIG 8-16.

Except that the expected strong carbonyl absorption by Polymer VI did not occur, analysis of the infrared spectra of the several polymers gave strong support to the structures as listed in Table IV.

Molecular Weight of Polymers.- Benzene and 1,2,4-trichlorobenzene were employed as the solvents in the molecular weight determinations. The values of the number average molecular weight, $\bar{M}n$, of the polymers listed in Table V, as well as the monomeric compounds listed in Table II, were determined by use of a "vapor pressure osmometer," Mechrolab Incorporated Model 302. The values of the weight average molecular weight, $\bar{M}w$, of the polymers listed in Table V were measured by the Battelle Memorial Institute by gel permeation chromatographic analysis calibrated by light scattering. While the results are incomplete because of the insolubility of several of the polymers, it can be seen by comparison of the physical properties in Table IV with the molecular weights in Table V that the tougher materials possessed the higher molecular weights.

Thermal Stability of Polymers.- Thermogravimetric analyses (TGA) of the polymers (except Polymer V) were made in a nitrogen atmosphere over the temperature range of 25-900°C at a heating rate of 4.1°C/min using TGA Instrument Model TR01 manufactured by Stanton Instruments, Ltd. The values of the percent weight loss, when the polymers were heated to 900°C, and the temperatures at which the weight loss was 10 percent of the original weight, listed in Table V, were taken from the TGA curves presented in FIG 17-25 in which the approximate percent weight loss is plotted against temperature. All of the polymers retained 48 percent or more of their original weight on heating to 900°C. Polymers II, III, and IV retained 90 percent of their original weight on heating to 520-568°C. Considering the several TGA curves collectively it will be seen that the decomposition which first became evident between 200 and 450°C appears to be essentially complete at about 650°C. For several of the polymers, the TGA curves above 650°C are relatively flat indicating that the decomposition has resulted in the formation of some highly stable material, possibly carbon or an organic silicon residue.

TABLE IV.- REACTION CONDITIONS AND CHARACTERISTICS OF POLYMERS

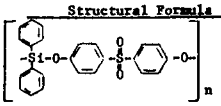
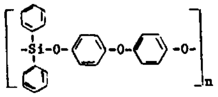
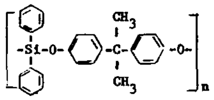
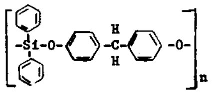
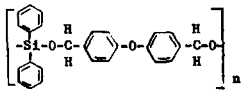
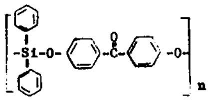
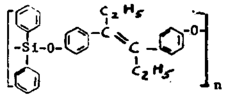
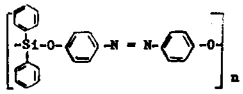
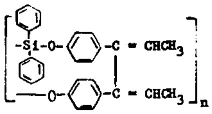
		Polymerization Conditions					
Polymer	Structural Formula	Time Hours	Temperature °C	Ability to Form Fibers	Brittleness	Appearance	Solubility
I		6	240	Fiber-forming; fibers flexible but weak.	Brittle but somewhat strong; softens at 148°C	Peach-colored	Slightly soluble chloroform; insoluble benzene, THF, 1,2,4-trichlorobenzene
II		6	230	Fiber-forming; fibers flexible and strong	Non-brittle; softens at 90°C	Green	Soluble THF, benzene, chloroform, 1,2,4-trichlorobenzene
III		6	230	Fiber-forming; fibers weak	Brittle, softens at 85°C	Cloudy, tan	Soluble THF, benzene, chloroform, 1,2,4-trichlorobenzene
IV		6	245	Fiber-forming; fibers flexible and strong	Non-brittle; softens at 87°C	Brown	Soluble THF, benzene, chloroform, 1,2,4-trichlorobenzene
V		6	225	Fiber-forming; fibers weak	Flexible when warm; brittle when cold, softens at 46°C	Cloudy yellow	Soluble THF, benzene, chloroform, 1,2,4-trichlorobenzene
VI		6-1/2	235	Fiber-forming; fibers weak and brittle	Very brittle; softens at 100°C	Clear, bright orange	Soluble THF, chloroform; slightly soluble benzene; insoluble 1,2,4-trichlorobenzene
VII		6	230	Fiber-forming; fibers strong and flexible	Non-brittle; softens at 89°C	Clear, pale yellow	Soluble THF, benzene, chloroform
VIII		6	230	Not readily fiber-forming; elastomeric when hot	Extremely tough; softens at 114°C	Dark brown	Insoluble benzene, soluble THF, chloroform, 1,2,4-trichlorobenzene
IX		6	235	Not fiber-forming; elastomeric when hot	Tough; softens at 86°C	Golden yellow	Insoluble THF, benzene, chloroform, 1,2,4-trichlorobenzene, toluene

TABLE V.- ANALYSIS OF POLYMERS

Polymer	Calculated			Found			M.W. x 10^3		Wt. Loss,%; at 900°C (TGA)	Temp, °C, of Exotherm (DSC)	Temp, °C, of 10% wt. Loss (TGA)
	%C	%H	%Si	%C	%H	%Si	M_n	M_w			
I(a)	66.95	4.22	6.52	68.56	4.07	6.82	(c)	-	50	395	468
II	75.36	4.74	7.35	74.82	4.58	7.52	8.8	86	40	427	568
III	79.37	5.92	6.88	78.05	5.53	6.92	11	-	52	454	520
IV	78.91	5.30	7.38	78.15	4.97	7.60	20	122	33	452	566
V	76.07	5.40	6.84	76.48	5.20	7.06	3.7	-	-	-	-
VI	76.11	4.60	7.12	75.45	4.63	7.86	(c)	-	41	361	410
VII	80.36	6.29	6.26	80.41	5.96	7.17	7.9	124	43	-	465
VIII(b)	73.07	4.60	7.12	71.82	4.36	7.25	(c)	-	37	-	390
IX	80.68	5.87	6.29	79.95	5.61	7.10	(c)	-	45	471	472

(a) Polymer I; S: Calculated - 7.45%; Found - 7.27%

(b) Polymer VIII; N: Calculated - 7.10%; Found - 7.32%

(c) Product was insoluble in benzene.

Finally, it can be seen in the comparison of FIG 20 and 21 that differences in molecular weight had little effect on the thermal stability of Polymer IV.

Differential Scanning Calorimetric (DSC)of the polymers were made by use of a Perkin-Elmer Model DSC-1 instrument at a heating rate of 10°C/min in an atmosphere of nitrogen over the temperature range of 305-773°K. Graphs of the heat change versus temperature are reproduced in FIG 26-32. For the several polymers, the curves are smooth and approximately horizontal showing no thermal reaction until the sample reached some high temperature at which time an exothermic process took place. The values listed in Table V under "T°C of Exotherm DSC" were selected to represent, approximately, the temperatures at which the curves showed maximum upward curvature. A rating of the polymers based on the DSC measurements again places Polymers III, IV, and II respectively, in high positions and in addition, indicates that Polymer IX may be noteworthy.

DISCUSSION

Comparison of the structures of Polymers I-IX in Table IV, with the weight loss at 900°C data in Table V, reveals a rough correlation between the molecular weight of the bridging group between the two phenylene units and percent loss in weight suffered by the polymer on being heated to 900°C. The Polymers VII and IX exhibit somewhat greater stability (lower weight loss) than might be expected on the basis of such a correlation, possibly because of the presence of unsaturated linkages in the bridging groups.

CONCLUSIONS

Several polymers having the structure,

$$\left[Si(C_6H_5)_2OC_6H_4XC_6H_4O \right]_n$$

where X is a bridging group, exhibited relatively high thermal stability and warrant further study for space applications as films, coatings, and possibly as fibers. The polymers in which the bridging groups were $-CH_2-$, -O-, Polymers IV, II, respectively, were judged to show the highest thermal stability of the group. Polymers IV and II were essentially comparable in thermal stability to the material referred to as Polymer A,

$$\left[Si(C_6H_5)_2OC_6H_4C_6H_4O \right]_n$$

which contains no bridging group between the two phenylene units, and which was found to possess the highest thermal stability in nitrogen atmosphere of the several aryloxysilane polymers previously studied.

APPENDIX

SECTION A

INFRARED SPECTRA OF MODEL COMPOUNDS AND POLYMERS

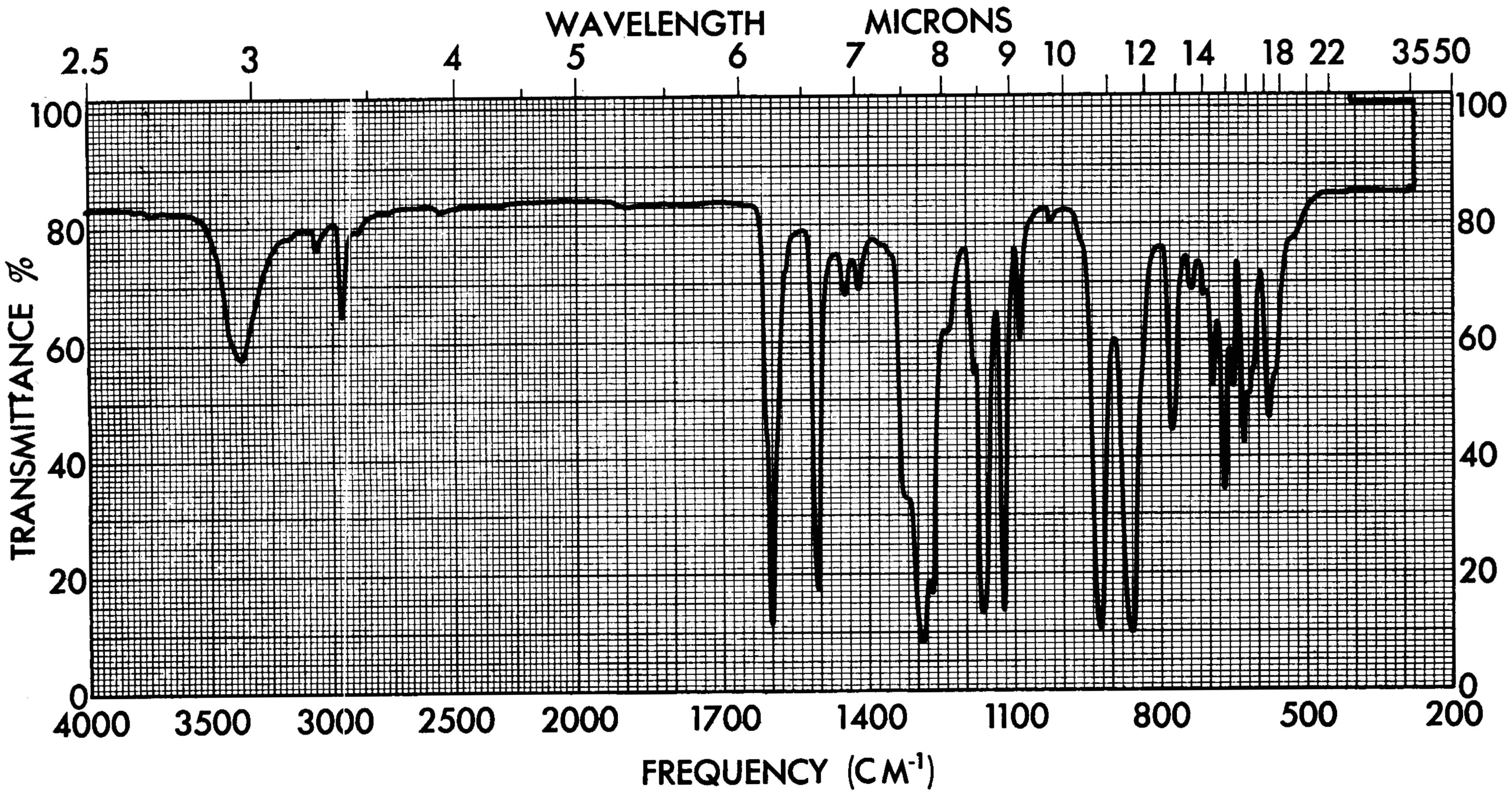
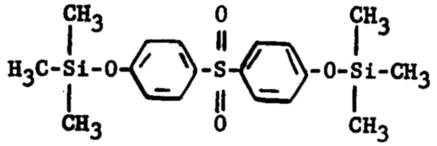


FIGURE 1.— INFRARED SPECTRUM OF COMPOUND I



4,4'-BIS(TRIMETHYLSILOXY)DIPHENYLSULFONE

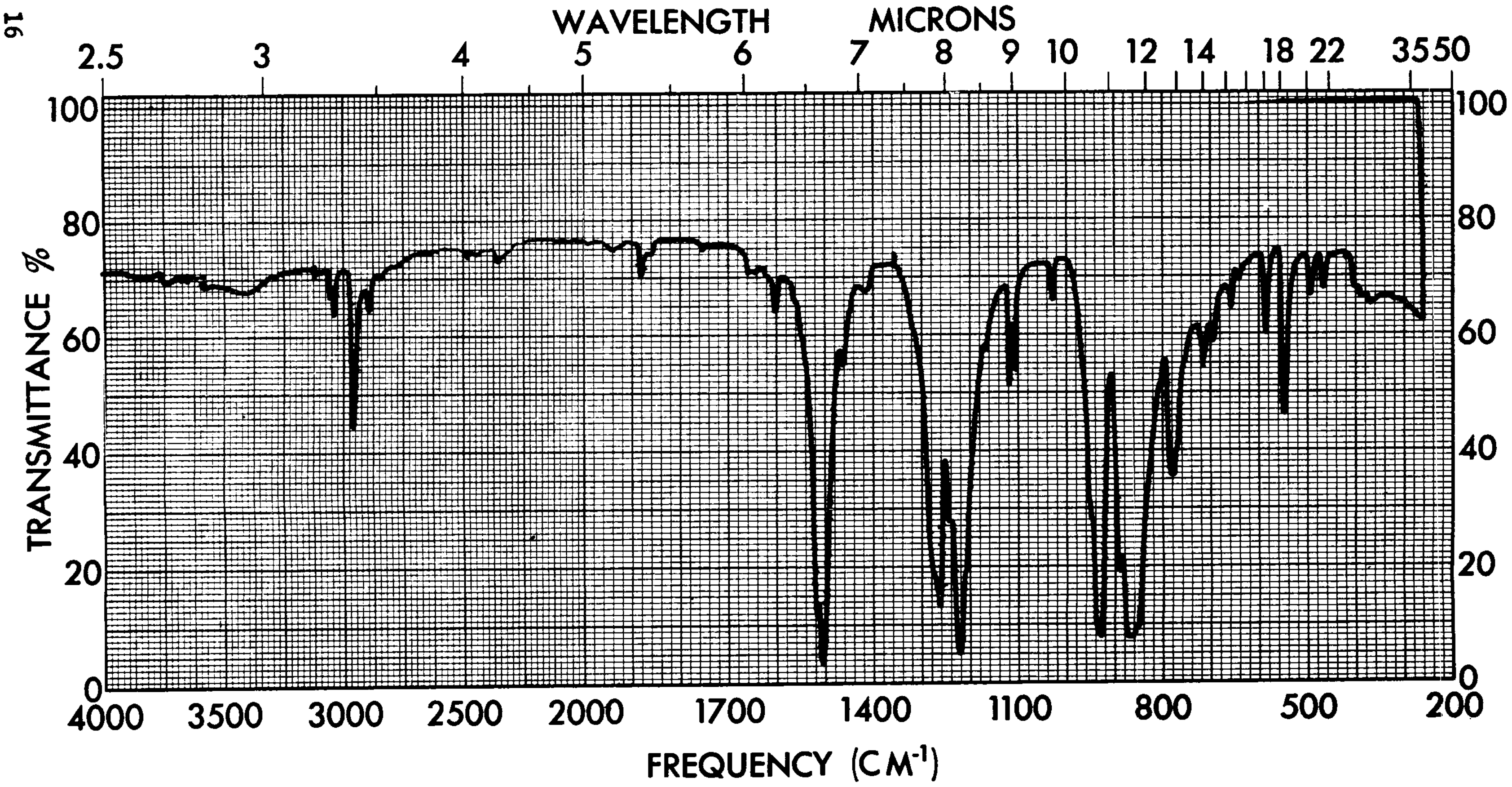
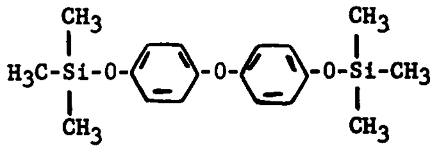


