SECOND ANNUAL SUMMARY REPORT

on

PROCESS DEVELOPMENT AND PILOT-PLANT PRODUCTION OF SILANE POLYMERS OF DIOLS

to

GEORGE C. MARSHALL SPACE FLIGHT CENTER

June 22, 1967

by

W. R. Dunnavant, R. A. Markle,
R. G. Sinclair, and P. B. Stickney

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BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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ABSTRACT

This report describes exploratory efforts to develop crosslinkable polyaryloxysilanes of a wide variety of types. A number of di- and trianilinosilane and tri- and tetraphenoxysilane compounds were prepared for use as monomers in these studies.

Linear polyaryloxysilanes having phenyl, methyl, or methyl and vinyl pendent groups were prepared and found to have potentially useful mechanical and electrical properties at ambient temperatures. The vinyl-substituted polymers were crosslinked by free-radical catalysts to provide insoluble and infusible materials, and crosslinking was found to improve their thermal and thermal-oxidative stabilities. Several allyl-substituted polyaryloxysilanes were also prepared and successfully crosslinked by free-radical catalysts to provide polymers that were insoluble and infusible. It was found that the response to free-radical crosslinking and the thermal-oxidative stabilities of certain polyaryloxysilanes were improved if contaminants (probably condensation side products and/or unreacted monomers) were removed from the polymers.

A series of three-dimensional polyaryloxysilane structures was prepared by crosslinking low molecular weight phenolic OH-terminated polymers with tetra- or triphenoxysilanes. Several of these cured polymers demonstrated exceptionally promising coating properties despite the fact that they underwent moderate weight losses upon prolonged exposure in air at 250 C.

Several of the polymer types explored during this program are believed to warrant further development efforts.

FOREWORD

This report was prepared by Battelle Memorial Institute under Contract NAS8-11837, "Process Development and Pilot-Plant Production of Silane Polymers of Diols", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch of the George C. Marshall Space Flight Center, with Dr. Lindsey Hobbs acting as project manager.

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PROCESS DEVELOPMENT AND PILOT-PLANT PRODUCTION OF SILANE POLYMERS OF DIOLS

by

W. R. Dunnavant, R. A. Markle,
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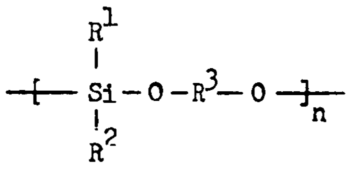
OBJECTIVES

(1) To develop syntheses of chemically crosslinkable resins and polyaryloxysilane elastomers having the general structure



$$-\!\!\left[\, \overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\mathrm{Si}}} - O - R^3 - O \,\right]_n\!\!-$$

which may prove useful in aerospace applications.

(2) To develop effective methods for curing the subject polymers at moderate temperatures (200 C or less) and evaluate the engineering potentials of the materials.

Novel silicon-containing polymers for potential use in adhesive, laminate, coating, molding, etc., applications where stability under extreme environmental conditions is required, will be prepared and evaluated. Efforts will be made to tailor polyaryloxysilane structures to meet specific present and anticipated aerospace requirements and to provide practical fabrication procedures and property evaluations for each of the more promising materials prepared during the program.

I. INTRODUCTION AND STATUS

This program is a logical extension of work accomplished under the basic NASA Contract NAS8-11837(1).* During the first year of this contract, the contractor developed a pilot-scale process for

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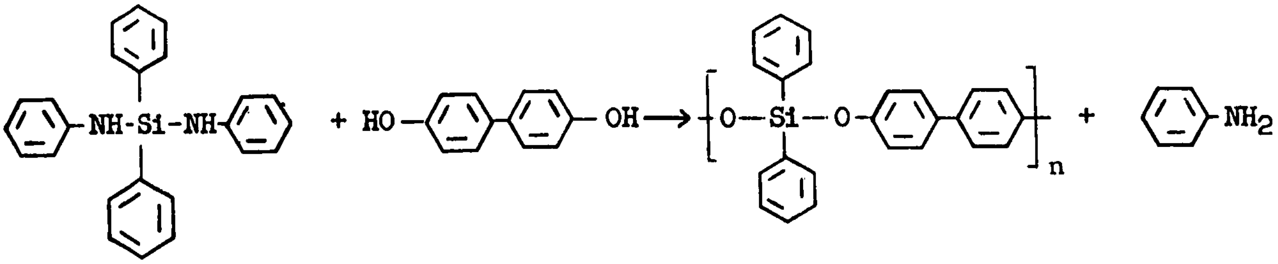
* References are on page 148.

preparing Polymer A by the condensation of bis(anilino)diphenylsilane (I) with p, p'-biphenol.



I p,p'-Biphenol Polymer A

In addition to establishing the feasibility of preparing polyaryloxysilanes, of which Polymer A is representative, on a pilot scale, the processability and properties of Polymer A were evaluated. It was found that the polymer possessed a unique set of properties, which include:

1. Excellent thermal stability to about 500 C in either air or nitrogen as measured by both differential and thermogravimetric analyses
2. Processability as a conventional thermoplastic material on standard equipment into useful engineering shapes (sheet, rod, fibers, molded objects, etc.)
3. Solubility in a variety of organic solvents from which the polymer could be advantageously applied as surface coatings
4. Room-temperature mechanical properties roughly comparable with those of several commercial molding resins
5. Ability to be self-extinguishing if ignited
6. Ability to be cooled to liquid-nitrogen temperature (-196 C) without embrittling.

The property deficiencies preventing the use of Polymer A as a heat-resistant engineering material were its relatively low softening temperature (about 150 C) that restricts its maximum service temperature and prevents the inherent stability of the polymer from being utilized, and its limited resistance toward hydrolysis(1).

Prolonged heating of Polymer A at high temperatures (250 C or higher) was observed to produce crosslinked forms of the polymer that were nonfusible and insoluble but still tough. While such crosslinked Polymer A specimens might be extremely interesting materials fur use in, for example, laminates, the curing conditions by which they were produced were considered to be too severe and not sufficiently reproducible for practical applications to be made.

It was evident that polyaryloxysilanes that could be controllably crosslinked at moderate temperatures (200 C or less) would allow the maximum stability of the polymer system to be utilized in practical end-use applications. In addition, the optimum use of crosslinking in polyaryloxysilanes might be expected to provide materials having significantly improved hydrolytic resistance.

During the second year of this contract (covered by this report), the following advances in polyaryloxysilane technology were made:

(1) Seven different di- and trianilinosilane monomers were successfully synthesized in good yields by condensing the corresponding chlorosilanes with aniline in the presence of s-collidine (an acid acceptor) and subsequently isolated in highly purified states by crystallization or distillation. These preparations illustrate the general utility of the synthetic route to anilinosilanes developed during this program. Tetraphenoxysilane, triphenoxyphenylsilane, and 3,3'-diallylbisphenol A were also synthesized for use in polymerization studies.

(2) A variety of linear, high molecular weight polyaryloxysilanes were prepared by melt-condensing dianilinosilanes with aromatic diols such as p,p'-biphenol, phenolphthalein, and 3,3'-diallylbisphenol A. Those polymers having pendent vinyl or allyl groups could be crosslinked to form insoluble and nonfusible materials by heating them with conventional free-radical catalysts. Each of the linear polyaryloxysilanes was a typical thermoplastic having a low softening temperature. Several of the polymers demonstrated potentially

useful mechanical and electrical properties at 25 C. For example, tenacities exceeding 4 grams per denier were obtained for drawn fibers of a dianilinodimethylsilane/p,p'-biphenol polymer. The mechanical properties and engineering potentials of the free radically crosslinked polyaryloxysilanes remain to be determined.

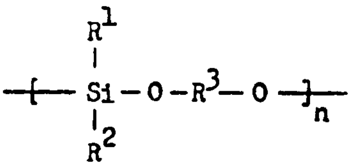
(3) Each of the thermoplastic polyaryloxysilanes prepared demonstrated excellent and similar thermal stabilities to temperatures above 400 C as measured by thermogravimetric analyses under air, a vacuum, or nitrogen. Isothermal analyses under air indicated those polymers with phenyl or vinyl pendent groups to be the more stable, but still susceptible to moderate thermal-oxidative degradation at temperatures in the 250 to 350 C temperature range. The exploratory studies have shown that the thermal-oxidative stabilities, and perhaps the hydrolytic resistance, of the polymers can be substantially enhanced by reducing their contaminant contents.

(4) Promising insoluble and infusible polyaryloxysilanes were prepared by condensing low molecular weight phenolic OH-terminated polyaryloxysilanes with tetraphenoxysilane, trianilinophenylsilane, triphenoxyphenylsilane, or with hexamethylenetetraamine. Similar polymers were prepared by condensing p,p'-biphenol with tetraphenoxysilane or triphenoxyphenylsilane. These polymers appear to possess good thermal stabilities and their processability was demonstrated by the conversion of certain of them into compression moldings or surface coatings on metals.

The phase of the program described in this report has been largely exploratory in nature. Several routes to promising heat-resistant, insoluble, and infusible polyaryloxysilanes have been discovered. These polymers are all processable at some stage in their preparation. The limited property data available for these materials suggest that, if properly developed, they could find use as engineering materials in a variety of industrial and aerospace applications.

A. Free-Radical Cures

The proper selection of R^1, R^2, and R^3 in the general formula for polyaryloxysilanes

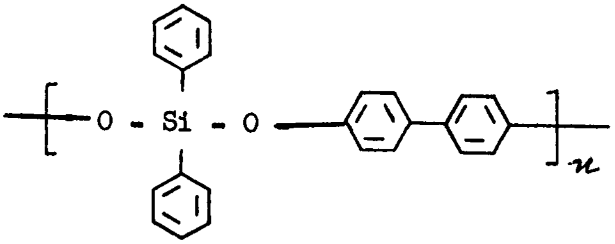


$$\left[\overset{R^1}{\underset{R^2}{\mathrm{Si}}} - O - R^3 - O \right]_n$$

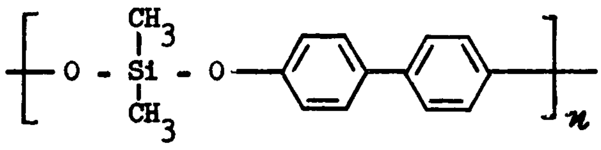
and the proper degree of crosslinking might be expected to provide a variety of either elastomeric or rigid resinous polymers.

A curing mechanism similar to that functional with the polysiloxanes should be operative also for these materials. Such cures should be facilitated if some vinyl-substituted silane units were inserted into polyaryloxysilane chains during their syntheses.

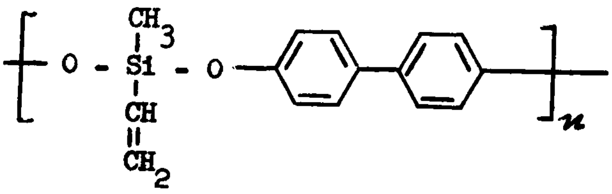
Some typical polyaryloxysilanes which were prepared in the course of this program are the following:



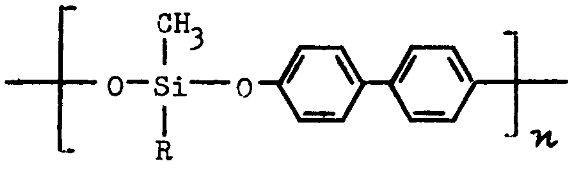
Polymer A



Polymer B



Polymer C



Polymer D

R = part methyl, part vinyl

Emphasis was placed on evaluating the potential of polyaryloxysilanes as heat-resistant coating materials during this program. The various polymers were screened for thermal stability by thermogravimetric analysis (TGA) in an inert atmosphere, and for oxidative thermal stability by isothermal aging of thin films in air at 250 to 350 C. The isothermal aging test provided valuable performance data on the polymers under realistic application conditions.

The various types of polyaryloxysilanes produced to date have all shown good resistance to heat. In some cases, their resistance to extreme thermal-oxidative environments has been found to compare favorably with many well-developed contemporary polymers. The results indicated that as the crosslink densities of the polymers were increased, reductions in the isothermal weight losses were observed.

The presently available data indicate that polyaryloxysilanes crosslinked via free radical mechanisms involving pendent methyl and vinyl groups may show useful stabilities in air at temperatures up to about 300 C. Their stabilities under a vacuum or inert atmosphere should be considerably enhanced.

Representative programmed thermogravimetric analyses under nitrogen or a vacuum (Figure 1) of polyaryloxysilanes having either aromatic or aliphatic pendent groups show weight losses of 5 percent or less at temperatures below 400 C. These polymers also show similar weight losses below 400 C and comparable breakdown temperatures under air (Figure 2), but higher ultimate weight losses are experienced than under a vacuum or inert atmosphere.

If only programmed thermogravimetric analyses are considered, it appears that polyaryloxysilanes with either alkyl or aromatic pendent groups have excellent stabilities in air or an inert atmosphere, with the all-phenyl-substituted polymer being slightly superior to the others.

A clearer picture of the relative stabilities of different polyaryloxysilane structures was provided by isothermal analyses (Figure 3) carried out under air. Despite their excellent TGA-indicated stabilities under air, the polyaryloxysilanes showed substantial weight losses in relatively short periods of time under isothermal heating in air at 250 C or 350 C.

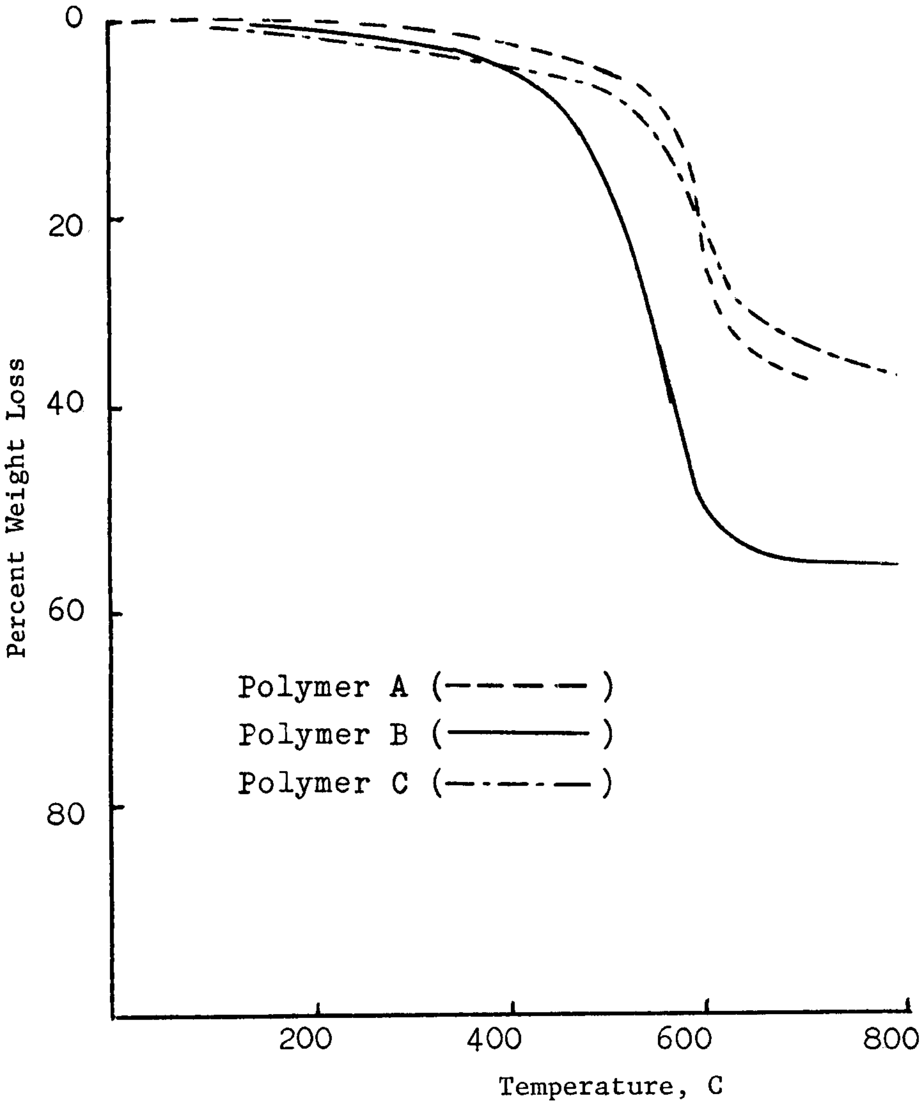


FIGURE 1. PROGRAMMED THERMOGRAVIMETRIC ANALYSES OF REPRESENTATIVE POLYARYLOXYSILANES UNDER NITROGEN OR A VACUUM

(Heating Rate = 4 C/minute.)

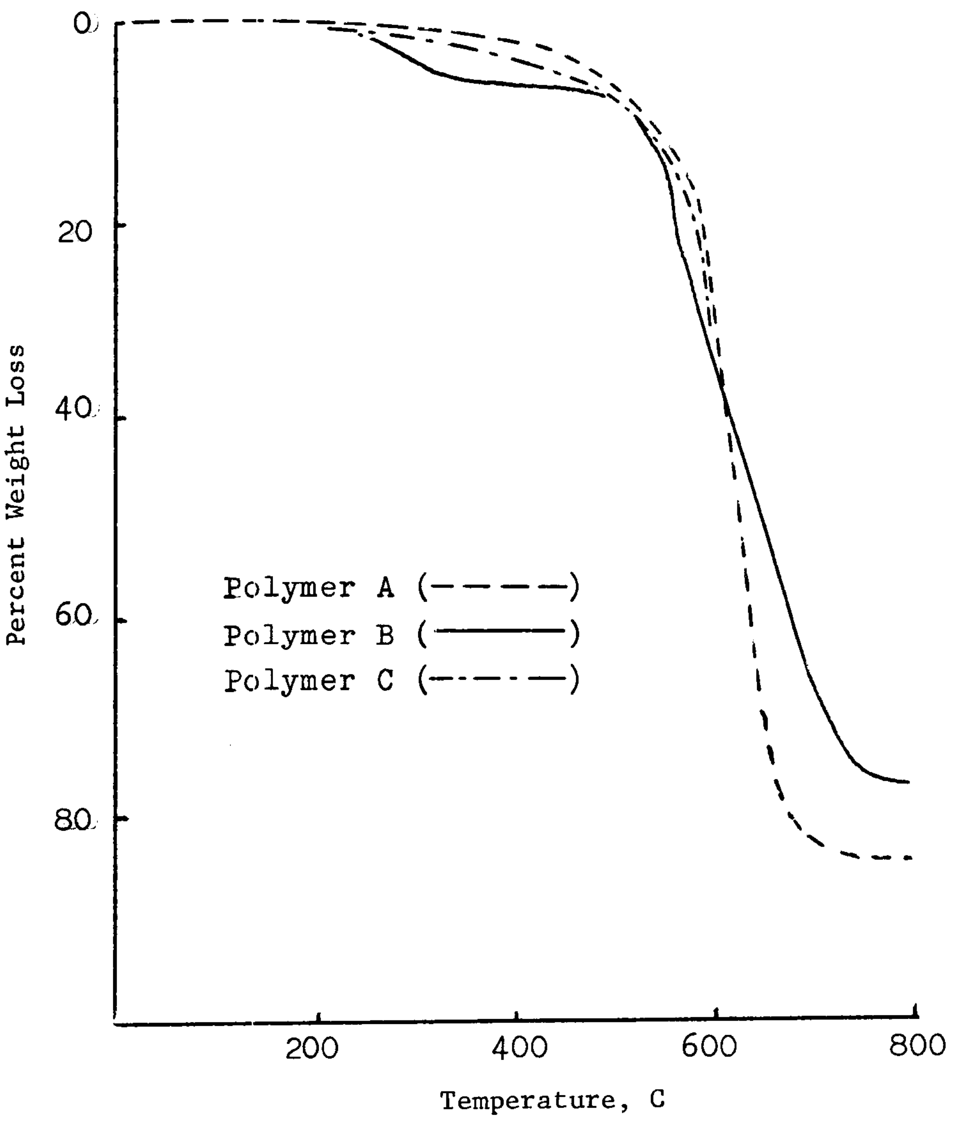


FIGURE 2. PROGRAMMED THERMOGRAVIMETRIC ANALYSES OF REPRESENTATIVE POLYARYLOXYSILANES UNDER AIR

(Heating Rate = 4 C/minute.)

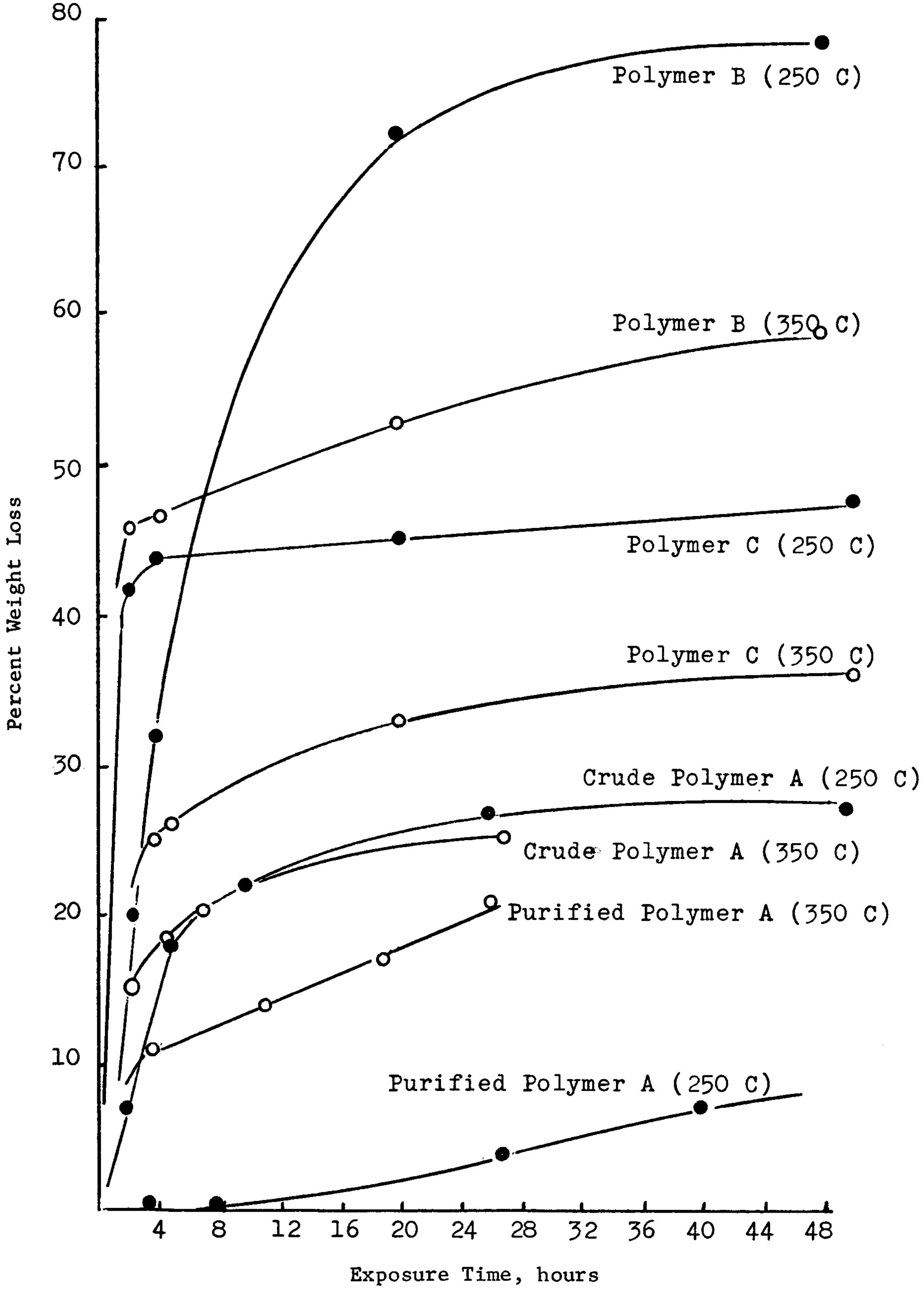


FIGURE 3. ISOTHERMAL THERMOGRAVIMETRIC ANALYSES OF REPRESENTATIVE POLYARYLOXYSILANES UNDER AMBIENT AIR AT 250 C AND 350 C

It should be pointed out, however, that the isothermal aging studies were performed on thin films (approximately 3 mils thick) and weight losses for such polymer specimens are substantially greater than for thick specimens. Thin films of the all-phenyl-substituted Polymer A showed significant weight losses at either 250 to 350 C, but the weight losses were much lower than those found for the methyl- and vinyl-substituted Polymers B, C, and D.

The alkyl- and vinyl-substituted polyaryloxysilanes showed higher final weight losses after isothermal heating in air for 48 hours at 250 C than at 350 C. This behavior is attributed to more rapid thermal or thermal-oxidation-induced crosslinking of these polymers at the higher temperature, resulting in the formation of more stable residues.

Polymer A showed similar isothermal weight losses at both 250 and 350 C. Probably because its pendent groups are less subject to thermal-oxidative cleavage, weight losses were much lower for Polymer A than Polymers B, C, and D.

The magnitudes of the isothermal weight losses experienced by the polyaryloxysilanes investigated prove unequivocally that both backbone and pendent group degradation occur. Infrared analyses of the residues resulting from the heating of Polymer C in air revealed carbonyl absorptions indicating that alkyl or vinyl group oxidation had occurred.

Pyrolysis studies performed in the absence of air on both Polymer A and crosslinked Polymer C established that p,p'-biphenol was lost from the polymers' backbones. One other identified decomposition product of Polymer A was benzene, presumably resulting from cleavage of pendent groups. The infrared spectra of all types of polyaryloxysilanes following pyrolysis indicate Si-O-Si absorptions (1100-1000 cm^{-1}), providing further evidence that chain scissions occur.

As shown in Figure 3, purified Polymer A, obtained by polymerizing carefully purified monomers and then precipitating the polymer from solution, shows a markedly improved stability in air as compared to the less pure specimen of Polymer A. This difference was not apparent from programmed thermogravimetric analyses of the pure and impure materials. While the impurities in Polymer A can have a profound effect on the rate of degradation, the purified Polymer A still provided p,p'-biphenol and benzene as decomposition products upon pyrolysis at 250 C under an inert atmosphere.

Films of highly purified Polymer A underwent rapid weight losses at 350 C but weight losses of less than 10 percent occurred when similar isothermal aging was performed in ambient air at 250 C for 48 hours. Comparable weight losses were obtained at 300 C under either dry breathing air (approximately 0.02 percent water) or air saturated with water (Table 5, this report). These data suggest that purified Polymer A is not appreciably sensitive to moisture and degrades rapidly only at temperatures above 300 C.

It was observed earlier in this program that films and compression moldings of nonpurified Polymer A slowly embrittled upon aging in ambient air. It now seems likely that this aging phenomenon might be due to a combination of moisture and impurities, and that high-purity Polymer A would exhibit improved aging characteristics.

The basic objective of this program was to develop a crosslinkable polyaryloxysilane which would possess useful engineering properties at elevated temperatures. The initial approach to this goal involved the preparation of linear, high molecular weight polyaryloxysilanes containing pendent methyl and/or vinyl groups. In general, these polymers, like all of the linear polyaryloxysilanes that have been prepared, had undesirably low softening temperatures. The softening temperatures were, in most cases, below 100 C. The vinyl-substituted resins did crosslink when heated with free-radical catalysts as evidenced by their becoming insoluble and nonfusible. Unless the crosslink densities were high, their low softening temperatures were not raised appreciably by crosslinking and the polymers are unsuitable for certain high-temperature applications in which structural rigidity is required.

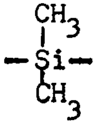
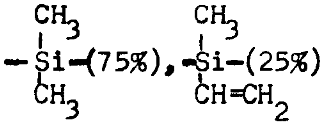
The vinylpolyaryloxysilanes probably undergo free-radical cures somewhat less readily than do vinyl-substituted polysiloxanes. In both cases, the response of vinyl groups on silicon atoms to free radicals is probably relatively poor, as compared to the response of vinyl groups on carbon atoms. It is conceivable that the vinyl-substituted polyaryloxysilanes and polysiloxanes do crosslink with comparable efficiencies. However, the polyaryloxysilanes have much lower molecular weights than the conventional crosslinkable polysiloxanes and would be expected to provide fewer crosslinks per polymer chain than the latter. It is also possible that the bulky aromatic rings in the chains of the polyaryloxysilanes interfere with the close approach of neighboring chains necessary for efficient intermolecular crosslinking reactions to occur. Nevertheless, crosslinked Polymer C and Polymer D specimens that were insoluble and did not soften or melt at 300 C were achieved. Crosslinked vinyl-substituted polyaryloxysilanes showed improved programmed and isothermal thermogravimetric analyses as compared to those of uncrosslinked specimens. However, it is apparent that no appreciable stability improvement should be expected by crosslinking via a free-radical mechanism that links polymer chains together by relatively thermally weak aliphatic units.

Some properties of several representative polyaryloxysilanes are summarized in Table 1. As in the case of Polymer A described in an earlier report(1), these polymers had low softening temperatures (70-90 C) and formed viscous melts at somewhat higher (94-170 C), but still relatively low temperatures. There was a slight trend toward higher softening and melt temperatures with increasing molecular weight, but the effect was not sufficient to make the formation of materials having structural rigidities much above 100 C likely. Oriented fibers having useful tenacities at room temperature could be drawn from these polymers, but again their high-temperature utility was restricted by their low softening temperatures.

The polymers containing only dimethylsilyl groups did not appear to respond to a free-radical catalyst except in the presence of an added vinyl monomer. However, the inclusion of vinyl pendent groups (Polymers C and D) provided crosslinkable materials. In this case, crosslinking was indicated by insolubilization of the polymer and the formation of a nonfusible material.

The electrical properties of several polyaryloxysilanes were determined during the program. The data were obtained on disks 2 inches in diameter and 1/8 inch in thickness compression-molded at 125 C in a laboratory press. The test specimens included samples of Polymer A,

TABLE 1. COMPARATIVE PROPERTIES OF METHYL- AND VINYL-SUBSTITUTED POLYARYLOXYSILANES FROM p,p' - BIPHENOL

Silyl Groups		 $-\mathrm{Si}(\mathrm{CH_3})_2-$			 $-\mathrm{Si}(\mathrm{CH_3})_2-$(75%), $-\mathrm{Si}(\mathrm{CH_3})(\mathrm{CH{=}CH_2})-$(25%)	
	Sample No. 23563-11-1	Sample No. 23563-15		Sample No. 23563-13-2	Sample No. 23563-27	
	(a)	(a)	(b)	(a)	(a)	(b)
Molecular Weight(M_w)$^{(c)}$	22,000	48,000	-	96,000	33,000	-
		Film Properties				
Tensile Strength, psi$^{(d)}$	-	3,895	-	-	4,486	3,912
Polymer Softening Temp.C$^{(e)}$	70	84	78	87	73	75
Polymer Melt Temp.C$^{(f)}$	94	144	152	170	122	>220
Solubility in o-Dichlorobenzene	Yes (Hot)$^{(g)}$	Yes (Hot)$^{(g)}$	Yes (Hot)$^{(g)}$	Yes (Hot)$^{(g)}$	Yes $^{(h)}$	No$^{(h)}$
		Fiber Properties				
Tenacity, g/denier$^{(d)}$	-	1.25	-	1.06	1.06	-
Cold Drawability	-	Fair	-	Good	Good	-

(a) Unoriented film specimen solvent-cast from o-dichlorobenzene and air-dried at 60-100 C (2 hours).

(b) Film prepared as in a, but containing 5 percent (based on polymer weight) of t-butyl perbenzoate and cured for 30 minutes at 160 C.

(c) By gel permeation chromatography

(d) Average figures from 10-15 test specimens.

(e) Temperature at which polymer becomes tacky on a melting point block heated at a rate of 4 degrees/min.

(f) Temperature on melting point block at which fibers can be drawn from polymer specimen

(g) Polymer dissolves in hot solvent, but becomes insoluble when cooled.

(h) In either hot or cool (room temperature) solvent.

a partially-purified sample of Polymer A obtained by precipitating the polymer from solution in benzene, and a sample of Polymer D obtained by condensing a mixture of dianilinodimethylsilane (90 percent) and dianilinomethylvinylsilane (10 percent) with p,p'-biphenol. The results of the tests (Table 2) indicated that the polyaryloxysilane-type materials might well be considered for use in applications requiring good electrical properties. No significant improvement in the electrical properties of Polymer A was achieved by the precipitation procedure used.

B. Condensation Cures

In view of the limited success achieved in controllably crosslinking preformed, high molecular weight polyaryloxysilanes, attention was turned to the possibility of building up three-dimensional polyaryloxysilane structures of the types shown in Figure 4 from low molecular weight precursors during fabrication.

Crosslinked Polymer A-type materials were prepared by condensing trianilinophenylsilane (5 parts) and dianilinodiphenylsilane (95 parts) with p,p'-biphenol (100 parts). Such polymers were insoluble and infusible but softened to a leathery consistency at elevated temperatures.

It is now believed that a promising route to curable polyaryloxysilanes may be through the use of phenoxy rather than anilino or aminosilane monomers in conjunction with aromatic diols. Previous work in this laboratory(2) revealed that polyaryloxysilanes similar to those obtained from dianilinosilanes and aromatic diols could be achieved by condensing diphenoxysilanes with aromatic diols.

There would appear to be several potential advantages for including as many siloxyphenyl linkages in a polyaryloxysilane as possible. For example, compounds containing the silicon-oxygen bond (89.3 kcal mole^{-1})(3) in phenoxysilane compounds are known to have excellent thermal stabilities(4) and, in our experience, phenoxysilanes are much less susceptible to hydrolysis than are the aminosilane compounds.

TABLE 2. ELECTRICAL PROPERTIES OF REPRESENTATIVE POLYARYLOXYSILANES

Sample	Specimen Number	Dielectric Constant[(a)]	Dissipation Factor[(a)]	Dielectric Strength, volts/mil[(b)]
Polymer A (21987-79-1)	1	2.95	0.0011	514
	2	3.00	0.0011	525
	3	2.84	0.0014	577
Polymer A (partially purified)	1	3.02	0.0013	513
Polymer D (23448-36)	1	3.21	0.0028	530
	2	3.13	0.0027	530

(a) Frequency = 1 mc.

(b) 500 volts/sec.

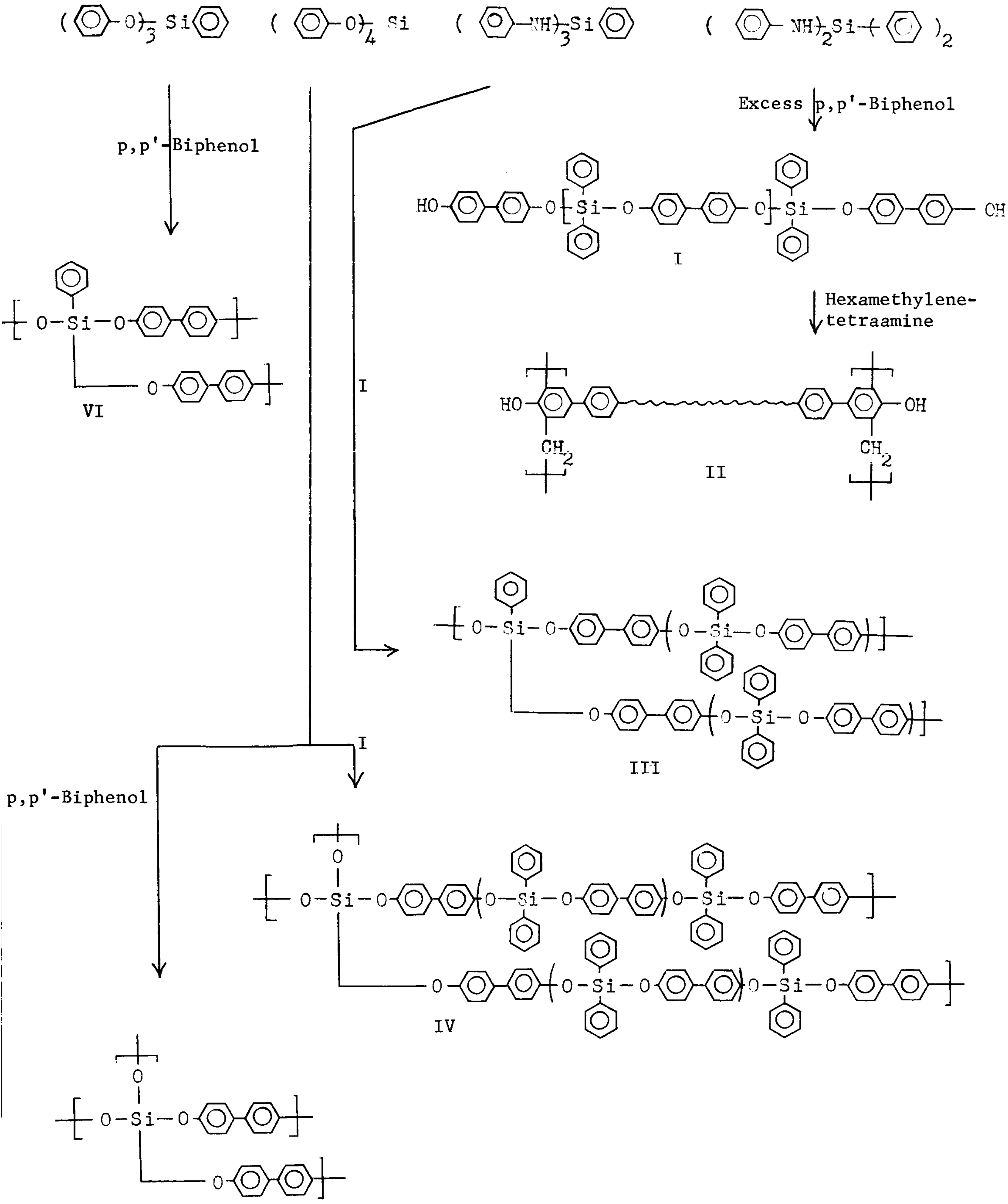


FIGURE 4. CONDENSATION CROSSLINKING OF POLYARYLOXYSILANES

Condensation of multifunctional silane monomers with aromatic diols would offer the following potential advantages:

(1) Elimination of the low softening point of Polymer A while retaining the latter's thermal stability

(2) Attainment of a range of physical properties through use of a variable crosslink density

(3) Elimination of the need for high molecular weight, linear polymers with its concomitant requirement for high-purity monomers and close control of stoichiometry of reacting monomers

(4) Achievement of crosslinked polymers which have a three-dimensional network more impervious to chemical attack than corresponding linear polymers

(5) Increase of thermal-oxidative stability. All previous studies indicated that crosslinking is of value in increasing high-temperature stability.

Recent results on polymerization of tetraphenoxysilane with p,p'-biphenol reveal that clear, tightly adhering films can be fabricated using this route and the resulting polymer is infusible, insoluble, and undergoes very low weight losses at 250 C for long intervals.