FIGURE 2.— INFRARED SPECTRUM OF COMPOUND II



4,4'-BIS(TRIMETHYLSILOXY)DIPHENYLETHER

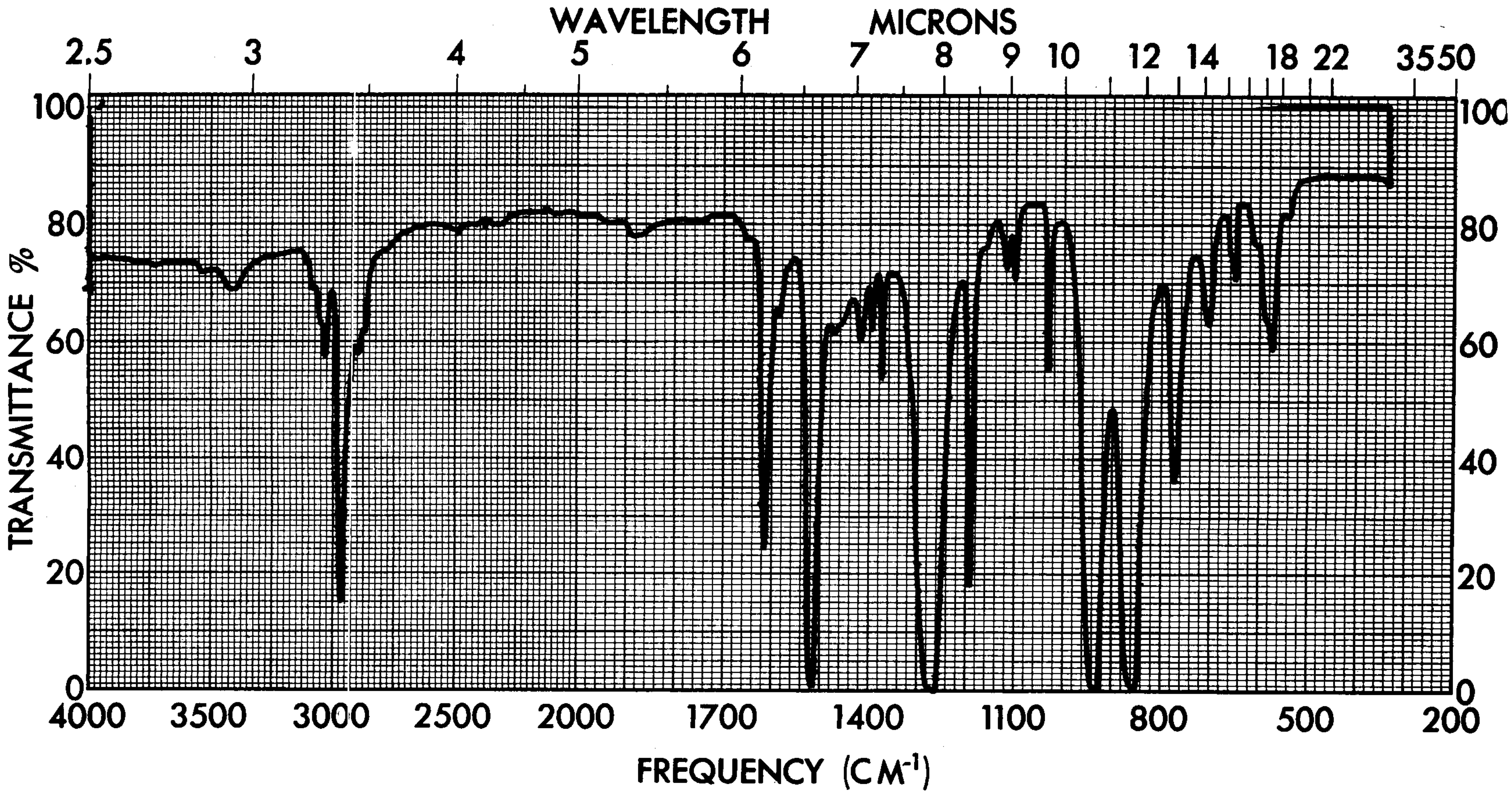
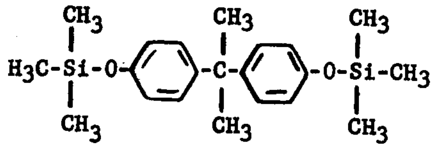


FIGURE 3.— INFRARED SPECTRUM OF COMPOUND III



4,4'-BIS(TRIMETHYLSILOXY)DIPHENYLISOPROPANE

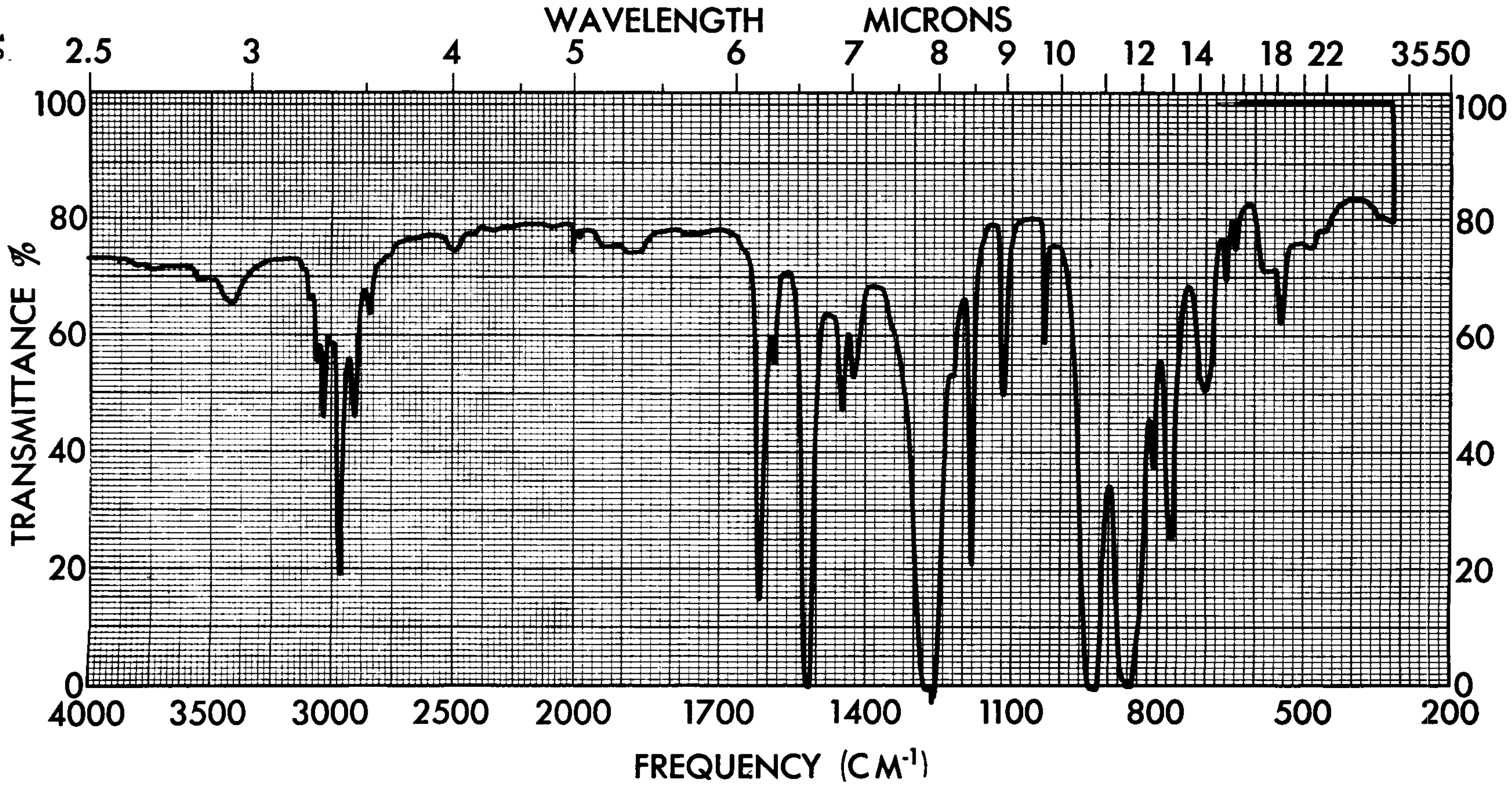
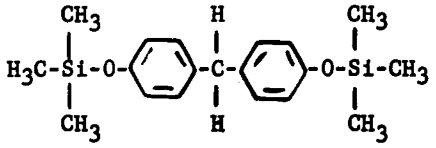


FIGURE 4.— INFRARED SPECTRUM OF COMPOUND IV



4,4'-BIS(TRIMETHYLSILOXY)DIPHENYLMETHANE

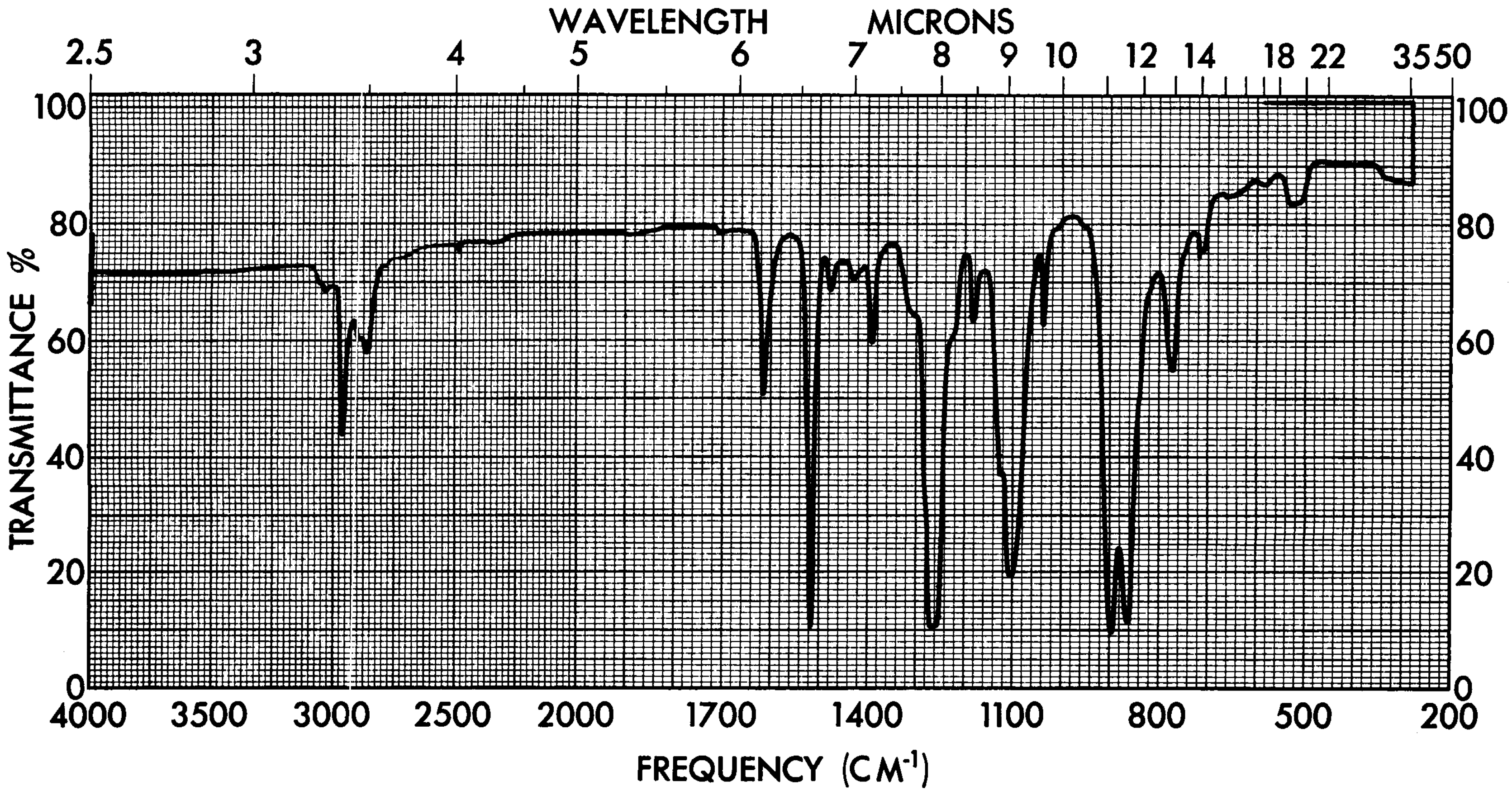
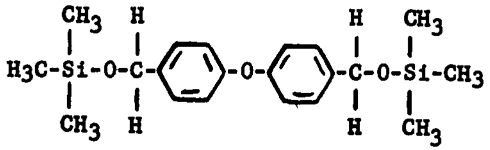


FIGURE 5.— INFRARED SPECTRUM OF COMPOUND V



4,4'-BIS(TRIMETHYLSILOXYMETHYL)DIPHENYLETHER

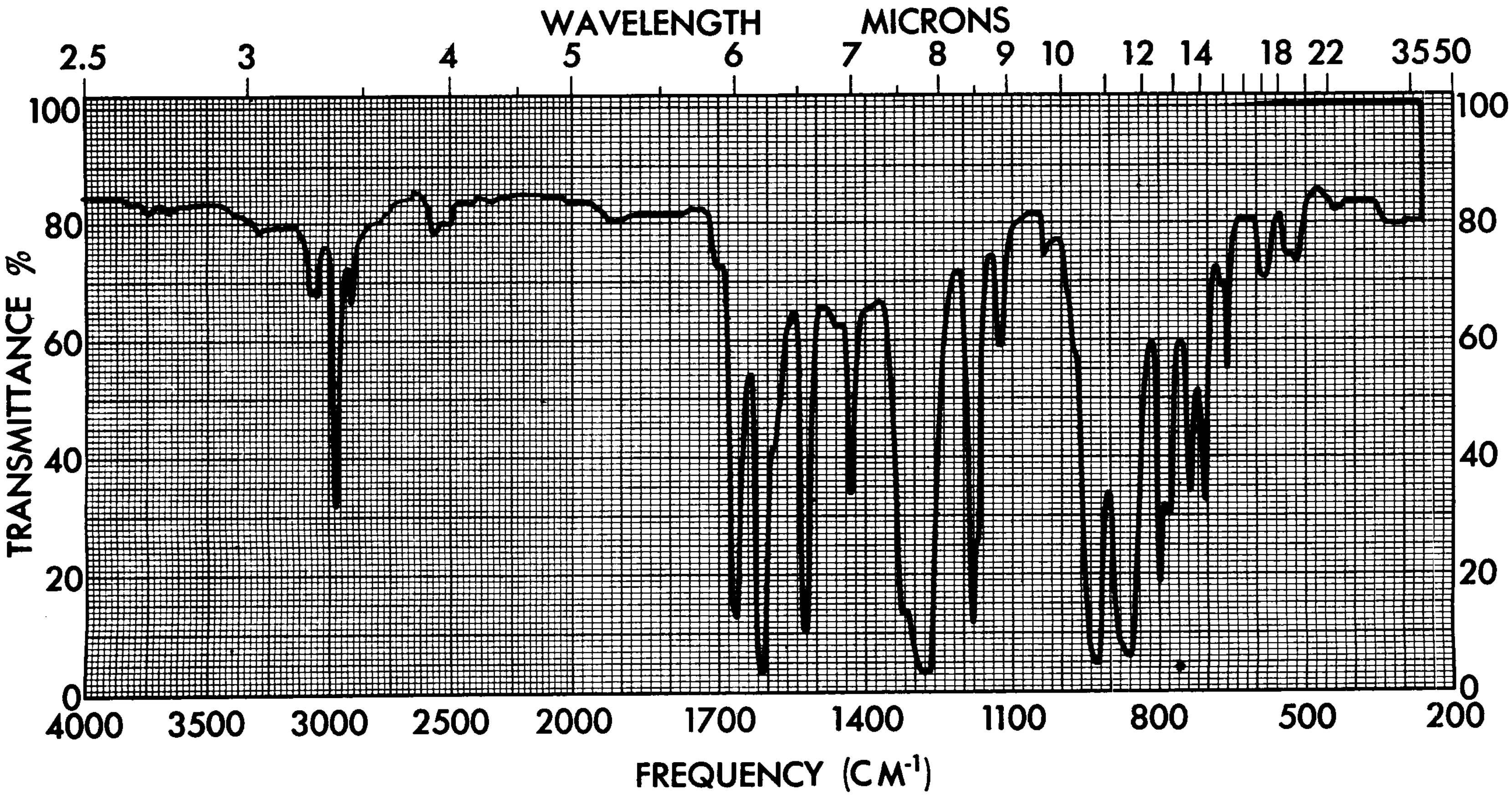
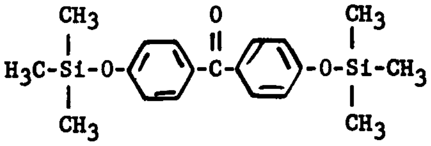