The above polymer is an example of a polyaryloxysilane in which all of the pendent groups are phenoxy units. The silicon atoms in such a polymer each carry four oxygen atoms and it might prove to be more thermally, oxidatively, and hydrolytically stable than any of the polyaryloxysilane types explored to date as a result.

The most promising polyaryloxysilanes prepared to date have resulted from the crosslinking of low molecular weight, phenolic OH-terminated polyaryloxysilanes by reaction with triphenoxyphenylsilane or tetraphenoxysilane. The resulting polymers have three-dimensional polyaryloxysilane structures--the crosslinks being formed through phenoxysilane linkages. Cured coatings prepared from polymers of these types have demonstrated good adhesion to aluminum, high clarity, absence of color, good solvent resistance, and flexibility. Even after 700 hours exposure in air at 250 C, these properties were retained to a considerable extent. However, some reduction in flexibility and development of a light-brown color were noted. Potentially useful coating properties appear to be retained in spite of the fact that moderate weight losses occur during the prolonged exposure tests.

It is thought that the weak links in polyaryloxysilane structures may be the silicon-carbon linkages binding the pendent groups to the backbones. Consequently, the next step in the development of thermosets may involve syntheses of polyaryloxysilanes having pendent phenoxy groups. Such structures would provide each silicon atom in polymer chains with a quartet of oxygen atoms which might be expected to provide optimum thermal-oxidative stability. If these polymers can be prepared, it may prove possible to crosslink them via their pendent phenoxy groups with aromatic diols.

II. MONOMERS

A. Discussion

A wide variety of potentially crosslinkable polyaryloxysilanes were prepared and evaluated during this program. Each of the polymers was obtained by melt-condensing an aromatic diol with a polyfunctional anilino-, dimethylamino-, or phenoxysilane. The melting and boiling temperatures and representative elemental analyses for the silane monomers prepared to support these studies are shown in Table 3.

Syntheses of seven anilinosilanes were accomplished by condensing the corresponding chlorosilanes with aniline in the presence of the acid acceptor s-collidine. This synthetic method was explored in depth earlier in this program when dianilinodiphenylsilane was prepared on a small pilot-scale, and is discussed in detail in the "First Annual Report on NASA Contract No. NAS8-11837, February 21, 1966".

Several of the anilinosilanes prepared during this program were not previously described in the literature. Those anilinosilanes that had been described earlier were prepared in generally higher yields and degrees of purity than previously reported(5,6).

Tris(dimethylamino)phenylsilane was prepared by the method of Burks and Covington(7). Several phenoxysilanes were prepared by the direct condensation of the corresponding chlorosilanes with phenol.

Three aromatic diols were used as monomers in this program. p,p'-Biphenol and phenolphthalein were obtained from commercial sources. The p,p'-biphenol was sublimed prior to use in polymerizations where exceptionally high monomer purity was required. 3,3'-Diallylbisphenol A was prepared from Bisphenol A using the procedure of Korshak, et al(8).

Detailed syntheses of the various monomers synthesized are presented in Table 3.

TABLE 3. PROPERTIES OF SILANE MONOMERS PREPARED

Monomer	M.P., C	B.P., C		Elemental Analysis C, %	Elemental Analysis H, %	Elemental Analysis N, %
$(C_6H_5NH)_2Si(C_6H_5)_2$	166-167	-	Calculated	78.65	4.95	7.66
			Found	78.78	5.23	7.92
$(C_6H_5NH)_2Si(CH_3)_2$	63.0-63.5	153.5/1.1 mm	Calculated	69.36	7.49	11.56
			Found	69.10	7.55	11.49
$(C_6H_5NH)_2Si(CH_3)(CH{=}CH_2)$	-	160.8-161.2/1.4 mm	Calculated	70.82	7.13	11.02
			Found	70.69	7.23	10.88
$(C_6H_5NH)_2Si(CH_3)(C_6H_5)$	65.5-67.0	-	Calculated	75.00	6.62	9.20
			Found	74.80	6.74	8.99
$(C_6H_5NH)_3Si(C_6H_5)$	139.5-142.0	-	Calculated	75.55	6.07	11.01
			Found	75.35	5.94	10.92
$(C_6H_5NH)_2Si(C_6H_5)(CH{=}CH_2)$	-	195.8-196.0/0.70 mm	Calculated	75.90	6.37	8.85
			Found	75.85	6.45	8.79
$(C_6H_5NH)_2Si(CH_3)(CH_2{-}CH{=}CH_2)$	-	146.0-148.3/0.50 mm	Calculated	71.59	7.51	10.44
			Found	71.64	7.74	10.61
$(C_6H_5O)_4Si$	-	214-215/1.2 mm	-	-	-	-
			-	-	-	-
$(C_6H_5O)_3Si(C_6H_5)$	44.0-44.2	192.0/0.20 mm	Calculated	74.97	5.24	-
			Found	74.81	5.20	-

B. Experimental

1. Preparation of Dianilinodiphenylsilane (23563-73). The reaction was carried out in a 1-liter, 3-necked flask fitted with a Trubore stirrer, reflux condenser with a drying tube attached, and a dropping funnel. The apparatus was flame-dried under a nitrogen sweep. In the reaction flask were placed 133 grams (1.68 moles) distilled aniline, 424 grams (3.50 moles) distilled s-collidine, and 100 ml tetrahydrofuran (THF dried over CaH_2). In the dropping funnel were placed 177 grams (0.700 mole) dichlorodiphenylsilane (Dow Corning, as received) and 50 ml dry THF. The dichlorodiphenylsilane solution was added to the rapidly stirred aniline solution over a 30-minute period. The temperature of the reaction mixture rose from room temperature to about 65 C. A thick white slurry resulted which was stirred for 1 hour, then filtered with suction while still warm (about 40 C) through a coarse sintered glass funnel. The white filter cake was washed with a 250-ml portion of boiling THF. The initial filtrate had to be refiltered three times to remove additional s-collidine hydrochloride which separated on standing. The combined filtrates were stripped, using a rotary evaporator at reduced pressure to remove THF and unreacted s-collidine. The yield from this procedure was a clear, yellow, viscous liquid which began to crystallize as it was allowed to cool. To this mixture was added, while swirling rapidly, 800 ml of dry, low-boiling petroleum ether (30-60 C). Rapid crystallization resulted, yielding a thick, tan crystalline mass. After standing overnight, this material was suction filtered and washed with a small amount of petroleum ether. The product was vacuum dried to yield 190 grams (74 percent of theoretical) of a light-tan crystalline solid. The filtrate was partially evaporated and further crystallization occurred. When recovered and dried, an additional 8 grams of tan, crystalline solid was obtained. Total yield of crude dianilinodiphenylsilane was 198 grams (77 percent of theoretical). The white s-collidine hydrochloride salt when dried and weighed produced 224 grams of material (102 percent of theoretical). Evidently not all the dianilinodiphenylsilane was removed from the salt.

A 70-gram portion (about one-third) of the crude dianilinodiphenylsilane was vacuum distilled (219-224 C at 0.36 mm). A 7-gram forecut was discarded and a 52-gram (74 percent of starting material) yellow maincut was obtained. Undistilled residue consisted of 9 grams (13 percent of starting material) of brown solid which solidified at the distillation temperature (>220 C). The 52-gram maincut was redistilled (200-203 C at 0.15 mm), yielding 45 grams (86.5 percent of starting material) of very light-yellow dianilinodiphenylsilane. A 4-gram forecut and 2 grams of pot residue (molten at distillation temperature) were discarded. The 45-gram maincut from the second distillation was twice recrystallized by dissolving in the minimum amount of boiling, dry benzene and then rapidly adding an equal amount of dry, 30-60 C petroleum ether to the hot solution. Rapid crystallization occurred, yielding a white, microcrystalline powder which was suction filtered and washed with a small amount of petroleum ether. The final, dry product was 39 grams (87 percent recovery of the distilled material) of pure white, microcrystalline dianilinodiphenylsilane, mp 167-168 C. The recovery of pure monomer based on 70 grams impure starting material was 56 percent. Based on an original 77 percent yield of impure monomer, the overall yield of pure white dianilinodiphenylsilane was 43 percent of theoretical. This high-purity monomer was prepared for use in synthesizing high-purity Polymer A for stability studies.

2. Preparation of Dianilinodimethylsilane a. The preparation was carried out in a 1-liter, 3-necked flask equipped with a Trubore stirrer, reflux condenser with a drying tube affixed, and a dropping funnel. The apparatus was flame-dried and then swept with nitrogen until cool. A solution of 38.7 grams (0.30 mole) of dimethyldichlorosilane in 100 ml of petroleum ether (30-60 C) was placed in the dropping funnel and 109.1 grams (0.90 mole) of freshly distilled s-collidine was mixed with 55.9 grams (0.60 mole) of aniline and 300 ml of petroleum ether in the reaction flask. The aniline/s-collidine solution was heated to reflux on a steam bath and the dimethyldichlorosilane solution was added dropwise over a period of 1 hour while the reaction mixture was stirred

rapidly. The resulting thick white slurry was held at the reflux temperature while being stirred for 1 additional hour, and was then cooled slowly to about 30 C. The warm slurry was filtered with suction on a sintered glass funnel and the filter cake was washed with warm petroleum ether. The dried filter cake, consisting of s-collidine hydrochloride, weighed 93.0 grams (98 percent of theoretical). The combined petroleum ether filtrates were evaporated to a yellow viscous liquid by using a rotary evaporator at reduced pressure. The viscous yellow residue was dissolved in 100 ml of warm 30-60 C petroleum ether and allowed to stand at 23 C for 18 hours.

A 50.0-gram crop (about 70 percent yield) of yellow crystals, melting point 57-59 C, was obtained. Three crystallizations from petroleum ether provided 43.0 grams (60 percent yield) of pure white, crystalline dianilinodimethylsilane, m.p. 63.0-63.5 C.

Analysis for $C_{14}H_{18}SiN_2$ Calculated: C, 69.36; H, 7.49; N, 11.56
Found: C, 69.23; H, 7.60; N, 11.44

b. The preparation was carried out in a 5-liter Pyrex resin kettle equipped with a Trubore stirrer, reflux condenser with a drying tube affixed, and a dropping funnel. The apparatus was flame-dried, then swept with nitrogen until cool. A solution of 387 grams (3.00 mole) of dimethyldichlorosilane in 1 liter of petroleum ether (60-110 C)* was placed in the dropping funnel, and 559 grams (6.00 mole) of aniline and 1091 grams (9.00 mole) of s-collidine were mixed with 1.25 liters of petroleum ether and 0.75 liter of tetrahydrofuran (THF) in the kettle. The dimethyldichlorosilane solution was added slowly (over 5 hours) to the rapidly stirred reaction mixture heated to reflux on a steam bath. A thick white slurry resulted. This was stirred at reflux for 1 hour. The slurry was then allowed to cool overnight to room temperature and filtered with suction. The filter cake was washed twice with liter portions of hot petroleum ether, then dried on a steam bath to give

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* Petroleum ether was dried over CaH_2. All other reagents, except dichlorodimethylsilane, were dried over $CaSO_4$.

1094 grams of crude collidine hydrochloride (116 percent of theoretical). Some dianilinosilane product (as much as 149 grams or 20 percent of theoretical) was probably retained by the salt, accounting for the yield in excess of theory. Petroleum ether and THF were stripped from the orange filtrate by using a rotary evaporator at reduced pressure. Vacuum distillation of the clear red-brown residue afforded 485 grams (67 percent of theoretical) of clear, light yellow dimethyldianilinosilane, b.p. 153.5C/1.10 mm, b.p. 145.0C/0.70 mm, m.p. 59-61 C. The excess s-collidine came over in a low boiling forecut that was discarded. The yellow product (485 grams) was recrystallized three times from low-boiling (30-60 C) petroleum ether to yield 341 grams (47 percent of theoretical) of white crystals, m.p. 62.5-63.5 C. The yellow mother liquors were condensed and reworked, yielding an additional 34 grams of pure white solid, m.p. 62.5-63.5 C. The total yield of pure white crystalline product was 375 grams (52 percent of theoretical).

Analysis for $C_{14}H_{18}SiN_2$ Calculated: C, 69.36; H, 7.49; N, 11.56
Found: C, 69.19; H, 7.57; N, 11.96

3. Preparation of Dianilinomethylvinylsilane. a. The preparation was carried out in a 1-liter, 3-necked flask equipped with a Trubore stirrer, reflux condenser with a drying tube affixed, and a dropping funnel. The apparatus was flame-dried, then swept with nitrogen until cool. A solution of 41.7 grams (0.30 mole) of dichloromethylvinylsilane in 100 ml of petroleum ether (60-110 C)* was placed in the dropping funnel, and 57.7 grams (0.62 mole) of aniline and 109.1 grams (0.90 mole) of s-collidine were mixed with 300 ml of petroleum ether in the reaction flask. The rapidly stirred reaction mixture was heated to reflux on a steam bath and the dichloromethylvinylsilane solution was added dropwise over a period of 1 hour. The thick slurry was heated an additional 10 minutes, rapidly cooled to about 30 C, and filtered with suction on a sintered glass funnel. The filter cake was washed with hot petroleum ether and dried, yielding 90 grams of s-collidine hydrochloride (95 percent of theoretical). The

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* Petroleum ether was dried over CaH_2. All other reagents, except dichlorodimethylsilane, were dried over $CaSO_4$.

petroleum ether was stripped from the red-orange filtrate using a rotary evaporator at reduced pressure. Vacuum distillation of the deep red-brown residue afforded 56 grams (74 percent of theoretical) clear, light yellow dianilinomethylvinylsilane (Sample No. 23563-25) b.p. 151.0-152.0 C/ 0.60 mm. The excess s-collidine and aniline were removed in a low-boiling forecut that was discarded.

<u>Analysis</u> for $C_{15}H_{18}SiN_2$ Calculated: C, 70.82; H, 7.13; N, 11.02
Found: C, 70.27; H, 7.25; N, 9.54

b. Gas-liquid chromatographic (GLC) analysis of dichloromethylvinylsilane, as received from Dow Corning, showed this compound to be about 85 percent pure, with over two dozen impurities, both higher and lower boiling than the desired starting material. Vacuum distillation of about 2 kg of this monomer through a 1-foot Vigreaux column afforded one high-purity cut of dichloromethylvinylsilane (175 grams, approximately 9 percent of the total) which proved to be 95 percent pure by GLC analysis. This higher purity material was used in the following preparation.

The preparation was carried out in a 5-liter Pyrex resin kettle equipped with a Trubore stirrer, reflux condenser with a drying tube affixed, and a dropping funnel. The apparatus was flame-dried, then swept with nitrogen until cool. A solution of 171.5 grams (1.216 mole) of dichloromethylvinylsilane in 400 ml of petroleum ether (60-100 C) was placed in the 1-liter dropping funnel, and 226.5 grams (2.432 mole) of aniline and 442 grams (3.65 mole) of s-collidine were mixed with 800 ml of petroleum ether (60-110 C) in the reactor. The dichloromethylvinylsilane was added over a 1.5-hour period to the rapidly stirred reaction mixture, heated to reflux on a steam bath. A thick white slurry resulted. This was stirred at reflux for 1.75 hours. The slurry was allowed to cool overnight to room temperature and filtered with suction. The filter cake was washed with hot petroleum ether, then dried on a steam bath to give a 366-gram (95.4 percent) yield of s-collidine hydrochloride salt. Petroleum ether was stripped from the filtrate using a rotary evaporator at reduced pressure. The clear, yellow residue was transferred to a 1-neck, 2-liter, round-bottomed flask and vacuum distilled. The excess s-collidine distilled at approximately 45 C at 2 mm. The dianilinomethylvinylsilane distilled at 160.8-161.2 C at 1.40 mm. The yield was 212 grams (69 percent) of light-yellow, oily liquid that could not be crystallized either in mass or in solvents. GLC analysis indicated 94 percent purity.

Analysis for $C_{15}H_{18}SiN_2$	Calculated:	C, 70.82; H, 7.13; N, 11.02
	Found:	C, 70.69; H, 7.23; N, 10.88

4. Preparation of Dianilinomethylphenylsilane. The same apparatus and procedure as described for preparing dianilinodimethylsilane were used. The quantities of reactants and solvents used were as follows:

56.0 grams (0.30 mole) methylphenyldichlorosilane
57.0 grams (0.31 mole) freshly distilled aniline
109.0 grams (0.90 mole) freshly distilled s-collidine
400 ml petroleum ether (60-110 C)

The crude product (yellow crystals) obtained by evaporation of the reaction mixture weighed 32.0 grams (35 percent of theoretical) and was apparently contaminated with s-collidine hydrochloride. The crude silane monomer, having a melting point range of 45 to 55 C, was redissolved in petroleum ether (30-60 C) and chromatographed on a silica gel column, using additional petroleum ether as the eluent. A 15-gram (17 percent yield) of colorless, crystalline dianilinomethylphenylsilane, m.p. 65.5-67.0 C, was obtained by crystallization from the eluting solvent. The elemental analyses were in close agreement with the calculated values.

Analysis for $C_{19}H_{20}SiN_2$	Calculated:	C, 75.00; H, 6.62; N, 9.20
	Found:	C, 74.80; H, 6.74; N, 8.99

The above synthesis is suitable for the preparation of small quantities of polymerization grade dianilinomethylphenylsilane, but not for providing sizable quantities of the monomer. It is probable that a significantly higher yield of monomer can be obtained by modifying the reaction conditions somewhat, and that the purified monomer could be obtained more readily by distillation than by the chromatographic method described above.

5. Preparation of Trianilinophenylsilane (TAPS). The reaction was carried out in a 1-liter, 3-necked flask equipped with a Trubore stirrer, reflux condenser with a drying tube attached, and a dropping funnel. The apparatus was swept with nitrogen for 30 minutes. In the reaction flask was placed 134.0 grams (1.44 moles) distilled aniline, 262.9 grams (2.16 moles) distilled s-collidine, and 250 ml benzene (dried over CaH_2). In the dropping funnel was placed 101.6 grams (0.480 mole) trichlorophenylsilane and 50 ml dry benzene. The phenyltrichlorosilane solution was added to the aniline solution over a 1-hour period while the reaction mixture was stirred vigorously. The reaction mixture was then heated to reflux temperature for about 1 hour. After standing overnight at about 25 C in a dry atmosphere, the thick white slurry was suction filtered. The filter cake was washed twice with dry benzene, then dried on a steam bath overnight to give a 210-gram (93.2 percent) yield of s-collidine hydrochloride. The combined filtrates were stripped of benzene and s-collidine using a rotary evaporator at reduced pressure. A viscous, dark-brown melt was obtained. To this was added 100 ml of benzene and the mixture was heated to effect complete solution. Then dry petroleum ether (60-110 C) was added slowly until the white precipitate which formed just barely redissolved in the hot solution (incipient precipitation point). As the solution was cooled and precipitation began, 15 ml benzene was slowly added to maintain a clear solution.

This solution was allowed to stand overnight at about 25 C. A bottom layer of an extremely viscous, dark-brown material separated. However, large tan crystalline masses of a material presumed to be the product formed in the upper, clear, light-brown layer. Crystallization continued slowly for 3 days, then the crystalline masses in the upper layers were removed as completely as possible. These light-tan, very hard, half-spheres of tightly packed small crystals weighed 98 grams (54 percent of theory). Two recrystallizations from dry toluene yielded 65 grams (36 percent) of an off-white microcrystalline powder with a sharp melting point at 148 C (DTA, under nitrogen). The sharpness of the melting endotherm indicates a high-purity sample. Infrared analysis supports this deduction, as does the elemental analysis given below. However, determination of the melting point under dry air in a capillary tube yields a melting point of 139.5-142.0 C. The reason for the discrepancy between DTA and capillary melting points is not yet known.

Analysis for $C_{24}H_{23}N_3Si$	Calculated:	C, 75.55; H, 6.07; N, 11.01; Cl, 0
	Found:	C, 75.35; H, 5.94; N, 10.92; Cl, 0.84

6. Preparation of Tris(dimethylamino)phenylsilane. The method of Burks and Covington(9) was used to prepare tris(dimethylamino)phenylsilane. A 46 percent yield was obtained of water-white liquid, b.p. 70-73 C/0.4-0.6 mm. Burks and Covington have reported 58-59 C/0.2 mm as a boiling point.

7. Preparation of Dianilinophenylvinylsilane (23563-76). Using the same approach as in Experiment 23563-73 described above, 126 grams (79 percent of theoretical) of crude, tan, microcrystalline dianilinophenylvinylsilane was prepared from a monomer charge of 102.9 grams (0.507 mole) dichlorophenylvinylsilane (Penninsular ChemResearch), 96.5 grams (1.03 moles) aniline, 307 grams (2.54 moles) s-collidine, and 250 ml THF. The yield of s-collidine hydrochloride salt was 155 grams (98 percent of theoretical). A 76-gram portion of crude dianilinophenylvinylsilane was distilled, b.p. 195.8-196.0 C/0.70 mm, and recrystallized, yielding 50 grams (66 percent recovery) of white monomer.

Analysis for $C_{20}H_{20}N_2Si$	Calculated:	C, 75.90; H, 6.37; N, 8.85
	Found:	C, 75.85; H, 6.45; N, 8.79

8. Preparation of Dianilinomethylallylsilane (23563-81). Similarly, 147 grams (94 percent of theoretical) of viscous, brown, liquid dianilinomethylallylsilane was prepared from a reactant charge of 90.2 grams (0.581 mole) dichloromethylallylsilane (Penninsular ChemResearch), 110 grams (1.18 moles) aniline, 352 grams (2.90 moles) s-collidine, and 300 ml THF. S-collidine hydrochloride salt yield was 186 grams (99 percent of theoretical). After three distillations,

100 grams (64 percent of theoretical) of very light-yellow, viscous liquid dianilinomethylallylsilane was realized. The final distillation was carried out at 0.50 mm pressure. The boiling range was 146.0-148.3 C.

Analysis for $C_{16}H_{20}N_2Si$	Calculated:	C, 71.59; H, 7.51; N, 10.44
	Found:	C, 71.64; H, 7.74; N, 10.61

9. Preparation of Tetraphenoxysilane (23563-84). The reaction was carried out in a 500-ml, 1-neck flask fitted with a reflux condenser connected to a water scrubbing tower to dissolve the by-product HCl gas. A trap was included between the condenser and the tower to prevent water back-up into the reaction mixture. The apparatus was purged with a flow of dry nitrogen gas for 30 minutes. Then 100 grams (1.062 moles) of phenol (J. T. Baker Chemical Company) and 30 grams (0.177 moles of $SiCl_4$ (Matheson, Coleman, and Bell Semiconducting Grade No. 7426) was placed in the flask. The $SiCl_4$ was analyzed by gas chromatography and found to be 99.99+ percent pure. Only one peak was observed in the chromatogram. Evolution of HCl commenced as soon as the $SiCl_4$ was added to the phenol. Gentle heating with a heating mantle for a few minutes was sufficient to initiate a vigorous reaction which continued without further application of heat for about 2 hours. As the spontaneous reaction began to subside, a pinch of anhydrous $MgCl_2$ (K and K Chemicals) catalyst was added, causing the reaction to speed up again. After another hour the reaction rate had slowed substantially and heat was applied with a heating mantle. Over a 2-hour period, the voltage supplied the mantle was raised gradually to 70 volts. The temperature of the reaction mixture rose to about 200 C and phenol began refluxing. Heating was continued for 4 days, but very slow HCl evolution was still evident (litmus test). A nitrogen sparge was introduced into the reaction mixture and the last traces of HCl removed. The clear, light-tan reaction mixture was distilled. Phenol distilled first, then the pressure was reduced and the tetraphenoxysilane product was distilled, b.p. 214-215 C/1.2 mm. The product was 45 grams (62 percent of theoretical) of a clear, very light-yellow liquid which crystallized to a white solid on standing 2 days in

the distillation receiver. Gas chromatography revealed no unreacted $SiCl_4$ or phenol in the product. Only one sharp peak was detected, indicating product purity of better than 99.9 percent.

10. Preparation of Triphenoxyphenylsilane (24288-38). The reaction was carried out in the same apparatus as the preparation of tetraphenoxysilane, using essentially the same technique. To 168 grams (1.787 moles) of distilled phenol in the 500 ml flask was added 116 grams (0.550 mole) of phenyltrichlorosilane. After HCl evolution was complete, the light tan reaction mixture was distilled at reduced pressure, b.p. 192.0 C/ 0.20 mm. The clear, colorless product, obtained in 194-gram yield (92 percent of theoretical), crystallized after standing overnight to pure white needles, m.p. 44.0-44.2 C. GLC analysis indicated 99.4 percent purity.

Analysis for $C_{24}H_{20}O_3Si$ Calculated: C, 74.97; H, 5.24
Found: C, 74.81; H, 5.20

11. Purification of p,p'-Biphenol. This dihydroxyaromatic compound was purified for reaction with the high-purity dianilinodiphenylsilane described above (23563-73) to prepare Polymer A samples for stability studies. Distillation Product Industries doubly recrystallized p,p'-biphenol (used as received in the pilot-plant scale preparations of Polymer A) was purified by sublimation. Two sublimations of the off-white DPI material yielded white p,p'-biphenol (m.p. 280-283 C) in better than 90 percent recovery.

12. Preparation of 3,3'-Diallylbisphenol A. To 400 ml of acetone was added 228 grams (1.00 mole) bisphenol A, 270 grams (2.23 moles) allylbromide, and 300 grams (3.03 moles) K_2CO_3. The mixture was refluxed 8 hours and then allowed to stand for 4 days. Water (400 ml) was added and the mixture was extracted three times with 300-ml portions of ether. The ether extract was washed three times with 170 ml of 3 percent aqueous sodium hydroxide, then with water until neutral. The ether extract was washed three times with 170 ml of 3 percent aqueous sodium hydroxide, then with water until neutral. The ether solution was dried over Na_2SO_4 and evaporated using a rotary evaporator. The yield of crude diallylether of bisphenol A was 302 grams (98 percent of theoretical).

A 100-gram portion of the crude diallylether in 150 ml of dimethylaniline was refluxed while stirring under nitrogen for 4 hours. The product was taken up in 1 liter of ether and washed three times each with dilute aqueous sulfuric acid, 3 percent aqueous NaOH, and water until neutral. The ether solution was then dried over Na_2SO_4 and the ether stripped off with a rotary evaporator. The dark-brown product was vacuum distilled (180-190 C at 0.3 mm). The yield was 77 grams (77 percent theoretical) of clear, viscous, almost colorless, 3,3'-diallylbisphenol A. An infrared spectrum of this product was consistent with the expected structure.

Analysis for $C_{21}H_{24}O_2$ Calculated: C, 81.77; H, 7.83; O, 10.40
Found: C, 81.55; H, 8.05; O, 10.40 by diff.

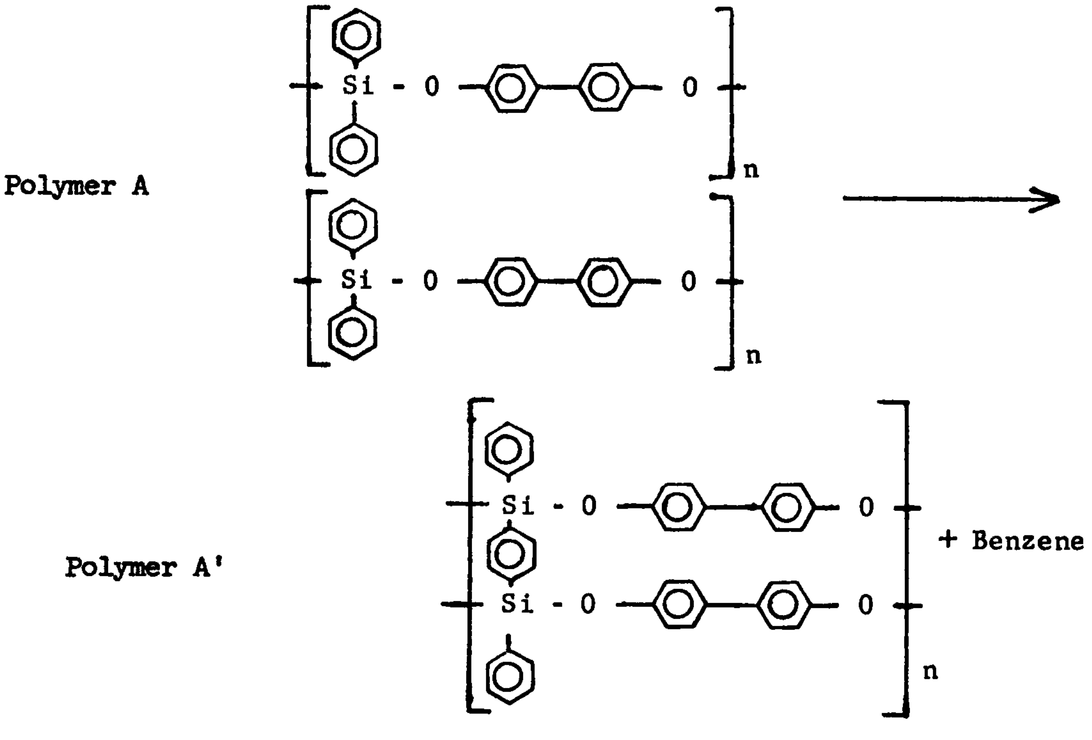
III. SYNTHESIS AND CHARACTERIZATION OF PHENYL-, METHYL-, AND VINYL-SUBSTITUTED POLYARYLOXYSILANES

A. Polymer A - Discussion

1. Programmed Thermogravimetric Analysis

Earlier in this program(1), it was observed that the condensation of dianilinodiphenylsilane with p,p'-biphenol in air or in a vacuum at temperatures exceeding about 250 C sometimes led to the formation of infusible and insoluble forms of the polyaryloxysilane-designated Polymer A. Polymer A has also undergone evaluations and shown promise in adhesive and coating applications after being cured at high temperatures(9,10).

It was reported(11) that heating Polymer A at 250 C to 440 C resulted in the formation of a crosslinked polymer with benzene as a side product, and a possible reaction mechanism for this reaction was proposed.



Thermogravimetric analyses of Polymer A samples under air normally show a catastrophic weight loss beginning at about 400 C, with the polymer probably being reduced essentially to a silica residue. Under nitrogen or a vacuum, approximately a 35 percent weight loss occurs between about 400 C and 700 C, with little more decomposition taking place on further heating to 900 C (Figure 5). The heat-stable residue remaining in this case above 700 C contains a major portion of the organic content of the original Polymer A and should correspond roughly to the structure proposed for Polymer A'. Thus, it was considered of interest to investigate the comparative thermal-oxidative stabilities of the Polymer A and Polymer A' structures.

A sample of Polymer A (Specimen No. 21987-79-1, Mw = 84,000) was heated to 750 C in nitrogen in a thermobalance and a typical 36 percent weight loss resulted (Figure 6). The sample was then cooled and reheated to 900 C in nitrogen. As might be expected, the weight loss during the second heating was only 3.6 percent up to 900 C. A second sample of the Polymer A was heated to 800 C under nitrogen. A thermogravimetric analysis of this residue was then obtained in air at 5 C/min (Figure 7). Decomposition began at about 450 C and a 60 percent weight loss was incurred up to 600 C. This behavior is essentially identical to that observed with nonthermally-treated Polymer A (Figure 5).

These observations, together with the isothermal aging studies of polymer coatings in air reported later in this report, indicate that crosslinking may improve the heat resistance, but not necessarily the thermal-oxidative stability, of a polyaryloxysilane-type material.

2. Impurity Associated Stability Trends

The degradation of Polymer A during heating in air may be the result of several general types of reactions, including pyrolysis, oxidation, and hydrolysis. Each of these reactions could be catalyzed by traces of impurities. This possibility was singled out of many factors as having an important influence on the stability of Polymer A.

Four Polymer A samples were used in a comparative stability study:

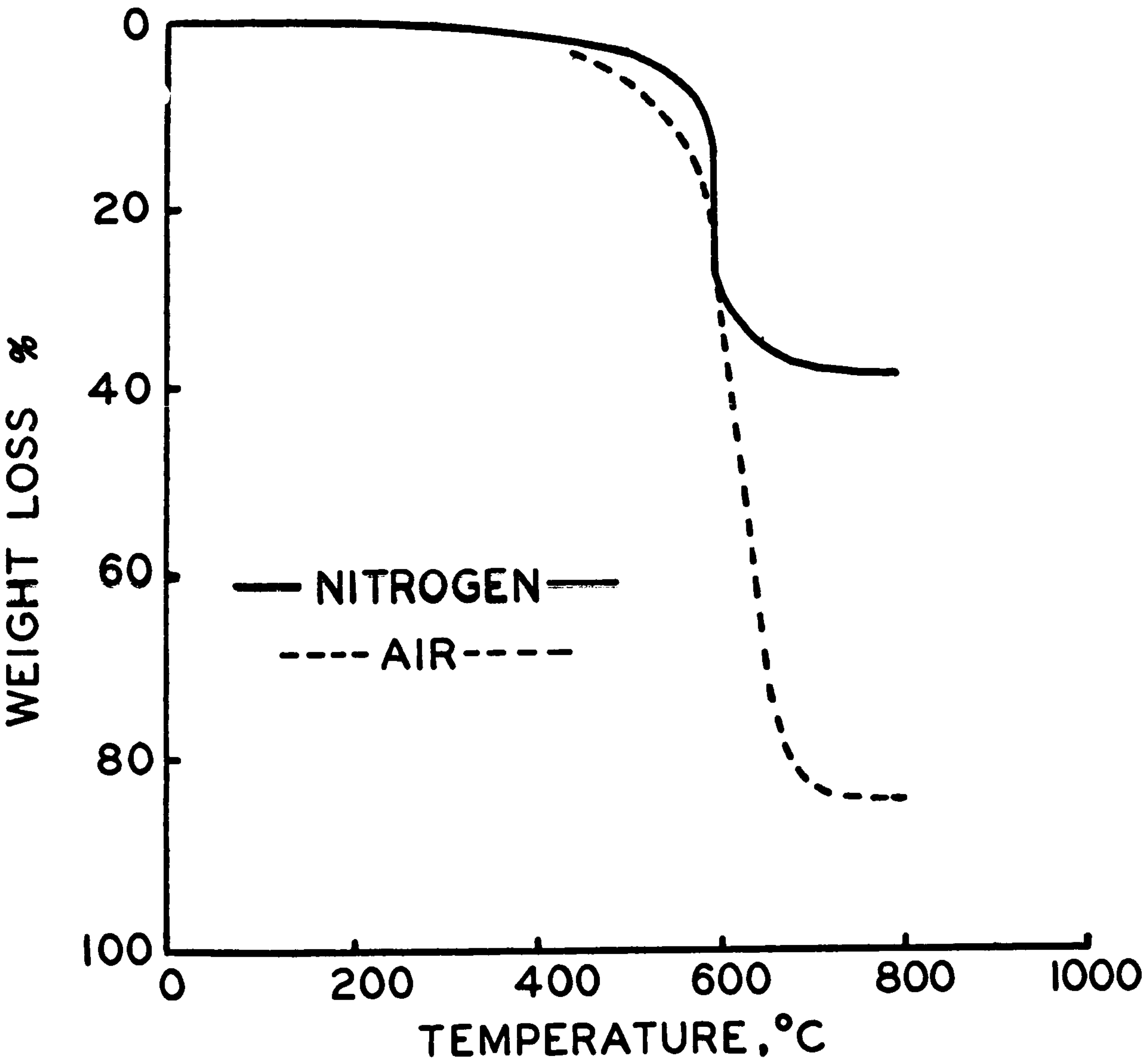


Figure 5. Thermogravimetric Analyses of Polymer A. No. 21987-79-1 Under Nitrogen (——) and Under Air (----)

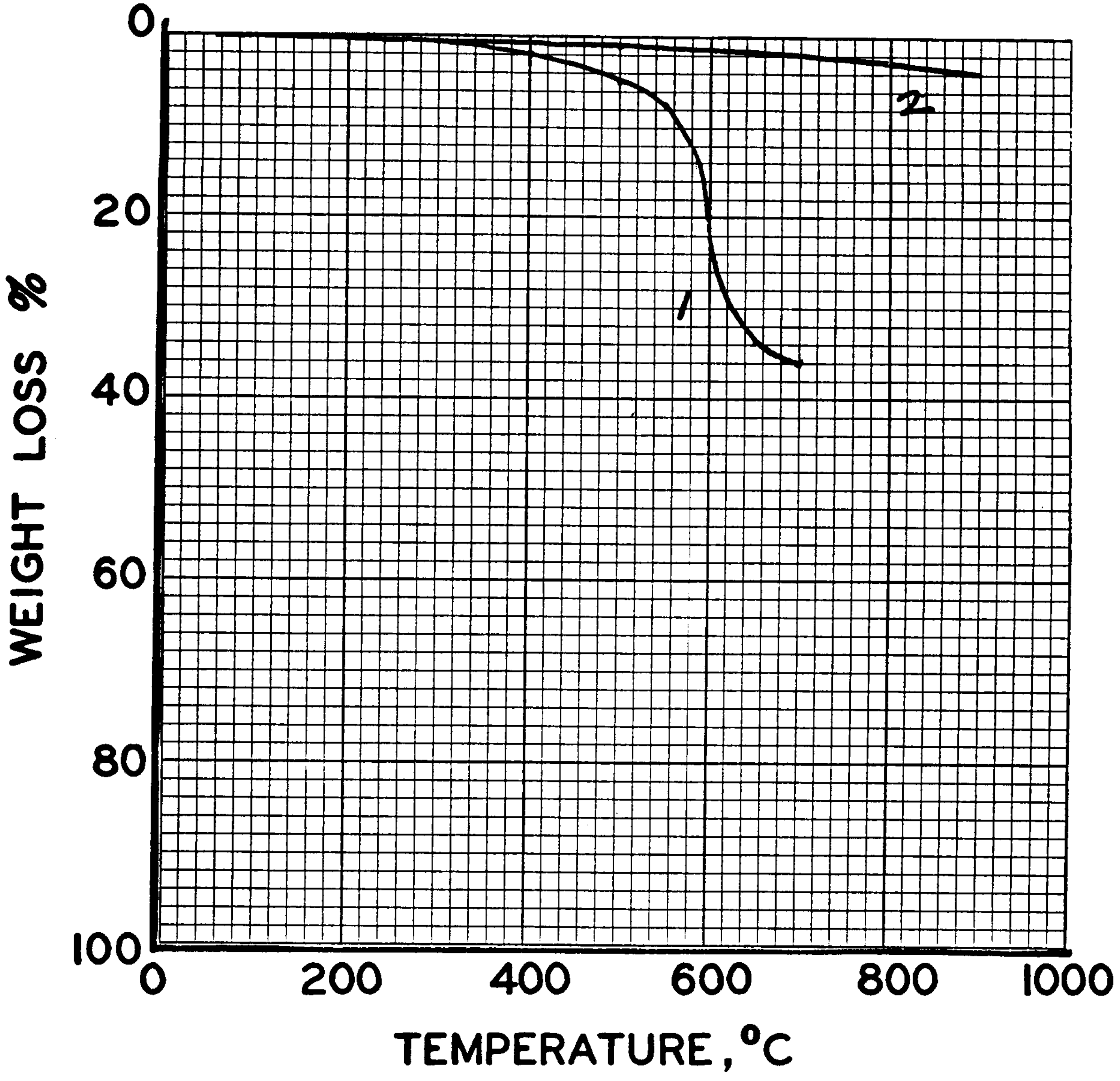


Figure 6. Thermogravimetric Analyses of Polymer No. 21987-79-1 Heated Under Nitrogen (Curve 1), Then Cooled and Reheated Under Nitrogen (Curve 2)

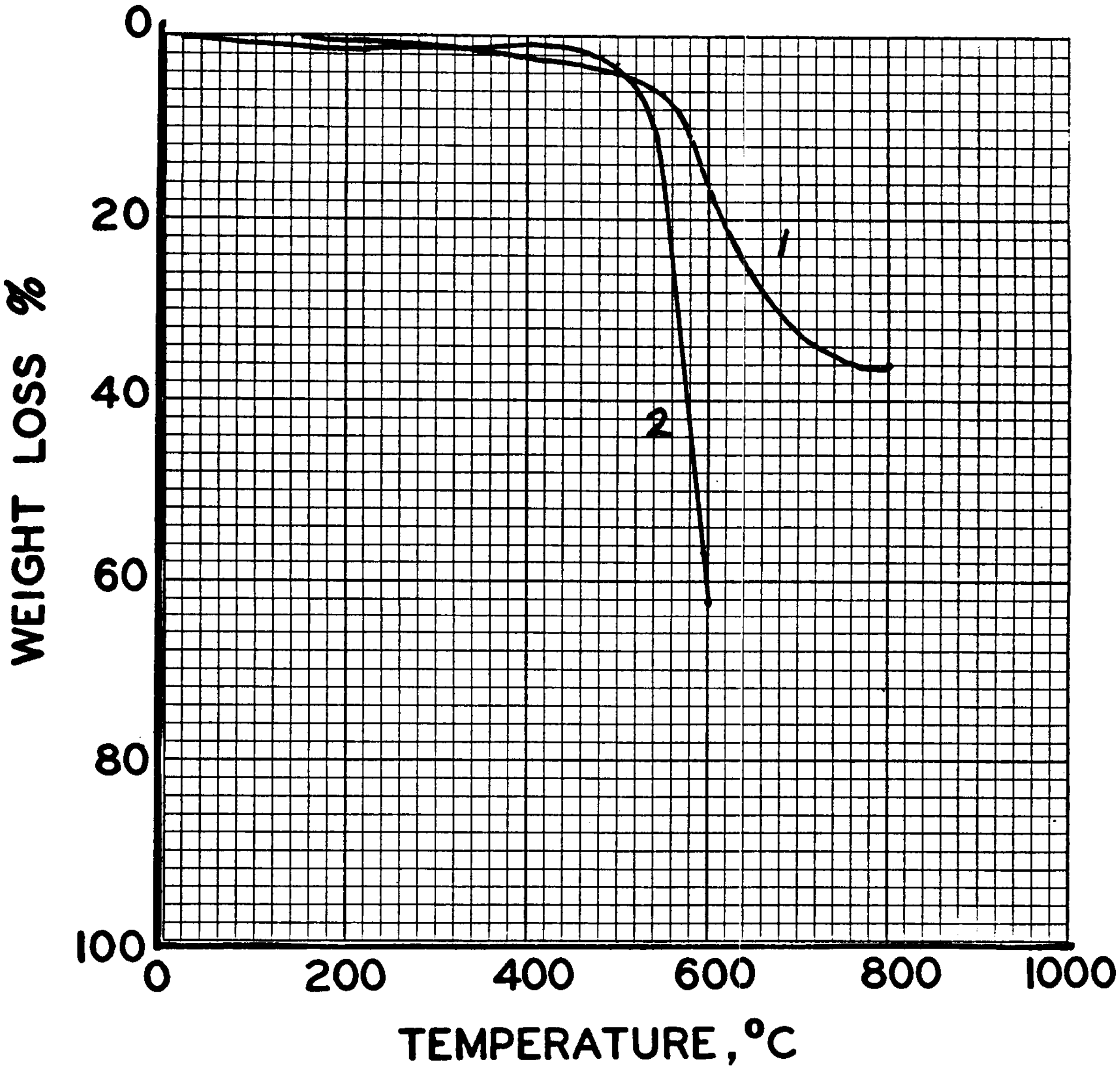


Figure 7. Thermogravimetric Analyses of Polymer A No. 21987-79-1 Heated Under Nitrogen (Curve 1), Then Cooled and Reheated Under Air (Curve 2)

1. Polymer A No. 21987-79-1, a crude black polymer (prepared on a pilot scale) having a weight average molecular weight of 5.73×10^4
2. A sample of Polymer A No. 21987-79-1 purified by precipitation from benzene by methanol to provide a gray-white Polymer A (No. 23753-86)
3. A higher purity pure white Polymer A (No. 23563-90-2) with a weight average molecular weight of 5.88×10^4 prepared using extremely pure monomers in the polymerization and then further purified by precipitation from benzene
4. A p-phenylphenol end-capped Polymer A No. 23563-99-2 having a weight average molecular weight of 3.71×10^4 prepared by condensing high purity dianilinodiphenylsilane with p,p'-biphenol and p-phenylphenol.

Comparisons of thermograms obtained (Figures 8, 9, and 10) for Polymer A samples (23753-86, 21987-79-1, 23563-90-2, and 23563-99-2) of differing purity show only small differences with no well-defined trend associated with purity. The inflection points and weight losses at higher temperature show no sensitivity to purity. Perhaps more significant are the weight losses incurred at lower temperatures. The losses incurred by the high-purity Polymer A samples are very low in the 50 to 400 C region and are an improvement over TGA stability data previously found. The data comprising Figures 9 and 10 are listed in Table 4 to emphasize the very low weight losses incurred in both air or vacuum in the 50 to 400 C range.

The results obtained by isothermal aging of thin films of Polymer A (Figure 11) have shown the influence of purity more clearly than have either programmed thermogravimetric analyses (TGA) or spectroscopy. Thin films of the four different Polymer A specimens were isothermally aged in a circulating air oven at 250 C (Figure 11). The less pure specimens (Nos. 23753-86 and 21987-79-1) underwent significantly more rapid and larger weight losses than did the Polymer A specimens that were prepared with specially purified monomers and further purified by precipitation from benzene solution by methanol.

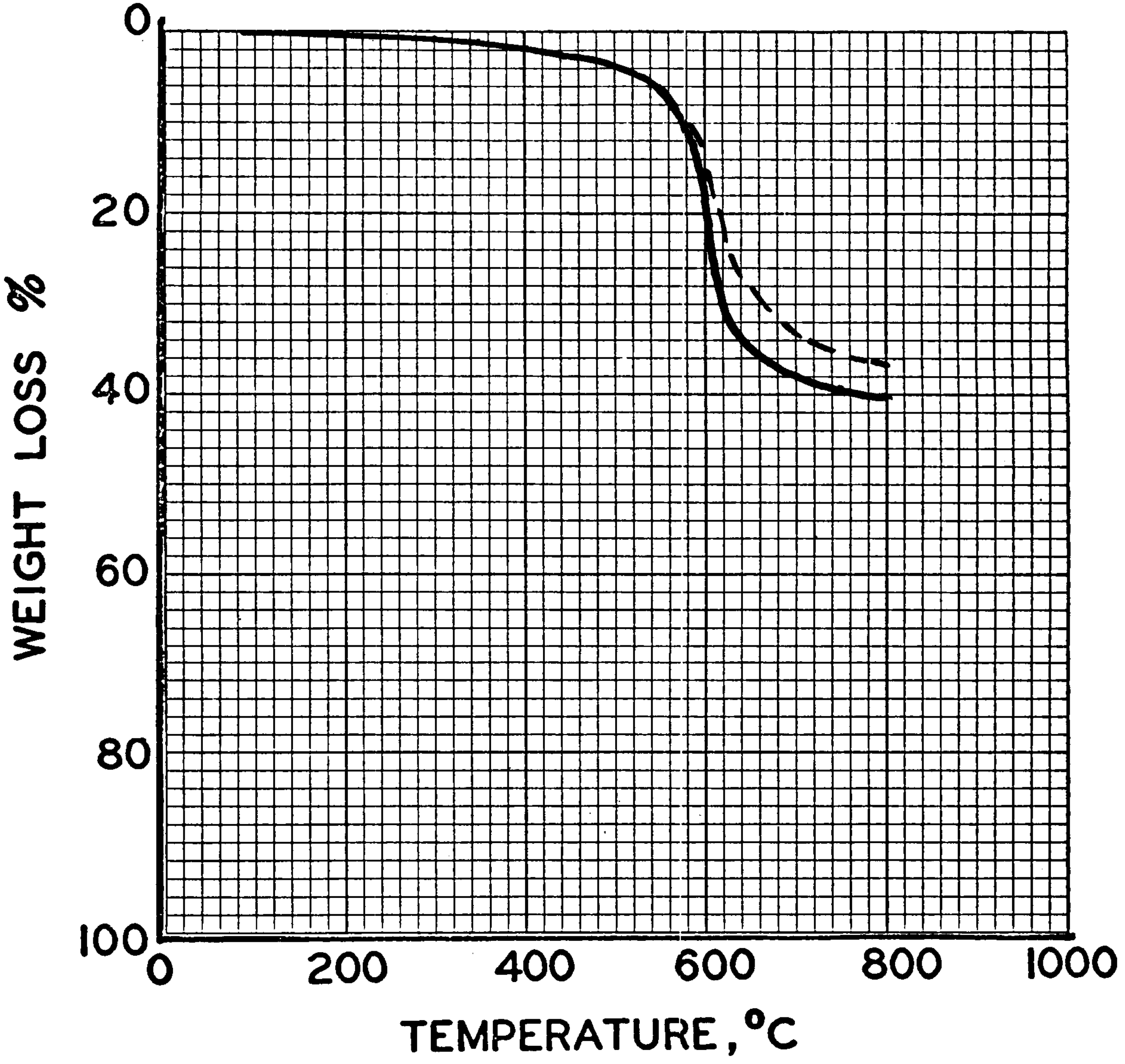


Figure 8. Thermogravimetric Analyses of Purified Sample No. 23753-86 (——) and Crude Sample No. 21987-79-1 (----) Polymer A

Thermogram obtained under nitrogen at 4 C/minute.

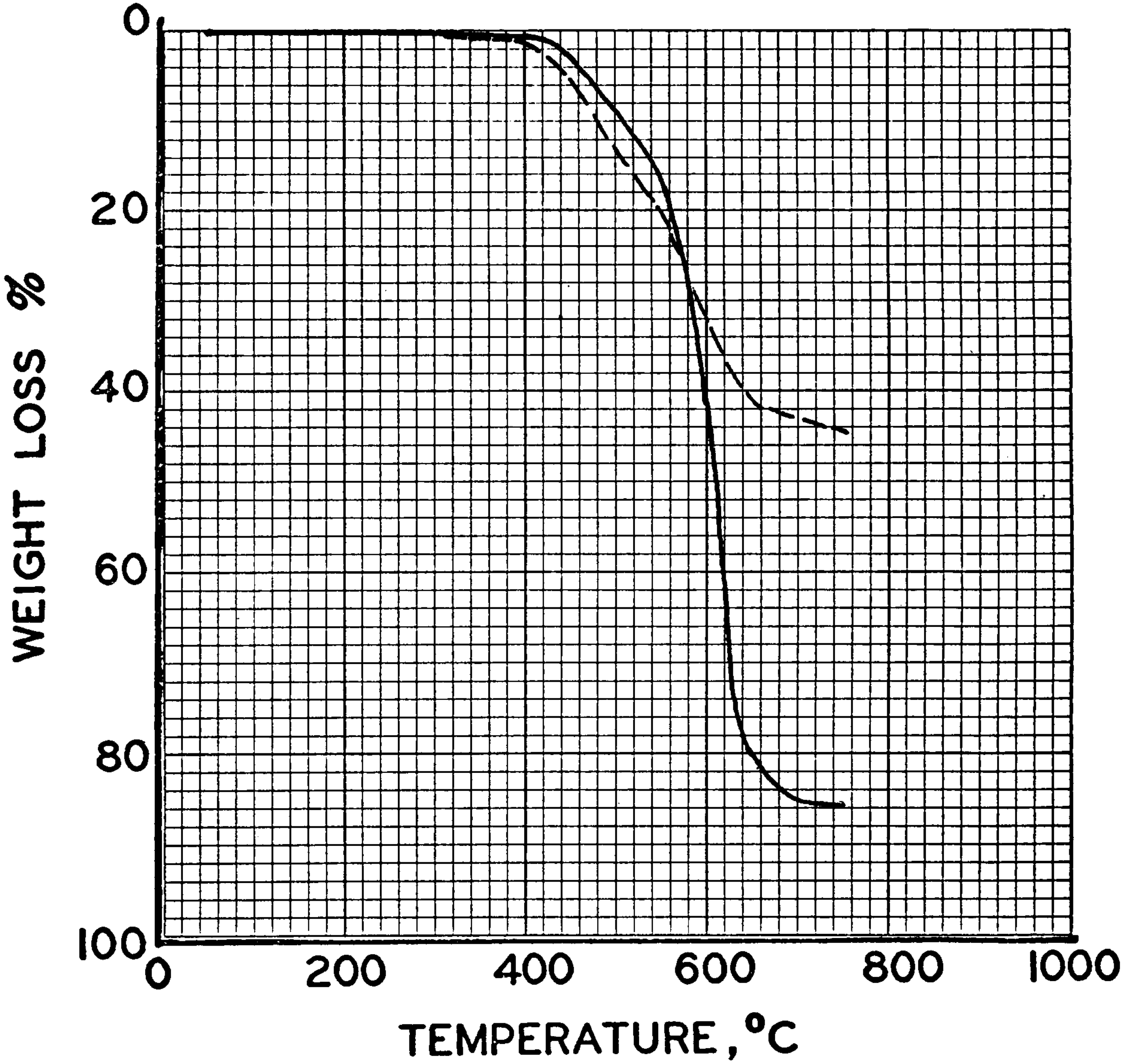


Figure 9. Thermogravimetric Analyses of Highly Pure Polymer A No. 23563-90-2 Thermogram obtained at 4 C/minute in air (——) and in vacuum (----).

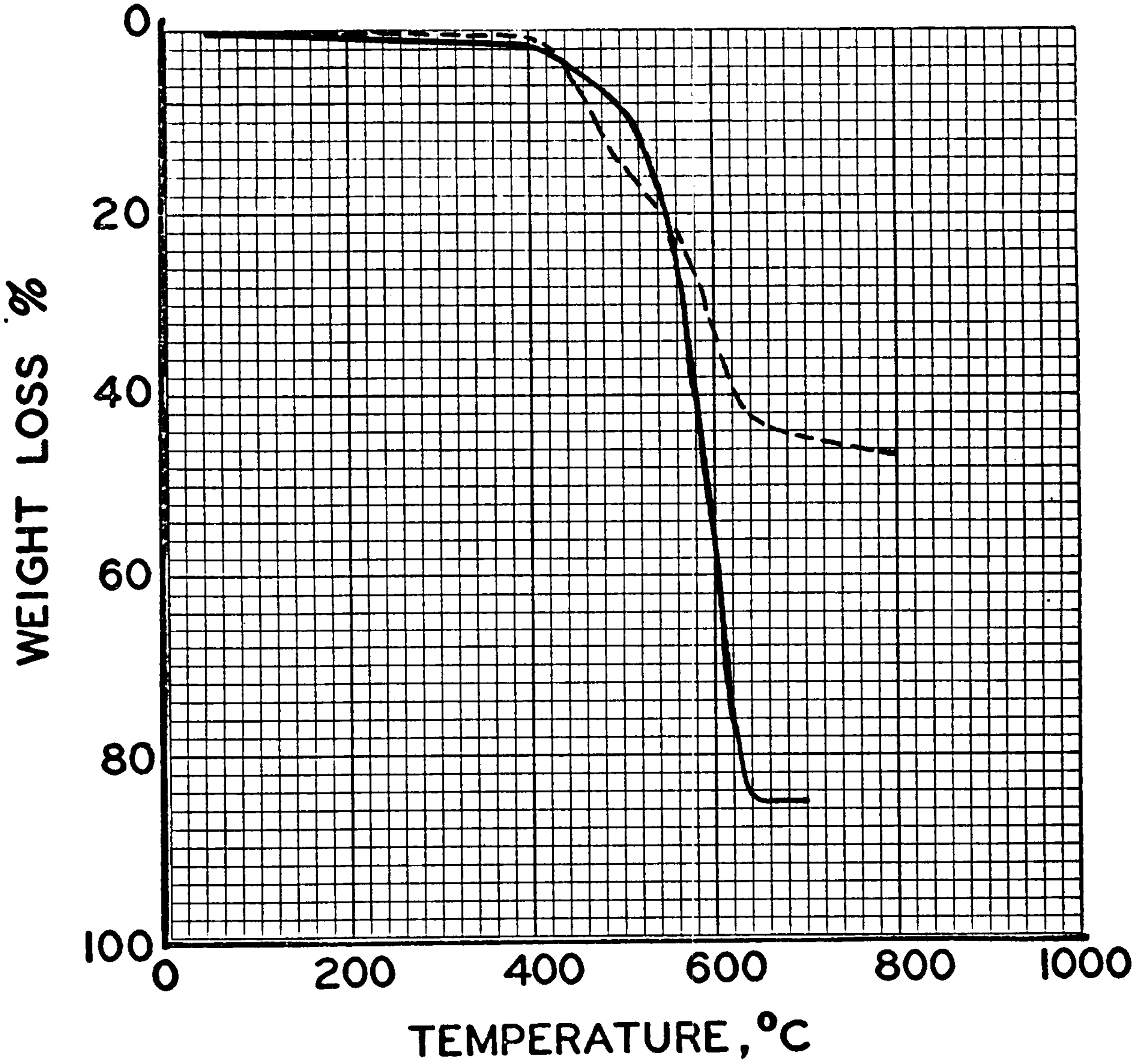


Figure 10. Thermogravimetric Analyses of End-Capped Polymer A No. 23563-99-2 Thermogram obtained at 4 C/minute in air (——) and in vacuum (----)

TABLE 4. THERMOGRAVIMETRIC ANALYSES OF POLYMER A

Sample No. 23563-99-2 Purified and End-Capped Polymer A(a)			Sample No. 23563-90-2 Purified Polymer A(b)		
Temp, C(c)	% In Air(d)	% In Vacuum(e)	Temp, C(c)	% In Air(d)	% In Vacuum(e)
50	0.0	0.0	50	0.1	0.1
100	0.1	0.0	100	0.1	0.1
150	0.3	0.1	150	0.1	0.1
200	0.6	0.1	200	0.1	0.1
250	0.7	0.2	250	0.2	0.3
300	0.8	0.3	300	0.2	0.4
350	1.0	0.5	350	0.4	0.5
400	1.6	1.3	400	0.8	1.4
450	4.4	5.4	450	3.9	4.8
500	8.1	14.4	500	8.4	13.3
550	21.0	20.3	550	16.8	19.4
600	55.5	32.3	600	41.1	32.6
650	85.0	43.0	650	80.0	41.1
700	85.0	44.5	700	85.2	42.9
750	-	45.3	750	85.2	44.2
800	-	46.3	-	-	-

(a) $\overline{\mathrm{Mw}}$ by GPC = 37100, $\overline{\mathrm{Mn}}$ by GPC = 16600.

(b) $\overline{\mathrm{Mw}}$ by GPC = 52200, $\overline{\mathrm{Mn}}$ by GPC = 25800.

(c) Programmed heating rate of 4 C/min.

(d) % weight loss in static air.

(e) % weight loss in vacuum, 0.1 mm Hg.

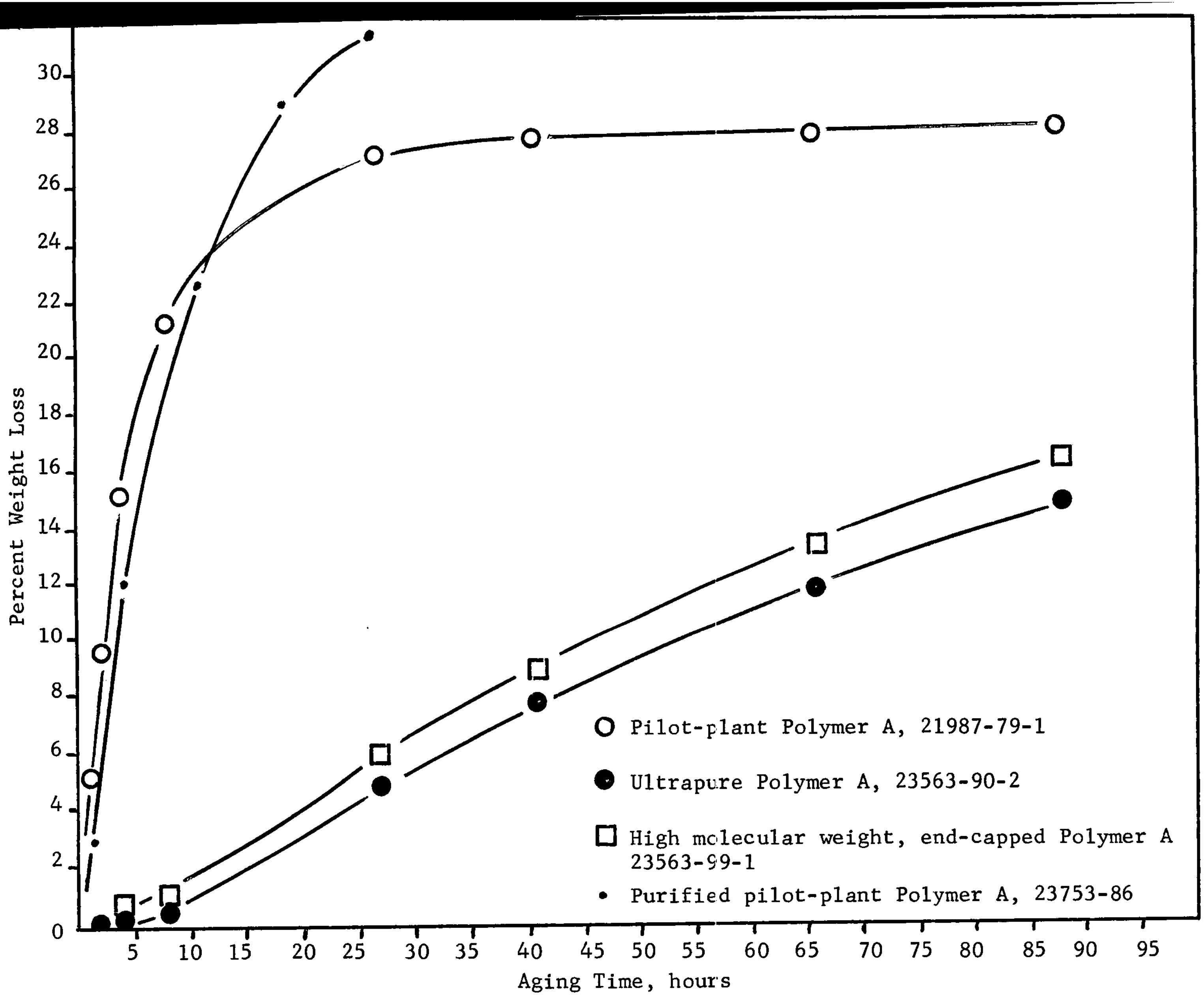


Figure 11. Isothermal Oven Aging of Polymer A Films (250 C)

The purest sample of Polymer A (23563-90-2) lost weight much more slowly (4 percent after 24 hours). The important difference in aging patterns lies in the extremely low initial rate of weight loss observed for the purer Polymer A. In fact, Sample 23563-90-2 did not lose any weight (within experimental error) in the first 2 to 4 hours while Sample 23753-86 lost 10 to 15 percent. Following this, Sample 23563-90-2 exhibited an increasing rate of weight loss up to about 25 to 30 hours aging, after which the rate begins to decrease. The opposite was true for Sample 23753-86. This polymer shows an initial high rate of weight loss which slowly decreases. This type of behavior suggests that a catalyzed thermal and/or thermal oxidative degradation is occurring. When impurities are present in very small concentration, or completely absent, as in Sample 23563-90-2, the polymer is initially much more stable. Even though Sample 23753-86 had been purified by precipitation, the polymer solutions were light-brown, indicating that impurities of some sort, perhaps as part of the molecular structure, were still present.

It is not known if Polymer A No. 23563-90-2 is completely pure or still contained a small but important quantity of impurities. If the former is the case, then it appears that the aging behavior observed is the best that can be hoped for. During aging, an initially pure Polymer A may be slowly degrading, giving rise to impurities which cause the degradation rate to accelerate. On the other hand, a very small impurity content could be causing the initial, very slow degradation which accelerates as the impurity content builds up. Precipitation in a nonsolvent, such as was done in the case of Sample 23563-90-2, should remove much of the free molecular debris while use of a monofunctional end-cap, such as p-phenyl phenol, should reduce or eliminate the "reactive" end group content. An attempt in the latter direction is represented by Sample 23563-99-2 which was also precipitated from solution. While the method of end-capping used cannot be guaranteed to completely eliminate "reactive" end groups, it can be assumed that the concentration of such groups was greatly reduced. The end-capped product was seen to have essentially the same stability as the pure, nonend-capped Polymer A.

Reference to Figure 12 shows that, at 350 C, all the Polymer A samples exhibited high initial rates of weight loss. Although the initial rates for Samples 23563-90-2 and 23563-99-2 were lower than for the other polymers, they were quite high as compared to the behavior of the same polymers at 250 C. There was no evidence of induction periods. Thus, it would appear from Figures 11 and 12 that there is a possibility of significantly improving the stability of Polymer A at 250 C by increasing its purity, but not at 350 C.

3. Influence of Moisture on High-Temperature Stability

The influence of moisture on the aging behavior of Polymer A was studied by heating thin films in controlled air which was either dry or preconditioned by bubbling through water before entering the heating chamber. Inspection of the data from these experiments (see Table 5) reveals no difference, within experimental error, between moist and dry air on the aging of Polymer A. Inadvertently, in some of the experimental runs there was a near-blocking of the exit to the heating chamber. High weight losses occurred as a result of this, as shown in Table 2. This suggests that there was an accumulation of decomposition products in this essentially static atmosphere. These apparently further catalyzed the decomposition of polymer. The isothermal heating periods of both "pure" (Sample 23753-86) and "ultrapure" (Sample 23563-90-2) Polymer A samples clearly show that there is a marked improvement in aging performance with increasing polymer purity in this temperature range.

While Figure 12 indicated that Polymer A No. 23563-90-2 underwent fairly rapid decomposition in air at 350 C, Runs 3-5, Table 5 strongly suggests that the polymer has reasonably good stability in either wet or dry air at 300 C.

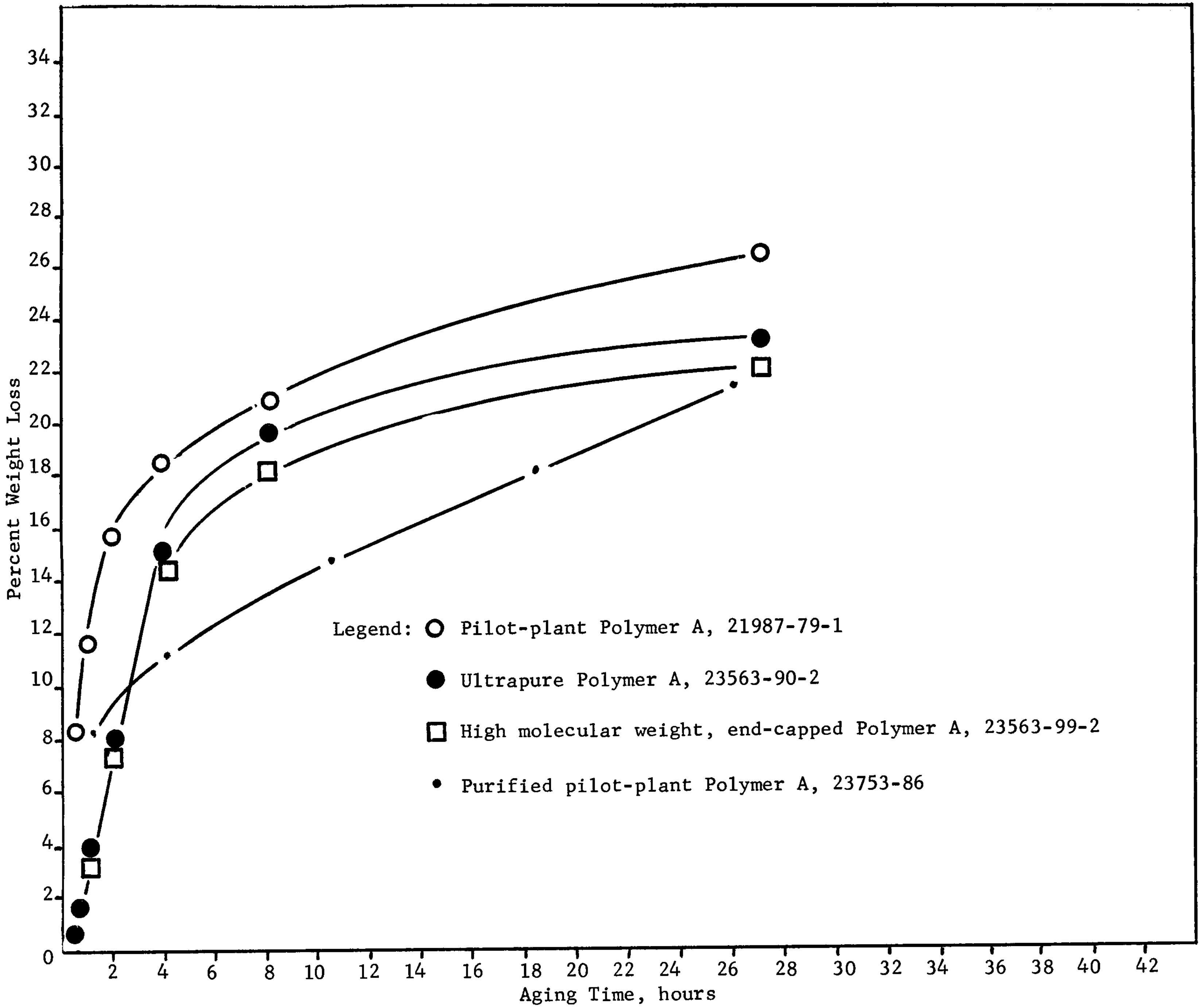


Figure 12. Isothermal Oven Aging of Polymer A Films (350 C)

TABLE 5. ISOTHERMAL WEIGHT LOSSES OF POLYMER A IN CONTROLLED ATMOSPHERES

Total Heating Time, hours	Percent Weight Losses(a)				
	Run 1	Run 2	Run 3	Run 4	Run 5
0.25	1.2	1.6	1.0	2.6	1.5
0.75	5.1	1.8	1.1	2.6	1.7
1.75	5.4	1.9	2.5	2.5	2.1
2.75			1.0		
3.75	5.5		1.9 1.5 (b)	2.6 3.3 (b)	1.7 1.9 (b)
18.75		1.7 2.2 1.7 1.9 1.9 1.4 1.7 (b)			
19.50			1.6 5.9 7.6 1.8 (b)		
24.50				2.7 4.0 10.7(c) 4.0 3.1 (b)	34.3(c) 36.4(c) 6.5 1.1 8.6 (b)
Temperature, C	250	250	300	300	300
Air	Dry(d)	Dry(d)	Wet(e)	Dry(d)	Wet(e)
Polymer	Pure(f)	Ultra pure(g)	Ultra pure(g)	Ultra pure(g)	Ultra pure(g)

(a) Percent weight loss of thin films (0.1 g/16 cm^2) during heating with 60 cc/min air flow across samples.

(b) Replicate analyses.

(c) Samples which had yellowed. After 4 hours, Runs 3, 4, and 5 incurred a partially blocked exit tube from the heating chamber.

(d) Compressed air (breathing grade, National Cylinder Gas Company), estimated as approximately 0.02% water.

(e) Air saturated with water vapor at room temperature, estimated as approximately 2% water.

(f) Slightly gray in color (23753-86).

(g) Pure white in color (23563-90-2).

B. Polymer A - Experimental

Polymer Syntheses and Purification

1. Preparation of High-Purity Polymer A (23563-90). A mixture of 18.326 grams (0.05000 mole) dianilinodiphenylsilane (23563-73) and 9.310 grams (0.05000 mole) p,p'-biphenol (doubly sublimed) was fused under nitrogen in a single-neck, 100-ml, round-bottom flask, previously flamed under a nitrogen stream. The flask was heated to 225 C with a Wood's metal bath. The reactants required about 15 minutes at 225 C before they were completely fused to a clear, colorless melt which was refluxing steadily (aniline evolution). After an additional 10 minutes of reflux at 225 C under 1 atmosphere of nitrogen, the pressure was gradually reduced over a 30-minute period to about 0.5 mm Hg. Aniline distilled rapidly during the period of reducing pressure so that by the time 0.5 mm pressure was obtained, aniline was no longer visible in the flask, and the reaction mixture was a clear, almost colorless, viscous, rapidly bubbling melt. After 30 minutes at 225 C and 0.5 mm, the melt was quite viscous and bubbling very slowly. The temperature was raised quickly to 250 C and a slight decrease in viscosity and increase in bubbling rate were noted. After 2 hours at 250 C and 0.5 mm, the bubbling had ceased entirely, yielding an extremely viscous, clear, very light-tan melt. The flask was flushed to atmospheric pressure with nitrogen and fibers hand-drawn from the melt. These fibers were readily hand cold-drawn to tough, flexible, glossy monofilaments. Samples of this fiber were stored in a dry chamber.

The bulk of the Polymer A was left in the flask and allowed to cool overnight in a dry chamber. The flask broke from the strains induced by the cooling polymer. The polymer plug was carefully separated from the glass fragments, yielding 14.5 grams of Polymer A. A portion of this plug (6.8 grams) was dissolved in about 100 ml of AR benzene. The solution was filtered through a medium-porosity sintered funnel and precipitated in a tenfold excess of rapidly stirred AR methanol, yielding a pure white, fibrous precipitate. This was dried, then redissolved in about 70 ml of AR benzene and freeze-dried, yielding 6.8 grams of pure white, powdered Polymer A. The clear, colorless filtrate from the polymer precipitation step (~850 ml) was evaporated to dryness on a steam bath. About 10 mg of soft, drak-brown solid (about 0.1 percent by weight of the starting Polymer A) was recovered. Thus, the recovery of Polymer A was essentially quantitative (Polymer A is less than 0.1 percent soluble in excess methanol), yet a very small amount of some dark-colored impurity was removed by the purification procedure. This material yielded an infrared spectrum containing strong absorption due to hydroxyl, aliphatic, and carbonyl structures.

The purified, freeze-dried Polymer A was designated 23563-90-2 while the untreated crude product was labeled 23563-90-1. Some polymer had splashed onto the upper walls of the reaction flask during the polymerization and was recovered separately by dissolving in benzene, filtering, and precipitating in a tenfold excess of methanol. This white, fibrous polymer was also redissolved in benzene and freeze-dried, yielding 1.75 grams of pure white powder, which was labeled 23563-90-3. The molecular weights of all three samples of 23563-90 were determined by GPC in THF solution at 23.3 C. The molecular weights obtained were as follows:

Polymer Number	$\overline{Mn}$	$\overline{Mw}$	Ratio, $\overline{Mw}/\overline{Mn}$
23563-90-1	25,900	53,800	2.07
-2	25,800	52,200	2.02
-3	25,700	58,800	2.28

2. Preparation of End-Capped Polymer A (23563-92, 23563-99-1, and 23563-99-2). The polymerizations were carried out in essentially the same way as 23563-90 except that a small portion of the p,p'-biphenol was replaced by sublimation-purified p-phenyl phenol. Polymerization 23563-92 was carried out in a 100-ml, round-bottom flask while Polymerizations 23563-99-1 and -2 were accomplished in tubes of approximately 35 cc capacity. The reactant charges were as follows:

Polymerization Number	Dianilinodiphenylsilane (23563-73)		p,p'-Biphenol (Sublimed)		p-Phenyl Phenol (Sublimed)	
	Grams	Mole	Grams	Mole	Grams	Mole
23563-92	7.3997	0.0219	4.0592	0.0218	0.0340	2 x 10^{-4}
-99-1	3.6998	0.01095	2.0296	0.01090	0.0170	1 x 10^{-4}
-99-2	4.0094	0.01093	2.0306	0.010905	0.0113	6.67 x 10^{-5}

The monomers were fused under nitrogen at 215 C (Wood's metal bath). The reactants required about 15 minutes at 215 C to completely fuse. After an additional 5 minutes at 215 C under nitrogen, the pressure was gradually reduced over a 30-minute period to 0.4 mm. The temperature was raised to 225 C for 20 minutes and then to 235 C for an additional 2 hours. By then, the pressure was 0.33 mm and the melts were very light-colored and bubble-free. While Sample 23563-99-2 was quite viscous, Samples 23563-99-1 and 23563-92 were thin, free-flowing melts. The flasks were flushed with nitrogen and attempts made to draw fibers by hand. Weak fibers which could not be cold-drawn were pulled from Sample 23563-99-2, while fibers could not be drawn from the other two products. The melts were cooled and recovered. All three were purified in the same way as described for Sample 23563-90. Molecular weights were obtained by GPC in THF solution at 23.3 C and are listed below:

Polymer Number	$\overline{M}n$	$\overline{M}w$	Ratio, $\overline{M}w/\overline{M}n$
23563-92-1(a)	4,700	8,900	1.89
-2(b)	5,300	12,000	2.27
-99-1(b)	8,400	12,800	1.52
-2(b)	16,600	37,100	2.24

(a) Unpurified polymer.
(b) Purified polymer.

The expected molecular weights for these end-capped polymers would be of the order of 10 times those found. Earlier work has suggested that some anilino reactivity is lost in polymerization so that the polymer has predominantly phenolic end groups. If this is correct, it could also account for the low molecular weights of the end-capped polymers. The "excess" end groups would then be both phenolic and whatever structures are formed as a result of loss of anilino reactivity.

3. Isothermal Aging of Polymer A. Solutions of pure and crude Polymer A samples were evaporated, then vacuum heated at 60 C/ 0.5 mm for 16 hours in aluminum weighing dishes of 28 cm^2 area. The resulting clear, tightly adhering films weighed 0.2 ± 0.05 g. The samples were then aged in 250 and 350 C forced-draft ovens and the appearance and weight losses of each polymer were observed in duplicate. The films showed discoloration and loss of strength after aging to the point where a 10 percent weight loss was incurred.