FIGURE 6.— INFRARED SPECTRUM OF COMPOUND VI



4,4'-BIS(TRIMETHYLSILOXY)BENZOPHENONE

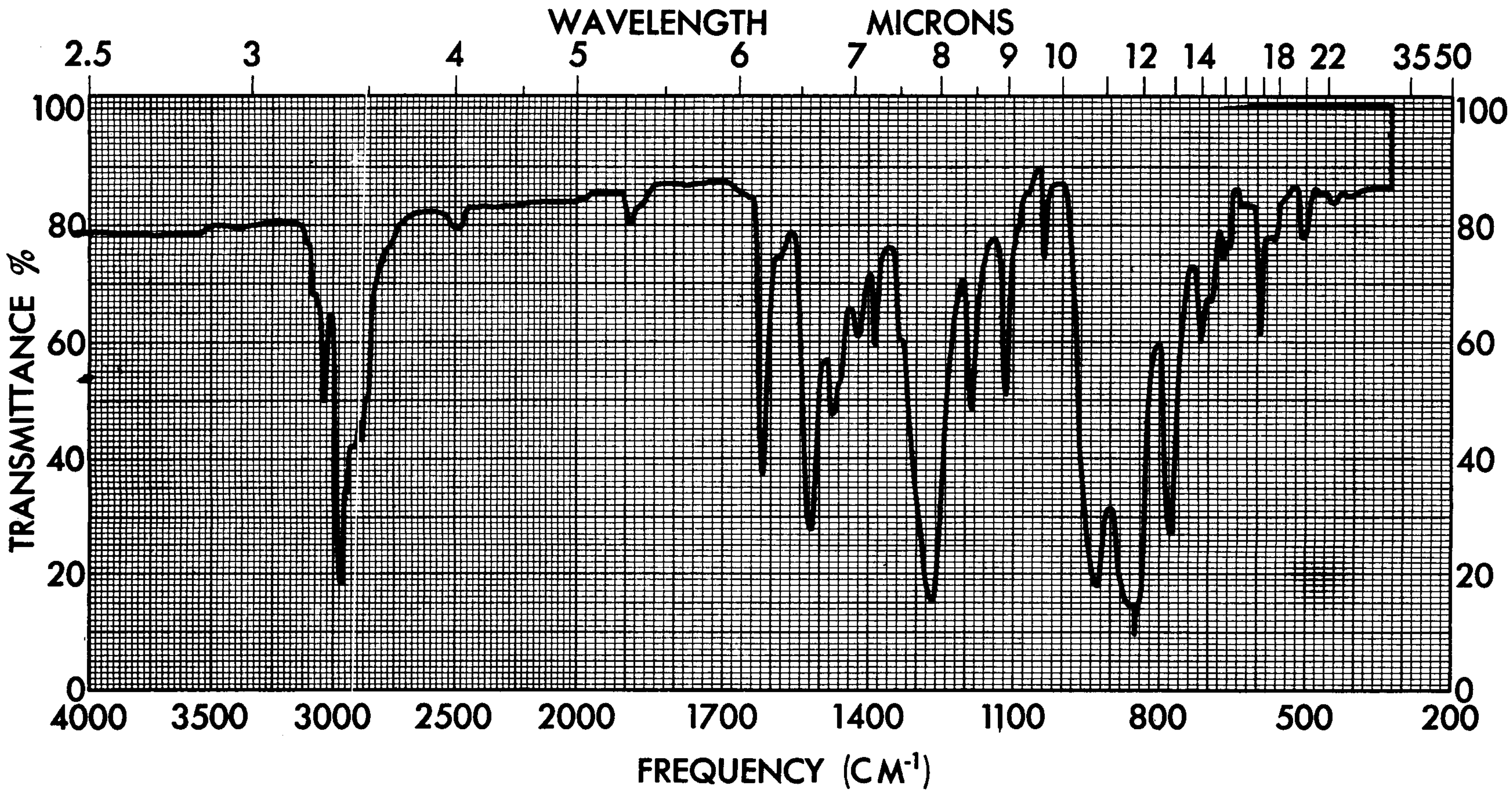
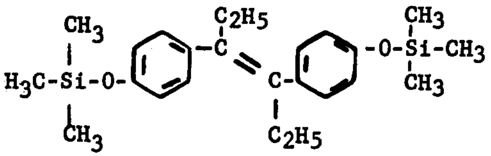


FIGURE 7.—INFRARED SPECTRUM OF COMPOUND VII



4,4'-BIS(TRIMETHYLSILOXY)DIPHENYL-α,α'-DIETHYLETHYLENE

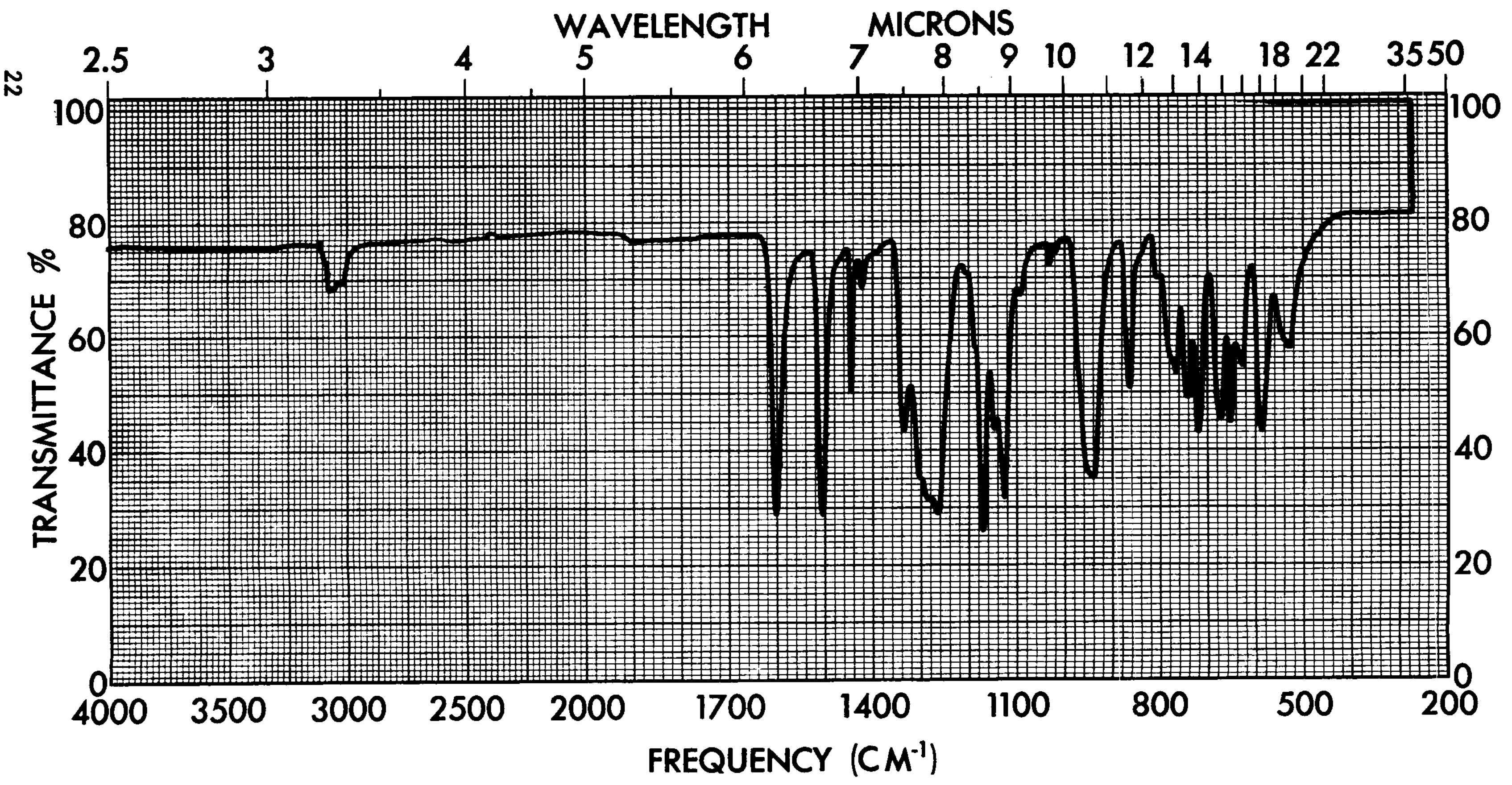
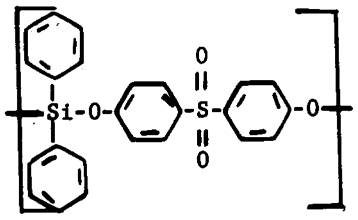


FIGURE 8.— INFRARED SPECTRUM OF POLYMER I



POLYDIPHENYLSILYL(4,4'-BISOXYDIPHENYLSULFONE)

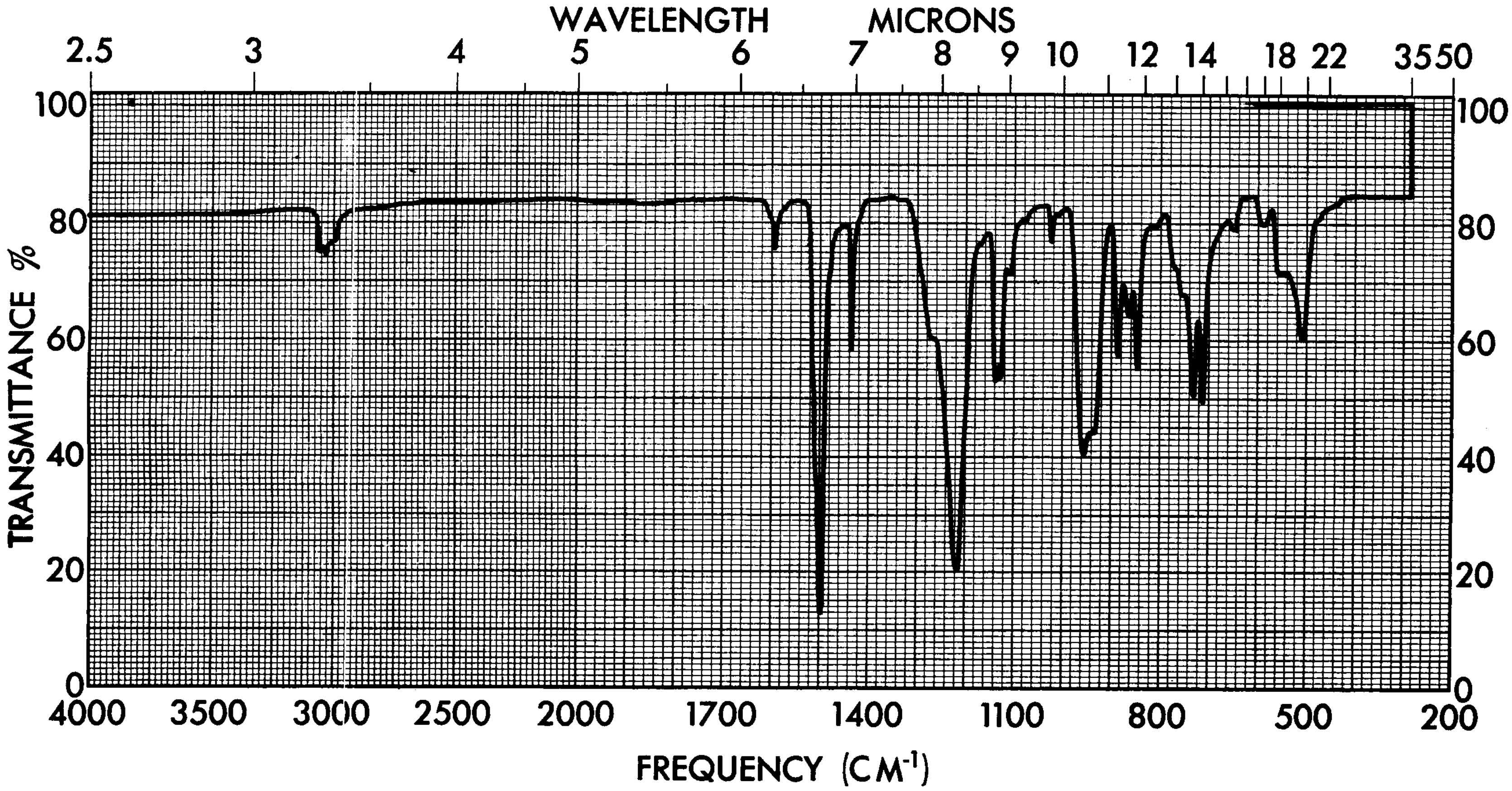
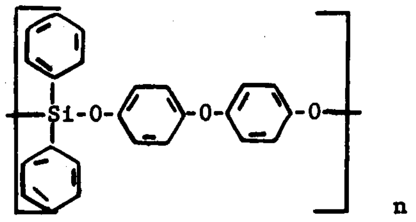


FIGURE 9.—INFRARED SPECTRUM OF POLYMER II



POLYDIPHENYLSILYL(4,4'-BISOXYDIPHENYLETHER)

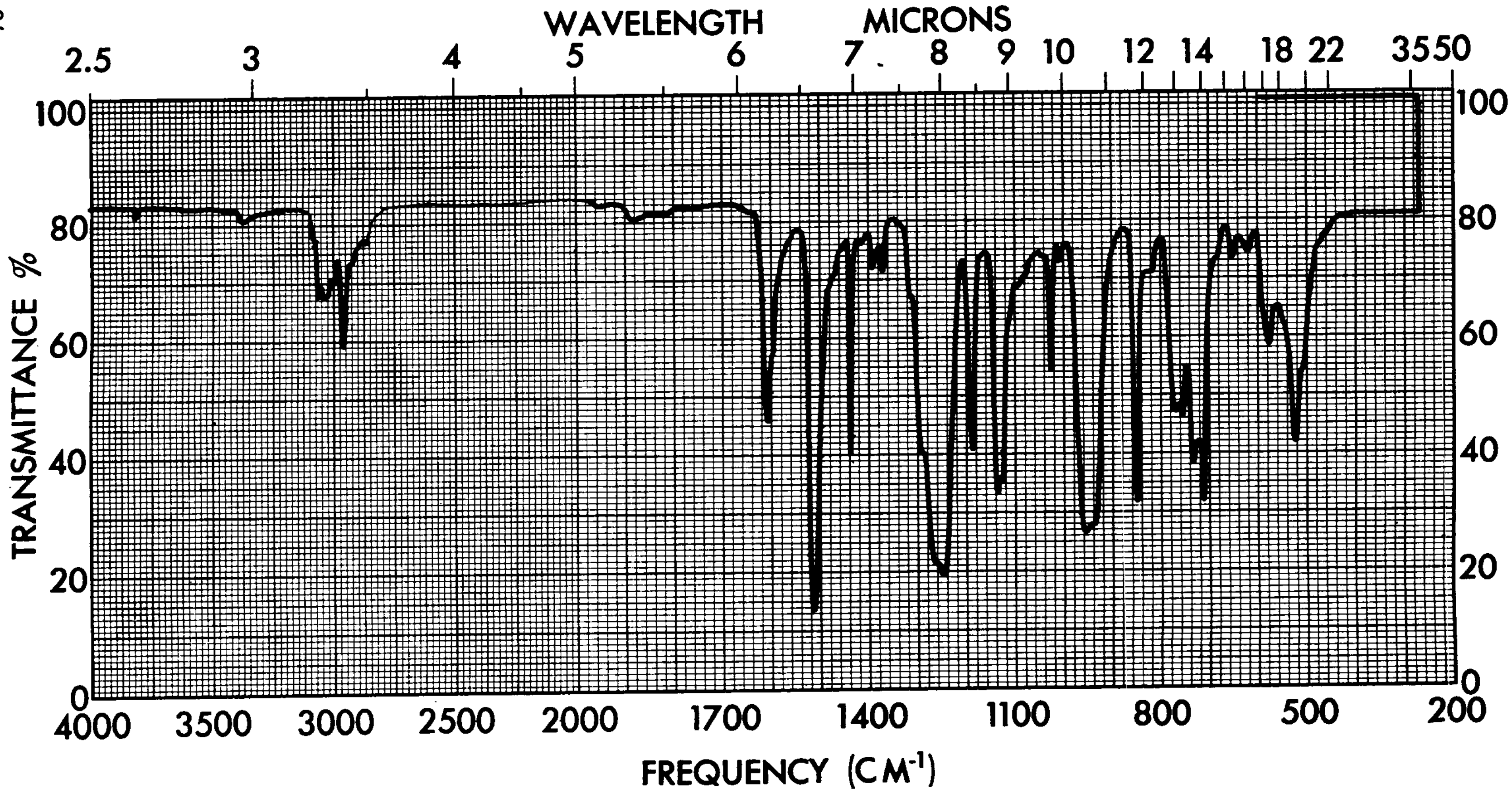
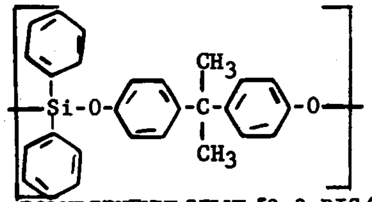


FIGURE 10.– INFRARED SPECTRUM OF POLYMER III



POLYDIPHENYLSILYL[2,2-BIS(4-OXYPHENYLENE)PROPANE]

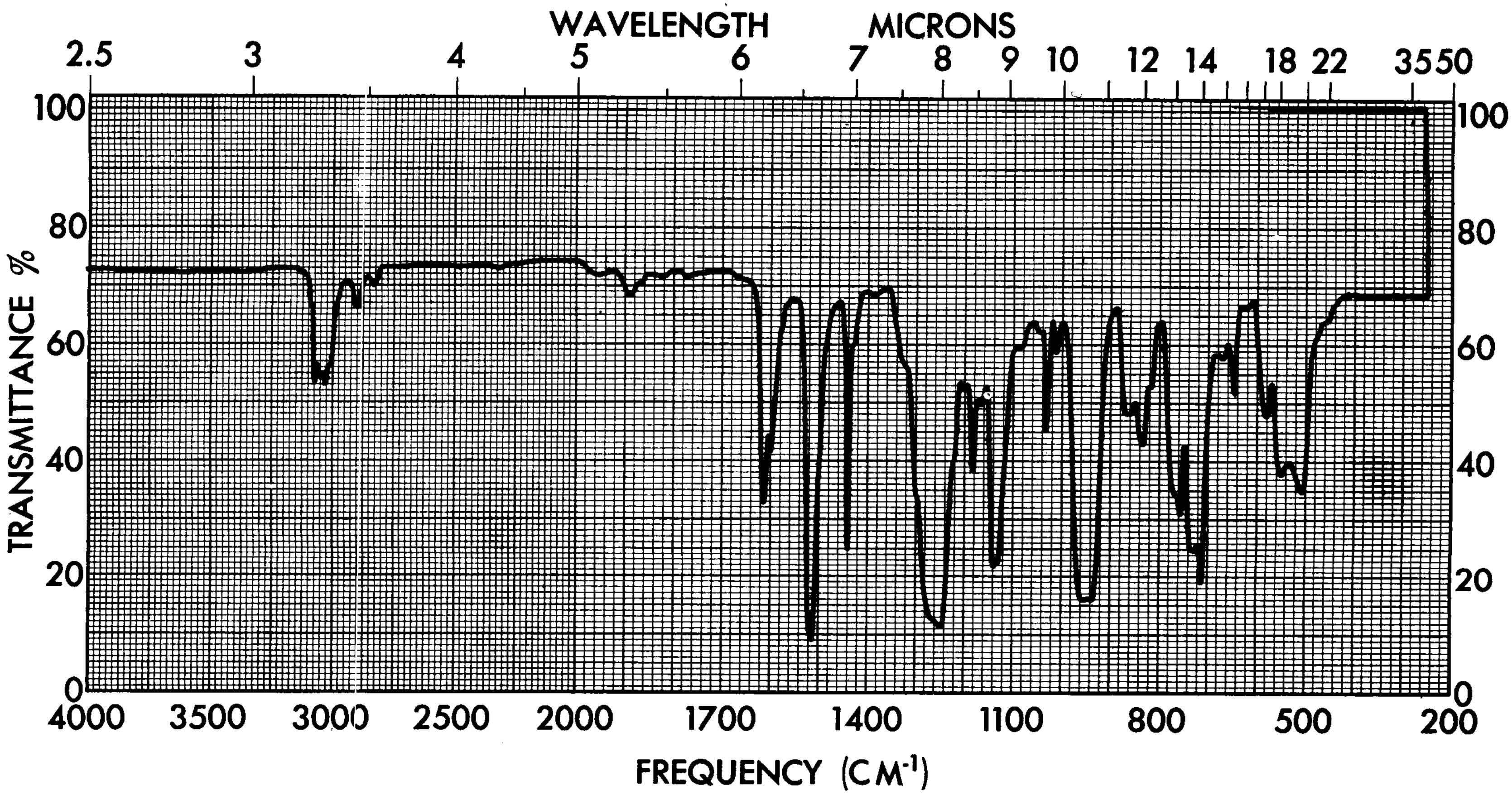
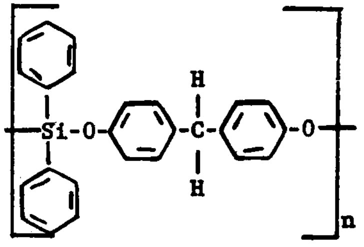