4. Isothermal Aging of Polymer A in Controlled Atmospheres. Polymer A from Samples 23563-90-2 and 23753-86 were solution-coated onto aluminum foil boats which had been cleansed of grease with refluxing benzene. The films weighed 0.1 gram with an area of 16 cm^2. They were placed in a cylindrical heating chamber, concentrically surrounded by heating elements and insulation. The all-glass cylinder contained flat glass trays to accommodate 10 samples. The inlet was connected to a cylinder of National Cylinder Gas Company, breathing grade air, which was regulated through the chamber at 60 cc/min. The exit tube passed through cold traps, which would allow isolation of volatile decomposition products. Where moist air was desired, the air was preconditioned by bubbling through a water trap prior to its entering the heating chamber. Infrared analyses of the residues after aging revealed Si-O-Si structures when the weight losses exceeded approximately 20 percent. A sublimate found near the exit tube proved by infrared spectroscopy to be p,p'-biphenol. In the third through fifth runs, the cold trap was discovered to be nearly blocked sometime subsequent to the 3.75-hour heating time.

5. Isothermal Pyrolysis of Polymer A. A pilot-scale preparation of Polymer A, Sample 21987-80-1, was purified by triple precipitation

from a benzene solution into excess methanol. The precipitate was freeze-dried from benzene to yield a gray-white polymer. A 0.1044-gram sample of this lyophilized polymer was pyrolyzed under an inert atmosphere at 250 C. The sample was placed in a 100-ml bottle that had one small neck sealed by a rubber septum and another neck connected by means of a three-way stopcock to either a vacuum pump or a dry nitrogen inlet. The sample was evaluated and then flushed with nitrogen several times. After the final nitrogen flush, the system was evacuated to 0.3 mm pressure and the system closed to both nitrogen and vacuum. The pyrolysis bottle was immersed to a depth of approximately 2 cm in a sand bath preheated to 250 C. The Polymer A melted almost immediately to form a brown liquid which noticeably outgased. The sample was pyrolyzed for 24 hours. The bottle was then cooled and nitrogen admitted into the sample chamber. On further cooling in solid carbon dioxide and acetone bath, white crystals were deposited on the walls of the pyrolysis chamber. The bottle was warmed to approximately 50 C and the head space was sampled by means of a gas syringe. A 5 cc sample of the gas was injected into a Perkin-Elmer, Model 800, double-column gas chromatograph using Porapak Q columns, 6 feet by 1/8 inch, 50 C programmed to 225 C, and flame detection. A 3 cc sample of the same head space was put through an equivalent column in an aerograph oven (HY-Fi, Model 500). The column eluate exited into a high resolution mass spectrometer (MS9, Associated Electrical Industries) where the major components were positively identified.

A white, finely divided sublimate on the upper walls of the pyrolysis bottle was separated from the residue in the bottom of the bottle by washing down the walls with acetone. The nonvolatile residue was completely insoluble in acetone and benzene. The acetone solution of the sublimate was evaporated to yield 0.0124 gram (12 percent of initial weight) of white solid which was submitted to infrared analysis as a KBr pellet.

The pyrolysis residue was weighed and found to be 0.0827 gram (79 percent of initial weight). This residue was not softened by benzene after 24 hours and the clear benzene was found to be free of any dissolved solids upon evaporation. The residue was attacked by sulfuric dichromate very slowly. An infrared spectrum of the residue was difficult to obtain because the material grinds to smaller size in KBr with difficulty. Nevertheless, a KBr pellet revealed a spectrum which, relative to the spectrum of undegraded Polymer A, showed new bands at 8.9-9.8 microns (1125-1025 cm^{-1}) and 2.9 microns (3450 cm^{-1}). Other details of the spectra were the same.

6. Pyrolysis Product Studies. a. Air Aging of Polymer A. During the present reporting period, the oxidation and pyrolysis products of several polyaryloxysilanes under simulated extreme environments were investigated. The purpose of the study was to determine whether the substituents or the backbone of the polymer decompose under the thermal-oxidative conditions. For this purpose, instrumental methods were employed to identify products originating from thin films of Polymers A, B, and C subjected to heating under an air flow. The following sequence of analytical operations was followed: thin films of polymers were exposed to an air flow in a cylindrical heating chamber; from time to time the aged polymer residue was removed for infrared analysis (IR); the effluent air stream passed through a room temperature trap, then into a trap cooled by dry ice - acetone, then into a gas bottle. Any effluent fractions that appeared in the traps were analyzed by gas-liquid chromatography (GLC) and by IR. Isolation of components from the GLC eluate by a cold trap makes possible analyses by mass spectrometry (MS) of either pure components or simple mixtures. The latter are further resolved by a gas chromatograph feeding directly into a high resolution mass spectrometer.

Table 5 lists the weight losses observed in these experiments. A heavy deposit which formed at both ends of the heating tube was shown by IR to be p,p'-biphenol. An IR of the total dry ice - acetone trapped material showed the presence of water, some Si-O-Si bands, no detectable CH bands, and an unidentified broad band at 1500 cm^{-1}. Infrared spectra of the polymer samples after aging showed no change in the original Polymer A spectrum until a high weight loss had occurred. The IR of the aged Polymer A having the greatest weight loss (Run 5, 36.4 percent weight loss after 24.5 hours), and which had turned yellow, showed that the residue was a mixture of Polymer A and Si-O-Si structures.

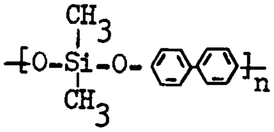
b. Isothermal Pyrolysis of Polymer A. Pilot-scale Polymer A (Sample 21987-80-1) was rendered nearly color-free (sample then designated No. 23753-86) by precipitation from solvent. A sample of this purified Polymer A was subjected to a 24-hour pyrolysis in a static, 250 C, inert nitrogen atmosphere at reduced pressure. A sublimate found on the upper walls of the pyrolysis chamber accounted for 12 percent of the initial material. The material had an infrared spectrum identical with that of p,p'-biphenol. The residue of the polymer was infusible and insoluble, and corresponded to 79 percent of the initial weight of the polymer. An infrared spectrum of this residue revealed two significant changes in the structure of the polymer. A moderate amount of Si-O-Si structure and a small amount of O-H structure appeared. Analyses of the head space in the pyrolysis chamber by gas chromatography and mass spectrometry showed the major gas components to be nitrogen and benzene. Flame detection yielded 19 trace components which ranged from 0.004 to 0.087 area percent relative to the chromatograph area of benzene of 99.4 percent (nitrogen was not detected). Using mass spectrometry for detection (which was not sensitive to the trace components), benzene was positively identified. The benzene chromatograph area was 21.4 percent and nitrogen (carrier gas) was 77.3 percent (uncorrected for ionization efficiencies). These findings indicate that Polymer A slowly undergoes both silicon-to-phenyl and silicon-to-oxygen bond cleavages during heating, and that Si-O-Si structures are more thermally stable than Si-O-biphenol.

The foregoing experiment was repeated on a very pure Polymer A, Sample 23563-90-2. A 0.1476-gram sample was pyrolyzed for approximately 10 to 15 hours, and 13.3 mg of p,p'-biphenol (identified by IR) was isolated as a decomposition product. Benzene was again identified by gas chromatography as the major gaseous product.

C. Polymer B - Discussion

1. Preparation and General Properties

A series of polyaryloxysilanes of type B



were prepared by melt condensing dianilinodimethylsilane with p,p'-biphenol (Table 6) using polymerization times of 1.5 to 5.0 hours at 225 C. In each case, the polymerizations were initiated under nitrogen and were then completed under a vacuum to achieve the maximum removal of the condensation side product, aniline. As in the case of condensations of dianilinodiphenylsilane with p,p'-biphenol, the reactions of dianilinodimethylsilane with the diol appeared to begin at approximately 200 C and proceeded very rapidly. The polymerization time had no apparent effect on the molecular weights obtained.

TABLE 6. CONDENSATIONS OF DIANILINODIMETHYLSILANE WITH p,p'-BIPHENOL

Sample No. 23563-13	Polymerization Time (Hours) at 225 C	Polymerization Time (Hours) at 0.3 mm	M_w(a)
1	1.5	1.0	82,400
4	2.5	2.0	88,000
3	3.5	3.0	86,100
2	5.0	4.5	96,300

(a) By gel permeation chromatography using 1,2,4-trichlorobenzene as the solvent at 130 C using 10^5, 10^4, 10^3, and 10^2 columns.

The molecular weights (Mw) of the polymers shown in Table 6 were determined by gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene as the solvent and based on previous GPC data obtained for Polymer A(1); they ranged from 82,000 to 96,000. These data indicate that it may be somewhat easier to consistently obtain high molecular weight polymers from dianilinodimethylsilane than from dianilinodiphenylsilane. The dimethylsilyl-containing polyaryloxysilanes were found to exhibit good thermal stability in both air and nitrogen (Figure 13). The thermogravimetric analyses showed a somewhat higher thermal breakdown temperature under air than nitrogen, suggesting that oxidation-induced crosslinking during heating produced a more stable species.

The polymers shown in Table 6 were readily soluble in warm o-dichlorobenzene or 1,2,4-trichlorobenzene. Good quality films were prepared by casting solutions of Polymer No. 23563-15 (Mw = 48,000) from o-dichlorobenzene on a chrome-plated casting surface heated to 100 C (Table 7). The cooled films released readily from the plate at room temperature (~23 C), were colorless, transparent, and tough. The softening temperature of the film as determined on a Fisher-Johns melting point block was 85-90 C. The same polymer was easily converted to transparent, tough sheet by compression molding at low pressure between sheets of aluminum foil in a laboratory press with platens heated to 125 C. Test specimens of the compression molded sheet and solvent cast film showed elongations up to about 150 percent at room temperature and tensile strengths up to about 4,700 psi.

A number of fibers were drawn from a melt of Polymer No. 23563-15 (Mw = 48,000 by GPC). These fibers could be cold-drawn by hand approximately 130-150 percent of their original lengths to provide filaments having tensile strengths as high as 50,000 psi and tenacities in some cases exceeding 4 grams per denier (Table 8). The higher strength values were obtained from the smallest diameter fibers. An evaluation of cold-drawn fibers (Table 9) from a similar polymer having a molecular weight (Mw) of 96,000 indicated tenacities roughly comparable to those obtained for the lower molecular weight polymer. These data suggest that biaxial orientation of the polymer film might also provide strength

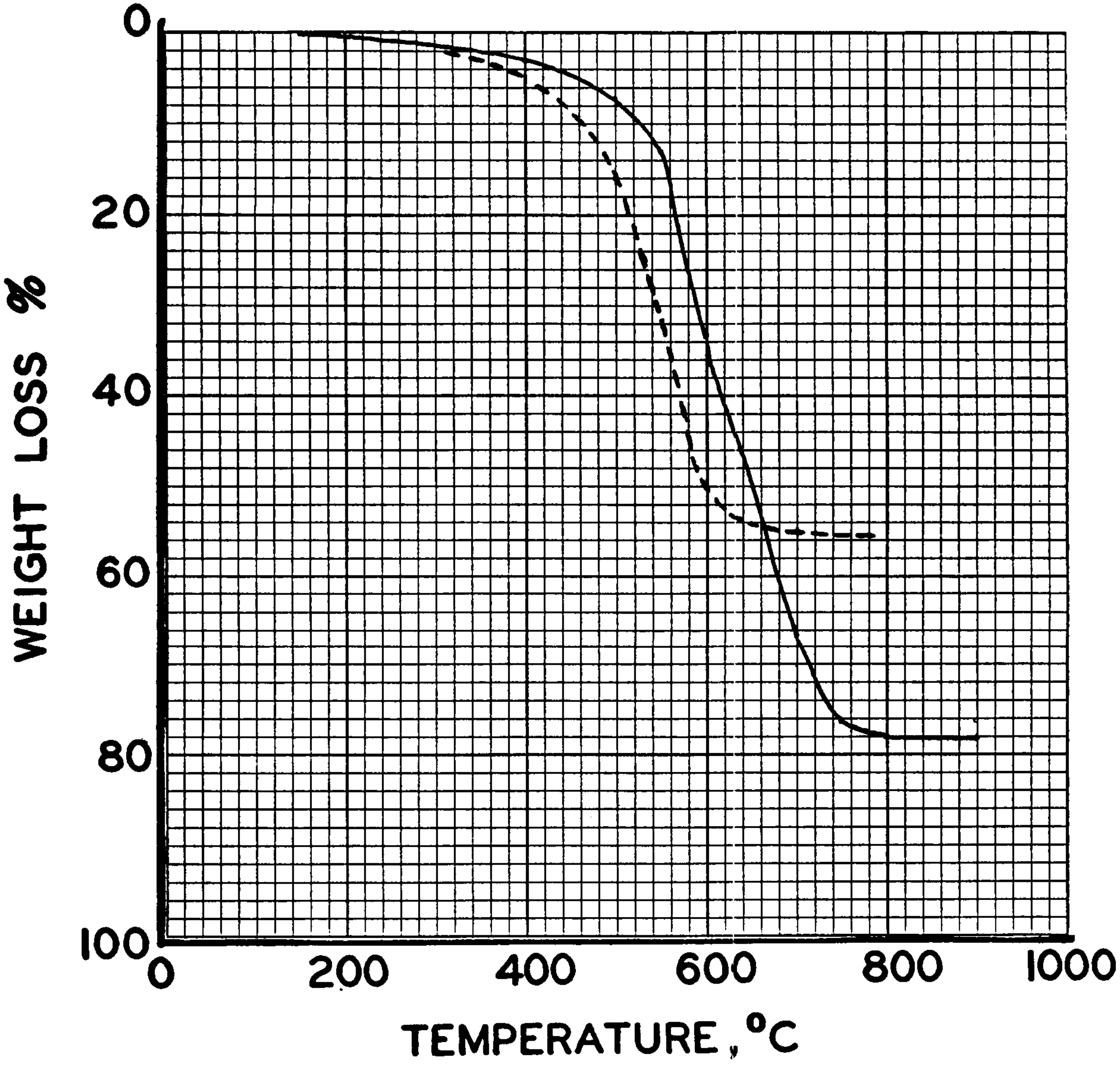


Figure 13. Thermogravimetric Analyses Under Air (——) and Nitrogen (----) of Polymer B No. 23448-5-A

TABLE 7. TEST RESULTS FOR FILM FROM POLYMER B NO. 23563-15

	Thickness, mils	Tensile Strength, psi
A. Solvent-Cast Film(a)	3.2	4,186
	3.2	3,125
	3.3	4,576
	3.5	4,514
	3.6	4,000
	3.6	3,556
	3.6	2,667
	3.7	4,432
	3.8	4,000
		3,895
B. Solvent-Cast Film After 53 Hour Immersion in Distilled Water (23 C)(a)	3.3	2,636
	3.4	4,147
	3.5	4,571
	3.6	4,194
	4.0	4,000
		3,910
C. Compression Molded Sheet(b)	24.0	3,467
	25.0	3,104
	26.5	4,135
	30.0	4,773
	35.0	4,685
		4,032

(a) Pulled as 3 x 1-inch strips.
(b) Molded at 125 C.

TABLE 8. TEST RESULTS FOR HAND-DRAWN FIBERS FROM POLYMER B NO. 23653-15

	Fiber Diameter, mils	Tenacity, grams/denier	Tensile Strength, psi
A. As Cold-Drawn	6.0	1.69	22,913
	7.0	1.27	17,219
	8.0	1.17	15,863
	9.0	1.40	18,981
	9.0	1.35	18,303
	9.0	1.26	17,083
	9.5	1.63	22,100
	11.0	1.56	21,151
	12.0	0.80	10,846
	12.0	0.39	5,287
		1.25	16,948
B. After 16-Hour Immersion in Distilled Water (23 C)	2.5	4.33	58,708
	5.5	1.82	24,676
	6.0	2.09	28,337
	6.0	1.21	16,405
	6.5	1.89	25,625
	7.0	1.43	19,388
	8.0	1.27	17,219
	8.0	1.24	16,812
	12.5	1.32	17,897
	12.5	0.96	13,016
		1.75	23,729
C. After 14-Day Immersion in Distilled Water (23 C)	2.2	4.19	56,809
	2.2	3.07	41,624
	4.5	3.82	51,793
	4.5	3.69	50,030
	5.0	1.07	14,507
	5.5	2.48	33,624
	7.0	1.20	16,270
	7.5	0.74	10,033
	17.0	0.57	7,728
		2.31	31,320

TABLE 9. TEST RESULTS FOR HAND-DRAWN FIBERS FROM POLYMER B NO. 23563-13-2 (Mw = 96,000)

Fiber Diameter, mils	Tenacity, grams/denier
8.5	1.04
8.5	1.01
13.0	1.39
10.5	0.70
5.5	1.66
10.0	1.23
10.0	1.37
11.0	1.27
8.0	1.01
7.0	1.04
9.5	1.63
5.0	1.17
5.0	1.08
7.5	0.41
7.0	1.18
	1.06

properties of considerable interest for use at ambient or perhaps cryogenic temperatures.

The relatively low softening temperature of these polymers precluded any mechanical tests on film to determine the effect of prolonged exposure of the polymer in boiling water. However, it is of interest to note that fiber specimens of Polymer B No. 23563-15 showed similar tensile and tenacity values (Table 8) before and after immersion in distilled water for 14 days, thus indicating no detectable sensitivity to moisture at room temperature.

X-ray measurements were made on several specimens of Polymer B, No. 23563-15. Solvent cast film (Figure 14A) and compression molded sheet (Figure 14B) gave X-ray diffraction spectra characteristic of amorphous materials. Undrawn (Figure 14C) and drawn (Figure 14D) fibers showed patterns of lines indicating orientation of differing degrees and more pronounced in the latter. The ability of the Polymer B to be cold-drawn while the diphenyl-substituted analogue (Polymer A) described earlier(1) could not probably results from closer lateral chain packing in the former as a consequence of its smaller pendent groups.

Differential thermal analyses of film, undrawn fiber, and drawn fiber specimens of Polymer B, Sample No. 23563-15, were obtained at 4 degrees C/minute to 500 C in dynamic nitrogen. There were no indications of any chemical or physical changes occurring below 500 C. In no case was an endotherm attributable to crystalline melting observed.

2. Crosslinking Studies

Attempts were made to crosslink Polymer B No. 23563-15 by means of peroxide catalysts. Films of the polymer were solvent cast from o-dichlorobenzene solutions containing either benzoyl peroxide (5 percent of weight of polymer) or t-butyl perbenzoate. The films were dried at 100 C, then the peroxide and perbenzoate films were heat-treated at 100 C and 200 C, respectively, for 1 hour. In both cases, the heat-treated films were soluble in hot 1,2,4-trichlorobenzene and could be compression molded in a laboratory press, indicating that gel formation had not occurred.

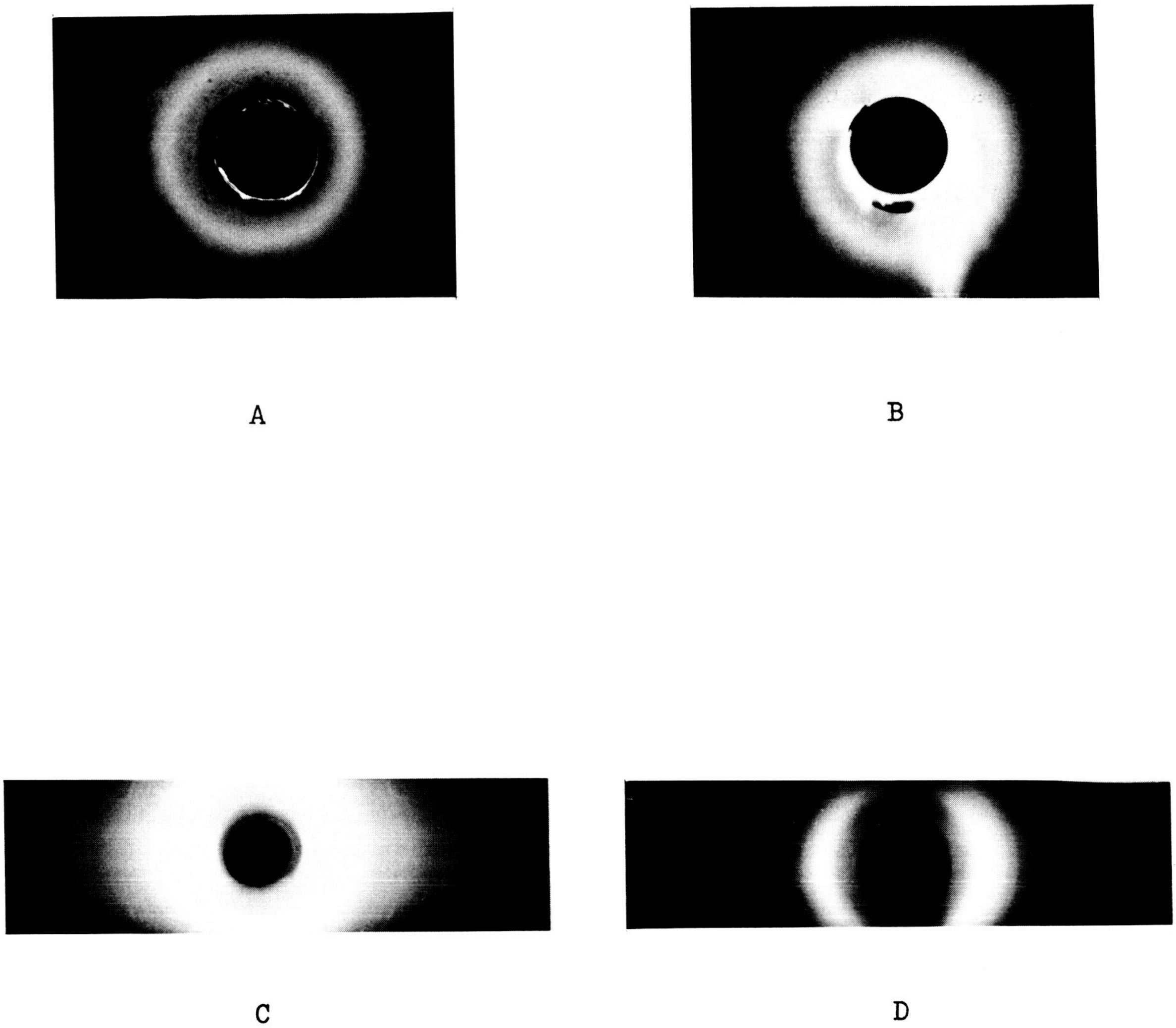
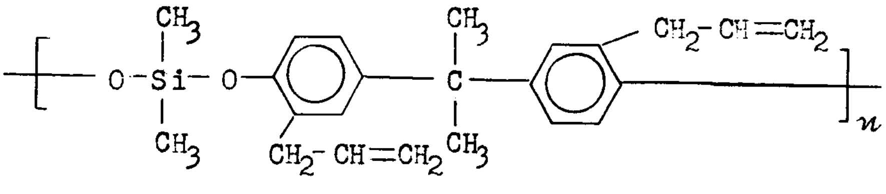


Figure 14. X-Ray Diffraction Patterns for Solvent Cast Film (A), Compression Molded Sheet (B), Undrawn Fibers (C), and Drawn Fibers (D) of Polymer B No. 23563-15

Positive evidence of crosslinking was obtained by casting a solution of Polymer B No. 23563-15 from 1,2,4-trichlorobenzene containing divinylbenzene and t-butyl perbenzoate. The film, cured for 1.5 hours at 170 C, did not dissolve upon being boiled for 2 hours in 1,2,4-trichlorobenzene. This film was brittle, and cracked during its preparation, indicating that the degree of crosslinking may have been excessive.

An allyl-substituted B-type polyaryloxysilane was prepared by condensing dianilinodimethylsilane with 3,3'-diallylbisphenol A.



This polymer was a very low-melting, transparent, tacky, gumlike material. It was readily converted to a tack-free, insoluble, infusible (at 250 C) product by heating it at 160 C with 2 parts of t-butyl perbenzoate. The cured resin was soft and semibrittle at room temperature and leatherlike at 250 C. A similar polymer having 75 percent of the 3,3'-diallylbisphenol A replaced by p,p'-biphenol could be cured effectively in the form of a thin coating but a thicker section failed to respond satisfactorily to free-radical catalysis.

The infrared spectrum of Polymer B No. 23448-5-A (Figure 15) was consistent with the spectra of previously examined polyaryloxysilanes, showing absorptions between 824 and 835 cm^{-1} due to C-H out-of-plane deformation contributed by 1,4-phenylene chain units, a broad band system between 1200 and 1300 cm^{-1} apparently characteristic of phenoxy-silicon linkages, and C-H stretch absorption at about 2900 cm^{-1} as a result of the methylsilyl chain components.

3. Thermogravimetric Analysis

Polymer B, before and after purification by precipitation from a solvent, yielded essentially the same TGA thermogram (cf Figure 16) under nitrogen. Improvement in its thermal-oxidative stability did not

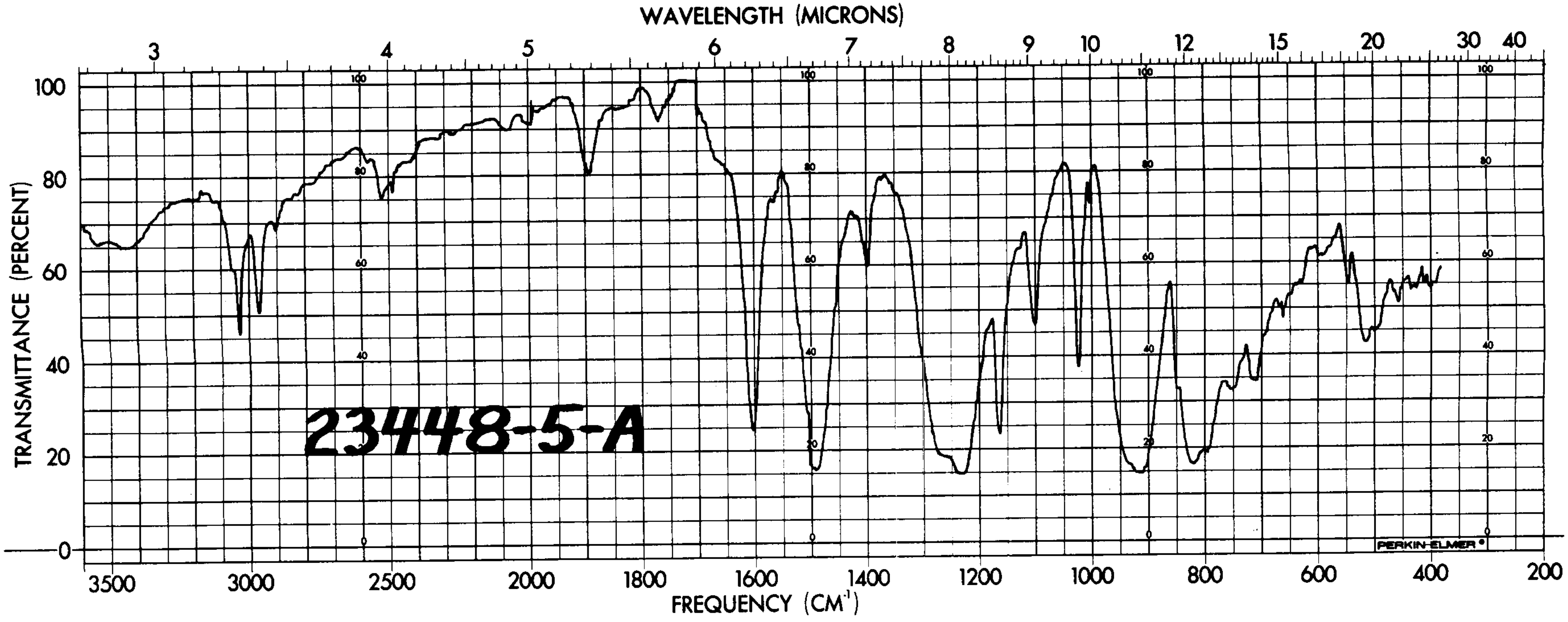


Figure 15. Infrared Spectrum of Polymer B No. 23448-5-A

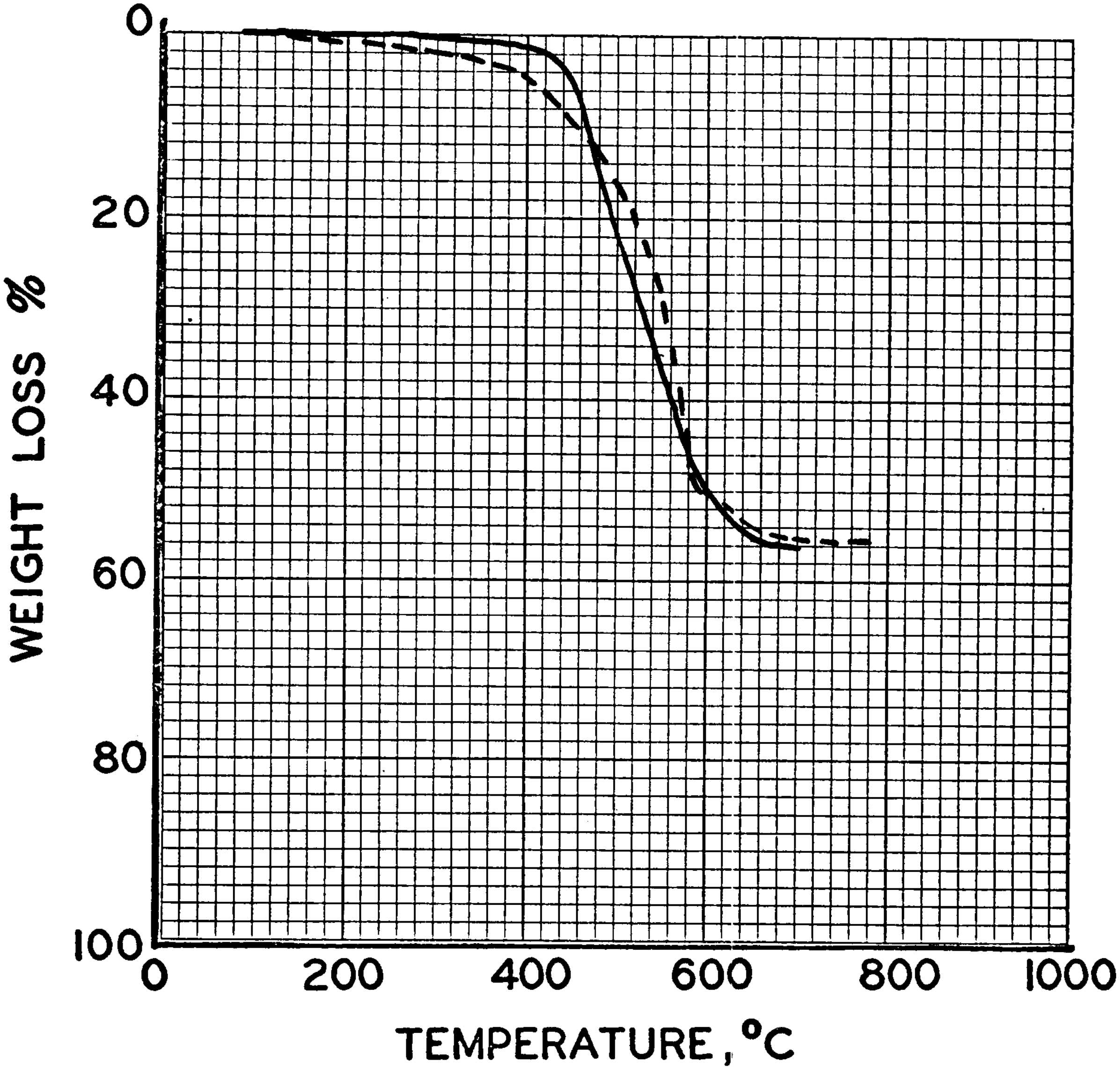


Figure 16. Thermogravimetric Analyses of Crude Sample 23448-5-A (----) and Purified Sample 23753-87-2 (——) Polymer B

Thermograms obtained under nitrogen at 4 C/minute.

result from purifying the polymer. As shown in Figure 17, the thermograms obtained on air heating for Polymer B indicate somewhat better (reason unknown) stability for the polymer before purification. Isothermal aging studies were made on Polymer B coatings on aluminum weighing dishes subjected to circulating air at temperatures ranging from 250 to 350 C.

The isothermal aging studies revealed that the lowest weight losses after 19 hours were obtained with samples heated at the highest temperature (350 C). These data suggest that two phenomena are occurring, a degradation mechanism, possibly oxidation or pyrolysis, and a thermally induced reaction, possibly crosslinking or cyclization. The two phenomena are apparently competitive in their influence on the weight loss.

It was noted earlier (Part III-B-4 of this report) that Polymer B did not show evidence of crosslinking when it was heated with either benzoyl peroxide or t-butyl perbenzoate. For this reason, it was expected that the aging characteristics of films of Polymer B alone and films of Polymer B containing t-butyl perbenzoate would be essentially the same. The experimental results (Figure 18) substantiated this conclusion.

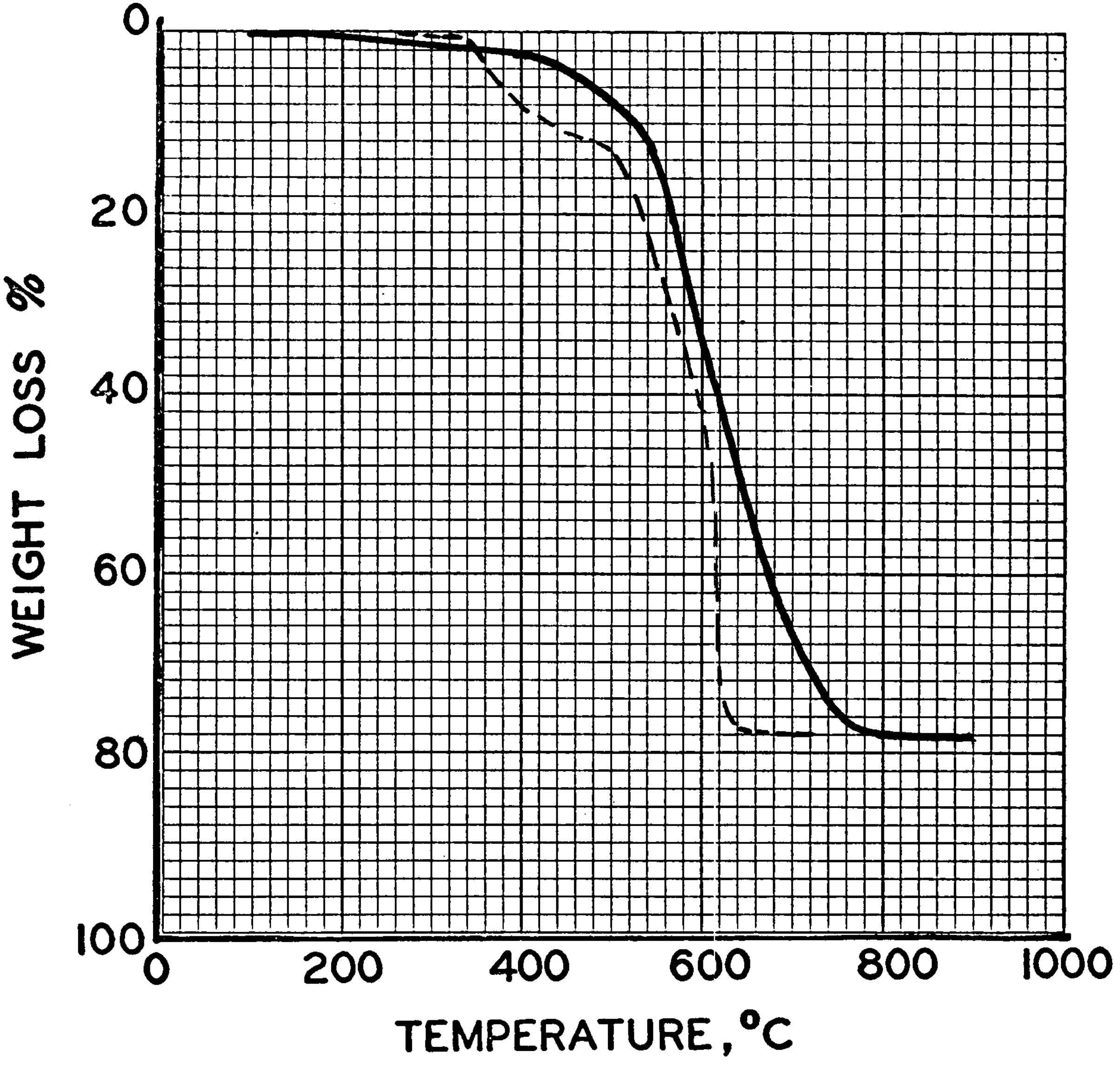


Figure 17. Thermogravimetric Analyses of Crude Sample No. 23448-5-A (——) and Purified Sample No. 23753-87-2 (----) Polymer B

Thermograms obtained under air at 4 C/minute.