FIGURE 11. – INFRARED SPECTRUM OF POLYMER IV



POLYDIPHENYLSILYL(4,4'-BISOXYDIPHENYLMETHANE)

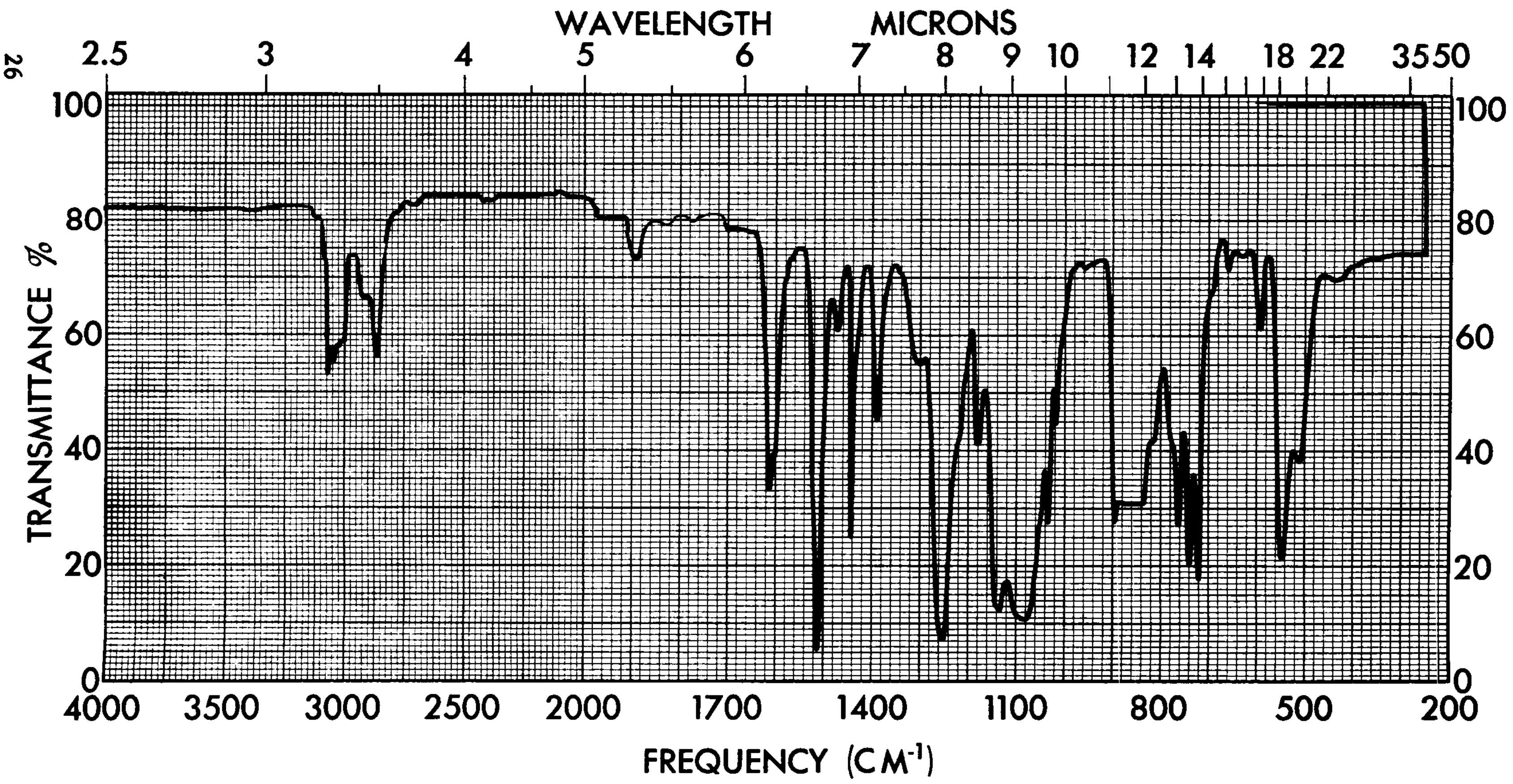
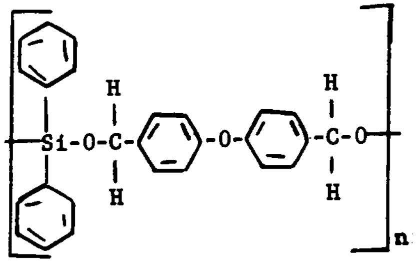


FIGURE 12. — INFRARED SPECTRUM OF POLYMER V



POLYDIPHENYLSILYL [4,4'-BIS(OXYMETHYLENE)DIPHENYLETHER]

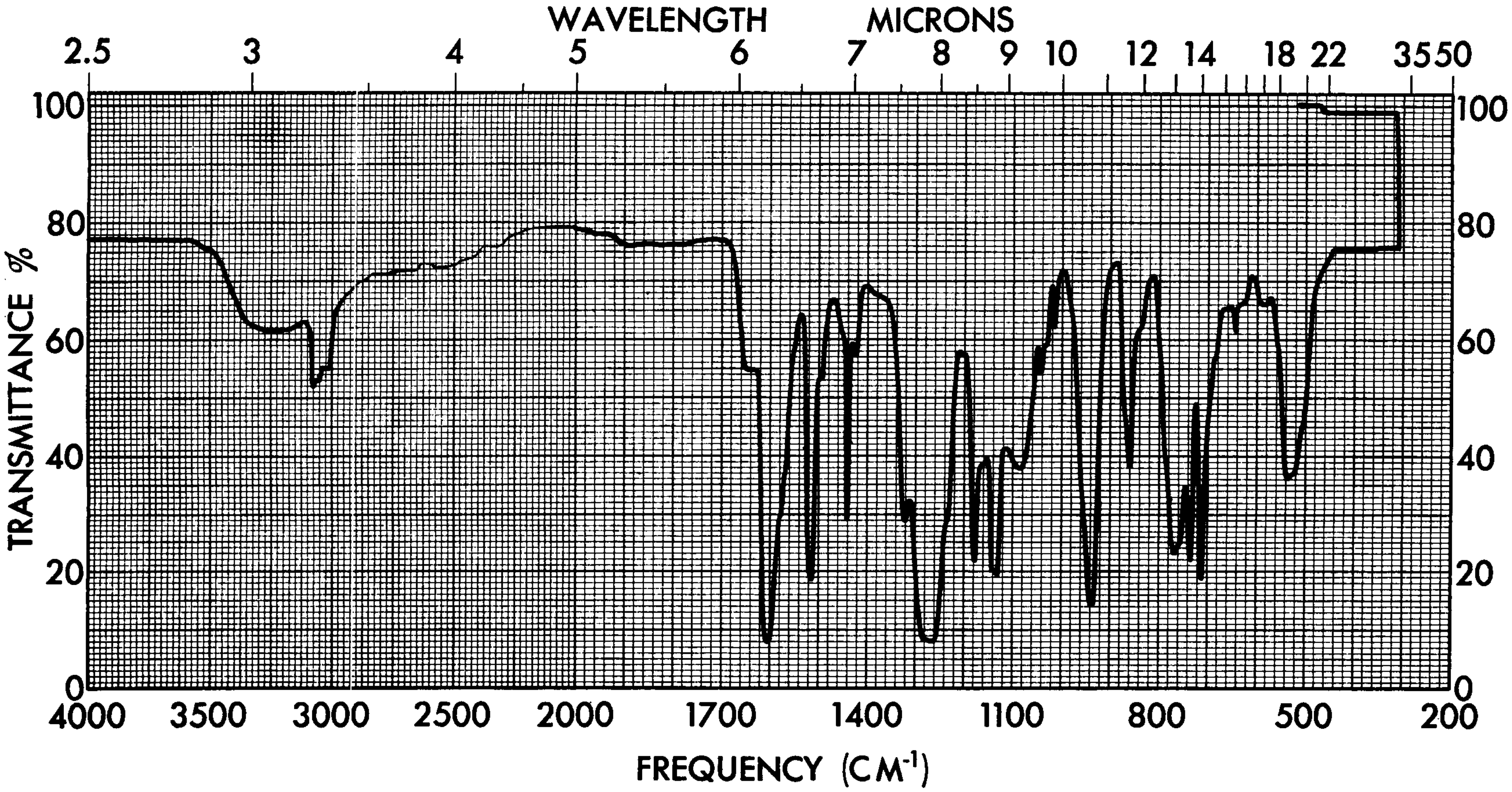
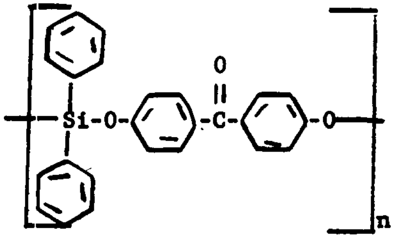


FIGURE 13.— INFRARED SPECTRUM OF POLYMER VI



POLYDIPHENYLSILYL(4,4'-BISOXYDIPHENYLKETONE)

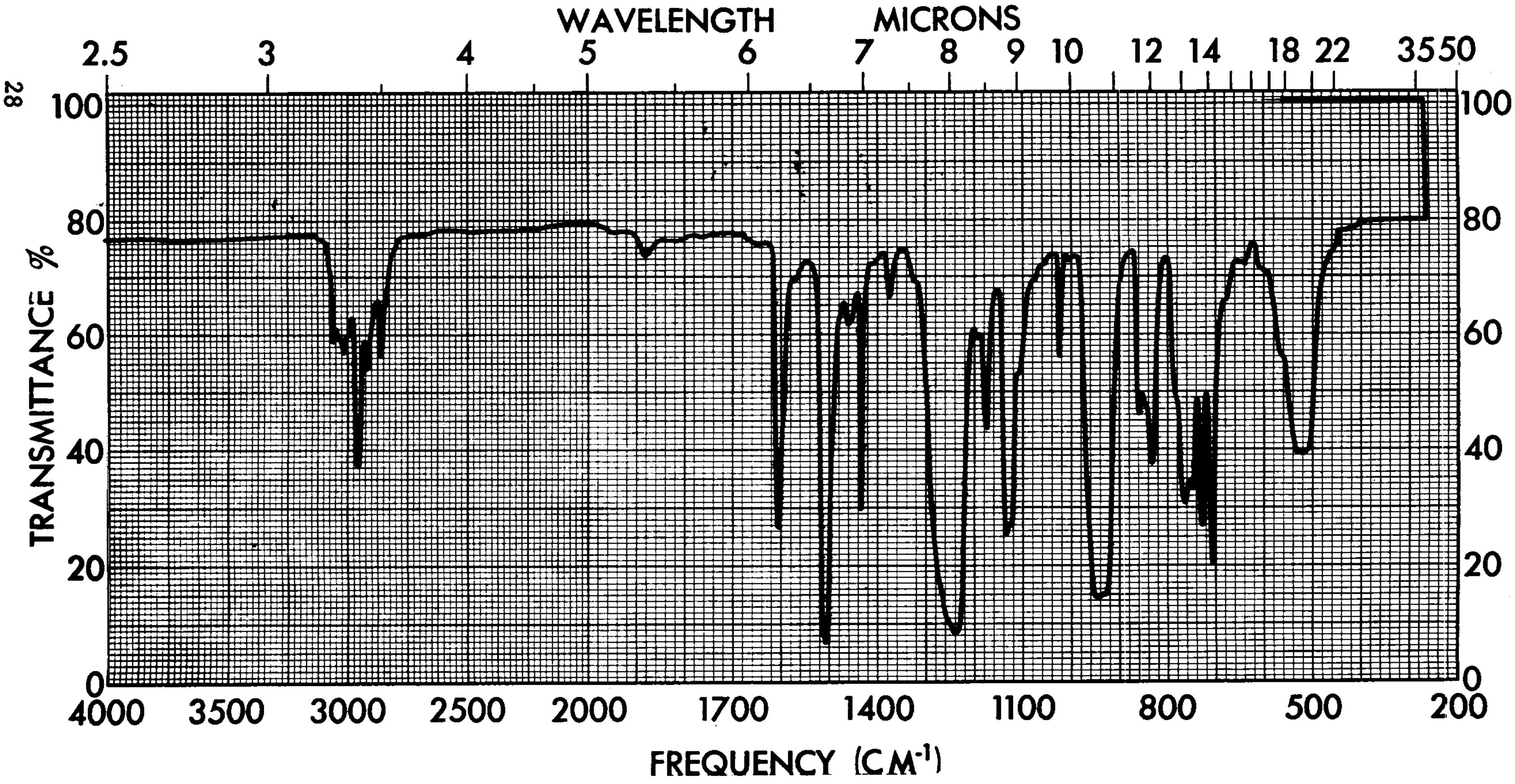
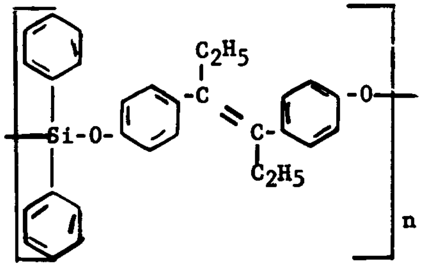


FIGURE 14.- INFRARED SPECTRUM OF POLYMER VII



POLYDIPHENYLSILYL(4,4'-BISOXYDIETHYLSTILBENE)

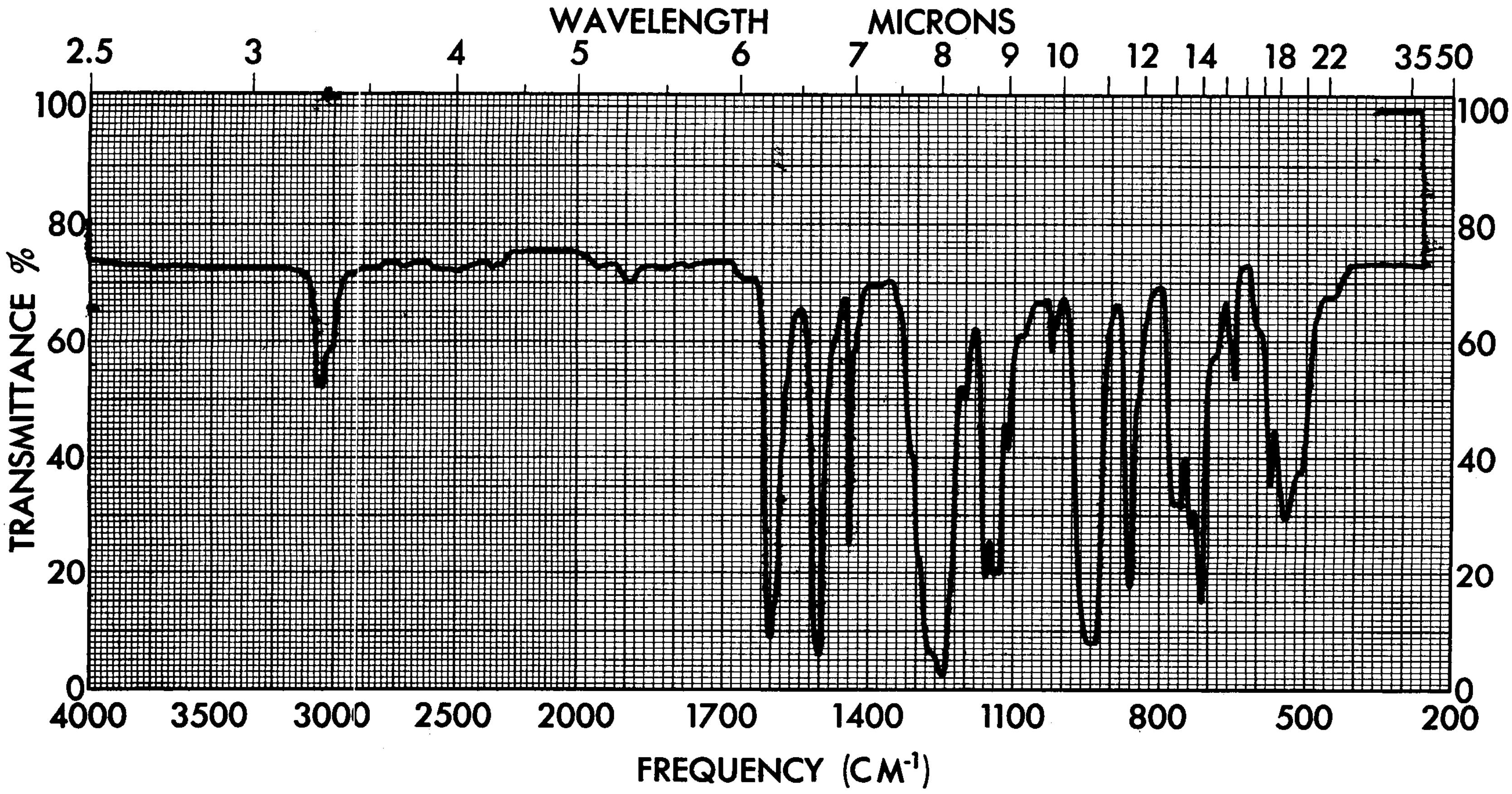
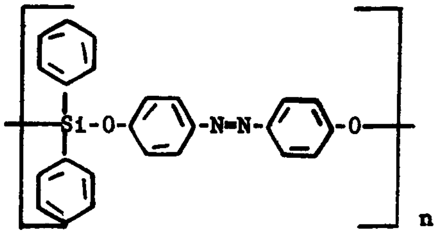