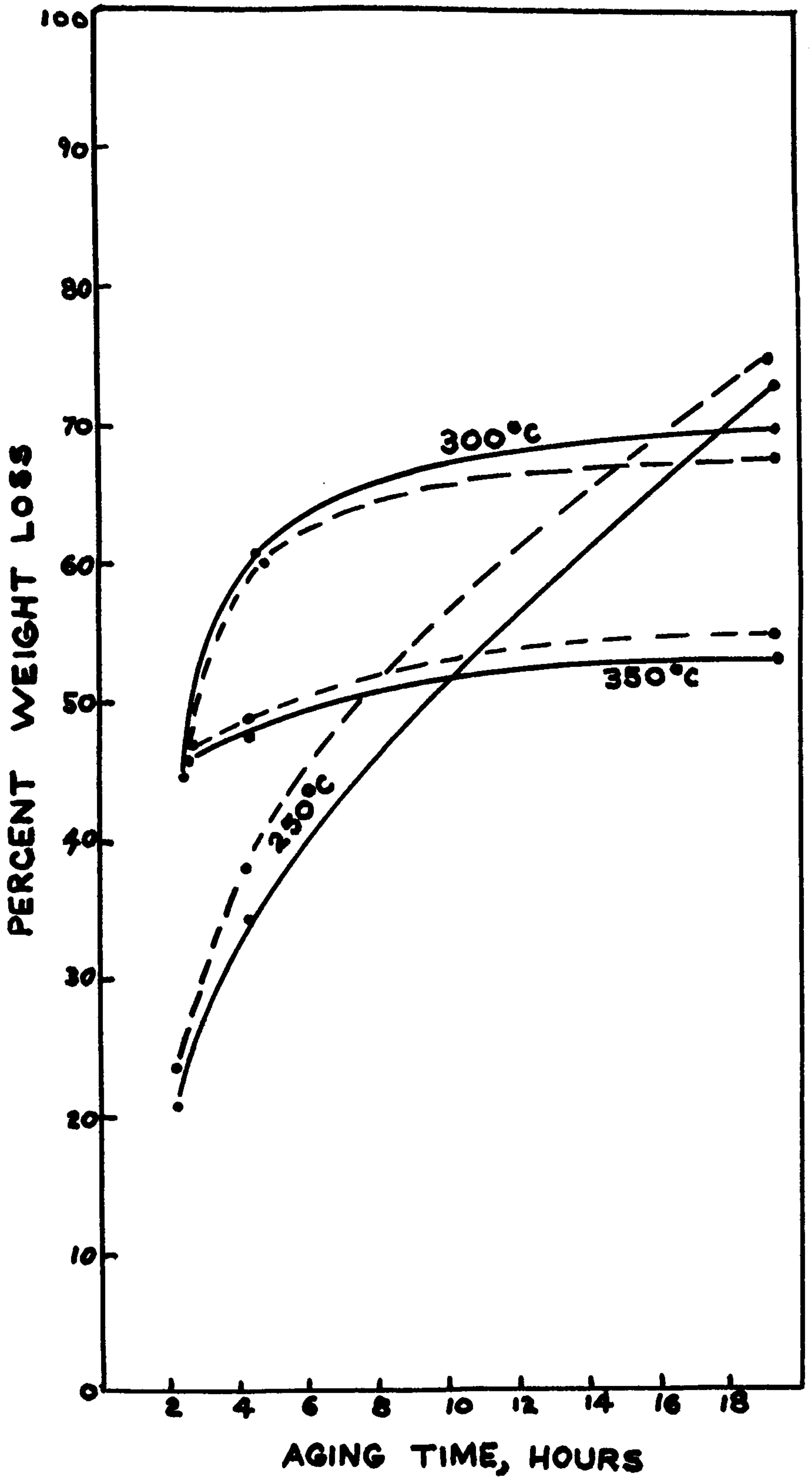


Figure 18. Isothermal Thermogravimetric Analyses of Polymer B No. 23563-23-1 with (——) and Without (----) t-Butyl Perbenzoate

D. Polymer B - Experimental

Polymerizations

1. Polycondensation of Dianilinodimethylsilane with p,p'-Biphenol. a. A mixture of 14.54 grams (0.06 mole) of dianilinodimethylsilane and 11.7 grams (0.06 mole) of p,p'-biphenol were fused under nitrogen at 230 C, then heated at 230 C under a vacuum for 75 minutes. The resulting polymer (No. 23448-5-A) was transparent, amber, and adhered tightly to the flask in which it was made. The fused polymer could be drawn into low-strength fibers and was easily compression molded between aluminum foil sheets in a laboratory press at 160 C to produce a hard waxlike, transparent, semibrittle film. The softening temperature of the polymer, as determined on a Fisher-Johns melting point block, was 75-80 C.

Analysis for $C_{14}H_{14}SiO_2$		
	Calculated:	C, 69.39; H, 5.82; Si, 11.58
	Found:	C, 68.87; H, 6.10; Si, 11.42

Thermogravimetric analyses (Figure 17) of Polymer No. 23448-5-A suggested that some low molecular weight polymeric material was being lost between 150 and 350 C, but that the heat stability of the polymer was good in both air and nitrogen. The TGA curves showed that the polymer underwent greater weight losses in nitrogen than in air in the 400 to 650 C temperature range. It is speculated that this unusual behavior may be due to the polymer crosslinking in the presence of air, thus producing a material more thermally stable between 400 and 650 C.

b. A polymerization, as in (a), was carried out by fusing 14.54 grams (0.06 mole) of dianilinodimethylsilane (m.p. 63 C) with 11.17 grams (0.06 mole) of p,p'-biphenol at 225 C under nitrogen, followed by heating for 150 minutes under a vacuum. This polymeric product (Sample 23448-11-1) was amber, transparent, and did not adhere to glass. Thin coatings of the polymer melt on glass provided highly flexible and tough films. Similar tough and flexible films could be cast from solutions of the polymer in 1,2,4-trichlorobenzene. The softening point of this polymer, as determined on a Fisher-Johns melting point block, was about 90 C.

The general properties of Sample 23448-11-1 prepared in (b) seem quite similar to those of the highest molecular weight Polymer A prepared earlier in this program. In addition, the dianilinodimethylsilane/p,p'-biphenol condensation product obtained in (b) is certainly of a significantly higher molecular weight than that obtained in (a).

2. Condensation of Dianilinodimethylsilane with p,p'-Biphenol in Polymerization Tubes. A representative tube polymerization is described. A mixture of 7.978 grams (0.03287 mole) dianilinodimethylsilane and 6.129 grams (0.03287 mole) p,p'-biphenol were fused in a Pyrex tube under nitrogen at 225 C. Polymerization was continued at atmospheric pressure for 15 minutes, then the pressure was reduced over a 15-minute period to 0.3 mm. During the second 15-minute period most of the aniline was removed from the reaction zone and an extremely viscous polymer melt was formed. After 1 hour at 0.3 mm the tube was removed from the Wood's metal bath and cooled quickly to room temperature. The tube was broken and the polymer recovered. Aniline was recovered from the cold trap received in theoretical yield. Results of four such polymerizations carried out for various heating periods are reported in Table 6.

3. Larger Scale Condensation of Dianilinodimethylsilane with p,p'-Biphenol (Sample No. 23563-15). A mixture of 100.00 grams (0.4126 mole) of dianilinodimethylsilane and 76.83 grams (0.4126 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 500-ml, round-bottomed flask heated to 225 C in a Wood's metal bath. The melt was held at 225 C at atmospheric pressure for 1 hour while aniline distilled off. The pressure was reduced to 0.2 mm during the second hour of heating at 225 C. The temperature was then raised to 250 C and the reaction continued for another hour at 0.2 mm. A near theoretical yield of aniline (76.5 grams, 99.6 percent) was realized.

At this point the flask was removed from the Wood's metal bath and a nitrogen atmosphere was placed over the resin. Fibers were drawn from the polymer melt. They were easily cold-drawn by hand, necking down and drawing out 130 to 150 percent to provide tough, flexible filaments. A number of these filaments were prepared and used for physical property measurements (Table 8). This batch of polymer was also used to prepare both hot-pressed and solvent-cast films for crosslinking and physical property studies (Table 7). The softening temperature of the polymer as determined on a Fisher-Johns melting point block was 128 C and the Mw as determined by GPC was 43,000.

Analysis for $C_{14}H_{14}SiO_2$		
	Calculated:	C, 69.39; H, 5.82
	Found:	C, 69.52; H, 6.03

4. Condensation of Dianilinodimethylsilane with 3,3'-Diallylbisphenol A. A mixture of 30.8 grams (0.1 mole) of 3,3'-diallylbisphenol A and 24.2 grams (0.1 mole) of dianilinodimethylsilane was fused under nitrogen. When the temperature of the melt reached 170 C, a rapid evolution of aniline was observed. Reflux of the aniline was continued for 30 minutes and the melt was then heated at 200 C under a vacuum for 2 hours. The resulting polymer was a light-orange, transparent, gumlike material (Sample 23448-40-1).

A solution of the resin in benzene containing 2 percent t-butyl perbenzoate (based on the weight of the resin) was brushed onto an aluminum panel and allowed to air dry. The panel was then heated at 160 C for 1 hour to provide a yellow, clear, flexible, nontacky coating that was no longer soluble in benzene. A mixture of 2 grams of Resin No. 23448-40-1 and 0.04 gram of t-butyl perbenzoate was heated on an aluminum weighing dish in air at 160 C for 1 hour. The product was semi-brittle at room temperature, softened when heated but did not melt, and was leathery and nontacky at 250 C.

5. Condensation of Dianilinodimethylsilane with p,p'-Biphenol and 3,3'-Diallylbisphenol A. An intimate mixture of 24.2 grams (0.1 mole) of dianilinodimethylsilane, 14.0 grams (0.075 mole) of p,p'-biphenol, and 7.7 grams (0.025 mole) of 3,3'-diallylbisphenol A was fused under nitrogen and heated at 200 C under a stream of nitrogen for 30 minutes. During this time, the evolution and reflux of aniline

was vigorous. The resulting polymer melt was heated at 210 C for 2 hours under a vacuum to remove the condensation side-product, aniline. The cooled polymeric product (Sample 23448-41-1) was hard, transparent, amber-colored, brittle, and slightly tacky. A 10 percent solution of the resin in benzene containing 2 percent t-butyl perbenzoate (based on the weight of the resin) was brushed on aluminum panels and the panels were then air dried. Upon heating the panels for 2 hours at 200 C, glossy, transparent, brown coatings were obtained that were nontacky at 200 C and that were no longer soluble in benzene. However, a mixture of 2 grams of the resin and 0.04 gram of t-butyl perbenzoate heated at 160 to 200 C for 18 hours in air did not, with the exception of its surface, appear to crosslink. Thus, this resin was not as responsive to the free-radical catalyst as was Resin No. 23448-40-1 in which the allyl-substituted chain component was not diluted with the nonreactive biphenyl unit.

E. Polymer C - Discussion

1. General Properties

A sample of Polymer C, No. 23753-9, a polyaryloxysilane containing only methylvinylsilyl and biphenyl chain units, was prepared by condensing dianilinomethylvinylsilane with p,p'-biphenol. This polymer was of relatively low molecular weight (29,000 by GPC), softened at 48 C, and melted at 78 C when heated at 4 degrees/minute on a Fisher-Johns melting point block. Low-tenacity fibers could be drawn from the melt of this polymer (Table 10) and it could be cast from o-dichlorobenzene to form clear and transparent, but relatively brittle, films. It was observed that samples of this polymer, which was initially soluble, became insoluble after exposure to air for several days indicating a ready tendency to crosslink.

The infrared spectrum (Figure 19) of Polymer C, No. 23563-53-9, showed bands at 1010 cm^{-1} and 1410 cm^{-1}, not present in Polymer B (Figure 15), and which indicate the presence of vinyl groups.

2. Crosslinking Studies

During this program, both crude and purified Polymer C specimens were successfully crosslinked by heating, in solution, with t-butyl peroxide (Table 11). The crosslinking tests were carried out as follows: Approximately 10 percent solutions of crude Polymer C, purified Polymer C (precipitated from benzene by methanol), benzoyl peroxide, t-butyl perbenzoate, and t-butyl peroxide in benzene or o-dichlorobenzene were prepared. About 5-milliliter portions of the polymer solutions together with an appropriate amount of an initiator solution were pipetted into polymerization tubes. The tubes were flushed with nitrogen or argon, the contents frozen, and the tubes sealed under a vacuum. The sealed tubes were heated in an oven at the temperatures, and/or the times, specified in Table 11. Positive evidence of crosslinking was provided by the polymers becoming insoluble, or gelled, in the solvents.

TABLE 10. TEST RESULTS FOR HAND-DRAWN FIBERS FROM POLYMER C NO. 23753-9-2

Fiber Diameter, mils	Tenacity, grams/denier
6	0.46
5	0.48
6.5	0.80
5.5	0.74
10.0	0.62
4.5	0.92
	0.67

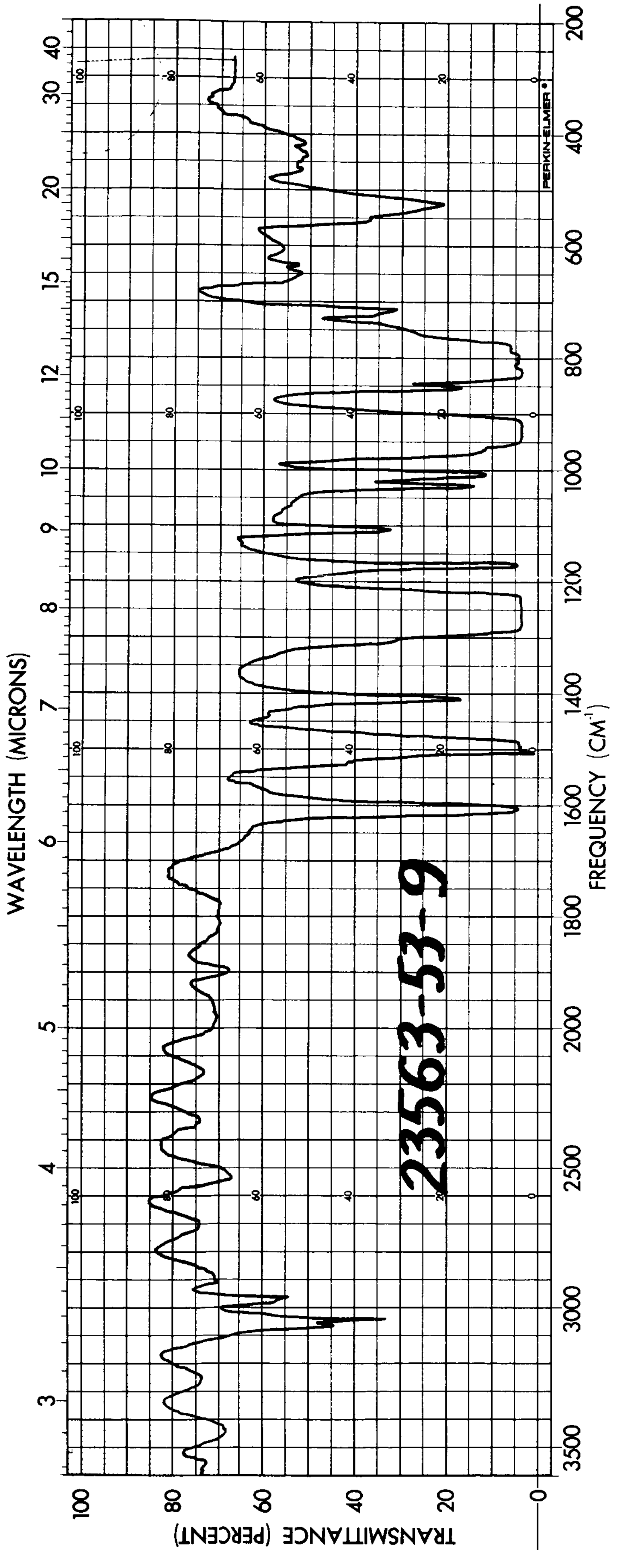


Figure 19. Infrared Spectrum of Polymer C No. 23563-53-9

TABLE 11. CROSSLINKING EXPERIMENTS[a]

	Sample	Catalyst Concentration, pphp[b]	Initiator	Solvent	T C/hr	Gelation
1.	0.50 g Polymer C	2	0.01 g t-butyl perbenzoate	o-dichlorobenzene	110/159	None
2.	0.50 g Polymer C	2	0.01 g dibenzoyl peroxide	o-dichlorobenzene	70/159	None
3.	0.50 g Polymer C	2	0.01 g dibenzoyl peroxide	benzene	70/159	None
4.	0.50 g Polymer C	1	0.005 g t-butyl peroxide	benzene	115/87	None
5.	0.50 g Polymer C	2	0.01 g t-butyl peroxide	benzene	110/159	Solid plug
6.	0.50 g Polymer C	5.0	0.025 g t-butyl peroxide	benzene	115/23	Gelled after 15 hrs, compact plug after 23 hrs, 0.34 g
7.	0.50 g Polymer C	10	0.05 g t-butyl peroxide	benzene	115/15	Solid plug, 0.39 g
8.	0.50 g Polymer C (freshly purified)	2.5	0.0125 g t-butyl peroxide	benzene	115/113	Gelled in 18-1/2 hrs, compact plug formed later, 0.343 g
9.	0.311 g Polymer C (freshly purified)	1.6	0.005 g t-butyl peroxide	benzene	115/40 115/135	Soft gel Soft gel
10.	0.311 g Polymer C (freshly purified)[c]	1.6	0.005 g t-butyl peroxide	benzene	115/135	None

(a) All reactions were carried out under a vacuum unless otherwise specified.

(b) pphp = parts per hundred parts of polymer.

(c) Reaction carried out in the presence of air.

Crude Polymer C failed to crosslink when heated for 159 hours with 2 parts (per hundred parts of polymer) of benzoyl peroxide (at 70 C) or t-butyl perbenzoate (at 110 C). However, it did form gelled structures when heated with 2 to 10 parts of t-butyl peroxide at 110 to 115 C.

Purified Polymer C also gelled in benzene when heated under a vacuum with 1.6 and 2.5 parts of t-butyl peroxide at 115 C. A duplicate of the experiment containing 1.6 parts of initiator, but run in the presence of air, did not provide a gel. This suggests, not unexpectedly, that oxygen can inhibit free-radical cures of Polymer C.

Several experiments were carried out in which crude Polymer C was heated with exceptionally large amounts (40 parts) of t-butyl peroxide, t-butyl perbenzoate, or benzoyl peroxide. Crosslinked polymers were obtained with each catalyst, in some cases in the presence of air. Thus, while t-butyl peroxide appeared to be the most active of the three initiators tried at low concentrations (2 parts), Polymer C can undoubtedly be crosslinked successfully with a wide variety of initiators if the appropriate initiator concentrations and curing conditions are determined.

The crosslinked Polymer C specimens described in Table all required relatively long curing times under the conditions used. This is probably due in part to the fact that the cures were carried out in solution. Larger quantities of Polymer C having the initiator homogeneously dispersed in it by milling could conceivably be cured in a compression mold in considerably less time.

Experiments involving the curing of mixtures of Polymer C with curing aids such as diallyl phthalate, diallyl isophthalate, and triallyl isocyanurate by t-butyl peroxide were carried out (Table 12). In each case those mixtures containing purified Polymer C showed gel formation with 1.1 parts (based on monomer weight) of t-butyl peroxide. Similar mixtures, but using crude Polymer C, failed to provide gels despite the fact that they contained higher concentrations (1.5 to 2.3 parts) of t-butyl peroxide.

It is apparent that purified Polymer C responds more readily to free-radical crosslinking than does the impure polymer. This is

TABLE 12. CROSSLINKING EXPERIMENTS[(a)]

Sample	Catalyst Concentration, parts[(b)]	Initiator	Solvent	T C/hr	Gelation
0.50 g Polymer C 0.25 g diallyl phthalate (allyl/vinyl 1/1)	1.5	0.0125 g t-butyl peroxide	Benzene	115/113	None
0.50 g Polymer C 0.025 g diallyl phthalate	2.3	0.0125 g t-butyl peroxide	Benzene	115/113	None
0.50 g Polymer C 0.025 g diallyl isophthalate	2.3	0.0125 g t-butyl peroxide	Benzene	115/113	None
0.50 g Polymer C 0.025 g diallyl terphthalate	2.3	0.0125 g t-butyl peroxide	Benzene	115/113	None
0.50 g Polymer C 0.025 g triallyl isocyanurate	2.3	0.0125 g t-butyl peroxide	Benzene	115/113	None
0.311 g Polymer C (freshly purified) 0.125 g diallyl phthalate	1.1	0.005 g t-butyl peroxide	Benzene	115/40 115/135	Soft gel Soft gel
0.311 g Polymer C (freshly purified) 0.0125 g diallyl phthalate	1.1	0.005 g t-butyl peroxide (1.58%)	Benzene	115/40 115/135	Soft gel Soft gel
0.311 g Polymer C (freshly purified) 0.125 g diallyl terphthalate	1.1	0.005 g t-butyl peroxide	Benzene	115/40 115/135	Soft gel Soft gel
0.311 g Polymer C (freshly purified) 0.125 g triallyl isocyanurate	1.1	0.005 g t-butyl peroxide	Benzene	115/40 115/135	Soft gel Soft gel

(a) Based on 100 parts by weight of Polymer C and allylic monomer.

(b) Parts per hundred parts of polymer and monomer.

understandable since impure Polymer C (or any other polyaryloxysilane prepared by melt condensing a dianilinosilane with an aromatic diol) undoubtedly contains at least trace amounts of free aniline (condensation side-product) or unreacted anilinosilane monomer. Either of these impurities could function as an inhibitor of free-radical crosslinking. Infrared analysis of Polymer C showed a small decrease in absorption at 3400 cm^{-1} upon purification which could be attributed to removal of such N-H containing impurities from the polymer.

Several of the solvent swollen, crosslinked Polymer C samples were vacuum dried for 15 hours at 80 C. These polymers discolored, but failed to soften or fuse when heated in air at temperatures as high as 371 C. A specimen of crosslinked Polymer C subjected to a force of 40 tons at 204 C in a laboratory press was deformed, but not successfully compressed into a coherent sheet. This behavior was in marked contrast to the typical thermoplastic properties exhibited by uncrosslinked Polymer C. Despite this lack of processability, usable sheet specimens of crosslinked Polymer C were prepared by compression molding for use in thermogravimetric analyses. More loosely crosslinked polymer films prepared by simultaneously evaporating and crosslinking Polymer C solutions in open aluminum weighing dishes were also prepared for use in the thermal analysis studies.

3. Programmed Thermogravimetric Analysis

Thermogravimetric analyses (Figure 20) of Polymer C (Sample No. 23563-53-9) under both air and under a vacuum show weight losses of only about 7.5 percent at 500 C, at which temperature the major weight losses occurred.

Polymer C (Sample No. 23753-30) was pyrolyzed under nitrogen at a programmed rate on a thermobalance. Two attempts were made to obtain a TGA thermogram on this sample to 900 C, but in both cases the sample decomposed at 600 C in such a manner that a portion of the sample was lost and the analyses were discontinued. Further, the sample appeared nonuniform as reflected by the 5 to 9 percent

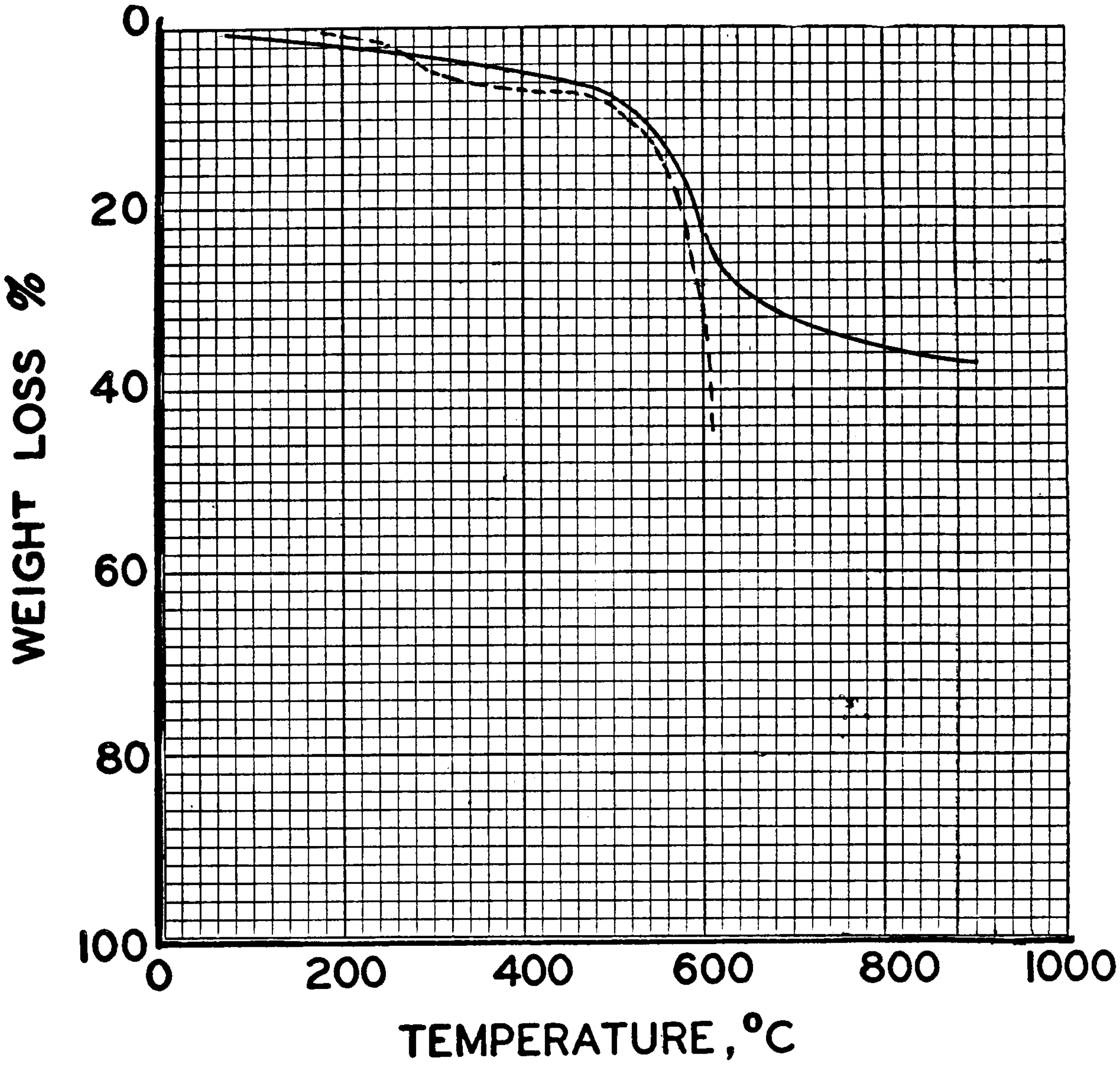


Figure 20. Thermogravimetric Analysis of Polymer C No. 23563-53-9 Under Air (----) and Under a Vacuum (——)

difference in weight loss between the two samples between 400 and 600 C. The data are shown in Figure 21. (Sample 23753-30 was purified by vacuum-heating during synthesis.)

Polymer C (Sample No. 23753-30) was precipitated twice from benzene solution to yield a white solid (23753-81). The thermogram of this polymer (Figure 22) showed that the sample lost 2.7 percent weight up to 500 C. In the region 600 to 800 C, a plateau is seen in the thermogram, indicating a thermally stable residue. The infrared spectra of the purified and unpurified materials did not differ appreciably. The spectrum of the purified polymer shows slightly more resolved bands and loss of a small absorption band in the vicinity of 3400 cm^{-1}.

Samples of Polymer C, which had been crosslinked (see previous section, this report) in nitrogen and in air, were compared by thermogravimetric analyses. Very little difference was seen in their thermograms (Figure 23). The thermal stability of Polymer C, purified and subsequently crosslinked, was studied and the thermogram (Figure 24) of this material is very similar to the above. The thermograms indicate that the uncrosslinked purified Polymer C is somewhat more stable than the crosslinked polymer. One possible explanation is that Polymer C thermally crosslinks during thermogravimetric analysis. The greater weight loss observed for the catalytically crosslinked material (Figures 22 and 24) may reflect initiator fragments or other impurities that entered the samples during crosslinking.

It should be pointed out that crosslinking during thermal analysis may provide an explanation for the improved TGA patterns observed when a vinyl group replaces a methyl group. Comparison of thermograms of Polymers B and C indicates a much lower weight loss in the 600 to 800 C range for the vinyl-substituted polymer.

4. Isothermal Analysis

As shown in Figure 25, the crosslinked Polymer C samples yielded a weight loss on aging at 350 C lower by a factor of 2 or 3 than the lowest weight loss obtained with uncrosslinked Polymer C (also

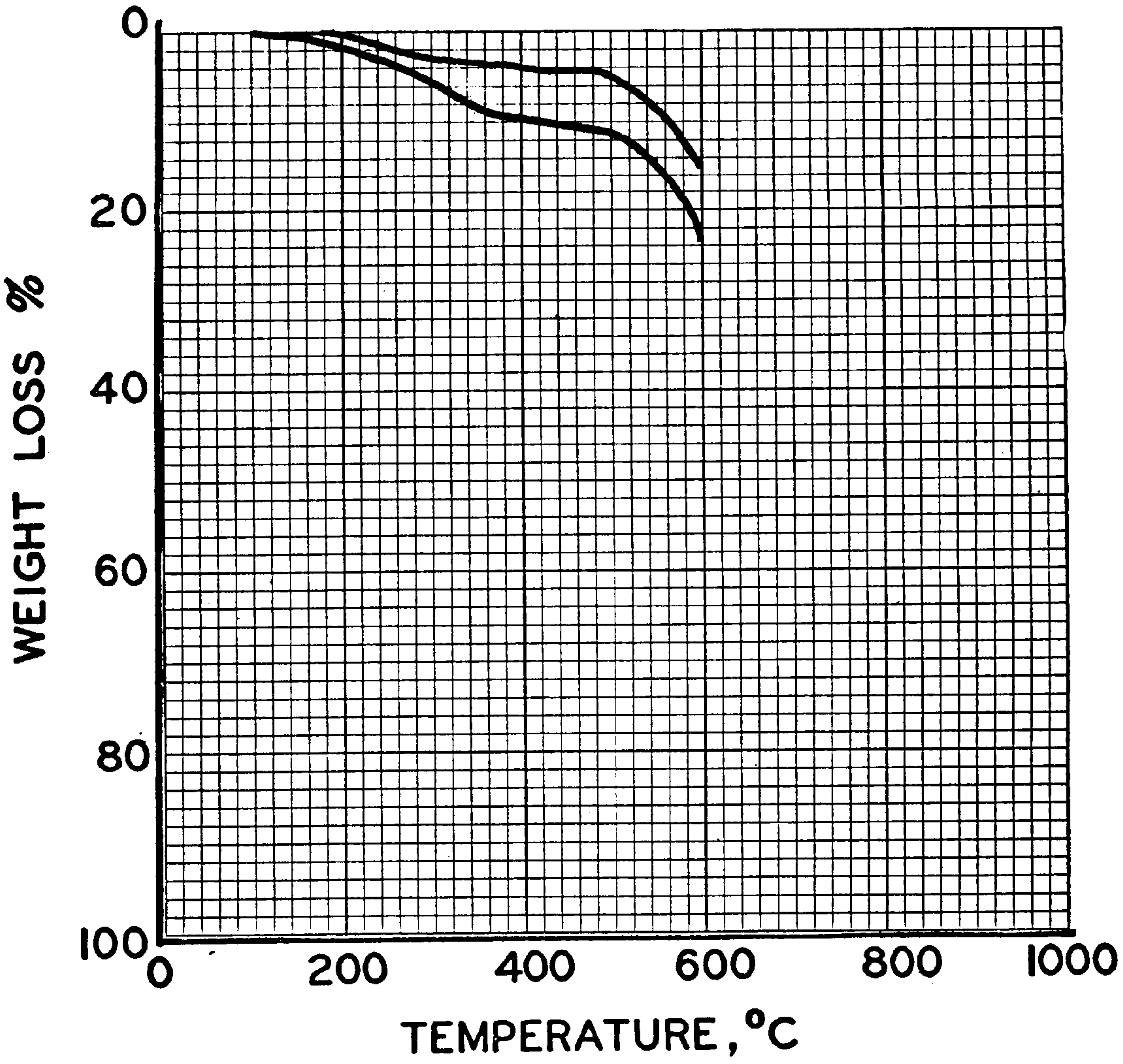


Figure 21. Thermogravimetric Analyses of Polymer C After Purification by Vacuum-Heating

At 600 C the decompositions became too erratic to plot. Thermograms obtained at 4 C/min in nitrogen.

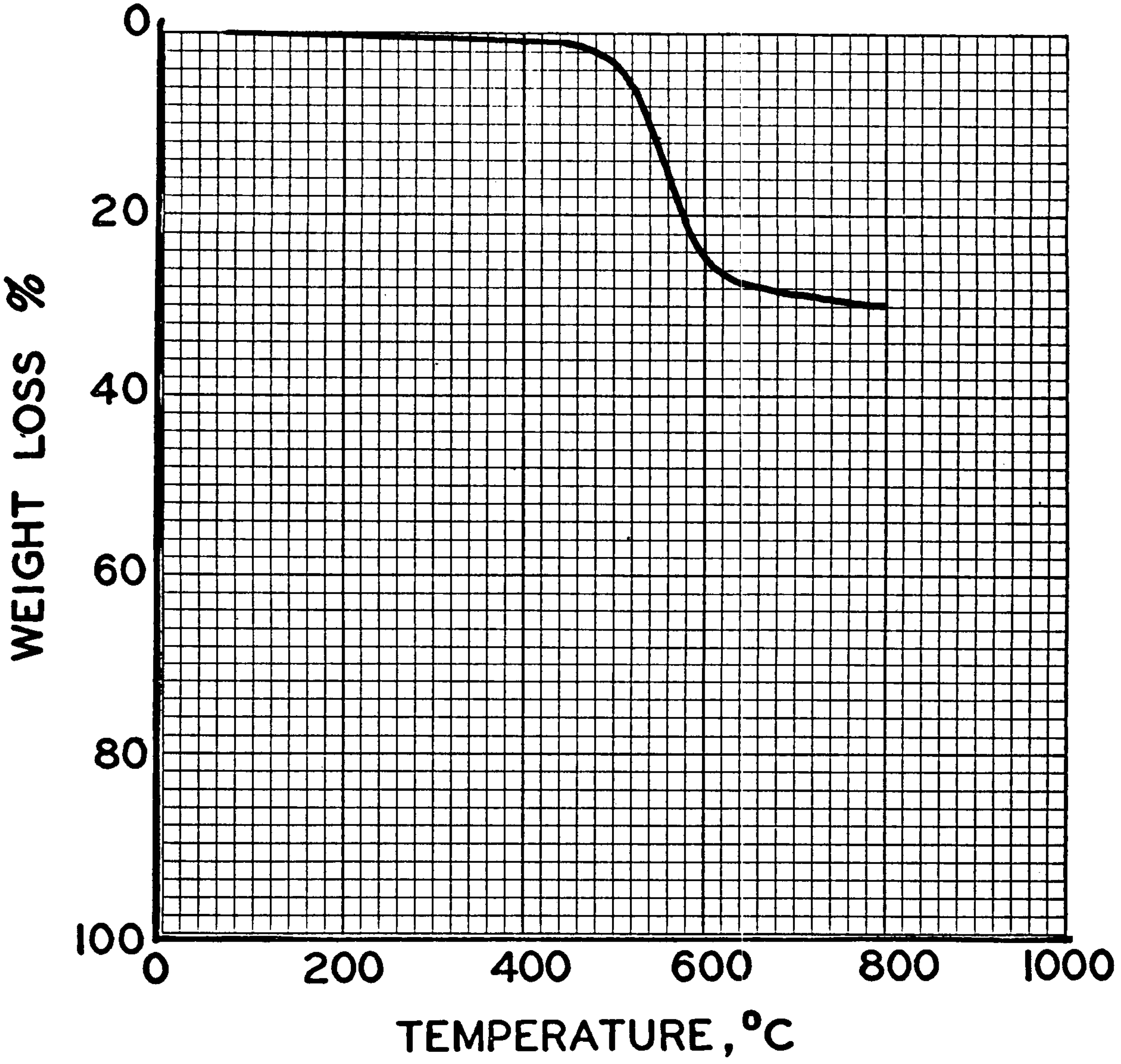


Figure 22. Thermogravimetric Analyses of Polymer C Purified by Precipitation from Solution Thermogram obtained at 4 C/min in nitrogen.

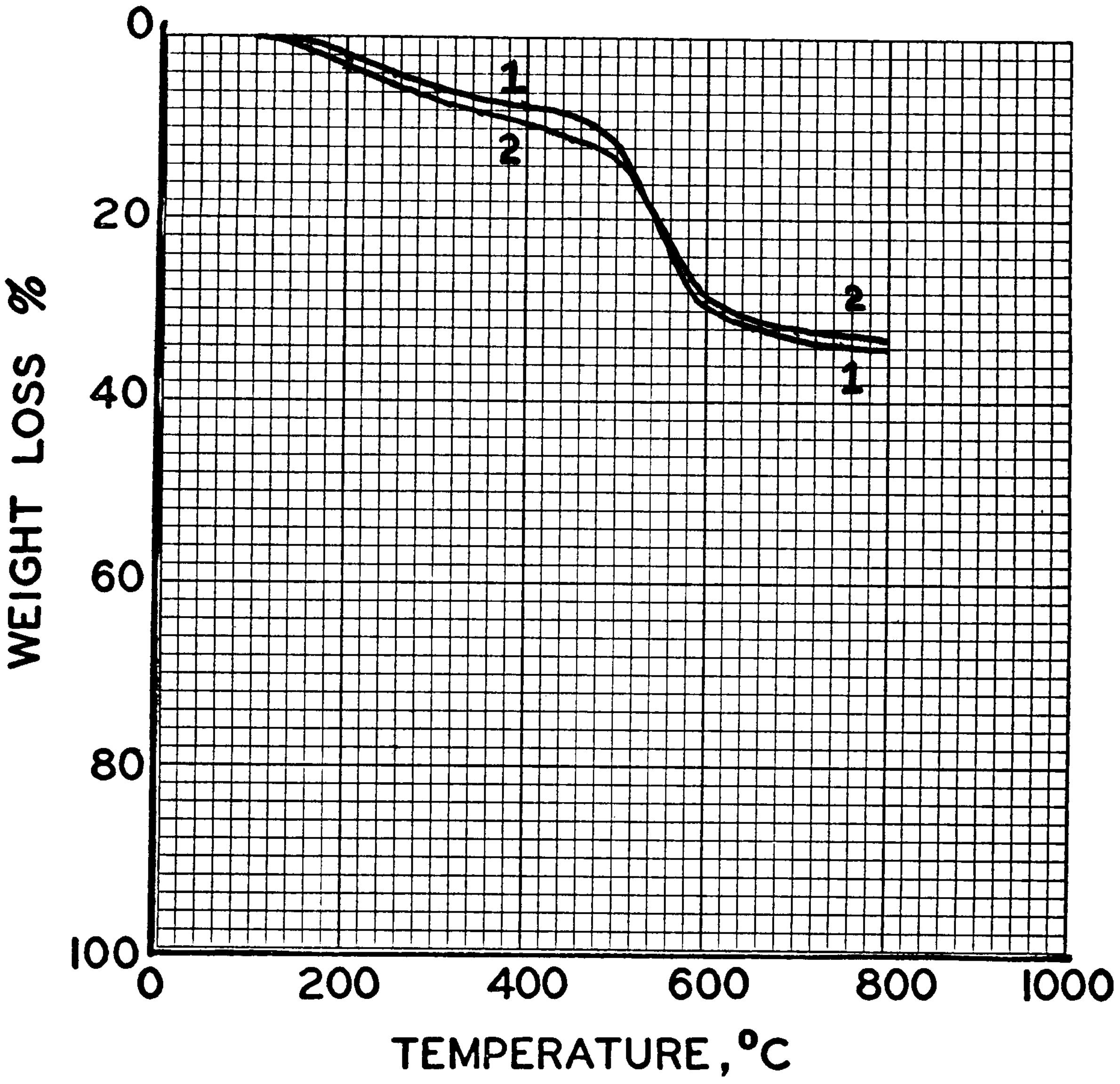


Figure 23. Thermogravimetric Analyses of Polymer C Crosslinked (1) in Nitrogen, and (2) in Air Thermogram obtained at 4 C/min in nitrogen.

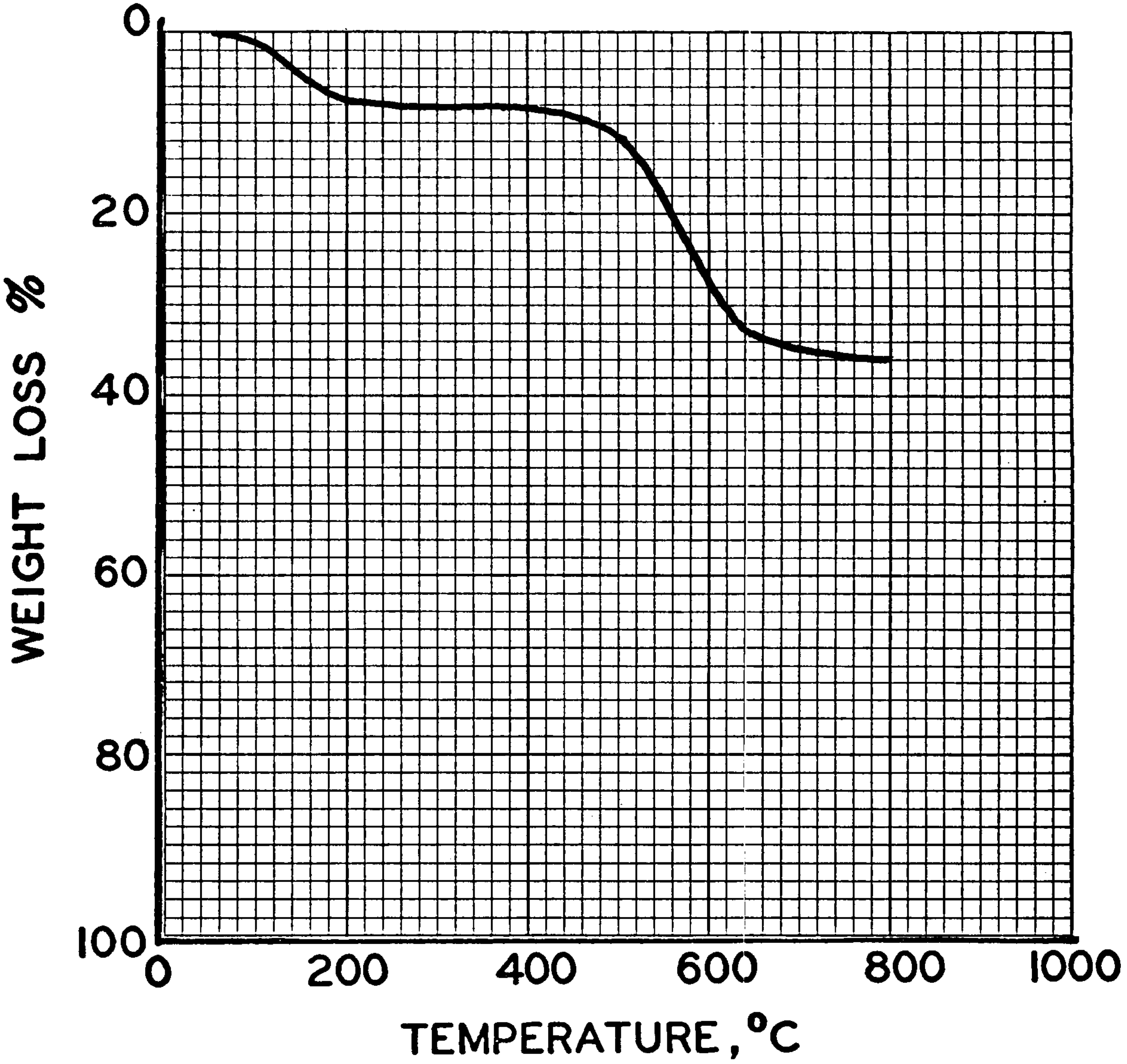


Figure 24. Thermogravimetric Analysis of Purified and Crosslinked Polymer C Thermogram obtained at 4 C/min in nitrogen.

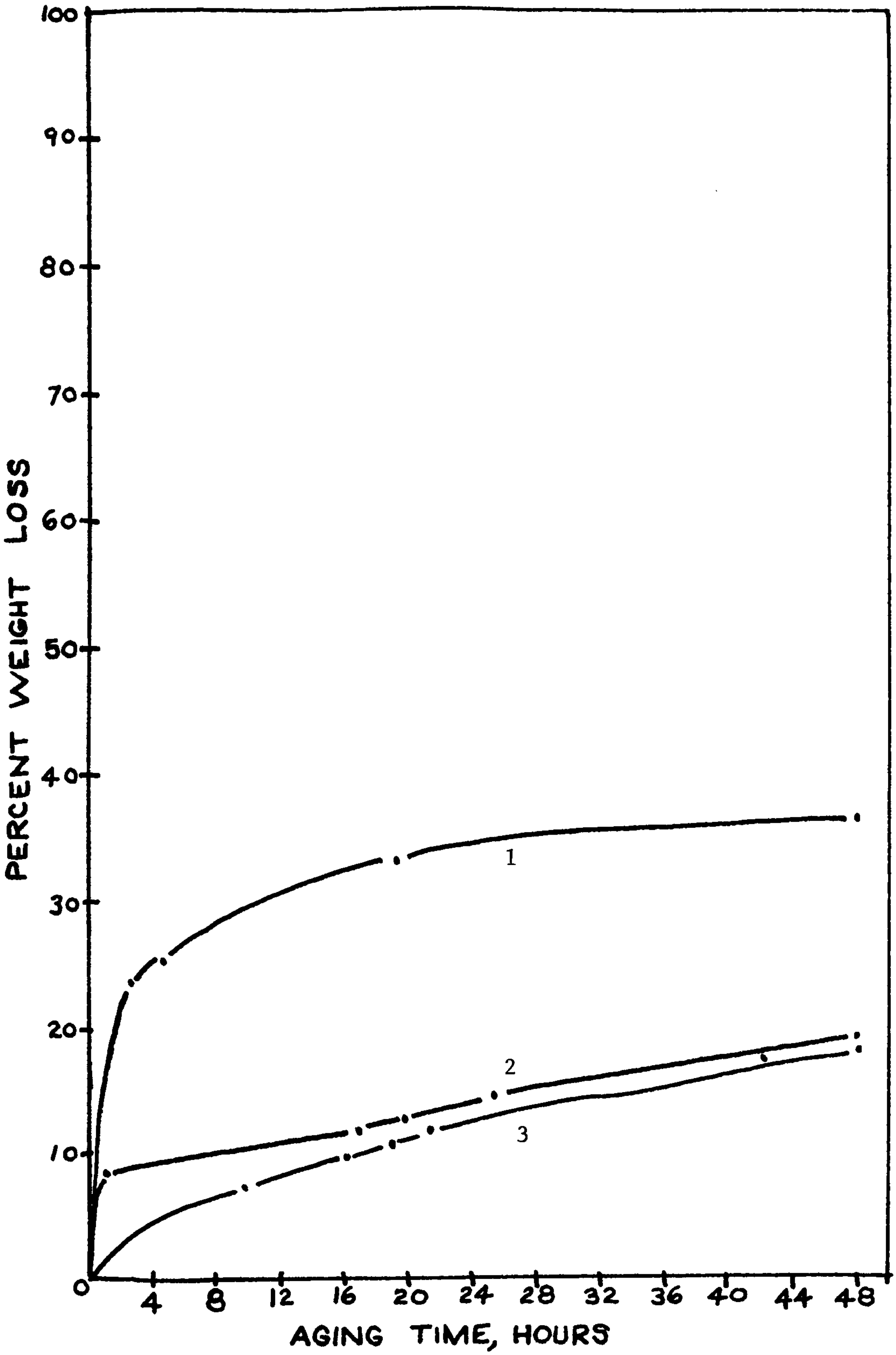


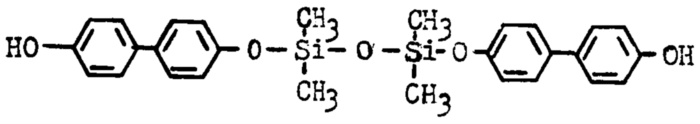
Figure 25. Isothermal Thermogravimetric Analyses of Polymer C at 350 C in Air

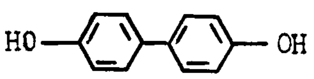
Curve 1: no prior crosslinking; 2: crosslinked in open dish; 3: crosslinked in sealed tube and pressed into film.

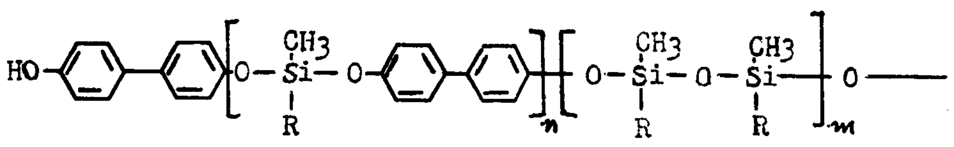
shown in Figure 25 for comparison purposes). This was found for both pressed and solvent-cast samples of the crosslinked polymer.

The isothermal weight losses for Polymer C in Figure 25 show initial steep slopes followed by gradual increases in weight loss. This is probably indicative of an early loss of thermally labile groups followed by gradual loss of more stable moieties of the polymer molecule. Upon aging the crosslinked Polymer C samples in air, they blackened and became brittle.

A pyrolysis of 150 mg of crosslinked Polymer C was conducted in an inert argon atmosphere and the products were investigated. After heating the polymer for 3.5 hours at 350-400 C in a static, low-pressure, argon atmosphere, it was observed that the products consisted of (1) a residue of polymer, the major product, which yielded an IR spectrum with new, strong bands at 3550 cm^{-1} (2.9 microns, probably a phenolic frequency) and 1125-1025 cm^{-1} (8.9-9.8 microns, probably a Si-O-Si frequency), and (2) about 10 mg of a sublimate, which condensed on the upper walls of the pyrolysis chamber. The sublimate was found to consist of an acetone-soluble fraction and an acetone-insoluble, benzene-soluble fraction. An IR of the former fraction and that of p,p'-biphenol were identical. The IR of the benzene-soluble fraction revealed evidence of Si-CH_3, Si-O-Si, phenolic O-H linkages, and p-substituted aromatic rings. The above evidence indicated that some p,p'-biphenol was split out of the polymer yielding as possible structures:







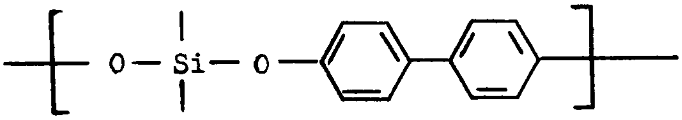
where R = aliphatic group or -O-Si-O-.

In light of the above results, the backbone of Polymer C appears to break up slowly under the experimental conditions.

In another investigation, the infrared spectrum of the residue of a thin film of Polymer C after 48 hours of aging in a 350 C forced-draft oven revealed the presence of Si-CH_3, Si-O-C, and para-substituted aromatic rings (all of which are present in unpyrolyzed Polymer C) as well as new, strong bands indicative of Si-O-Si and carbonyl groups. Elemental analysis revealed that the backbone of the polymer was severely degraded.

	Found, weight percent	Calculated for $C_{14}H_{14}O_2Si$ (Polymer C)	Calculated for $C_{12}H_8SiO_2$
Carbon	45.29	70.82	67.90
Hydrogen	3.30	5.55	3.80

The calculation for $C_{12}H_8SiO_2$ was based on



i.e., for the largest loss of carbon possible without change in the polymer backbone. Therefore, all portions of Polymer C must have undergone severe oxidation and pyrolysis under the experimental conditions.

F. Polymer C - Experimental

1. Preparation of Polymer C No. 23563-53-9

a. A mixture of 25.0 grams (0.09 mole) of dianilinomethylvinylsilane and 18.2 grams (0.09 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 250-ml, round-bottomed flask heated to 225 C by a Wood's metal bath. The melt was held at 225 C for 15 minutes while aniline distilled off. The pressure was reduced to 1.0 mm over a period of 1 hour while the temperature was held at 225 C. After 10 minutes at 1.0 mm and 225 C, the melt ceased bubbling, indicating that aniline evolution had ceased and the polymerization was complete. After an additional 10 minutes at 1 mm and 225 C, the reaction was terminated. A near theoretical yield of aniline (18.1 grams, 99 percent) was recovered. At this point the flask was flushed to atmospheric pressure with nitrogen and fibers were hand-drawn from the melt. These fibers were cold-drawn to filaments that were fairly tough and flexible, but not as strong as comparable filaments from Polymers 23563-15 or 23563-27. The softening point of this polymer as determined on a Fisher-Johns melting point block was about 48 C and the Mw as determined by GPC was 29,000.

Analysis for $C_{15}H_{14}SiO_2$		
	Calculated:	C, 70.84; H, 5.55
	Found:	C, 70.61; H, 5.58

b. Preparation of Polymer C No. 23753-30. A mixture of 54.56 grams (0.2145 mole) of dianilinomethylvinylsilane and 39.94 grams (0.2145 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 250-ml, round-bottomed flask heated to 220 C in a Wood's metal bath. After 25 minutes of rapid reaction, with aniline refluxing steadily, the pressure was gradually reduced over a 1-hour period to 0.5 mm. By the time 0.5 mm pressure was attained, there was no detectable quantity of aniline left in the reaction flask. Heating was continued for 2 hours at 0.5 mm. The melt had ceased bubbling by this time and the reactor was flushed to atmospheric pressure with nitrogen.

Aniline was obtained in 39.6-gram (98.9 percent) yield from the cold trap. At room temperature the polymer product was a hard, tough plastic which softened at 65 C and melted at 168 C. It was soluble in o-dichlorobenzene at room temperature and had a weight-average molecular weight by GPC of 42,000.

2. Film Casting

Films of both Polymer No. 23563-15 and Polymer No. 23563-27 (with 25 percent of the dimethylsilyl units replaced with methylvinylsilyl units) were cast from o-dichlorobenzene solution. Solutions of both polymers were prepared based on a recipe of 20 grams of polymer dissolved in 76.5 ml (100 grams) of o-dichlorobenzene. Thus, the solutions were 20 percent by volume (16.7 percent by weight). Films were cast on a polished chrome-steel plate heated to ~100 C by an embedded steam-heated coil. A film-casting blade with a 25-mil opening was used. The dry, free films averaged about 3 mils in thickness. The efficacy of benzoyl peroxide and t-butyl perbenzoate as crosslinking agents was studied by dissolving 5 percent of catalyst (based on polymer weight) in the solution just prior to casting. The films containing homogeneously dispersed free-radical catalysts were heat-treated and the effect on their abilities to melt or dissolve observed.

G. Polymer D - Discussion

1. General Properties

The failure of Polymer B to respond readily to free-radical-induced crosslinking, but positive response of Polymer C, prompted the synthesis of a polymer containing both dimethylsilyl and methylvinylsilyl chain units. A mixture of dianilinodimethylsilane and dianilinomethylvinylsilane (3:1 molar ratio) was melt condensed with p,p'-biphenol to provide a transparent, tough polymer (softening temperature 85-90 C) similar in general appearance and properties to Polymer B. This polymer (No. 23563-27) could be cast into tough, transparent film (that could be redissolved) from chlorinated aromatic solvents and could be drawn into fibers from its melt. As in the case of Polymer B, these fibers could be cold-drawn. Fiber tenacities up to 1.9 grams per denier and tensile strengths up to 26,000 psi were obtained from hand-drawn filaments (Table 13).

The tensile strength of Polymer D No. 23563-27 (Table 14) was comparable to that of Polymer B film No. 23563-15 reported earlier (Table 4). A comparison of the properties of films of cured and uncured Polymer D 23563-27 showed no significant difference in tensile strength (Table 8). Thus, free-radical cures of the vinyl-substituted polyaryloxysilanes can be achieved without destroying the strength and flexibility of the polymers.

The infrared spectrum of uncured Polymer D No. 23563-27 (Figure 26) showed evidence in the 900-1000 cm^{-1} region for vinyl-CH absorption and a weak band near 750 cm^{-1} contributed by CH_3-Si. The changes in the spectrum (Figure 27) of perbenzoate cured Polymer D No. 23563-27* were fairly small. The principal changes were apparently due to pickup of oxygen, i.e., appearance of an -OH band at 3430 cm^{-1} and C=O bands at 1760 and 1690 cm^{-1} (the latter may be due to residual catalyst or combined catalyst residues).

TABLE 13. TEST RESULTS FOR HAND-DRAWN FIBERS FROM POLYMER D NO. 23563-27(a)

Fiber Diameter, mils	Tenacity, grams/denier	Tensile Strength, psi
5.2	1.97	26,710
5.5	1.50	20,337
5.5	0.89	12,067
6.5	0.63	8,541
7.0	1.43	19,388
7.0	0.42	5,694
9.0	1.27	17,219
11.5	0.96	13,016
12.0	1.12	15,185
13.0	1.16	15,727
13.5	0.87	11,795
14.0	0.61	8,270
14.5	1.90	25,761
15.0	0.84	11,389
15.0	0.45	6,101
	1.06	14,371

(a) As cold-drawn.

TABLE 14. TEST RESULTS FOR SOLVENT-CAST FILM FROM POLYMER D NO. 23563-27, FROM MONOMER II, MONOMER IV, AND p,p'-BIPHENOL

	Film Thickness, mils	Tensile Strength, psi
A. Uncured	3.5	4,150
	3.0	4,798
	3.0	4,503
	3.0	4,209
	3.0	4,753
	3.0	4,768
	3.0	3,885
		4,486
B. Cured*	3.7	2,518
	3.6	4,464
	3.6	4,415
	3.5	4,125
	3.5	3,633
	3.5	3,898
	3.5	3,860
	3.5	3,154
	3.5	3,961
	3.5	4,289
	3.5	3,936
	3.5	3,292
		3,912

* Film containing t- butyl perbenzoate (5 percent of polymer weight) was cured for 30 minutes at 160 C.

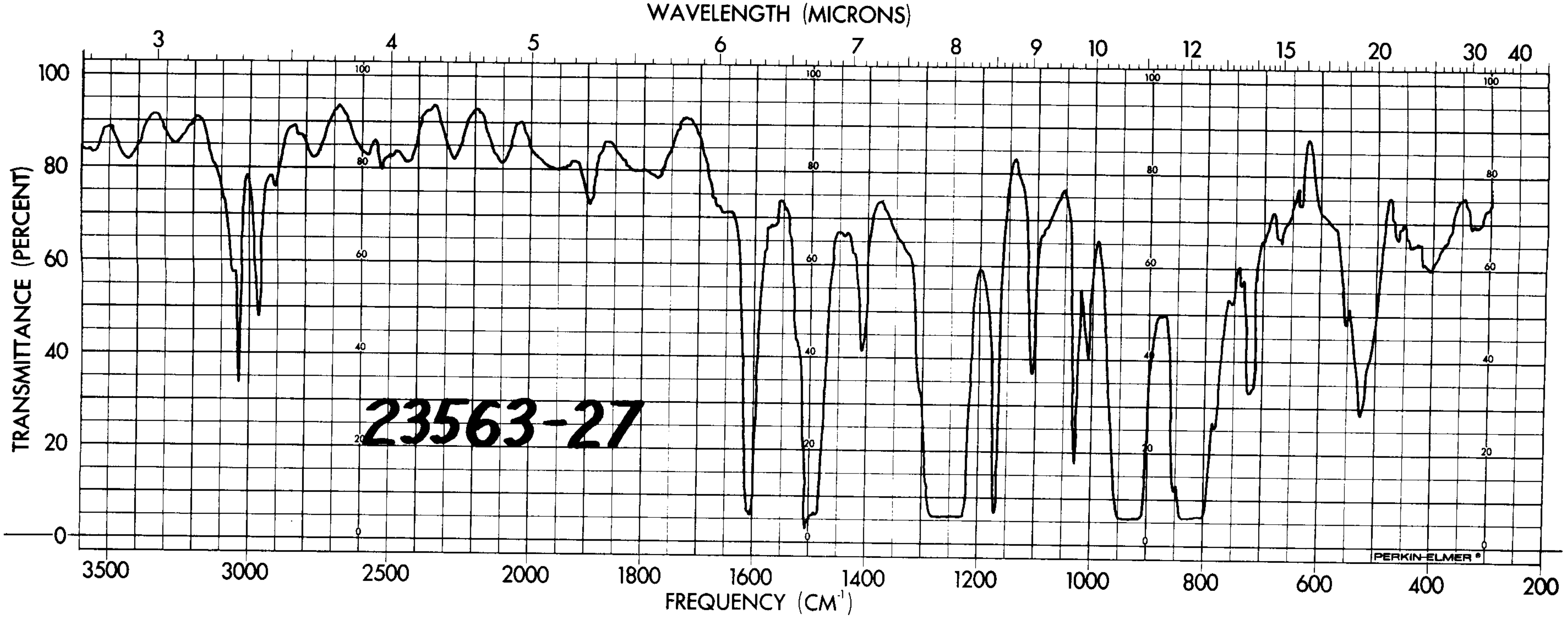


Figure 26. Infrared Spectrum of 1-Mil Film of Polymer D No. 23563-27

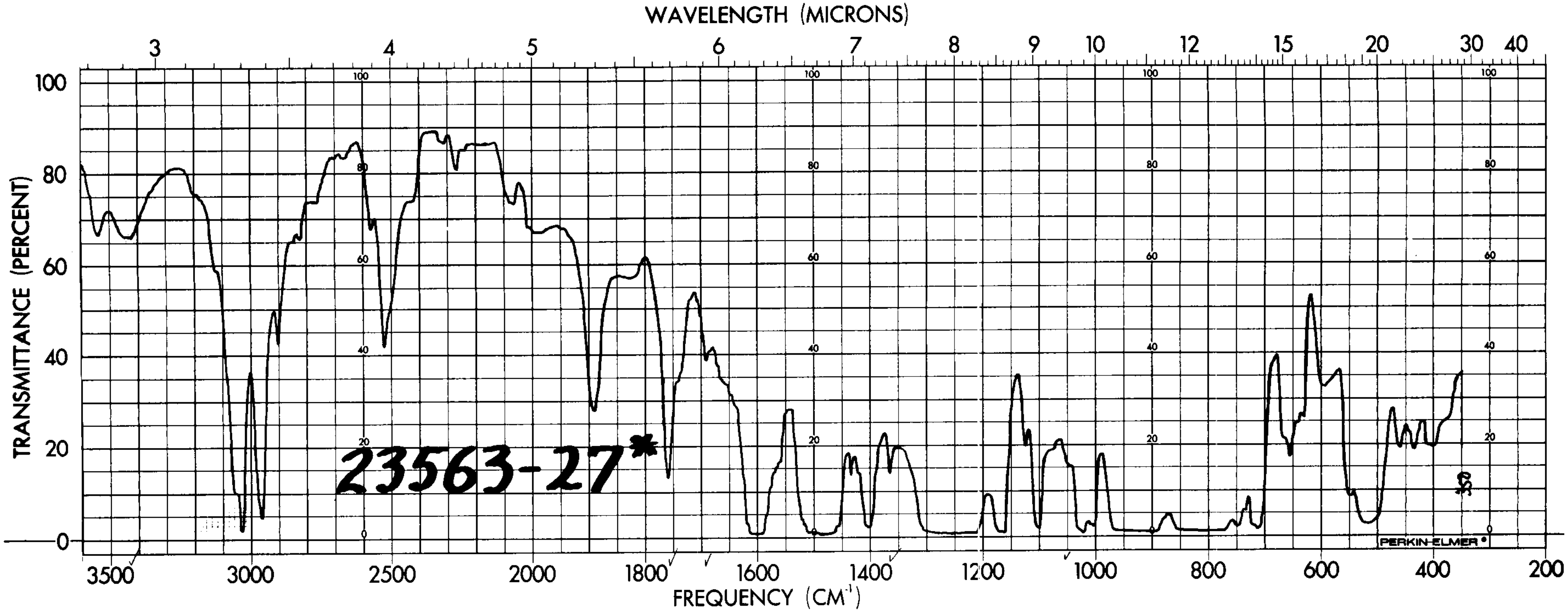


Figure 27. Infrared Spectrum of Crosslinked Polymer D No. 23563-27*

2. Crosslinking Studies

Studies of the curability of Polymer No. 23563-27 were carried out using film samples. Twenty percent (by volume) solutions of the polymer in o-dichlorobenzene both with and without t-butyl perbenzoate (5 percent of polymer weight) were prepared. Films were cast on a polished chrome surface heated at temperatures ranging from 60 to 100 C. The films were then stripped from the plates and cured in a vacuum oven at 160 C and 1 mm pressure for 1 hour.

To determine if the polymer films were crosslinked, their solubilities and melting points were determined. While polymer films cast without t-butyl perbenzoate readily redissolved in o-dichlorobenzene at 23 C, film treated as above swelled, but did not dissolve in boiling o-dichlorobenzene. Softening and melting temperatures of the films were determined on a Fisher-Johns melting point block. The films prepared without t-butyl perbenzoate softened at about 73 C, then became fluid at about 121 C. The perbenzoate-containing films softened at about 75 C, but did not become fluid when heated to 220 C.

3. Programmed Thermogravimetric Analysis

Thermogravimetric analyses of Polymer D No. 23563-27 (Figure 28) were obtained under air and under a vacuum. In both cases the weight loss at 400 C was only about 4.5 percent. Extensive weight loss began about 450 C under reduced pressure and at 500 C under air. The thermal-oxidative stability of this material appeared similar to that of Polymer B (Figure 13).

A programmed thermogram of crosslinked Polymer D (10 percent methylvinylsilyl groups) is shown in Figure 29. This polymer demonstrated a lower initial breakdown temperature and smaller amount of residue remaining at 800 C than did the crosslinked, highly-vinylated, Polymer C (Figure 24). This further indicates that as a polyaryloxysilane's crosslink density increases, its TGA-indicated thermal stability also increases.

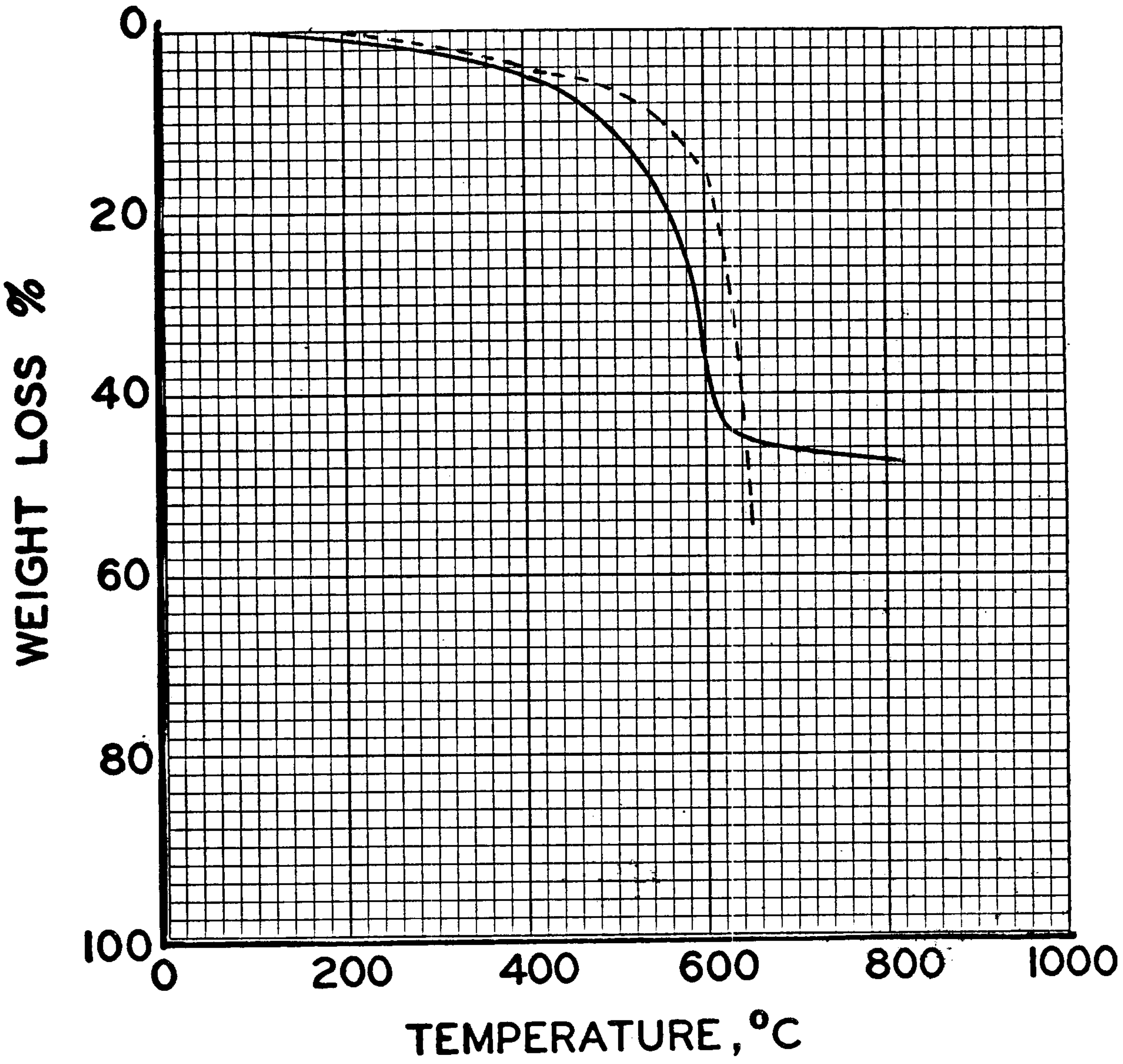


Figure 28. Thermogravimetric Analyses of Polymer D No. 23563-27 Under Air (----) and Under a Vacuum (——)

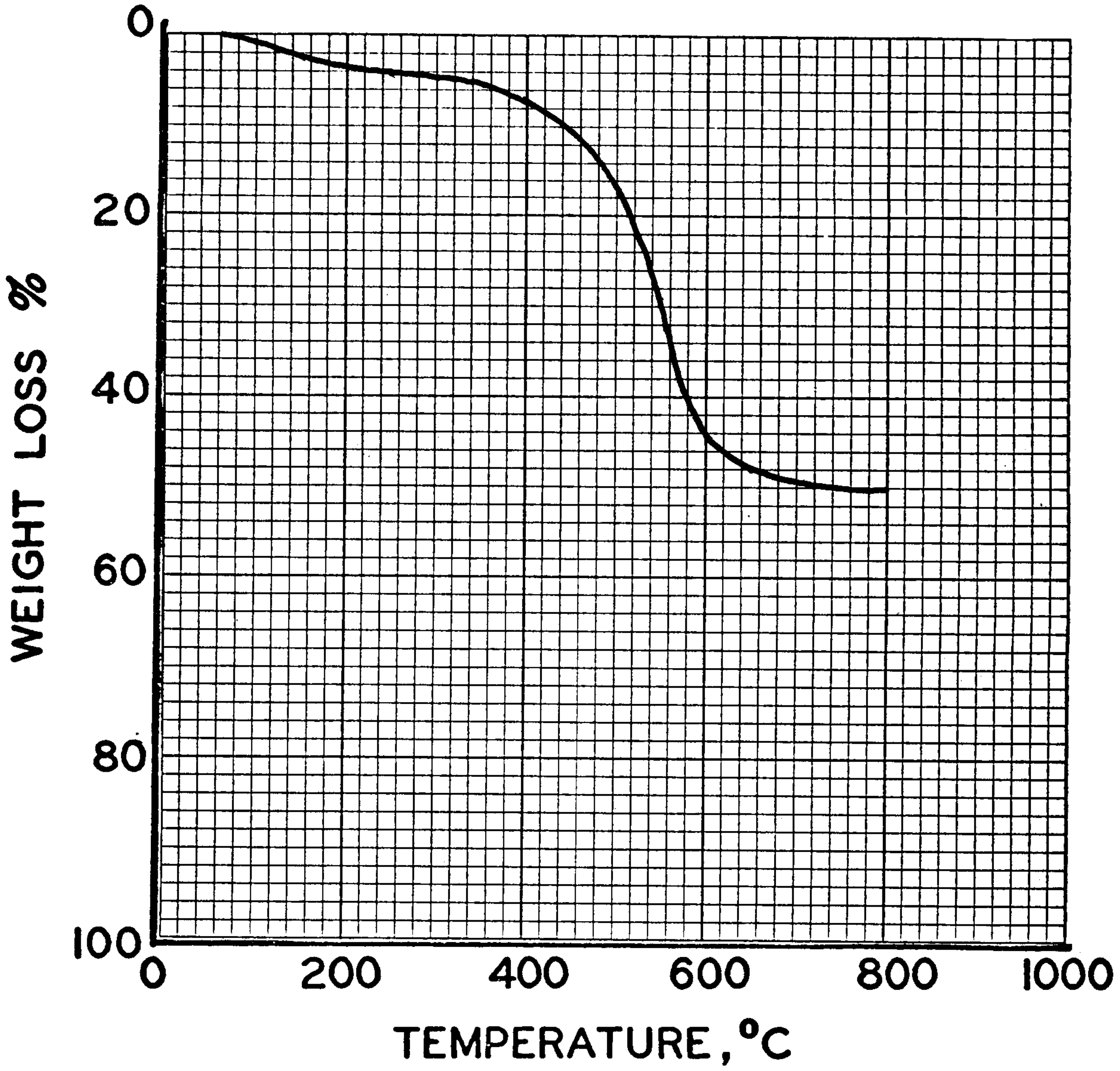


Figure 29. Thermogravimetric Analyses of Purified and Crosslinked Polymer D Thermogram obtained at 4 C/minute in nitrogen.

4. Isothermal Thermogravimetric Analysis

Coatings of Polymer D (Nos. 23448-36 and 23563-58) on aluminum weighing dishes were subjected to isothermal aging in circulating air at temperatures ranging from 250 to 350 C (Figures 30 and 31).

As in the case of Polymers B and C, the aging studies again revealed that the lowest weight losses after 19 hours were obtained with samples heated at the highest temperature. Polymer D No. 23448-36 had a methylvinylsilyl unit content of only 10 percent, while Polymer D No. 23563-58 contained equal numbers of dimethyl- and methylvinylsilyl units. Comparison of Figures 30 and 31 reveals that the more highly vinylated polymer (No. 23563-58) showed significantly lower weight losses than the other polymer at all three temperatures. Again, thermal stability was enhanced by increasing the crosslink density.