FIGURE 15.- INFRARED SPECTRUM OF POLYMER VIII



POLYDIPHENYLSILYL(4,4'-BISOXYDIPHENYLDIIMIDE)

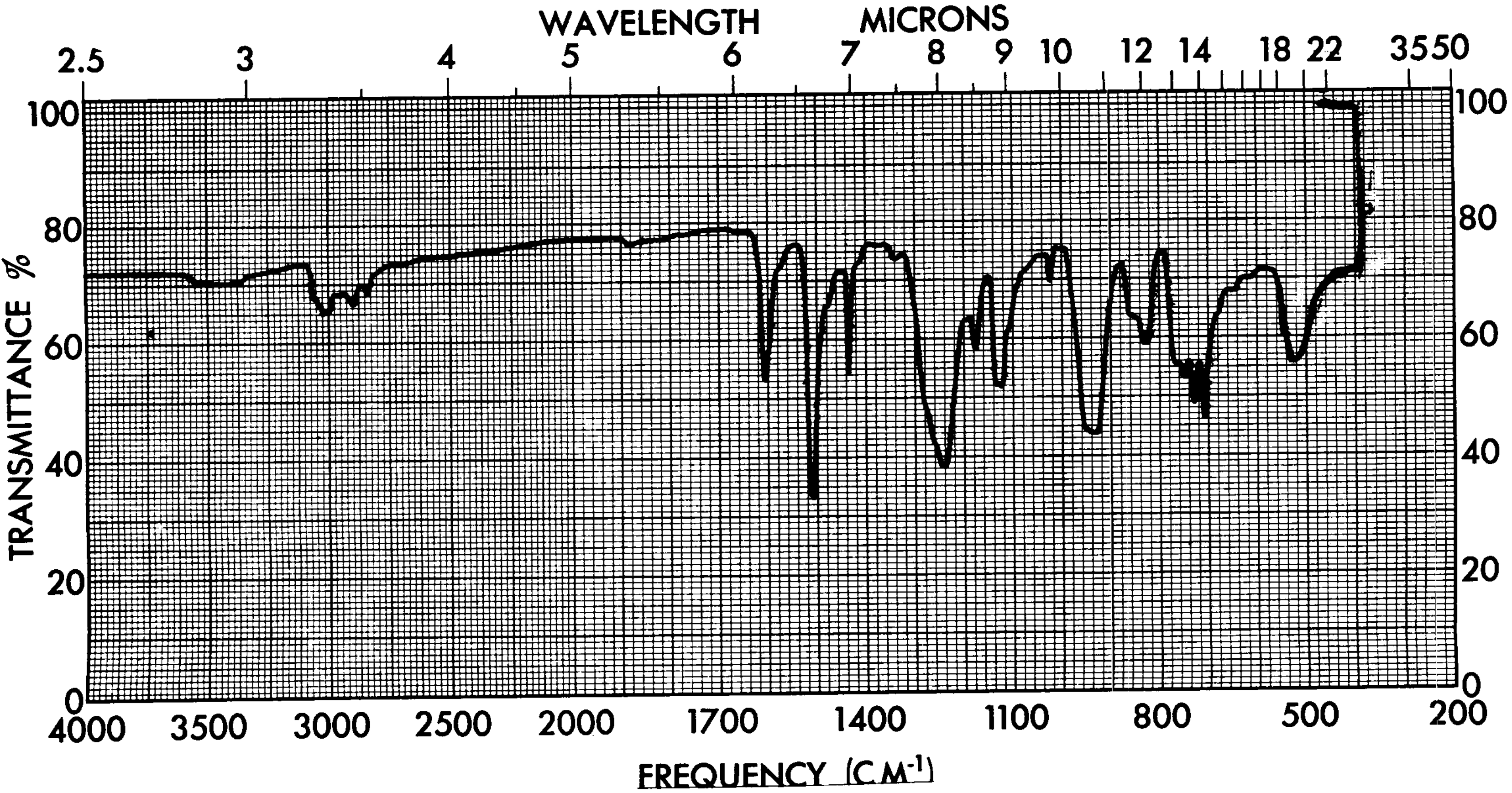
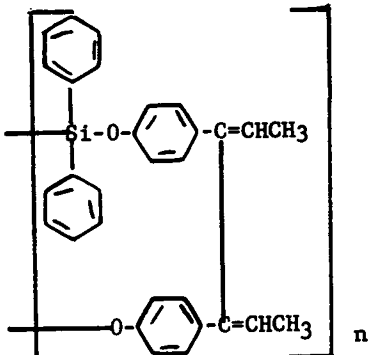


FIGURE 16.- INFRARED SPECTRUM OF POLYMER IX



POLYDIPHENYLSILYL [3,4-BIS(p-OXYPHENYL)-2,4-HEXADIENE]

SECTION B

THERMOGRAVIMETRIC ANALYSIS OF SELECTED POLYMERS

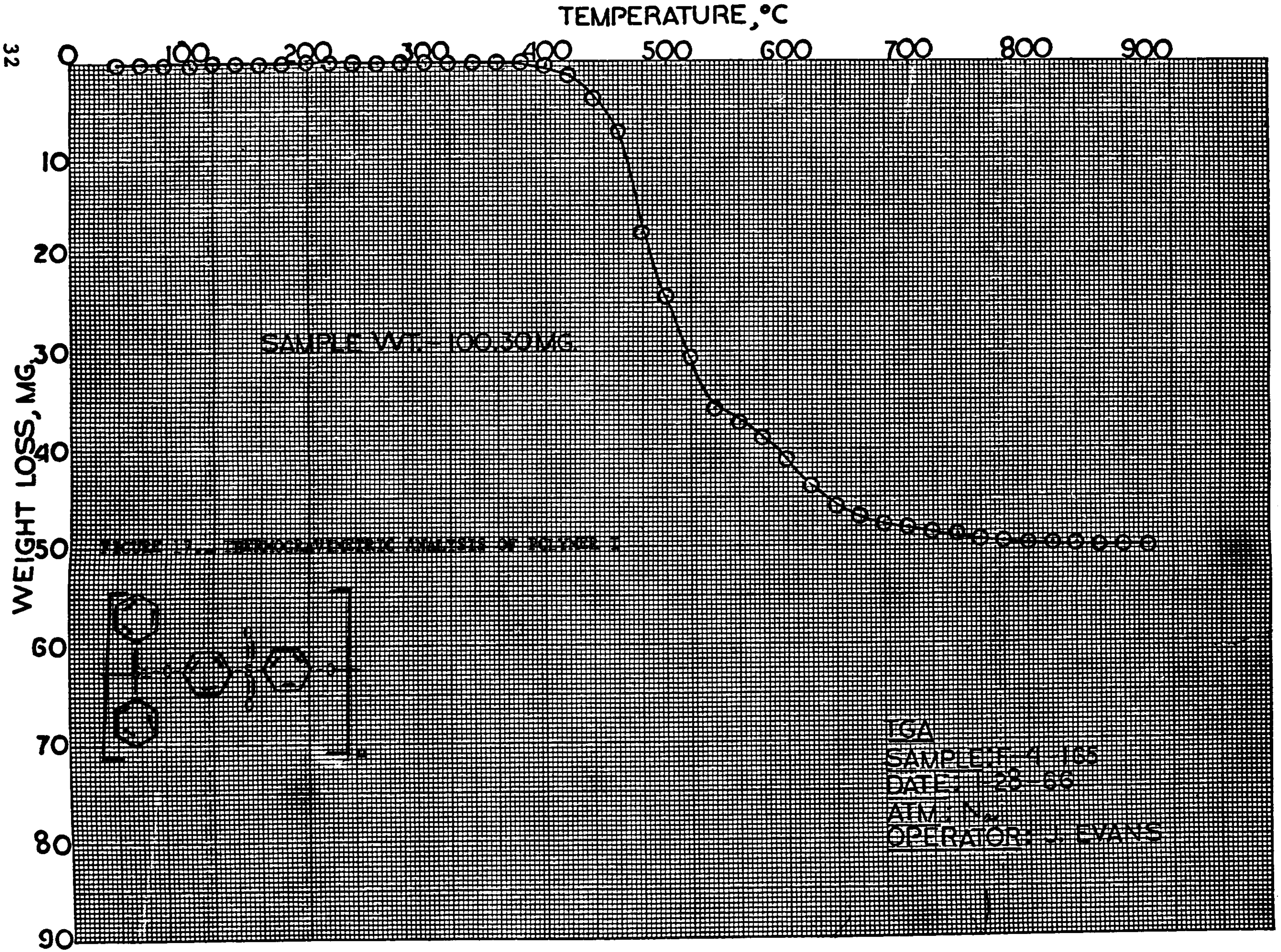


FIGURE 17. THERMOGRAVIMETRIC ANALYSIS OF POLYMER I

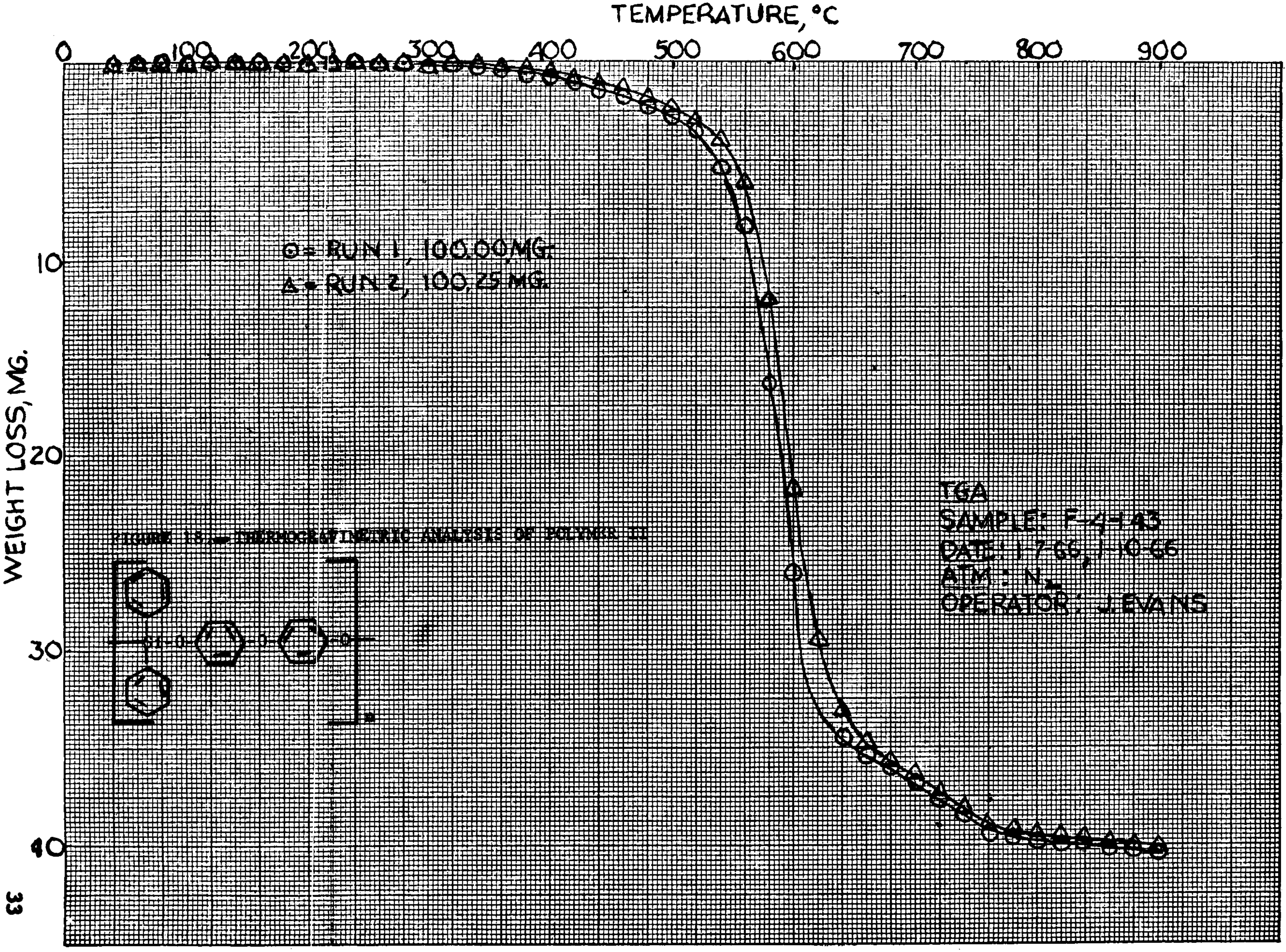


FIGURE 18. THERMOGRAVIMETRIC ANALYSIS OF POLYMER II

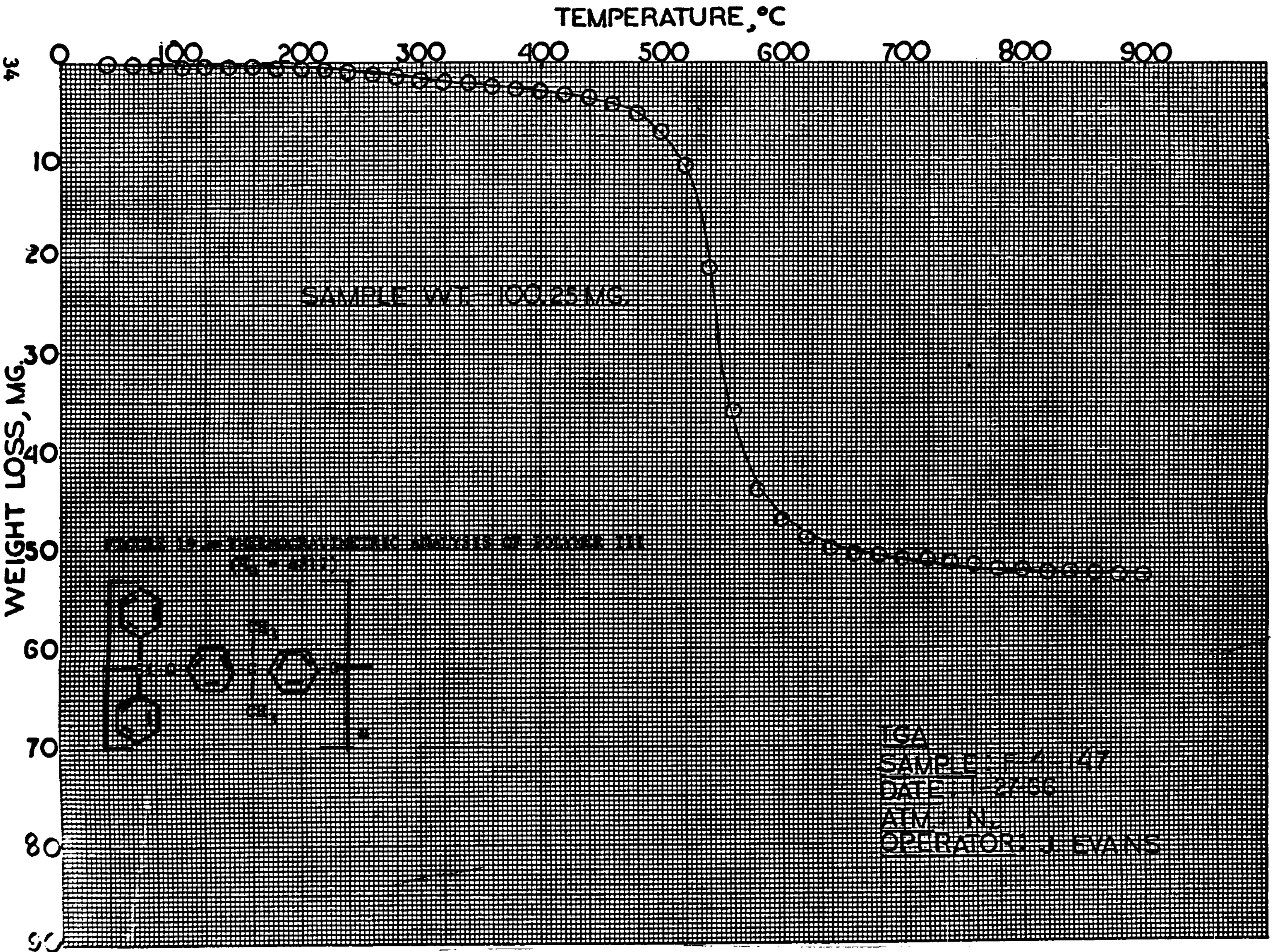


FIGURE 19. THERMOGRAVIMETRIC ANALYSIS OF POLYMER III ($\overline{M}_n$ = 4817)

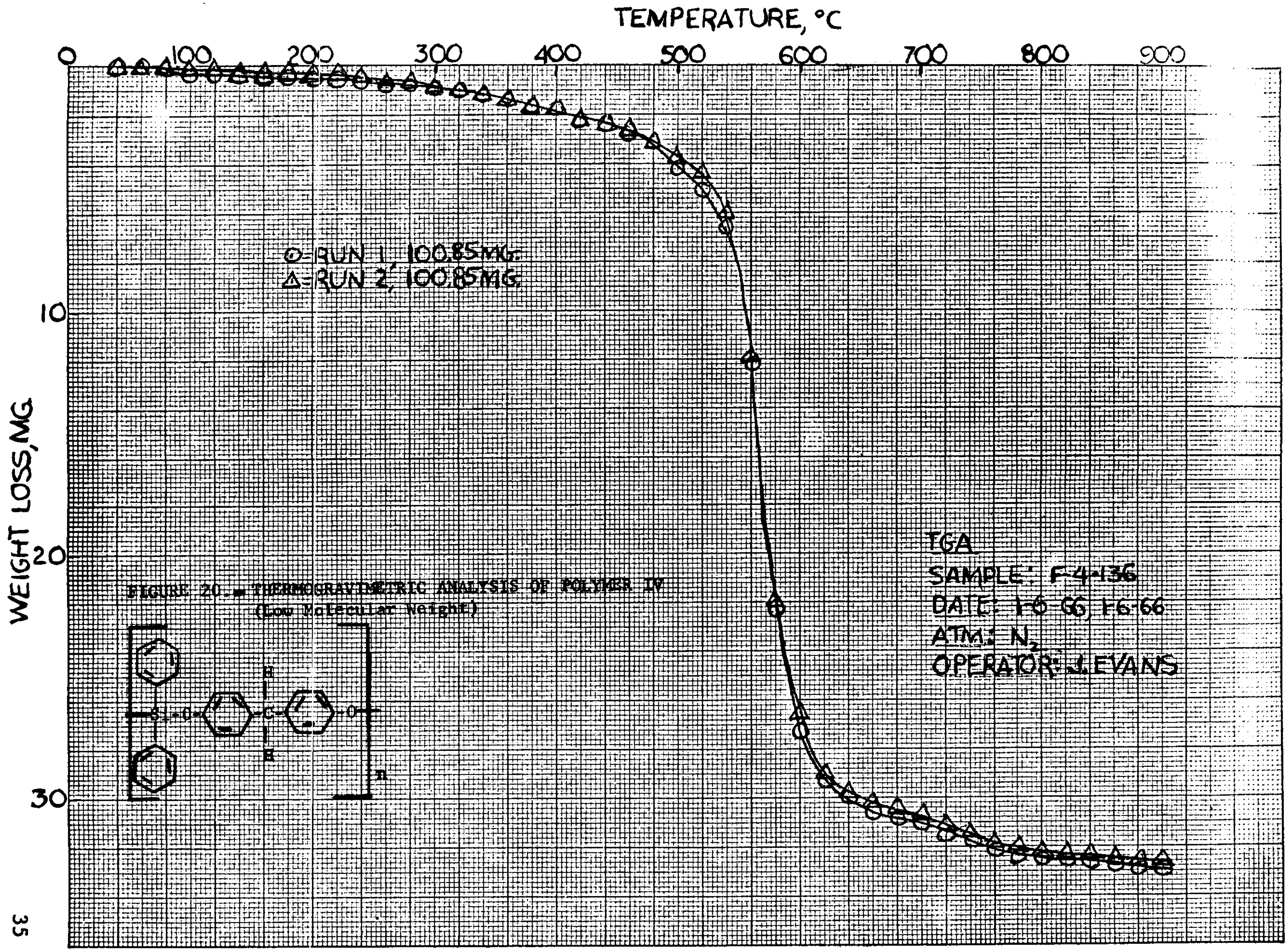


FIGURE 20. THERMOGRAVIMETRIC ANALYSIS OF POLYMER IV
(Low Molecular Weight)

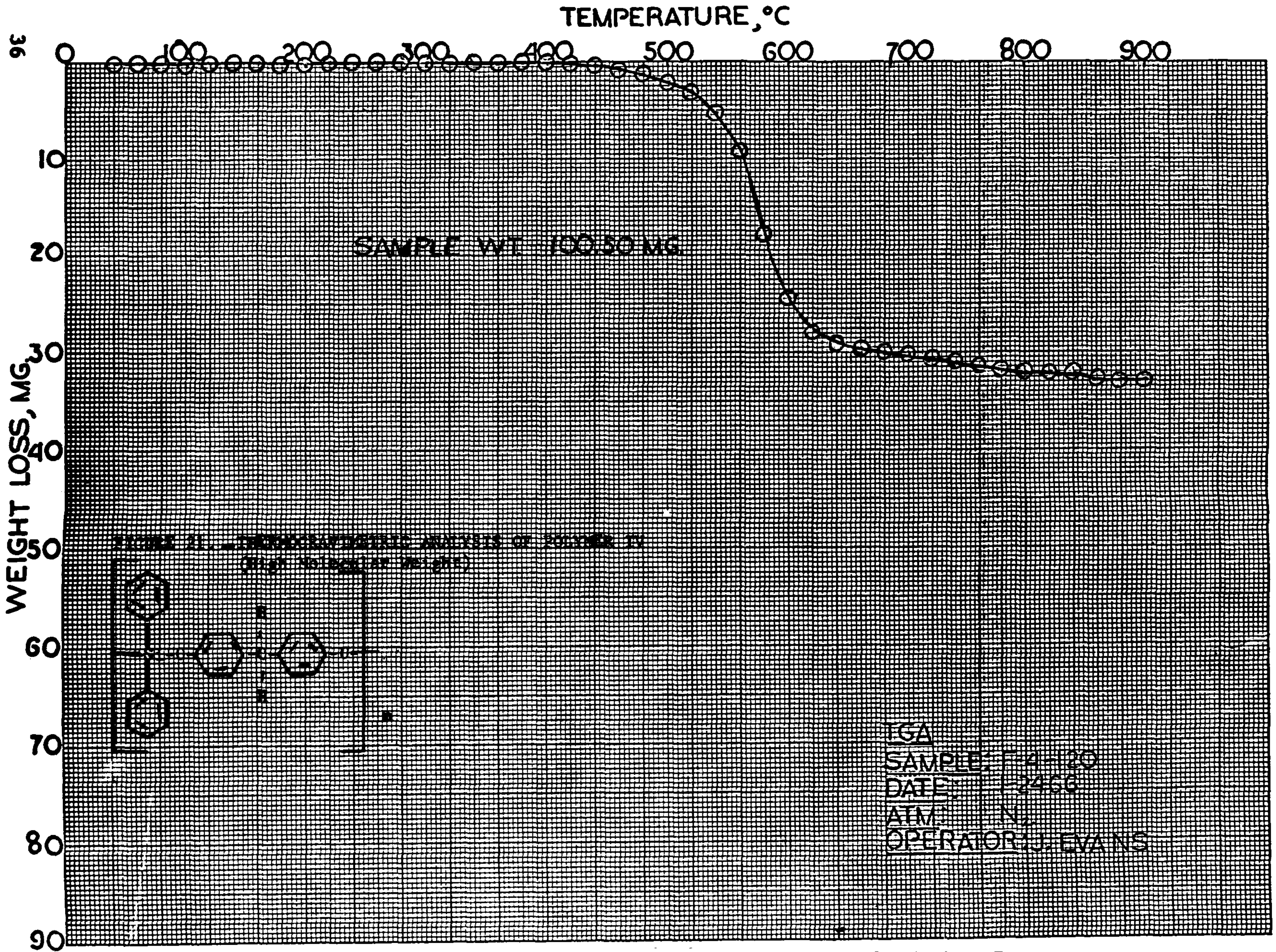


FIGURE 21. THERMOGRAVIMETRIC ANALYSIS OF POLYMER IV
(High Molecular Weight)