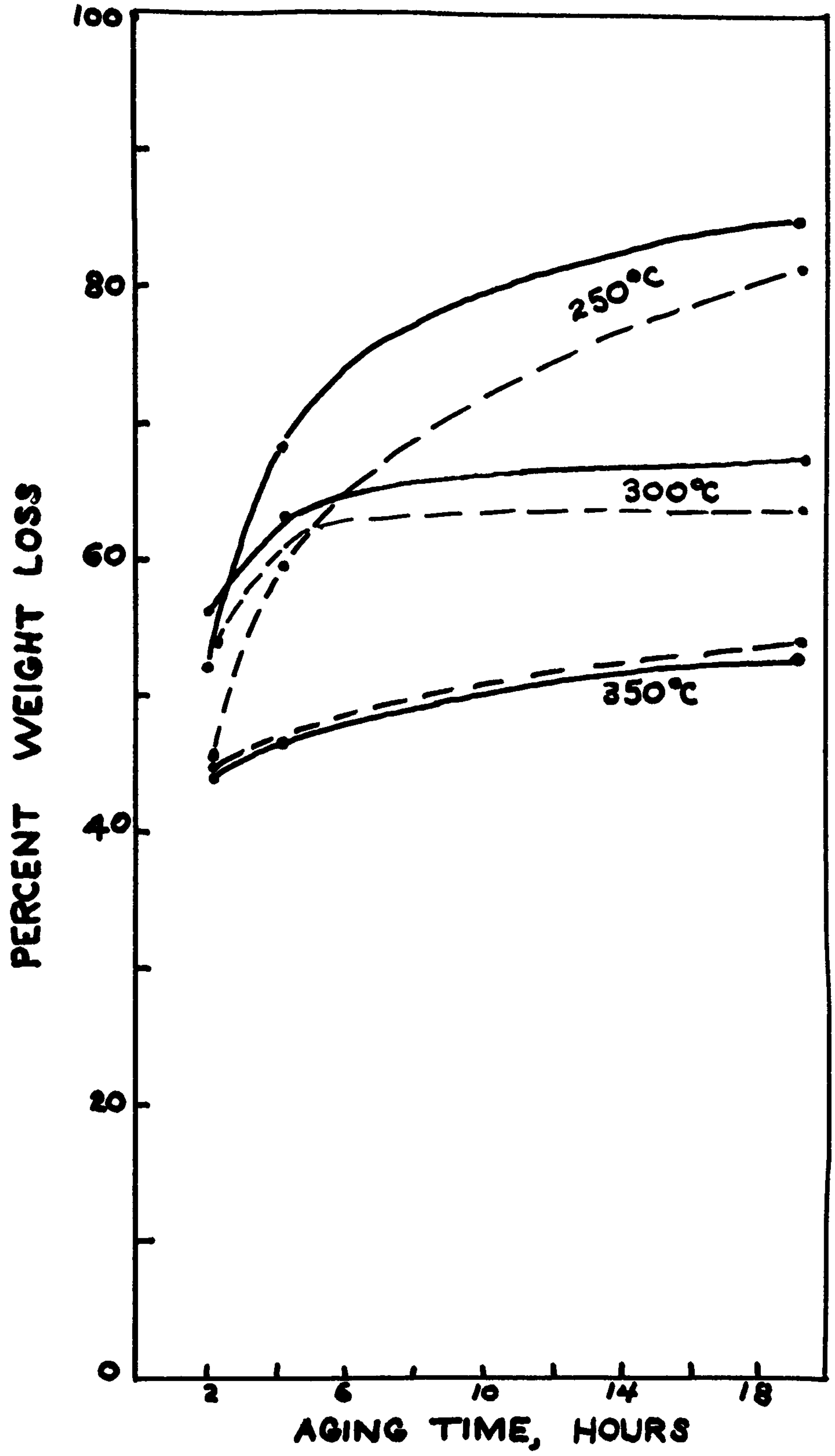


Figure 30. Isothermal Thermogravimetric Analyses of Polymer D No. 23448-36 With (——) and Without (----) t-Butyl Perbenzoate

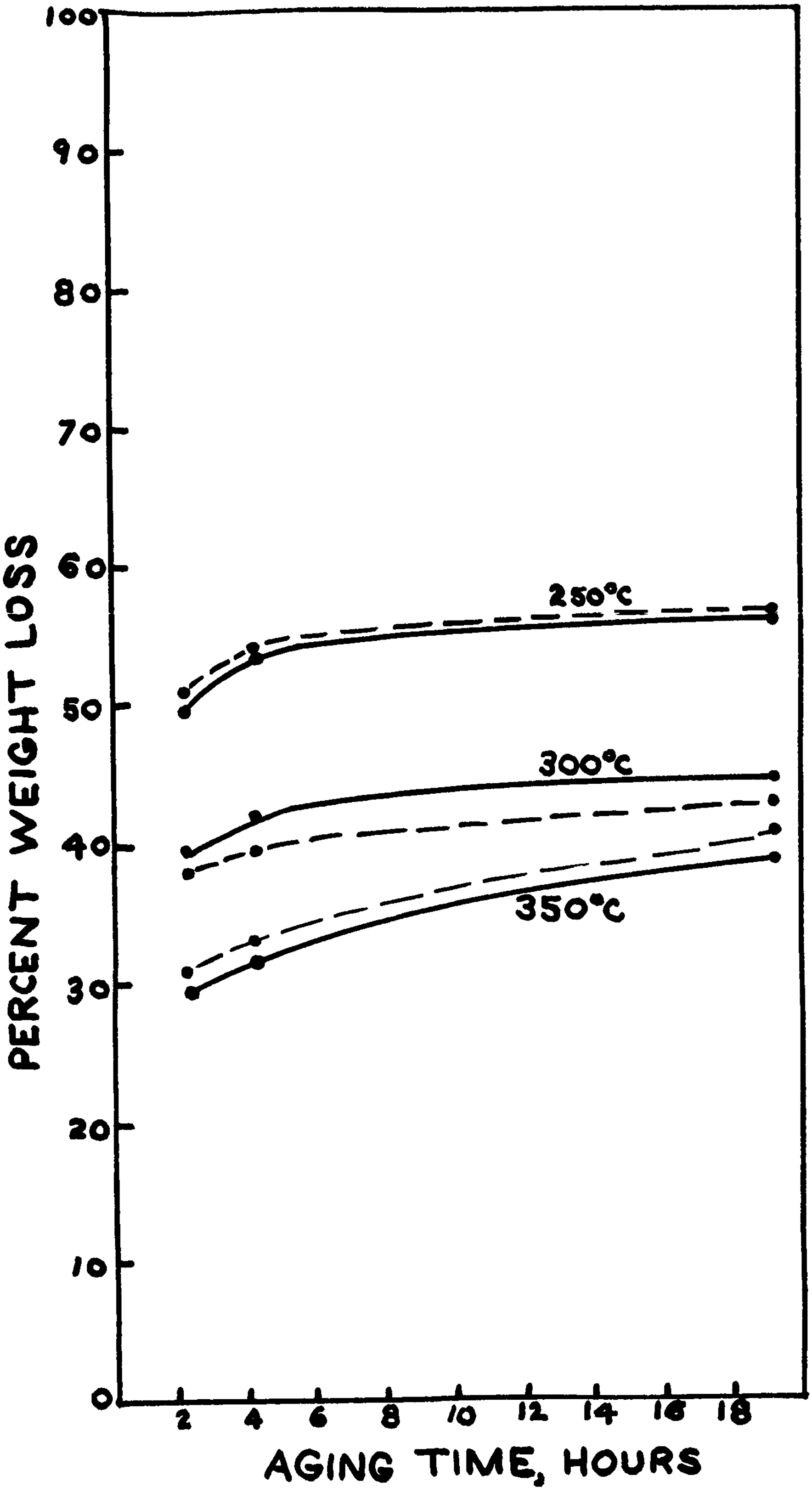


Figure 31. Isothermal Thermogravimetric Analyses of Polymer D No. 23563-58 With (———) and Without (----) t-Butyl Perbenzoate

H. Polymer D - Experimental

1. Preparation of Polymer D (No. 23563-27)

a. A mixture of 37.50 grams (0.1547 mole) of dianilinodimethylsilane, 12.50 grams (0.04913 mole) of dianilinomethylvinylsilane, and 37.96 grams (0.2038 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 500-ml, round-bottomed flask heated to 210 C in a Wood's metal bath. The melt was held at 210 C at atmospheric pressure for 1 hour. The pressure was then gradually reduced to 0.2 mm over a half-hour period, during which time most of the aniline distilled off. The temperature was then raised to 225 C and the reaction was continued for another hour at 0.2 mm. The flask was then flushed to atmospheric pressure with nitrogen. A theoretical yield (38.0 grams, 100 percent) of aniline was realized. Fibers pulled from the melt were easily cold-drawn by hand necking down and drawing out 130 to 150 percent to tough, flexible filaments, indicating that very little or no crosslinking via reaction at the double bond had occurred during the polymerization. A number of filaments were drawn for physical property measurements (Table 13). The polymer softening temperature as determined on a Fisher-Johns melting point block was 120 C. The molecular weight (Mw) of the polymer, determined by GPC, was 33,000.

Analysis for Copolymer Composition		
	Calculated:	C, 69.75; H, 5.75
	Found:	C, 69.62; H, 5.68

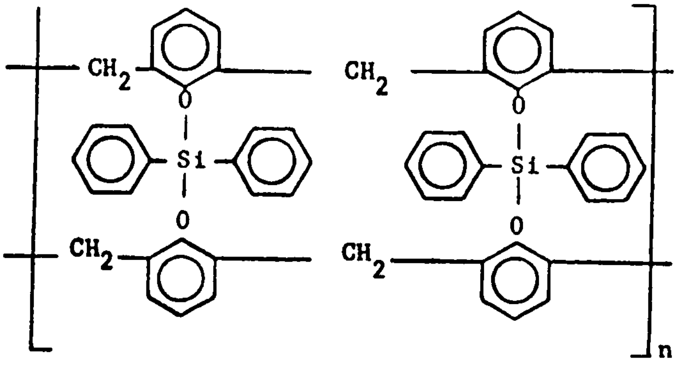
b. Condensation of Dianilinodimethylsilane (90 percent) and Dianilinomethylvinylsilane (10 percent) with p,p'-Biphenol. A mixture of 90.0 grams (0.37 mole) of dianilinodimethylsilane, 10.17 grams (0.04 mole) of dianilinomethylvinylsilane, and 76.2 grams (0.41 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 1000-ml, round-bottomed flask heated to 210 C by a Wood's metal bath. The melt was held at 210 C under a nitrogen sweep for 25 minutes while aniline distilled off. The reaction mixture was then heated under a vacuum at 210-225 C for 1.5 hours. Nitrogen was then admitted to the flask and the polymeric product (No. 23448-36) was cooled to room temperature. The resulting resin was transparent, light-yellow, and tough. It was readily compression-molded at 125 C to provide transparent sheet and could be milled on rolls heated to 150 C.

c. Polycondensation of Dianilinomethylvinylsilane (50 percent) and Dianilinodimethylsilane (50 percent) with p,p'-Biphenol (Polymer No. 23563-58). A mixture of 50.55 grams (0.1990 mole) of dianilinomethylvinylsilane (Monomer No. 23753-25), 48.16 grams (0.1990 mole) of dianilinodimethylsilane, and 74.00 grams (0.3974 mole) of p,p'-biphenol was fused under nitrogen in a single-neck, 500-ml, round-bottomed flask heated to 215 C in a Wood's metal bath. A vigorous reaction was noted immediately and aniline began to distill out of the reaction flask after approximately 10 minutes at reflux. After 15 minutes at 215-220 C, the pressure was gradually reduced over a 1-hour period to 0.20 mm. By this time, essentially all of the aniline was removed and the reaction mixture was a light-brown, highly viscous melt, bubbling very slowly. The temperature was raised to 250 C and heating continued for 1.5 hours at 0.17 mm. The polymer melt had ceased bubbling at this time. The flask was flushed to atmospheric pressure with nitrogen and an attempt was made to pull fibers from the melt. However, the product was an extremely viscous, rubbery mass and no fibers could be drawn. A small sample of the product only partly dissolved in boiling o-dichlorobenzene. A mixture of viscous solution and highly swollen, but insoluble, gel particles was observed. Evidently some thermally induced crosslinking occurred during the polymerization. However, the product was sufficiently soluble to allow preparation of solution (containing gel particles) for evaluation as a surface coating. By-product aniline was obtained in 73.8-gram (99.9 percent) yield.

IV. CURES INVOLVING NOVOLAKS AND SILANE MONOMERS

A. Discussion

One approach to crosslinked polyaryloxysilane resins explored during this program involved the condensation of novolak (phenolic) resins with dianilinodiphenyl- or dianilinodimethylsilanes. The resulting polymers would presumably have the basic polyaryloxysilane structure, but in a three-dimensional form.



Resins of this type could be relatively inexpensive to produce and might be useful in a wide variety of end-use applications, including that of a modified phenolic for use as an ablator.

Attempts were made to melt condense dianilinodiphenylsilane with both a commercial novolak (Union Carbide's BRZ-7541) and a novolak prepared in the laboratory. In neither case was there evidence of a chemical reaction. The product in each case was a low-viscosity fluid at 200 C having an infrared spectrum similar to that of the starting novolak. However, a melt condensation of dianilinodimethylsilane with a novolak appeared to be successful. Heating a fused mixture of Monomer II and the phenolic resin to 200 C resulted in a rapid evolution of aniline (detected by odor) and the immediate formation of a sponge-like, nonfusible, yellow-orange resin. These results suggest that steric hindrance may block the reaction of dianilinodiphenylsilane with a novolak.

It was subsequently found that a mixture of a novolak, dianilinodimethylsilane, and hexamethylenetetraamine could be successfully compression molded at 200 C to produce an orange, transparent thermoset (Polymer No. 23448-33-1) that failed to soften or melt when heated for 60 minutes in air at 315 C.

The infrared spectrum of this thermoset (Figure 32) showed the composite feature of the spectrum of a phenolic resin and of Polymer B. The CH_3-Si bands at 800, 920, and 1260 cm^{-1}, the aromatic substitution bands at 690 and 750 cm^{-1}, and the Si-O-phenyl band at 1250 cm^{-1} support the general aryloxysilane-modified phenolic structure shown above.

Thermogravimetric analysis (Figure 33) of Polymer 23448-33-1 in air showed a gradual weight loss above 200 C with a 50 percent weight loss at 575 C and an 84 percent weight loss at 700 C. Under a vacuum, only a 17 percent weight loss was incurred up to 500 C and 37 percent at 850 C.

In a further study, a quantity of novolak resin was synthesized (23563-66) and several condensations with dimethyldianilinosilane were carried out in an inert atmosphere. Infrared analysis showed that siloxy crosslinks were formed in each case but the extents of crosslinking were difficult to determine. When only 64 percent of the theoretically required amount of dianilinosilane monomer needed for complete reaction with the novolak's hydroxyl groups was used, no evidence for unreacted anilinosilane groups was found in the product's infrared spectrum. However, the use of the theoretical amount of dianilinosilane monomer resulted in unreacted anilinosilane being detected in the spectrum of the product.

A control resin was prepared by curing the novolak with hexamethylenetetraamine (Hexa). Thermogravimetric analyses were obtained on all the above products under a vacuum (Figure 34).

The results indicated that the dimethyldianilinosilane-crosslinked novolaks were somewhat less thermally stable than the hexamethylenetetraamine-crosslinked novolak. However, comparison of Curve 2 of Figure 34 with Figure 33 reveals that crosslinking with a mixture of dimethyldianilinosilane and hexamethylenetetraamine provided

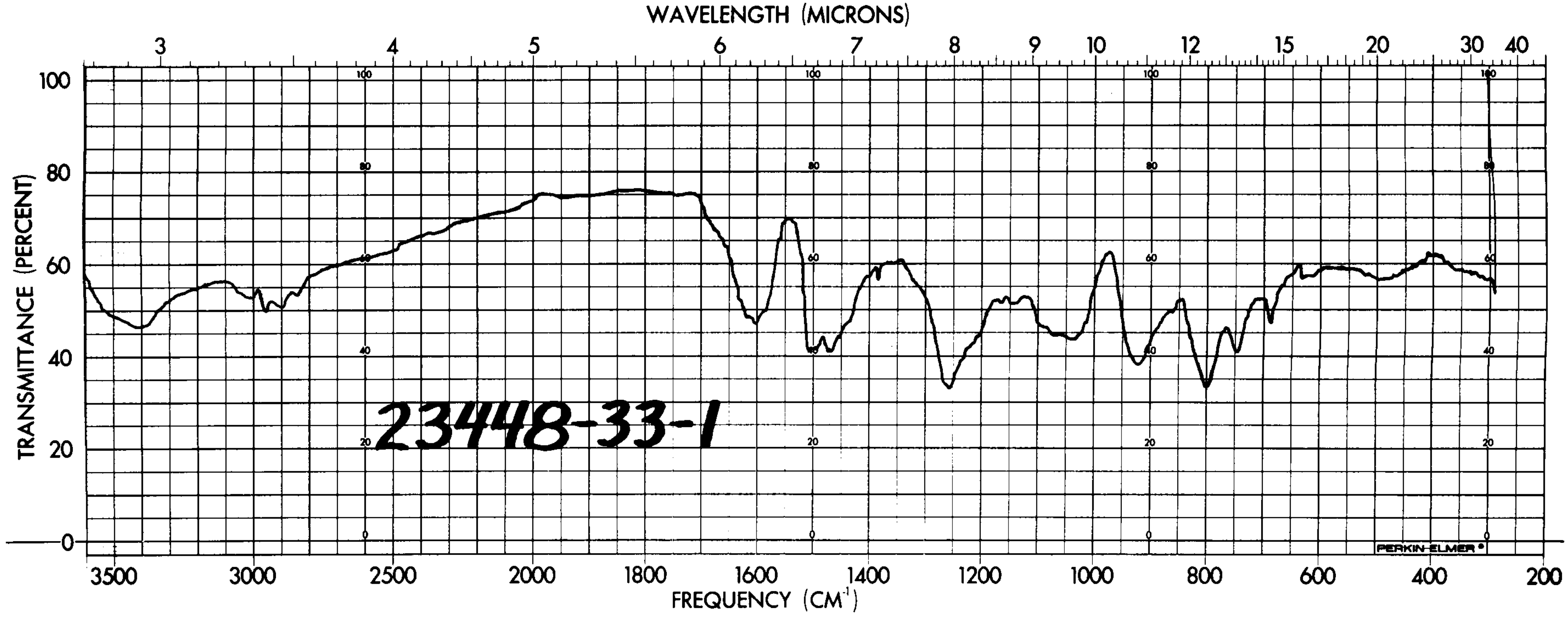


Figure 32. Infrared Spectrum of Silane-Modified Novolak No. 23448-33-1

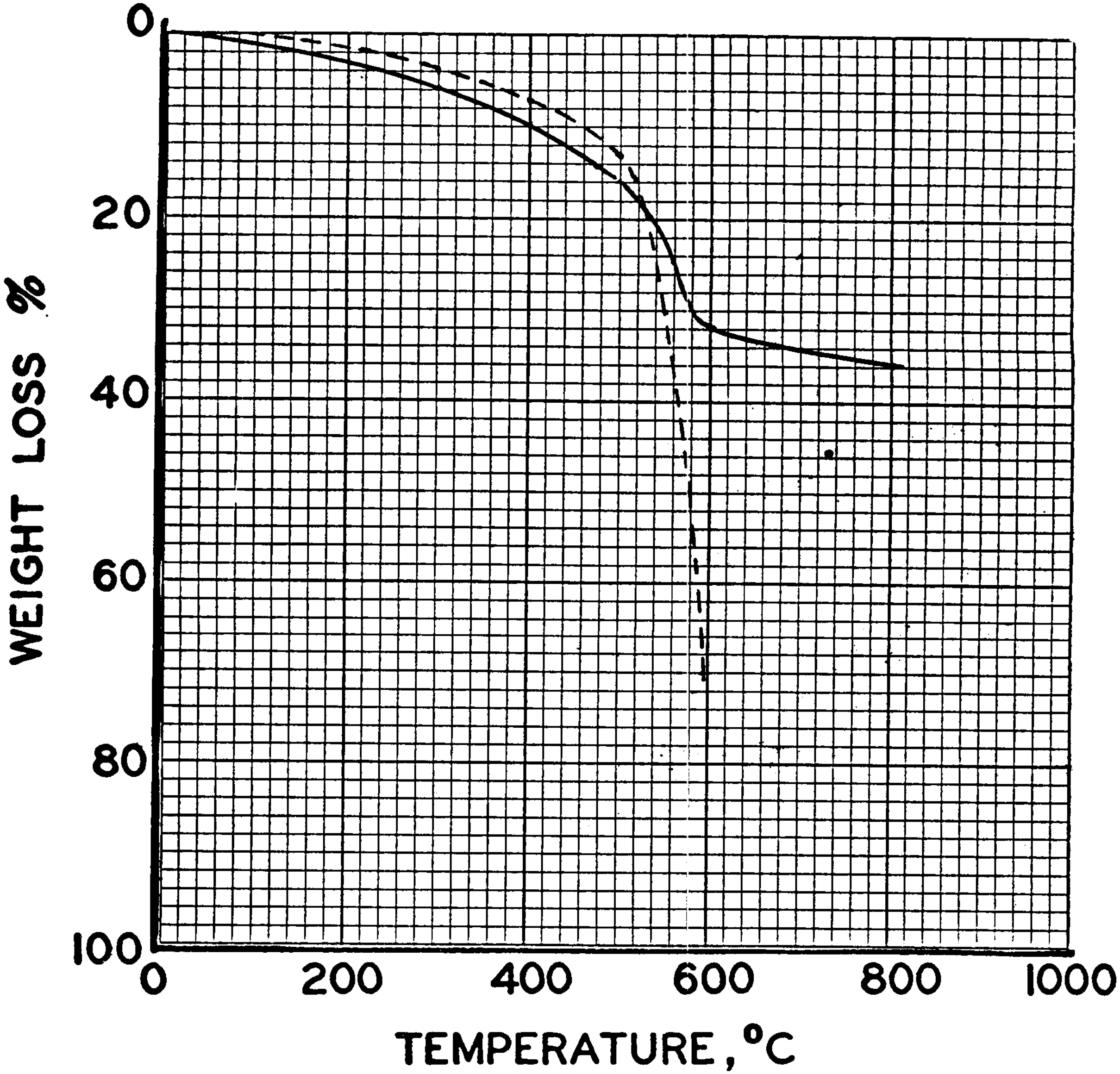


Figure 33. Thermogravimetric Analyses of Silane-Modified Novolak No. 23448-33-1 Under Air (----) and Under a Vacuum (——)

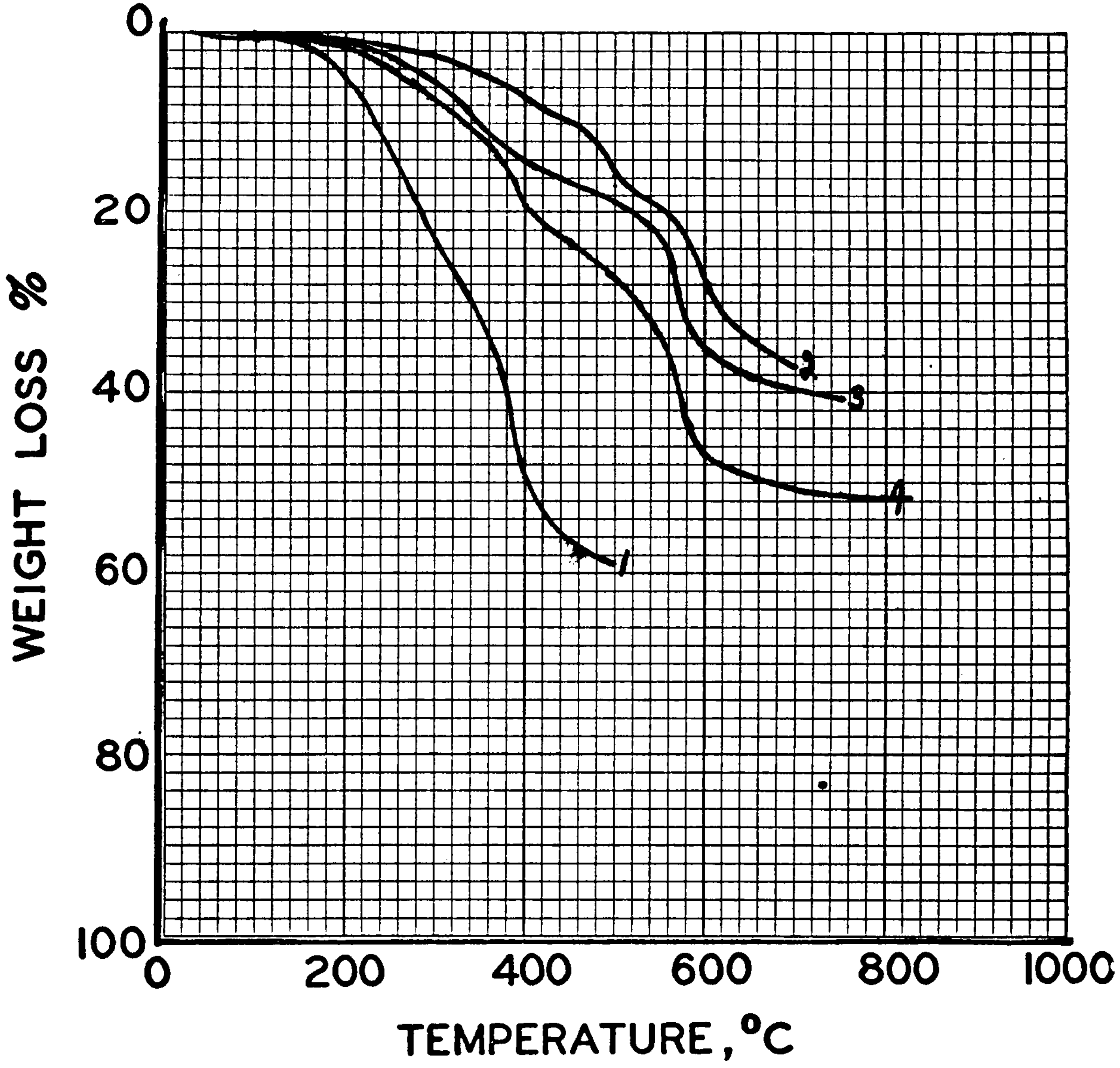


Figure 34. Thermogravimetric Analyses (4 C/min at 0.1 mm Hg) of Novolak Resin (23563-66) Crosslinked with Hexamethylenetetraamine and Dimethyldianilinosilane

1: Neat novolak resin; 2: Hexa-cured novolak resin (23563-69-4); 3: $(CH_3)_2Si(NHC_6H_5)_2$-cured novolak resin (23563-69-3); 4: $(CH_3)_2Si(NHC_6H_5)_2$-cured novolak resin (23563-69-2).

a product (23448-33-1) which was very similar to the conventional cured phenolic resin in thermal stability.

The phenolic resin cured with both Hexa and dianilinodimethylsilane might possess certain valuable property advantages not revealed by thermogravimetric analyses. For that reason, further work to optimize the cures, to determine the processability of the resin, and to evaluate the general properties of test specimens seems warranted.

B. Experimental

1. Preparation of Novolak Resin (Polymer No. 23563-66)

A novolak resin was prepared following, in part, the instructions in "Preparative Methods of Polymer Chemistry"(12), Preparation 257, page 294. The reaction was scaled up fivefold and run in a 5-liter resin kettle. The charge used was: phenol, 650 grams; 37 percent aqueous formaldehyde, 462 grams; water, 65 ml; oxalic acid dihydrate, 10 grams.

However, a difference between the present preparation and that described in Sorenson and Campbell should be pointed out. In their method, the reaction is stopped after the resin product reaches 120 C at a pressure of 50-100 mm. Polymer 23563-66 was prepared by gradually raising the temperature of the melt to 175 C at 0.5 mm over an 8-hour period to insure complete reaction of methylol groups and subsequent removal of water and unreacted phenol. According to Sorenson and Campbell, 700 grams of resin should be obtained. The actual yield was 628 grams of readily powdered, nontacky, clear, very light-yellow resin. Also recovered was 71 grams of phenol and 108 grams of water. The hydroxyl equivalent of the resin is estimated to be close to 103. That is, 103 grams of resin contain approximately 1 gram-mole of hydroxyl groups.

2. Condensations of Monomer I and Monomer II with Novolaks

a. A mixture of 8.5 grams of Union Carbide's BRZ-7541 phenolic resin and 1.5 grams of dianilinodiphenylsilane was melted under a stream of nitrogen in a polymerization tube heated by a Wood's metal bath. The melt was heated under nitrogen at 260 C for 15 minutes, then under a vacuum at 260 C for 90 minutes. The product was orange-yellow in color, a low-viscosity liquid when hot, and a brittle, transparent solid after being cooled to room temperature. The infrared spectrum of the product (Sample No. 23448-7) was essentially the same as that of the starting novolak. The silane monomer apparently failed to react with the phenolic resin and was distilled from the reaction tube under vacuum and lost.

b. A similar experiment was carried out using a novolak prepared according to the procedure of Sorenson and Campbell(12). A mixture of 16.0 grams of novolak and 5.0 grams of dianilinodiphenylsilane was heated under nitrogen at 215 C for 30 minutes, then under a vacuum at 225 C for 45 minutes. The product was a low-viscosity fluid that hardened upon cooling to a hard, transparent, yellow, brittle solid (Sample 23448-9-A).

c. A mixture of 2.13 grams of the novolak used in Example b and 2.42 grams of dianilinodimethylsilane was heated in an aluminum weighing dish on the surface of a Wood's metal bath heated to 200 C. A rapid evolution of aniline occurred (detected by odor of vapor) and a slightly tacky, spongelike, yellow-orange, infusible resin was formed within 1 minute. The resin was insoluble in boiling 1,2,4-trichlorobenzene.

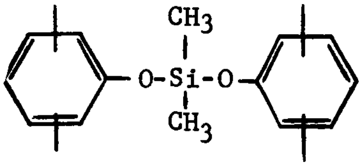
d. A mixture of 2.12 grams of the experimental novolak used in (b) and (c), 2.42 grams of dianilinodimethylsilane, and 0.5 gram of hexamethylenetetraamine was intimately ground together with a mortar and pestle. The mixture was placed in a small compression mold preheated to 205 C and a slight pressure was applied. Aniline was immediately evolved (detected by the odor) and the majority of the polymer flowed from the mold before it hardened to a light-orange, transparent, foamed resin. The resin was rubbery when hot and brittle at room temperature. The partially cured, foamed resin was pulverized, then remolded at 205 C to provide an orange, transparent, semiflexible but still brittle disk.

The compression molded polymer (No. 23448-33-1) darkened in color, but did not soften or melt when heated on a hot plate in air at 315 C for 60 minutes.

e. Three reactions were run in Pyres polymerization tubes. Preparations 23563-69-2 and -3 included 100 and 64 percent, respectively, of the amount of $(CH_3)_2Si(NHC_6H_5)_2$ theoretically required to react with all the hydroxyl groups of the phenolic resin. Preparation 23563-69-4 included 64 percent of the amount of hexamethylenetetraamine (Hexa) required to react with all the open ortho and para positions of the phenyl rings in the novolak. The following monomer charges were used:

Experiment Number	$(CH_3)_2Si(NHC_6H_5)_2$	Hexa, grams	Novolak 23563-66
23563-69-2	4.70 grams	-	4.00 grams
-3	4.50 grams	-	6.00 grams
-4	-	1.32	9.00 grams

The reactants were charged into tubes which were evacuated and flushed with nitrogen three times. The tubes were then immersed in a Wood's metal bath heated to 150 C. The mixtures all fused quickly to viscous melts. The melt containing Hexa soon began to foam and expanded three to four times the original volume. Both melts containing dianilinodimethylsilane gave off aniline almost immediately. After 30 minutes at 150 C, the temperature was raised to 210 C and rapid aniline reflux was noted in 23563-69-2 and -3. However, no signs of bubbling in the melt were noted and it is believed that mixtures were already crosslinked. (A reaction with the same charge as 23563-69-2, when carried out in an open beaker while hand-stirring, gave a melt at 80-100 C which set up at about 130 C.) The temperature was raised to 250 C and the pressure reduced to 0.5 mm. After 30 minutes, the tubes were flushed with nitrogen and cooled. The tubes were broken and the hard resin products recovered. Both 23563-69-2 and -3 were hard, light-yellow resins which were ground to a powder with difficulty in a mortar, while 23563-69-4 was a very hard, dark-brown resin almost impossible to grind to a powder in the mortar. Infrared analysis showed the presence of



groups in Resins 2 and 3, with evidence for unreacted aniline groups in Resin 2.

V. CROSSLINKING PHENOLIC OH-TERMINATED POLYARYLOXYSILANES

A. Discussion

A portion of the experimental work was devoted to preparing and evaluating polyaryloxysilanes that might be cured by intermolecular condensation reactions. It is believed that polyaryloxysilanes of this type offer the best possibility of providing useful structural properties at elevated temperatures that would exhibit optimum thermal stabilities for the polyaryloxysilane system of polymers. Examples of these polymer structures are shown in Figure 35. Each of these polymer types is currently in a very early stage of development and only preliminary synthesis and evaluation data are available at this time.

Although high molecular weight Polymer A contains phenoxy chain units and might be expected to undergo a novolak-type cure, it showed only a slight tendency to crosslink when heated (as a melt) with hexamethylenetetraamine. This may be due to the fact that phenolic cures with hexamethylene tetraamine are dependent on the presence of free phenolic -OH groups that are normally not present in any significant concentration in a high molecular weight polyaryloxysilane. A low molecular weight, presumably phenolic-terminated specimen of Polymer A was prepared by condensing Monomer I with an excess of p,p'-biphenol. The resin hardened appreciably when mixed and fused with hexamethylenetetraamine and formed a resin that was soft, but did not melt at 225 C. Fibers could not be drawn from the resin at 225 C. This experiment suggested that appropriate low molecular weight polymers of the type

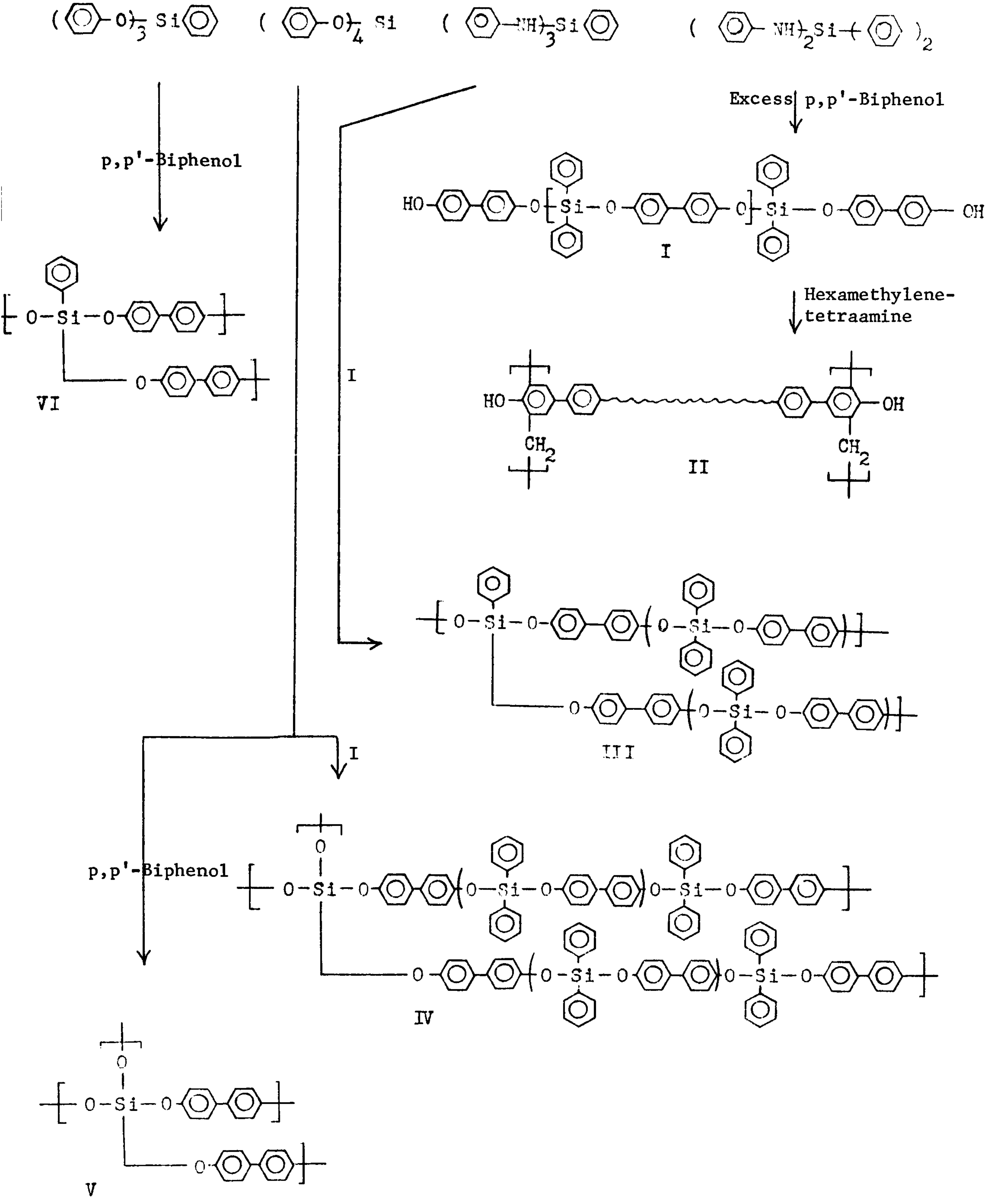


Figure 35. Condensation Crosslinking of Polyaryloxysilanes

might represent polyaryloxysilanelike novolaks that could be cured by hexamethylenetetraamine or paraformaldehyde. Presumably, the tightest cures would be obtained the more closely n approached zero.

One experimental low polymer of the above type was prepared by condensing dianilinodiphenylsilane with a fivefold excess of resorcinol followed by removal of the residual resorcinol by vacuum distillation. The resinous product (Polymer No. 23753-7) was a red material that was gummy at room temperature. The infrared spectrum of the resin (Figure 36) showed no conclusive evidence for the presence of phenolic OH. However, the material appeared to cure in the presence of hexamethylenetetraamine as a typical novolak. A compression molded mixture of Polymer 23753-7 and hexamethylenetetraamine was obtained as hard, transparent, deep-red, semibrittle material (Sample 23448-32-II) that did not soften or melt at 200 C. The infrared spectrum of the cured polymer (Figure 37) generally supports an aryloxysilane-modified phenolic structure, but contains certain features that have not been interpreted.

Thermogravimetric analyses (Figure 38) of Resin No. 23448-32-II under both air and vacuum showed weight losses of only about 20 percent up to 550 C. While the resin degraded rapidly in air above this temperature, it underwent only a 27 percent weight loss up to 750 C under a vacuum. On the basis of TGA results, the stability of this material appeared superior to that of a conventional cured phenolic (see Figure 34). Type II polymers should be further explored to determine the optimum curing conditions and the properties of suitably filled compression moldings. It is possible that Type II polymers might show improved thermal shock resistance as compared to phenolic resins and that they might prove useful as cocurable modifiers for phenolic resins.