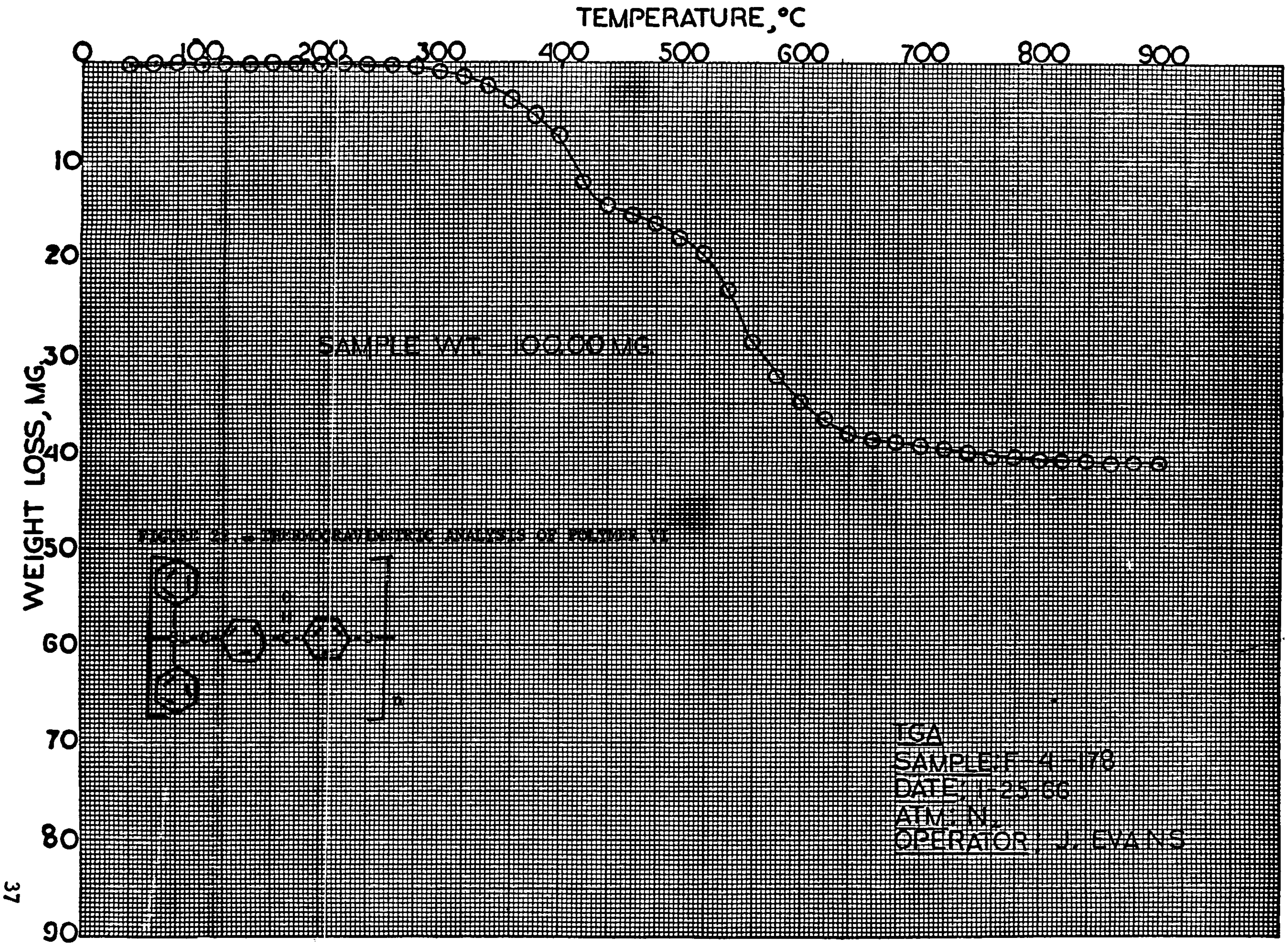


FIGURE 22. THERMOGRAVIMETRIC ANALYSIS OF POLYMER VI

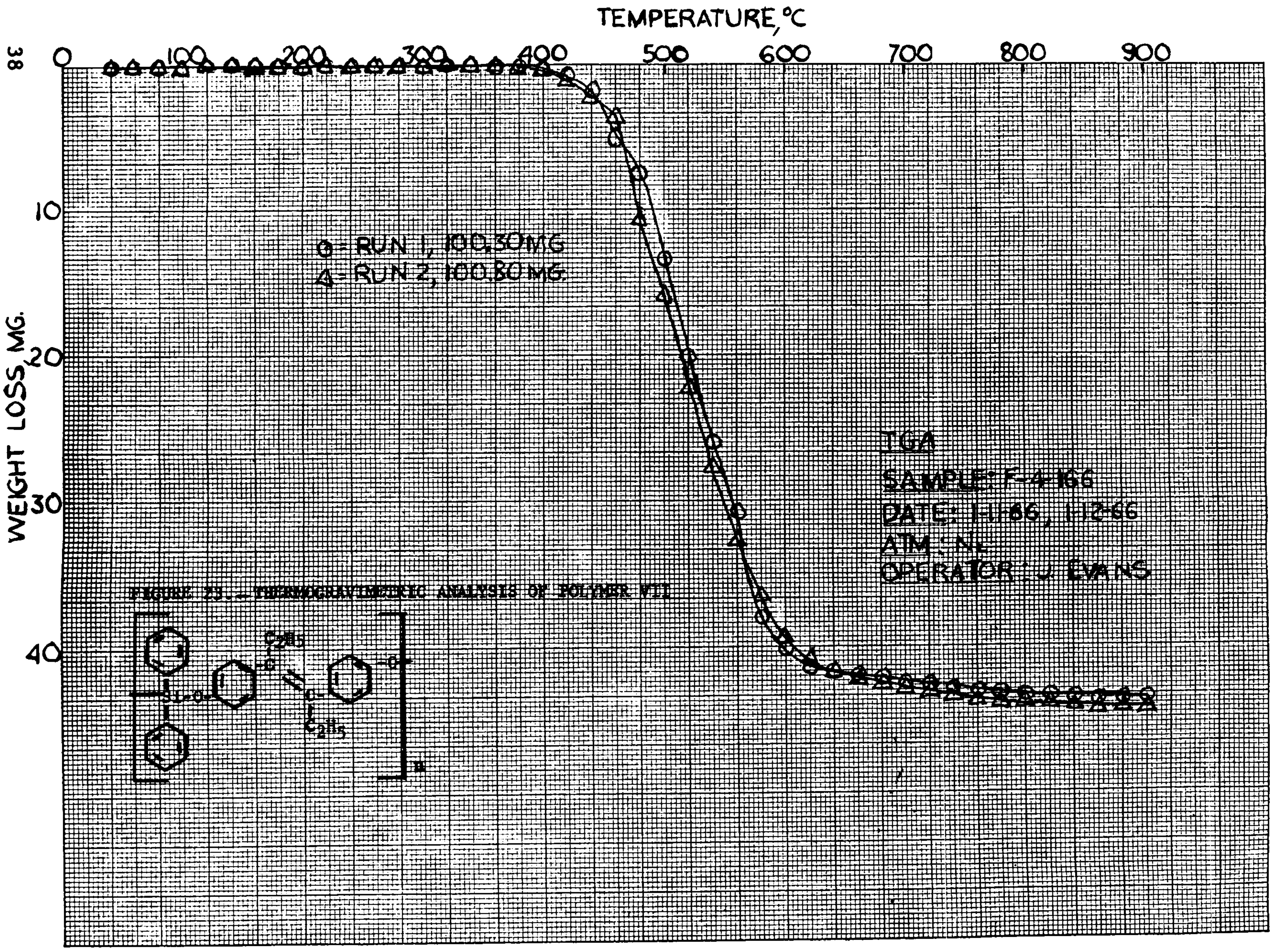


FIGURE 23. THERMOGRAVIMETRIC ANALYSIS OF POLYMER VII

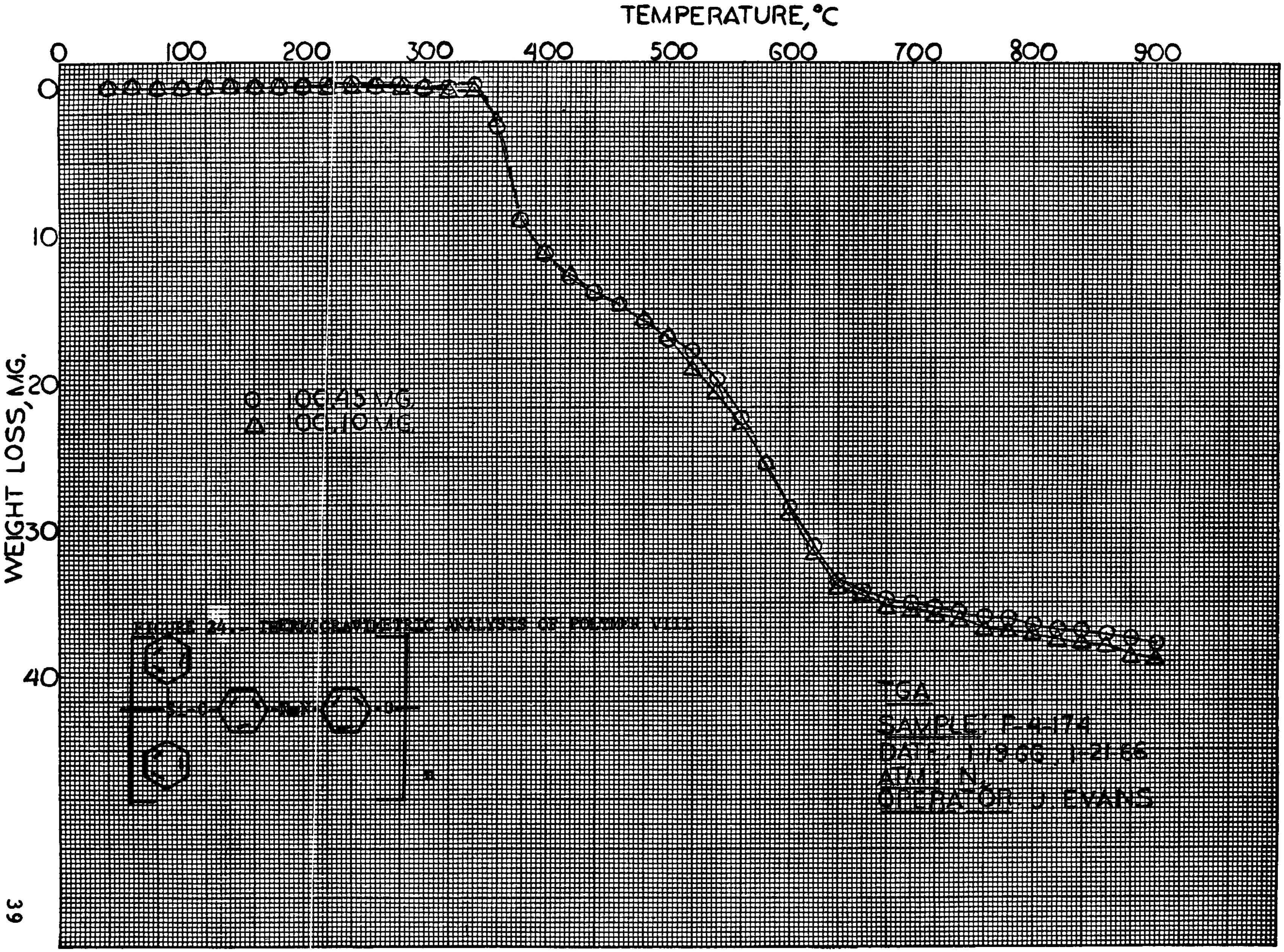


FIGURE 24. THERMOGRAVIMETRIC ANALYSIS OF POLYMER VIII

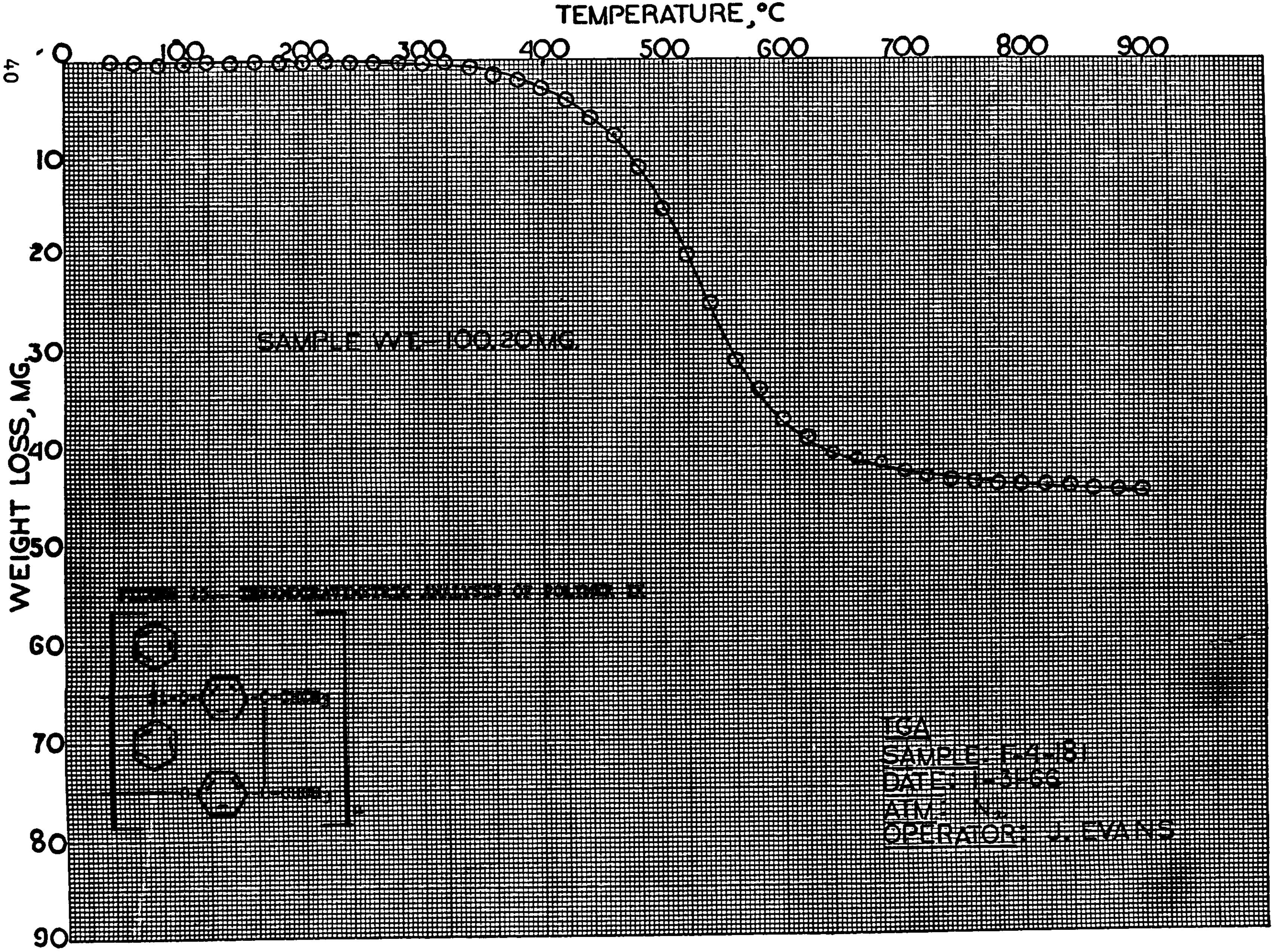
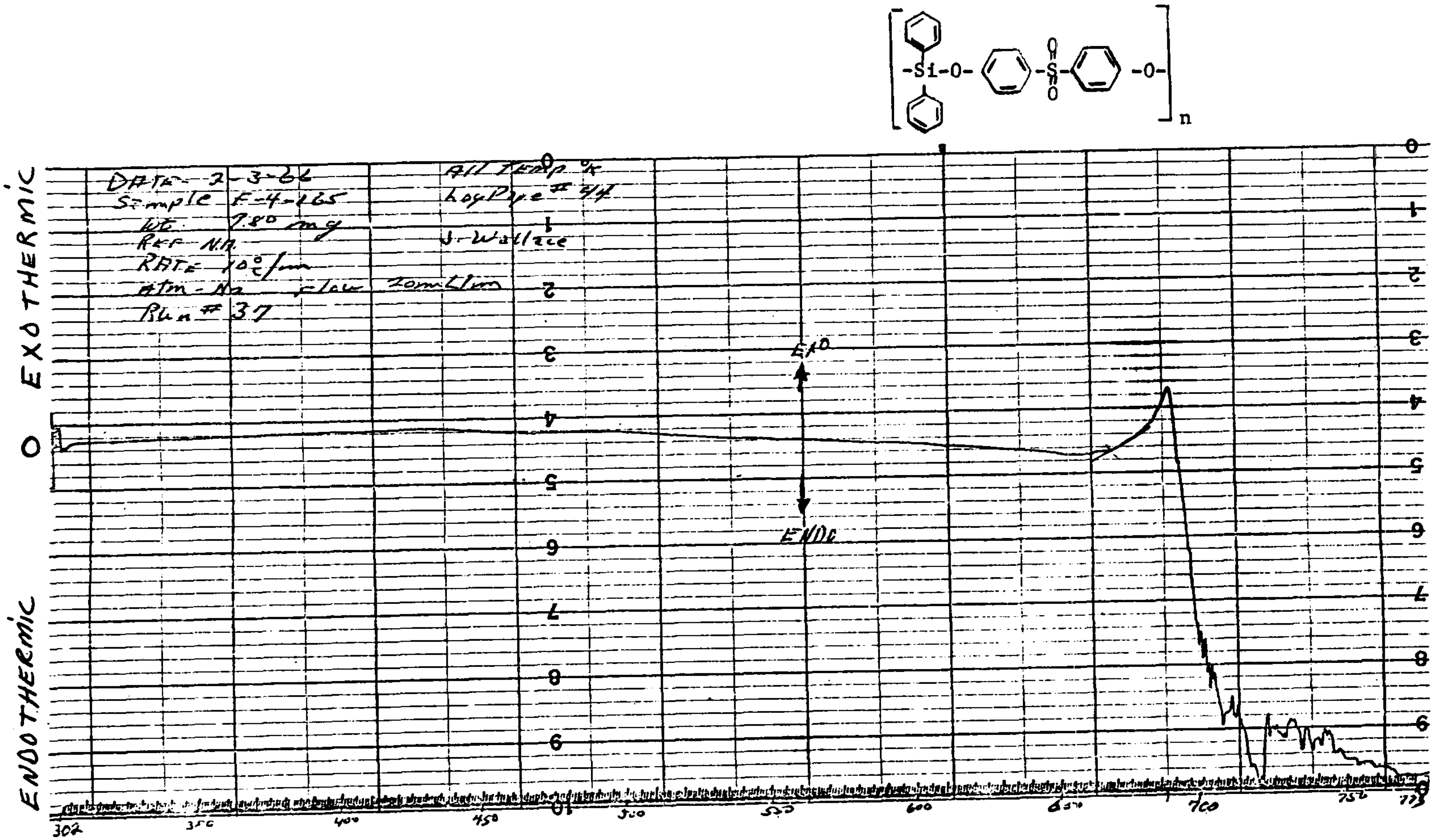


FIGURE 25. THERMOGRAVIMETRIC ANALYSIS OF POLYMER IX

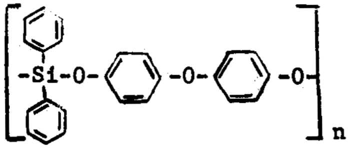
SECTION C

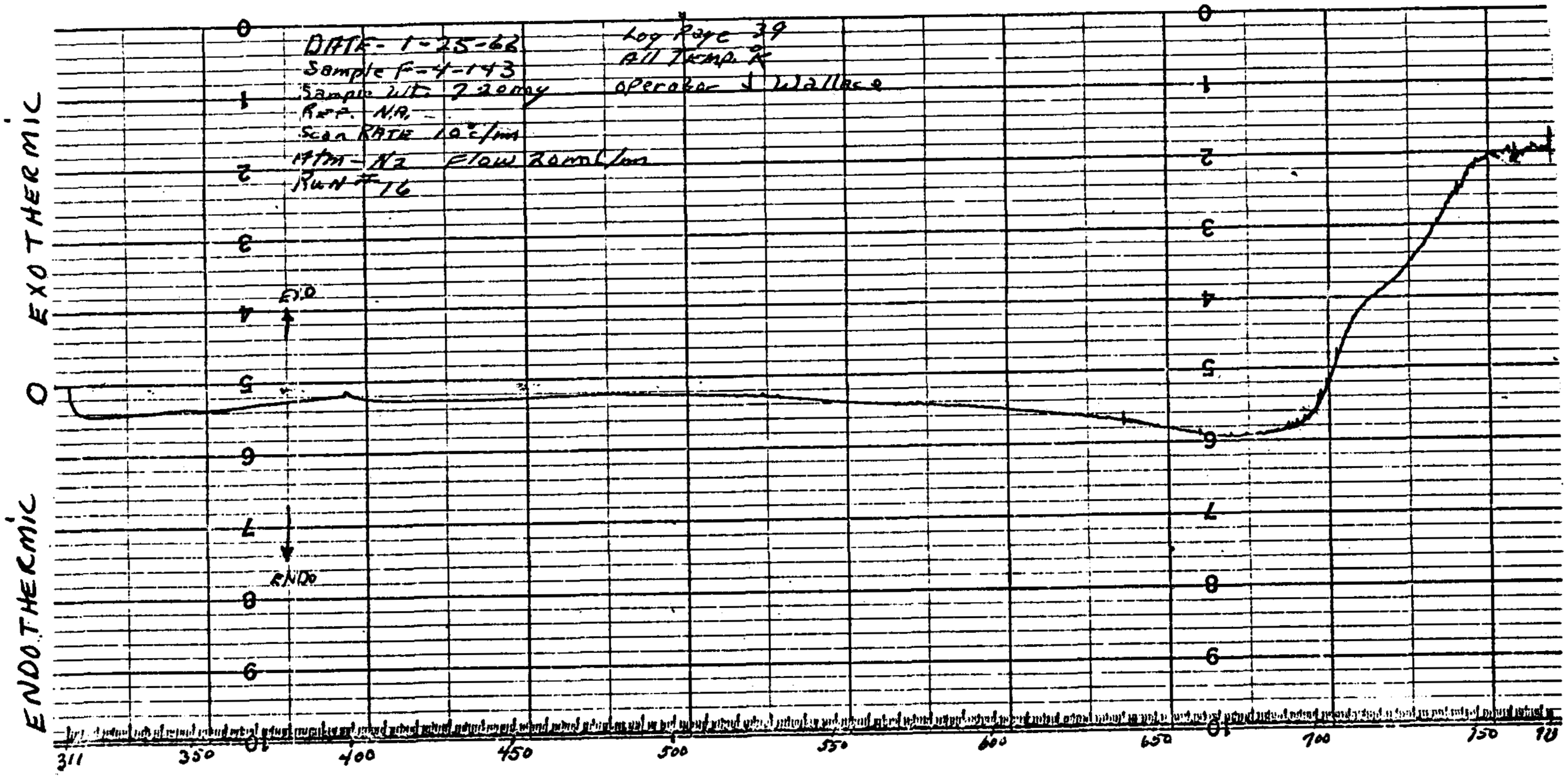
DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF MODEL COMPOUNDS AND POLYMERS



TEMPERATURE, °K

FIGURE 26.-DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER I

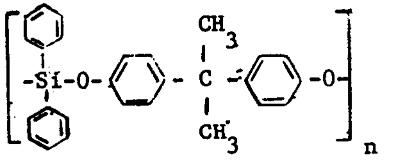




DATE - 1-25-62
Sample F-4-143
Sample Wt. 7.20mg
Ref. N.A. -
Scan RATE 10°c/min
Atm - N2 Flow 20ml/min
Run # 16
Log Page 39
All Temp °K
Operator J Wallace

TEMPERATURE, °K

FIGURE 27.- DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER II



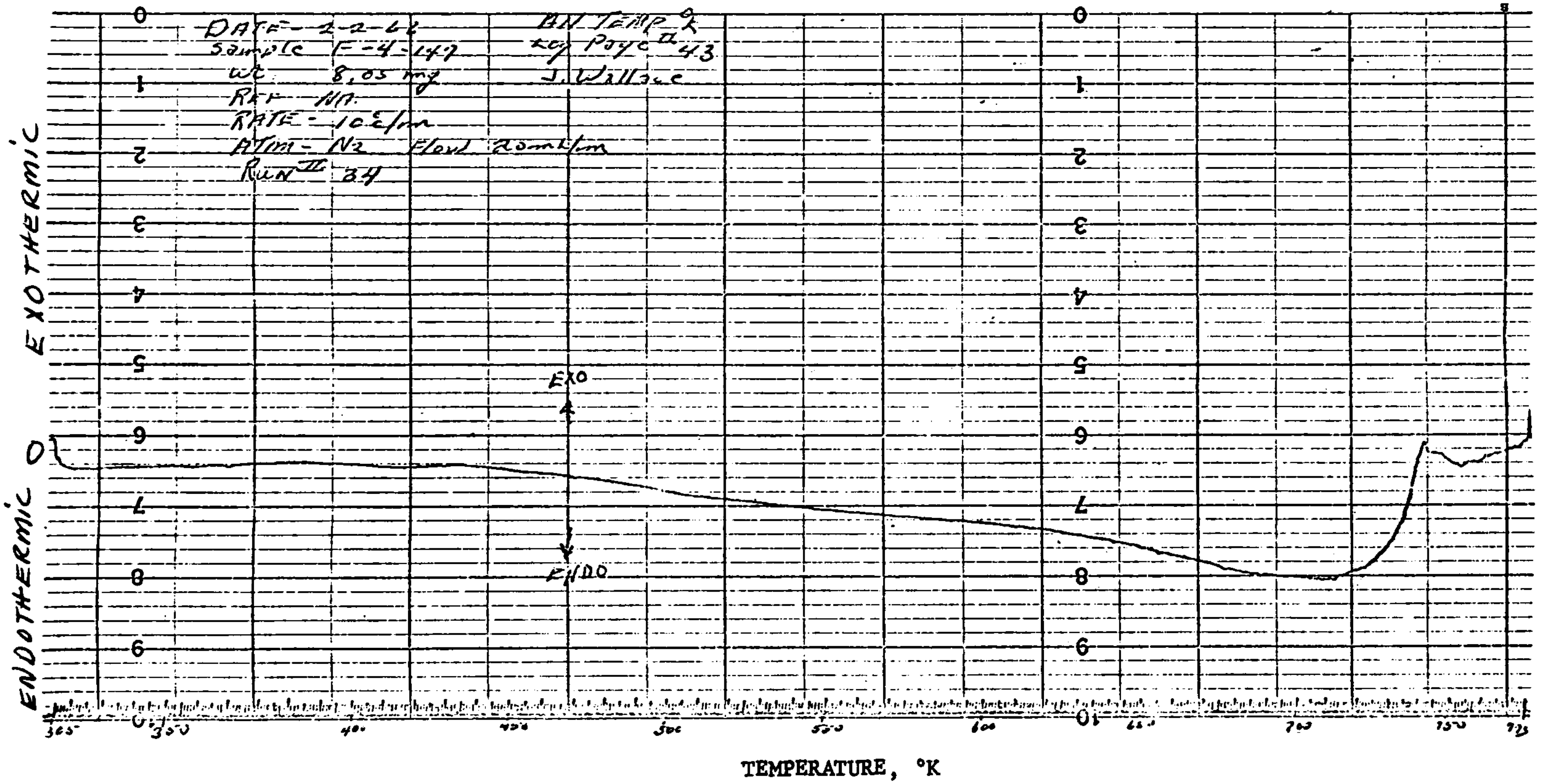
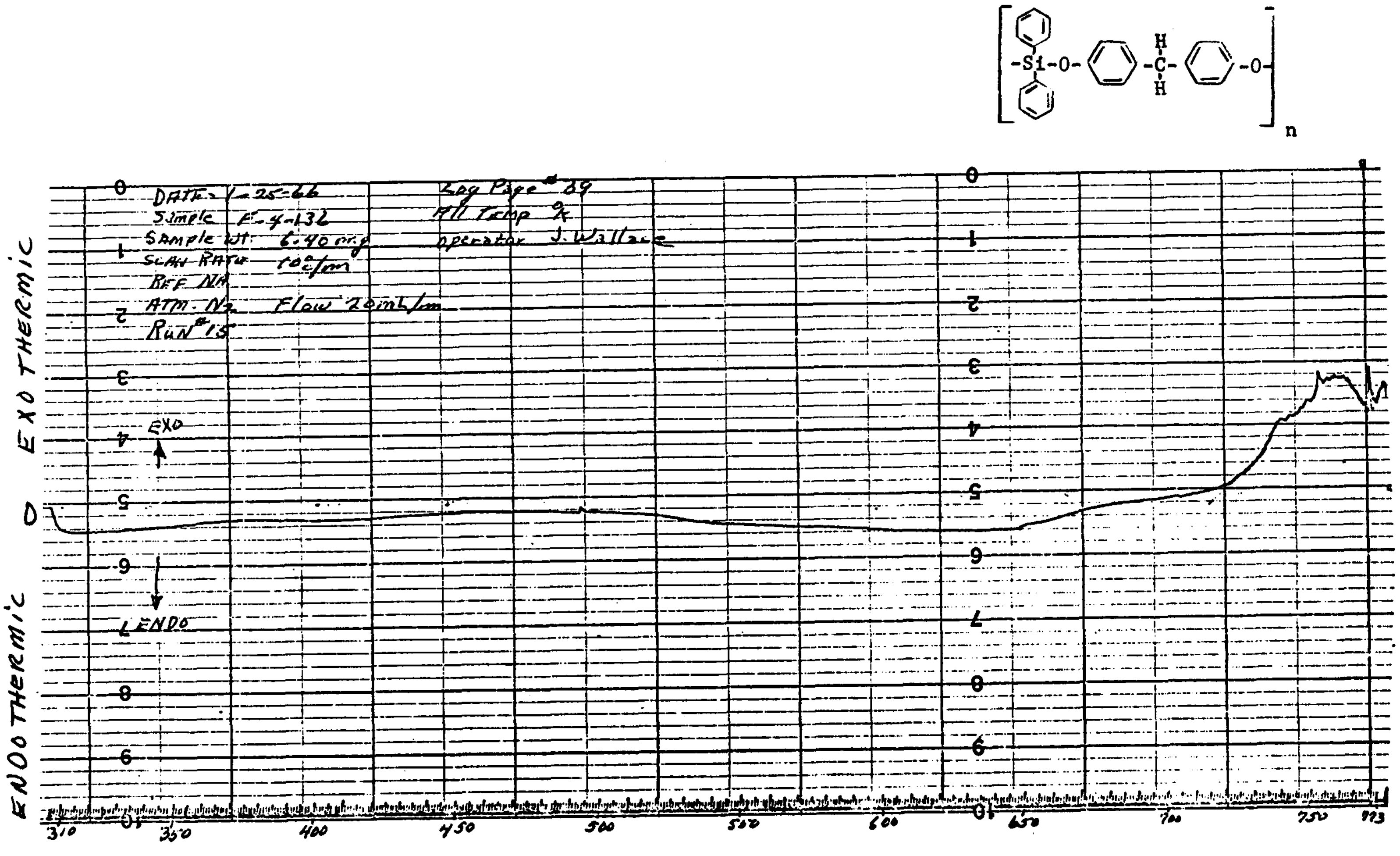


FIGURE 28.—DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER III



TEMPERATURE, °K

FIGURE 29.—DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER IV (LOW $\overline{M}_n$)

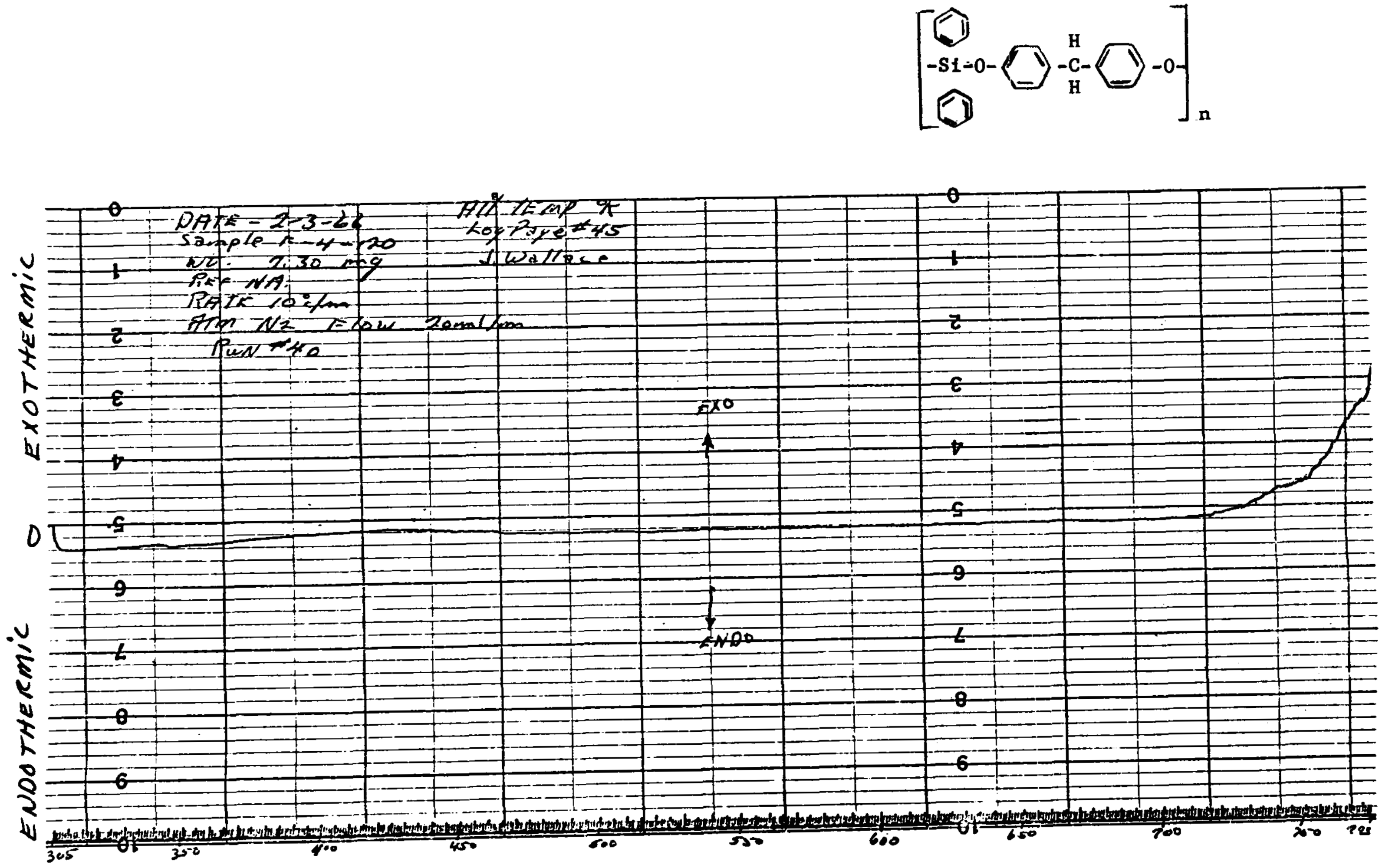
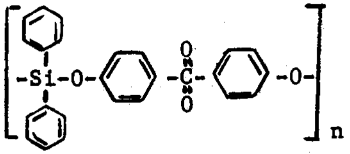
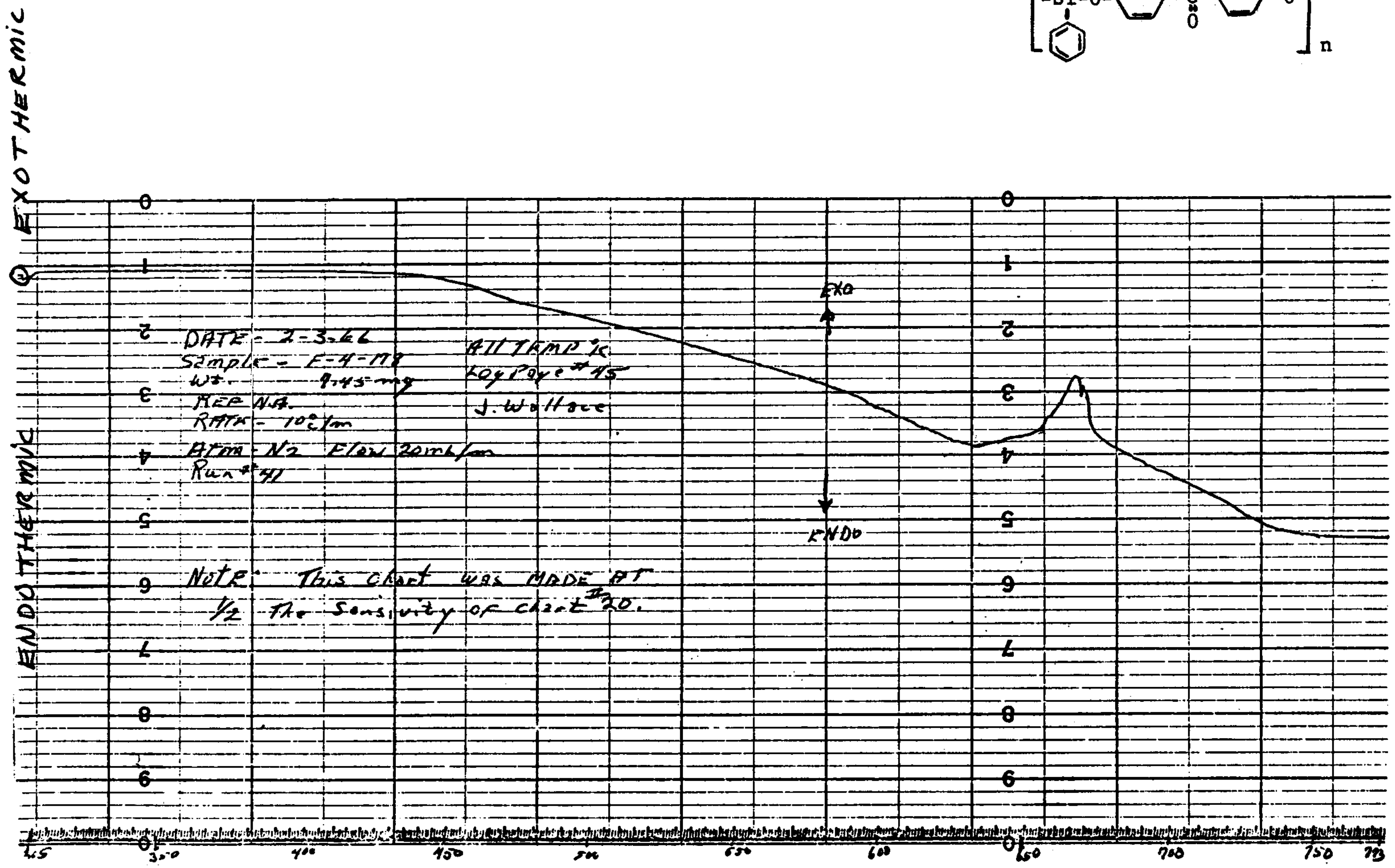


FIGURE 30.—DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER IV (HIGH $\overline{M}_n$)





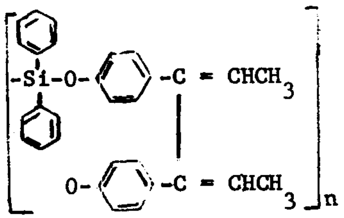
DATE - 2-3-66
Sample - F-4-178
Wt. 9.45 mg
REF N.A.
RATE - 10°c/m
Atm - N2 Flow 20ml/m
Run # 41

All TEMP °K
Log Page # 45
J. Wallace

Note: This chart was MADE AT 1/2 The Sensivity of chart #20.

TEMPERATURE, °K

FIGURE 31.—DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER VI



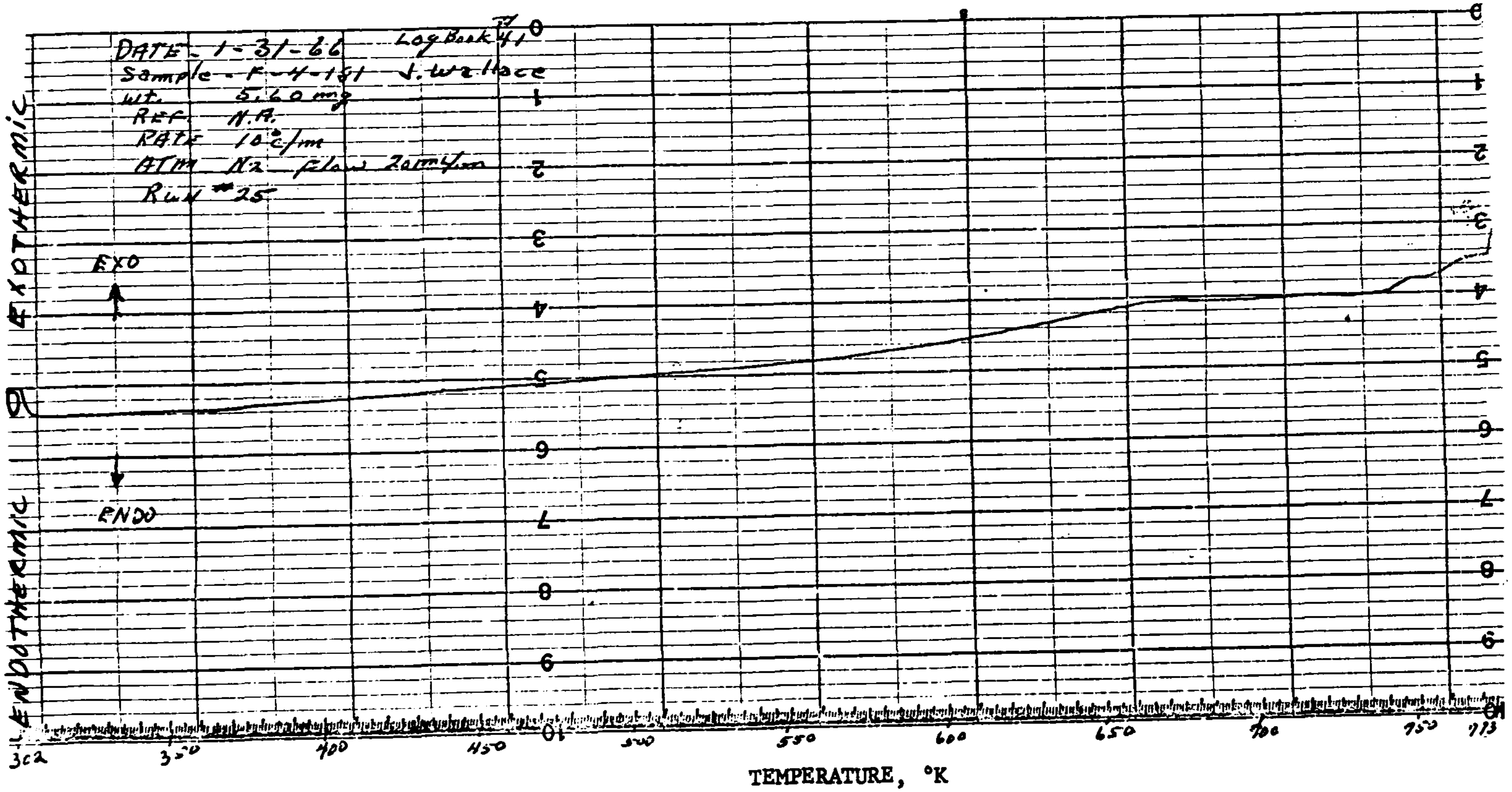


FIGURE 32.—DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF POLYMER IX

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November 14, 1966 APPROVAL NASA TM X- 53536

EFFECT OF MOLECULAR STRUCTURE ON PHYSICAL CHARACTERISTICS OF POLYARYLOXYSILANES AND RELATED COMPOUNDS

By Mary H. Fowler

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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