A lightly crosslinked Polymer A of Type III (Figure 35) was prepared by condensing dianilinodiphenylsilane (95 percent) and trianilinophenylsilane (5 percent) with p,p'-biphenol. The resulting polymer swelled in benzene but did not dissolve. The resin could not be compression-molded at 250 C/10,000 psi using press times up to 30 minutes. However, extending the press time to 5 hours (218 C/3000 psi)

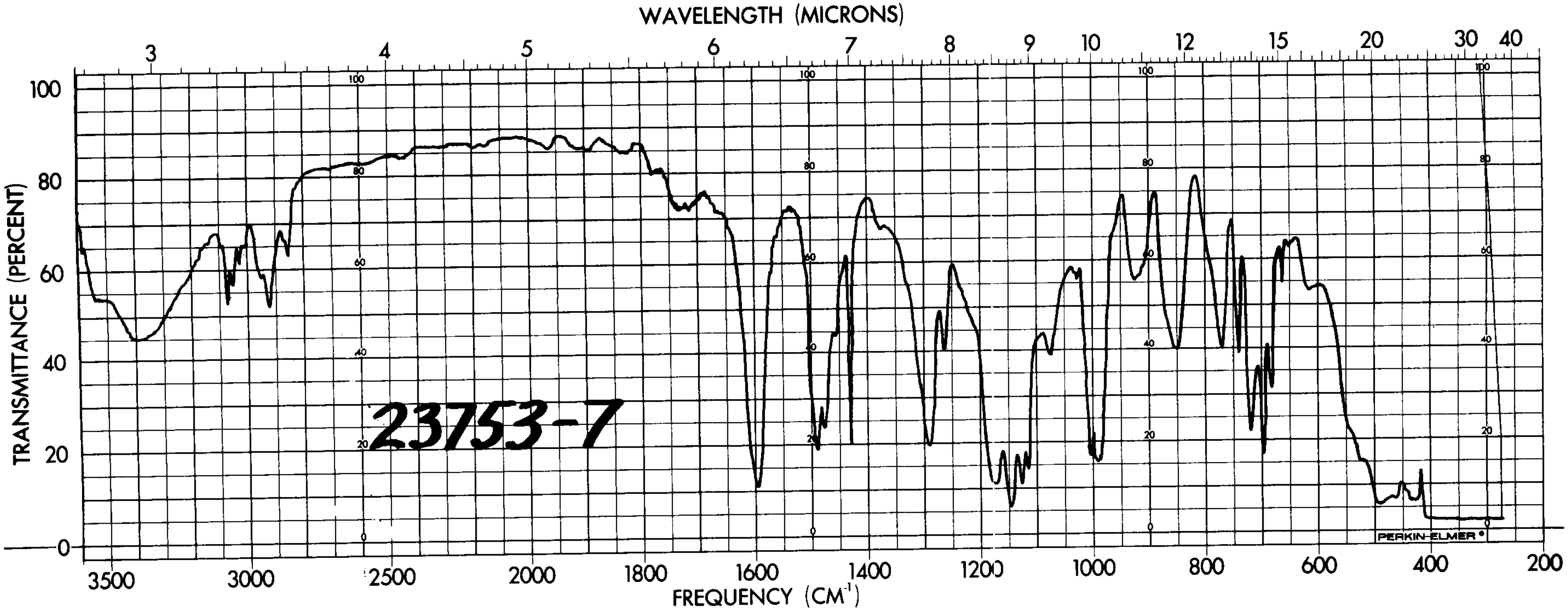


Figure 36. Infrared Spectrum of Resorcinol-Terminated Polyaryloxysilane 23753-7

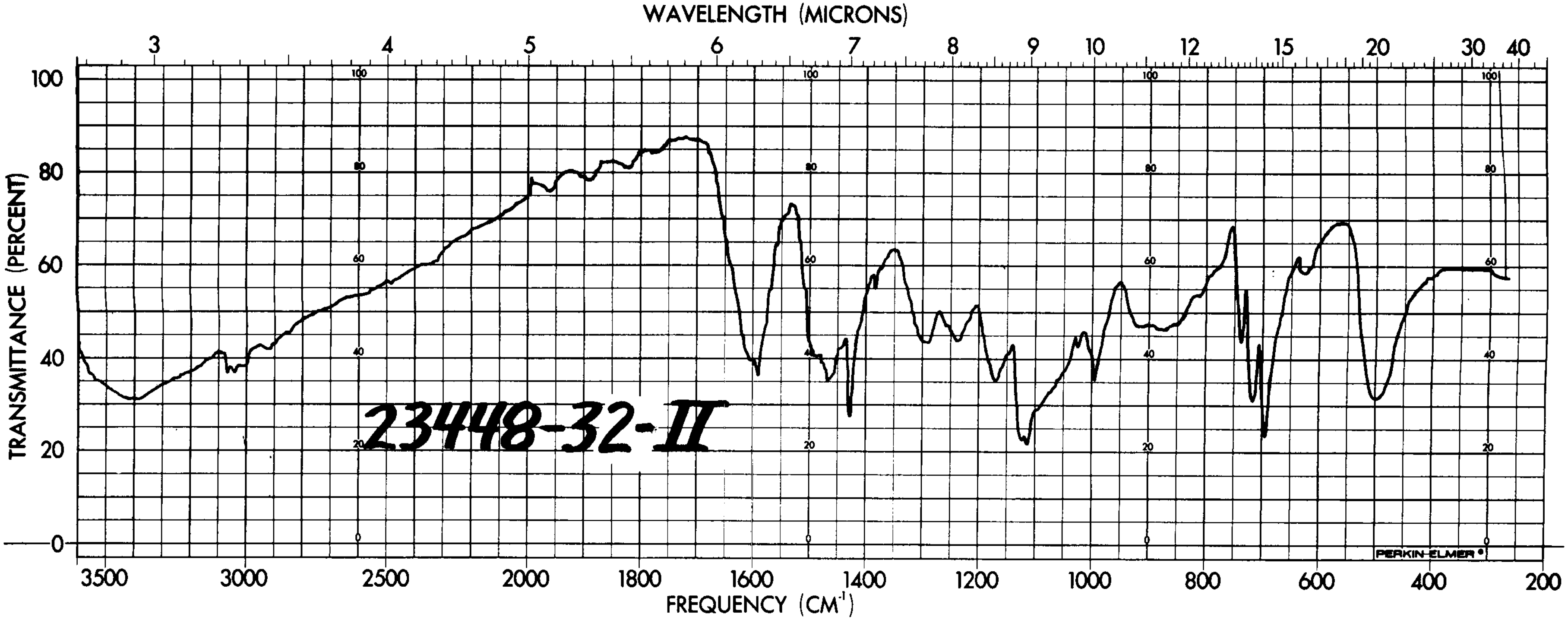


Figure 37. Infrared Spectrum of Hexamethylenetetraamine-Cured Resorcinol-Terminated Polyaryloxysilane No. 23448-32-II

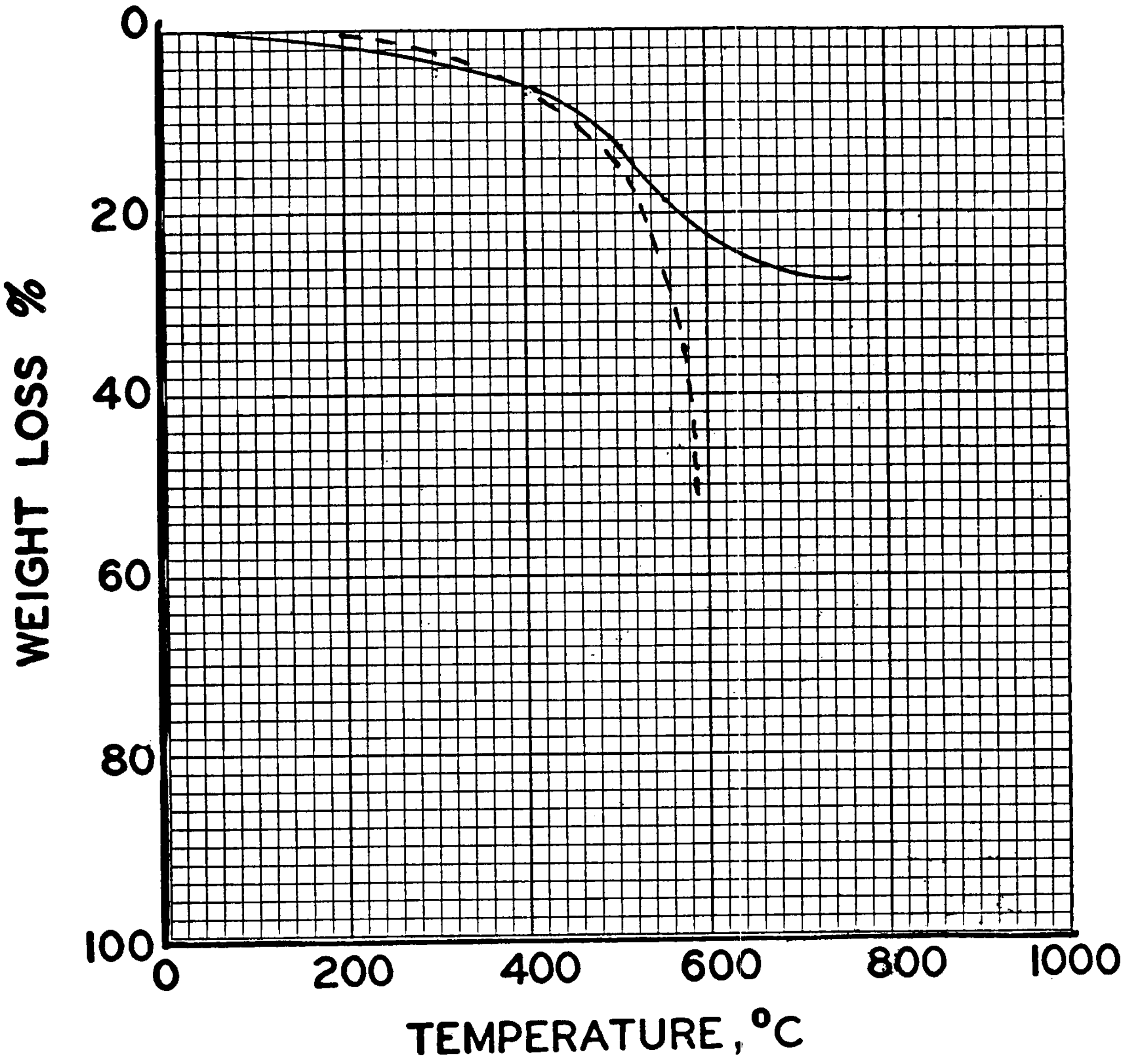


Figure 38. Thermogravimetric Analyses of Hexamethylenetetraamine-Cured Resorcinol-Terminated Polyaryloxysilane No. 23448-32-II Under Air (----) and a Vacuum (——)

did permit the preparation of a clear, homogeneous-appearing compression molding, suggesting that the degree of crosslinking was low.

The use of triphenoxy- and tetraphenoxysilanes as curing agents for phenolic OH-terminated polyaryloxysilanes was also explored. These curing agents have the potential advantage over the analogous anilinosilanes in that incomplete reactions (which are the rule in condensation-type cures) will not leave relatively thermally unstable and moisture-sensitive aminosilane linkages in the resulting polymers.

Several polymers of Type IV (Figure 35) were prepared by heating aryloxysilanes with tetraphenoxysilane. The polymers used in this study were a DP $\sim$ 11 Polymer A, a DP $\sim$ 5 Polymer A, and a DP $\sim$ 5 Polymer H. Polymer H was a modified polyaryloxysilane prepared from dianilinodiphenylsilane and resorcinol. Resorcinol was investigated in place of p,p'-biphenol since it is more readily available and relatively inexpensive. Since a three-dimensional network polymer was being investigated, it was felt that there was a possibility that a resorcinol-based resin might prove to be as stable as a biphenol-based resin.

The two low molecular weight, phenolic-terminated Polymer A products were crosslinked with 10 weight percent $\mathrm{Si(O\phi)_4}$ while the Polymer H was reacted with 15 weight percent $\mathrm{Si(O\phi)_4}$ to compensate for its lower equivalent weight. In all cases, the appropriate amounts of resin and curing agent were weighed into aluminum cups, dissolved in dry THF, and the THF evaporated to yield clear, uniform films. These coatings were then cured by heating 30 minutes in a forced-draft oven at 250 C. This treatment provided clear, colorless, nontacky, flexible films which were unaffected by rubbing with a cloth saturated with THF and which were no longer fusible at 250 C. Cured coatings obtained in this way were then aged in a forced-draft oven at 250 C for 700 hours. Even after 700 hours at 250 C and weight losses of 34-37 percent, these coatings were still intact, tightly adhering, and moderately flexible, although they became light brown in color. The weight loss data are presented in Figure 39 and Table 15. The two crosslinked Polymer A materials were similar to ultrapure Polymer A (23563-90-2) in stability.

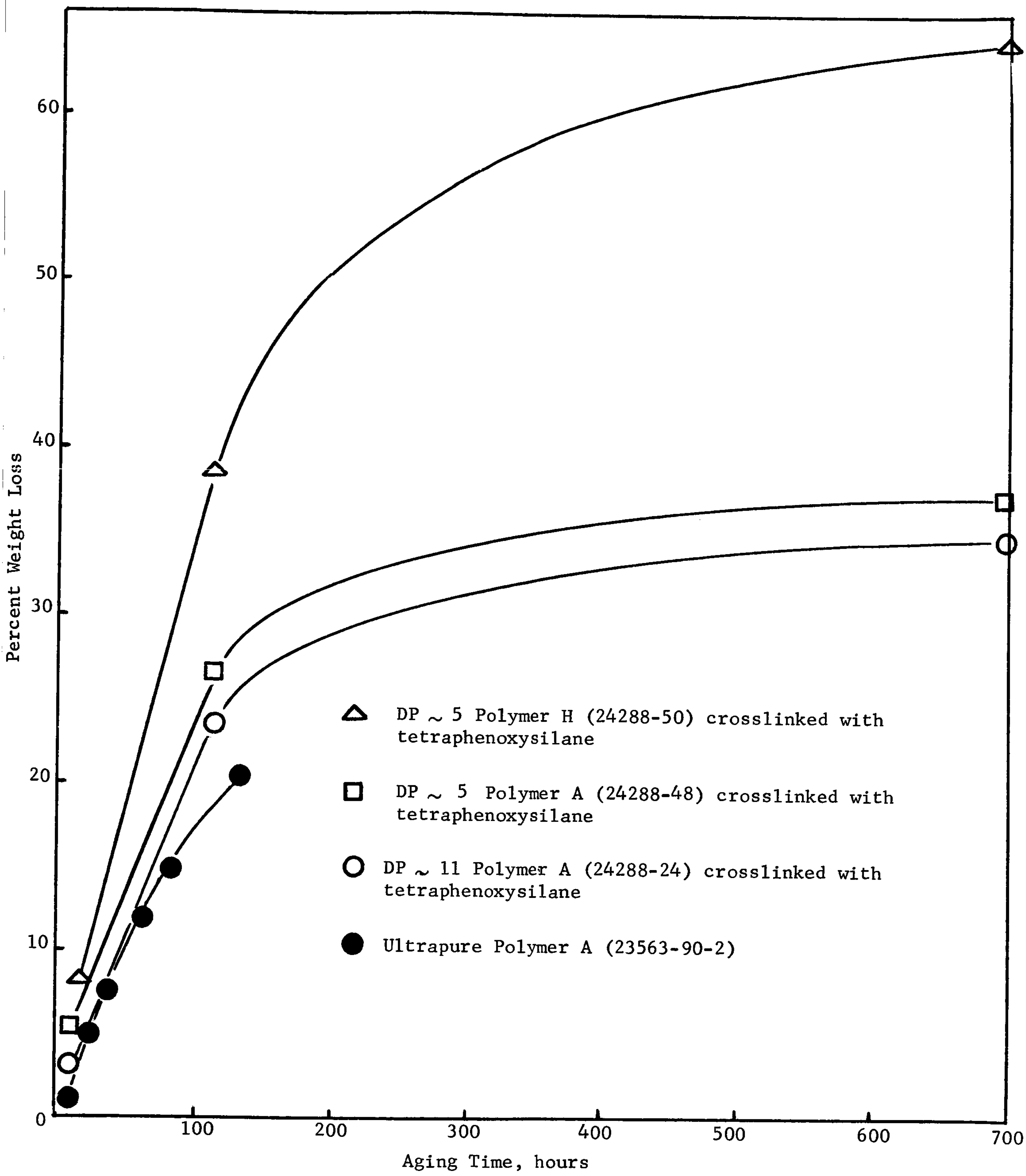


FIGURE 39. ISOTHERMAL OVEN AGING OF POLYMER FILMS AT 250 C

TABLE 15. WEIGHT LOSS ON AGING OF POLYMER A AND POLYMER H FILMS CROSSLINKED WITH $Si(O\phi)_4$ (a)

Aging Time, hours	Weight Loss in Percent			
	24288-24 (b)	24288-48 (c)	24288-50 (d)	Control 23563-90-2 (e)
8	-	-	-	0.8
15	3.0	5.5	6.4	-
19	3.8	6.0	7.9	-
27	-	-	-	5.0
40.8	-	-	-	7.8
65.8	-	-	-	11.8
87.8	-	-	-	14.8
115	23.0	26.7	38.6	-
135.1	-	-	-	21.0
700	34.7	37.2	64.2	-

(a) Heated in a forced-draft oven at 250 C.

(b) Hydroxy-terminated Polymer A, DP ~ 11, crosslinked with 10 percent $Si(O\phi)_4$.

(c) Same as (b) except DP ~ 5.

(d) Same as (c) escept Polymer H, where R is phenyl, crosslinked with 15 percent $Si(O\phi)_4$.

(e) Ultrapure Polymer A control (data from Seventh Quarterly Report, February 15, 1967, page 21).

However, crosslinked Polymer H showed appreciably greater weight losses upon prolonged aging than the crosslinked Polymer A coatings.

Modifications of the Type IV (Figure 35) were achieved by curing phenolic OH-terminated Polymer A with triphenoxyphenylsilane. Metal coatings were prepared from benzene solutions of these polymers. The coatings cured readily at about 200 C and were clear, colorless, and flexible. Their colors and flexibilities remained good after prolonged heating in air at 250 C. The isothermal weight losses in air at 250 C (Table 16) were found to be comparable to those experienced by ultrapure Polymer A under comparable conditions (op cit). It will be seen from Table 16 that the thermal decomposition rates of this polymer were greatly accelerated at temperatures above about 250 C. This is in general agreement with thermal stability data obtained for various types of polyaryloxysilanes during this program. A polymer (No. 24357-38) of the same type was prepared by condensing tris(dimethylamino)-phenylsilane with phenolic OH-terminated Polymer A. This resin was insoluble in benzene and was very difficult to compression-mold at 200 C, indicating a reasonably high degree of crosslinking. However, this resin had a strong aminelike odor suggesting that many of the silamine linkages remained intact in the polymer and were being acted upon by atmospheric moisture.

It is of interest to compare the weight loss data for triphenoxyphenylsilane-crosslinked 24288-24 coatings with the data of Figure 39. After 128 hours at 250 C, the weight loss of the triphenoxyphenylsilane-cured material was actually lower than any of the coatings represented in Figure 39, including the ultrapure Polymer A control.

TABLE 16. ISOTHERMAL AGING STUDIES ON TRIPHENOXYPHENYLSILANE-CURED, LOW MOLECULAR WEIGHT, PHENOLIC OH-TERMINATED POLYMER A[a]

	Pan No.	T1	T2	T7	T8	T5	T6	T3	T4	T9	T10
Exposure Time, hrs	Temp, C	250	250	250	250	300	300	350	350	350	350
0.5		<1	<1	<1	<1	-	-	5.3	5.5	5.2	5.3
17		4.8	4.9	4.6	4.9	-	-	18.4	18.4	24.1	23.8
21		-	-	-	-	21.4	21.4	-	-	-	-
24		6.0	6.0	5.8	6.1	-	-	19.4	20.0	25.8	25.8
40		8.8	8.8	8.5	8.8	-	-	24.3	24.1	31.3	30.1
64		11.0	11.5	11.3	11.5	-	-	-	-	-	-
85		-	-	-	-	30.1	29.4	-	-	-	-
128		17.8	17.9	17.3	17.9	-	-	-	-	-	-

(a) 1 to 2-mil-thick films in aluminum weighing dishes.

B. Experimental

1. Preparation of a Low Molecular Weight Polymer A (24288-24)

A low molecular weight, hydroxyl-terminated Polymer A was prepared for curing studies with tetraphenoxysilane. To 16.443 grams (0.0450 mole) dianilinodiphenylsilane (23563-73) in a 250-ml, 1-neck, round-bottomed flask was added 9.310 grams (0.0500 mole) of resublimed p,p'-biphenol (10 mole percent excess biphenol). The polymer resulting from this mixture of reactants would be predicted to have a $\overline{Mn}$ of about 4000 and a DP of about 9.

The reactants were fused under nitrogen at 225 C (Wood's metal bath). After 15 minutes, vigorous aniline reflux was in progress and the biphenol was all in solution. The pressure was reduced over a 10-minute period to 0.1 mm Hg. Aniline distilled rapidly. Also, some biphenol sublimed out of the reaction chamber, indicating that the pressure was reduced too soon. The melt was heated for 2.5 hours at 225 C. At this time, the product was a thin melt with no evidence of further reaction. The flask was flushed with nitrogen and cooled, yielding a clear, very light-yellow, brittle resin which was chipped out of the flask and readily ground to a white powder with a mortar and pestle. GPC indicated molecular weight in trichlorobenzene at 130 C was: $\overline{Mw} = 6708$; $\overline{Mn} = 4205$; ratio, $\overline{Mw}/\overline{Mn} = 1.59$. Based on an $\overline{Mn}$ of 4205, the DP is 11.5 (4205/366), very close to the predicted value. Samples of this resin were cured by dissolving in dry THF together with 10 percent by weight tetraphenoxysilane, casting films, and heating at 180 to 300 C.

2. Preparation of Low Molecular Weight Polymer A (24288-48)

A low molecular weight, hydroxyl-terminated Polymer A was prepared for use in curing studies with tetraphenoxysilane and triphenoxyphenylsilane. The procedure used in the preparation of phenolic-terminated Polymer A No. 24288-24 was followed, except that a larger excess of p,p'-biphenol was used so that a polymer with a DP of ~ 5, rather than 11, would be obtained. Thus, a 20 mole percent excess of p,p'-biphenol was used. The monomer charge was dianilinodiphenylsilane, 14,6608 grams (0.0400 mole), and p,p'-biphenol, 9.3100 grams (0.0500 mole). The mixture was fused under nitrogen at 215 C and held at 215 C for 45 minutes. The temperature was then raised to 225 C for 30 minutes before pressure reduction was started. The pressure was reduced to 0.5 mm Hg over a 1-hour period. The resulting thin, light-tan melt was held at 225 C and 0.5 mm for 1.5 hours. By this time, no further bubbling of the melt was observed and a small amount of biphenol sublimate (<0.1 gram) had collected on the upper flask walls. The reaction chamber was flushed with nitrogen and the melt was cooled to room temperature. The product was a brittle, light-tan solid.

3. Phenolic-Terminated Polyaryloxysilane

A mixture of 7.32 grams (0.02 mole) of dianilinodiphenylsilane and 4.09 grams (0.02 mole plus 10 percent excess) of p,p'-biphenol was fused under nitrogen at 225 C. When the rapid evolution of aniline had abated, the melt was heated under a vacuum at 225 C for 60 minutes to produce a light-yellow, brittle resin having a softening temperature of 125 C (Sample No. 23448-22-1). A 1.0-gram sample of the polymer was fused in an aluminum weighing dish floating on the surface of a Wood's metal bath heated to 225 C. A 0.1-gram quantity of hexamethylenetetraamine was stirred into the melt. Within 3 minutes the melt had hardened to a yellow-orange, tough, gumlike foam (Sample No. 23448-23-1). Fibers could not be drawn from the resin at 225 C.

4. Preparation of Resorcinol-Terminated Polymer No. 24288-50

The preparation No. 24288-48 was repeated, using resorcinol (sublimed) in place of p,p'-biphenol. Thus, 14.6608 grams (0.040 mole) dianilinodiphenylsilane and 5.5054 grams (0.0500 mole) of resorcinol were fused under nitrogen at 215 C. The mixture fused rapidly to produce a light-yellow melt which bubbled slowly. After 20 minutes at 215 C, the reaction was still quite sluggish so the melt was heated to 220 C. Rapid boiling and aniline reflux began at once and aniline began to distill. Most of the aniline was distilled out of the reaction vessel and pressure reduction was started after 15 minutes at 220 C. The pressure was reduced to 0.5 mm Hg after 10 minutes. A light-yellow melt, bubbling slowly, resulted. The temperature was raised to 225 C and held there for 2 hours at 0.5 mm. After this treatment, no bubbling or other indication of further reaction was evident and the reaction vessel was flooded with nitrogen and cooled to room temperature. The product was a very brittle, transparent, light-yellow resin.

5. Preparation of Resorcinol-Terminated Polymer No. 23753-7

To 59.8 grams (0.54 mole) of resorcinol in a 250-ml, single-neck, round-bottomed flask was added 20 ml of acetonitrile. The acetonitrile was distilled off at atmospheric pressure to azeotropically removed (acetonitrile b.p. 81.5 C, water azeotrope b.p. 76.0 C) any water present in the resorcinol. Forty grams (0.109 mole) of dianilinodiphenylsilane was then added, and the mixture was fused under nitrogen using a Wood's metal bath heated to 170 C. No evidence of reaction was observed so the temperature was gradually raised to 210 C, at which time aniline reflux began. After 15 minutes at 210 C, the pressure was reduced over a period of 1 hour to 0.2 mm. The temperature was then raised to 225 C and the reaction continued for 2 hours at 225 C and 0.2 mm. The flask was then flushed to atmospheric pressure with nitrogen and cooled to room temperature. The product was a dark red-brown, extremely viscous semisolid at room temperature which fused to a water-thin liquid at 50-60 C.

Analysis for $C_{24}H_{20}SiO_4$		
	Calculated:	C, 71.98; H, 5.03
	Found:	C, 73.15; H, 5.27

6. Condensation of Dianilinodiphenylsilane, Trianilinophenylsilane, and p,p'-Biphenol

In a 100-ml round-bottomed flask was placed 1.473 grams (0.00402 mole) of diphenyldianilinosilane, 0.087 gram of phenyltrianilinosilane (0.000228 mole), and 0.824 gram (0.00443 mole or 0.00007 mole excess phenol groups vs anilino groups) of p,p'-biphenol. The open flask was purged with dry nitrogen while heating at 190 C to fuse the monomers. A retort head was placed on the flask and the heat increased. As the reaction temperature rose to 200-210 C, evolution of aniline began. A vacuum pump and nitrogen back-flushing were used alternately for brief periods to remove the aniline slowly and provide mixing of the reactants. The last distillation of aniline was performed while heating 15 minutes at 270 C in vacuo. The alternate application and release of vacuum left the polymer product as a colorless, foamlike, tough material. The polymer product was heated 15 hours at 90 C/0.5 torr and then placed in refluxing benzene for 15 hours. The mixture was filtered while hot and washed three times with boiling benzene. The polymer swelled in benzene but did not dissolve. Evaporation of the filtrate and drying yielded 0.23 gram of soluble polymer. The insoluble polymer was mixed with benzene and lyophilized. A pure white, partially fused polymer was obtained. A thermogravimetric analysis (4 C/minute) of the product (Sample 24357-5-2) under a vacuum indicated a thermal breakdown temperature at 400 C with a 34 percent weight loss incurred up to 600 C.

A 0.3-gram sample of the latter was molded at 3000 psi, 218 C, over a 5-hour interval, using a 0.50-inch-diameter, cylindrical mold. The molded specimen was clear, transparent, and free of voids and opaque regions. Temperatures as high as 250 C and pressures of 10,000 psi, individually or together, did not mold the polymer into transparent specimens when the molding time was 30 minutes or less.

7. Curing of Resorcinol-Terminated Polyaryloxysilane

a. A 2.5-gram sample of Resin No. 23753-7 was heated to 100 C in an aluminum weighing dish and 0.12 gram of hexamethylenetetraamine was stirred into the melt. Upon heating the melt to 160 C, a rapid evolution of gas occurred and the resin set to a leathery, yellow-orange foam (Sample No. 23448-30-1). This foam was insoluble in boiling 1,2,4-trichlorobenzene and did not soften or melt when heated on a hot plate at 315 C.

b. An 8.0-gram sample of resorcinol-terminated polyaryloxysilane No. 23753-7 was fused at 100 C and 1.0 gram of hexamethylenetetraamine was stirred into the melt. The homogeneous melt was then heated to 160 C and a rapid evolution of gas occurred and a leathery, orange-yellow foam was obtained. The foam was pulverized, then compression molded at 205 C to provide a hard, deep-red, transparent, semibrittle disk (Sample No. 23448-32-II) that did not melt or soften at 200 C.

8. Crosslinking Low Molecular Weight HO-Terminated Polymer A with Hexamethylenetetraamine

A mixture of 1.0 gram of low molecular weight HO-terminated Polymer A No. 24228-48 ($\overline{DP} \sim 5$) and 0.15 gram of hexamethylenetetraamine was placed in an aluminum weighing dish and heated, in air, by means of a Wood's metal bath. A homogeneous, light-yellow, soft, nontacky melt was obtained when the temperature reached 130 C. The melt was heated slowly to 180 C, at which temperature evolution of a gaseous product was evident, and the resin began to harden. The polymer was heated for an additional hour at 380 C. The resulting product (Resin 23448-39-1) was yellow, brittle, at room temperature, but somewhat leathery at 200 C. The resin was compression molded at 195 C to provide a transparent, but brittle disk. A substantially stronger disk could probably be obtained by treating the resin as a phenolic molding compound and filling it with a suitable reinforcing agent prior to molding.

9. Condensation of Tetraphenoxylsilane with Low Molecular Weight OH-Terminated Polymer A

A 0.915-gram sample of OH-terminated Polymer A No. 24288-48 ($\overline{Mn} = 1830$, $\overline{DP} = 5$) and 0.10 gram of tetraphenoxysilane were intimately ground together using a mortar and pestle. The mixture was placed in a 97 by 12 mm test tube, then heated under a vacuum at 150-160 C until fusion occurred. The resulting melt was heated at 240-250 C for 30 minutes, then at 220 C/20 mm for 18 hours to provide a foamed polymer (No. 24357-36) that was infusible at 270 C. Four 1/2-inch diameter by 0.5-2 mm thick disks were compression-molded from the foamed resin.

Sample No.	Molding Conditions		
24357-37-	Temp., C	Time, hrs	Force, lbs
1	200	15	3000
2	200	1	3000
3	200	0.5	3000
4	200	15	3000

Each of the molded disks was tough and transparent, but appeared to contain small inhomogeneous areas.

Molded Specimen 24357-37-1 was aged in a circulating air oven at 300 C for 5, 17, and 23 hours, and showed weight losses of 10.8, 21.6, and 22.8 percent, respectively. Specimen 24357-37-2 was broken into quarters and the pieces were immersed in water, 6N HCl, 3N NaOH, and benzene. After 64 hours, the benzene-immersed section had swollen considerably, but the samples exposed to the other three reagents were essentially unchanged in appearance. Specimen 24357-37-4 was exposed to boiling water for 24 hours and became brittle and opaque (white).

10. Condensation of Tetraphenoxysilane with Low Molecular Weight HO-Terminated Polymer A

A mixture of 7.3 grams of HO-terminated low molecular weight Polymer A No. 24288-48 ($\overline{DP} \cong 5$) and 0.80 gram of tetraphenoxysilane was added to a 250-ml Erlenmeyer flask and fused under nitrogen at 150-160 C to form a viscous melt. The melt was stirred with a glass rod until it became rigid, and was then heated for 24 hours at 250 C under a vacuum. The resulting resin was infusible and rubbery at 280 C and remained so down to 230 C, below which temperature it became leathery. At 25 C the product was a tough, straw-colored foam. The resin was compression-molded at 250 C (force of 8000 pounds) to provide a clear, tough, flexible disk which swelled to two or three times its original volume when immersed in benzene. This polymer was severely attacked by 3N NaOH and 6N HCl at room temperature, and by boiling water, within 2 hours.

11. Condensation of Triphenoxyphenylsilane with Low Molecular Weight OH-Terminated Polymer A

A solution (A) of hydroxyl-terminated low molecular weight Polymer A was prepared by dissolving 4.00 grams of Polymer A No. 24288-24 ($\overline{Mn}$ = 4205, $\overline{DP}$ = 11.5) in 100 milliliters of benzene. A second solution (B) was prepared by dissolving 0.244 gram of triphenoxyphenylsilane (bp 192 ± 0.5 C/0.2 ± 0.05 torr) in 100 milliliters of benzene. Five milliliters of these solutions contained 9.51×10^{-5} equivalents of ether phenoxy or phenolic hydroxyl groups, assuming that Polymer A has two OH groups (terminal) per chain.

To each of five aluminum weighing dishes (T1 through T5) was added 5 milliliters of solutions A and B. Five additional weighing dishes (T6 through T10) were prepared, each containing 5 milliliters of Solution A and 10 milliliters of Solution B. The weighing dishes were then heated on a steam bath to evaporate the solvent, and were then aged at temperatures ranging from 200 to 350 C in a forced draft oven. The dishes were periodically removed from the oven, inspected, weighed, and then replaced. The weight losses experienced by the polymer films are shown in Table 16. At 250 C, the films remained colorless after aging up to 128 hours. At 350 C, the films began to yellow after 17 hours.

VI. POLYMERS PREPARED FROM MULTIFUNCTIONAL SILANES AND p,p'-BIPHENOL

A. Discussion

The condensation of tetraphenoxysilane with p,p'-biphenol was investigated. The reaction proceeded readily without the need for basic catalysts as in the condensation of diphenoxydiphenylsilane with p,p'-biphenol. Qualitatively, the reaction proceeded at about the same rate (at 225 to 250 C) as the reaction of dianilinodiphenylsilane and p,p'-biphenol, with phenol evolving smoothly and rapidly from the reaction mixture after an initial heating period (about 15 minutes) to establish an equilibrium. The condensation of a tetrafunctional with a bifunctional reagent leads, of course, to crosslinking relatively early in the reaction. In practice, gelation occurred when only slightly more than one of the four available phenoxy groups on an average was removed, i.e., at about 30 percent reaction. Therefore, the reaction was stopped at about 25 to 28 percent completion and the product was then taken up in a solvent. Films were then cast from solution and oven cured at temperatures ranging from 180 to 300 C. Clear, colorless, insoluble, infusible, moderately flexible, tightly adhering films were obtained on aluminum in this way. These films exhibited good stability on air-aging at 250 C. For example, a film cured 20 minutes at 240 C showed the following weight losses at 250 C: 8.6 percent after 11 hours, 12.5 percent after 54 hours, 15.0 percent after 99 hours, and 15.1 percent after 122 hours. After 122 hours, the residual coating was still clear, colorless, and moderately flexible. After the first 10 hours aging at 250 C, the rate of weight loss slowed considerably and the film did not discolor on prolonged aging. The nature of the material is such that an appreciable amount of the volatilization observed on aging at 250 C could be due to (1) evaporation of low molecular weight species trapped in the crosslinked film, or (2) continued slow reaction of phenoxysilane and hydroxyl groups immobilized in a matrix of crosslinked polymer.

A condensation of equimolar amounts of p,p'-biphenol and trianilinophenylsilane was found to provide a nearly white, brittle, foamed polymer (No. 23563-69-1) that was infusible at 250 C. A programmed thermogravimetric analysis of this polymer (Figure 40) in a vacuum showed weight losses of 4.5 percent at 400 C, 11.5 percent at 500 C, and only 25 percent at 700 C. This compares favorably with Polymer A which shows a limiting weight loss of about 37 percent by 700 to 800 C.

B. Experimental

1. Preparation of Tetraphenoxysilane/ p,p'-Biphenol Resin (24288-23)

A mixture of 10.012 grams (0.025 mole) tetraphenoxysilane and 4.655 grams (0.025 mole) p,p'-biphenol was heated under nitrogen in a 100-ml, single-neck, round-bottom flask. A 1-to-7 mole ratio of reactants was used to insure complete reaction of all available hydroxyl groups. The p,p'-biphenol was not soluble in the tetraphenoxysilane but went into solution as the reaction proceeded. At 225 C (Wood's metal bath), the reaction started slowly. After 2 minutes, only a faint trace of volatile material, probably phenol, had collected on the upper, cold walls of the flask. After 15 minutes, about half the biphenol was in solution and the mixture was boiling slightly. However, in only 5 more minutes (20 minutes total), vigorous boiling and reflux of phenol set in and the biphenol was practically all dissolved. The upper flask walls were then heated to drive phenol out of the reaction vessel into a trap connected to the flask via a short path retort head. Several minutes were required before sufficient additional phenol had formed to require heating the flask walls to drive it off. Thus, the bath temperature was raised to 250 C to speed up the reaction. After several cycles of heating and driving off a portion of the phenol by-product, followed by a short waiting period for more phenol to form, the reaction mixture had become moderately viscous. Then, with 2.7 grams of phenol (57 percent reaction of available hydroxyls, or

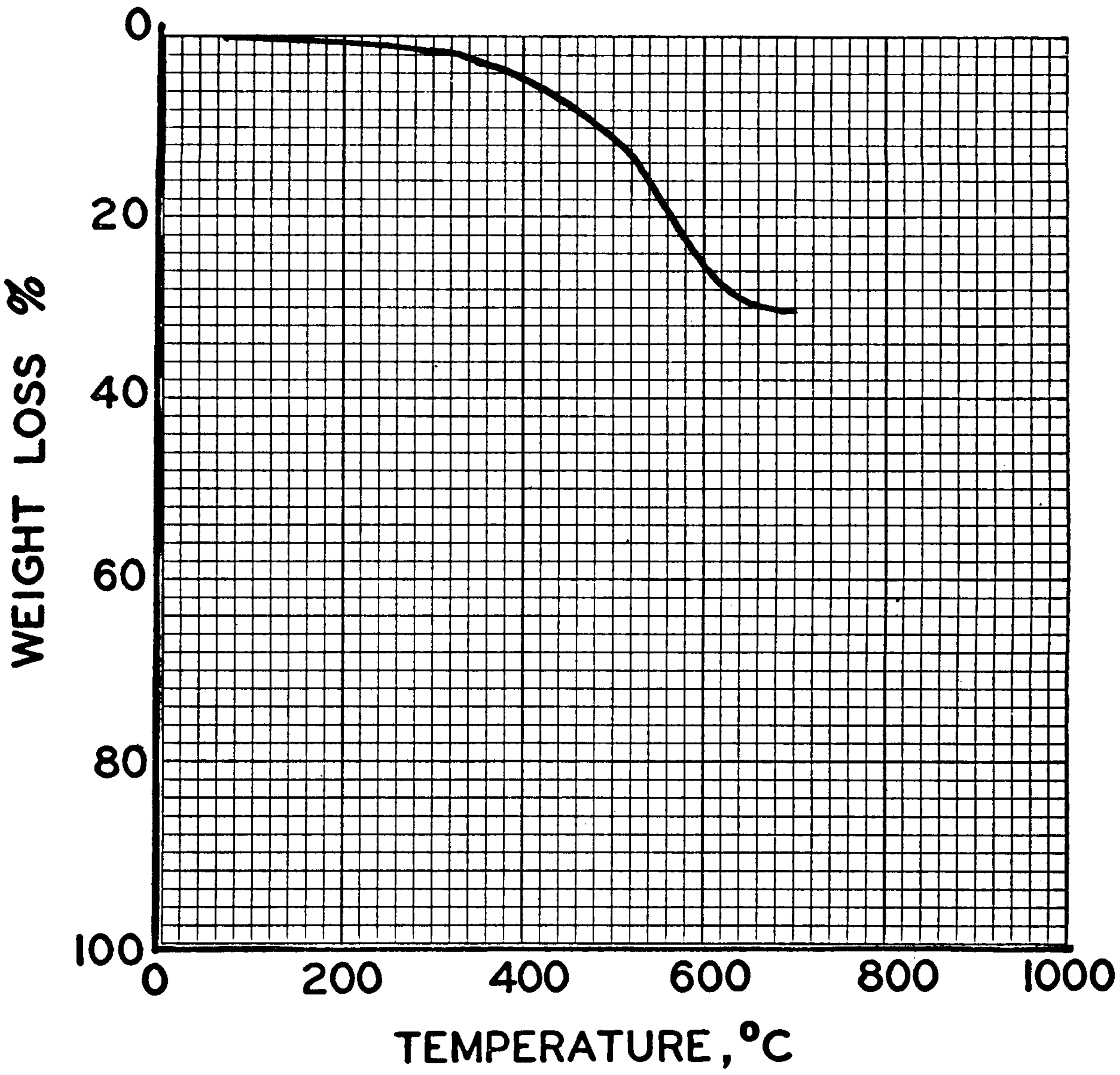


Figure 40. Thermogravimetric Analysis of Polymer No. 23563-69-1 Prepared from p,p'-Biphenol, Dianilinodiphenylsilane, and Trianilinophenylsilane

Heated 4 C/minute at 0.1 mm Hg.

28.5 percent removal of phenoxy groups of tetraphenoxysilane) collected, the reaction mixture gelled (1.5 hours after the start of heating). When a small portion of this phenol (two- or three-tenths of a gram) was returned to the reaction mixture, the gel dissolved, a convincing qualitative observation that an equilibrium process is involved. At room temperature, the product was a cloudy, off-white, viscous liquid which readily dissolved in THF to give a clear, very light-yellow solution.

An example of the preparation and aging of a cured film of this product was as follows. A 0.2450-gram portion of the product was weighed into an aluminum cup. It was dissolved in several milliliters of dry THF and the solution was evaporated to give a fairly uniform coating. After drying several minutes at 100 C to insure removal of most of the THF, the coating was cured in a forced-draft oven at 240 C. After 10 minutes at 240 C, the coating weighed 0.1729 gram (29.4 percent weight loss), while after 20 minutes at 240 C it weighed 0.1688 gram (31.1 percent weight loss). At this point, a clear, colorless, firmly adhering, flexible, nontacky, insoluble coating was obtained. It was also observed to be firm and nontacky at 240 C. Thus, a 31 percent weight loss occurred during the curing of a thin coating of Resin 23488-23 at the arbitrary condition of 20 minutes at 240 C. Theoretically, only a 17.4 percent weight loss should have been observed (additional phenol loss to completion of biphenol hydroxyl reaction). On aging in a forced-draft oven at 250 C, the 0.1688-gram coating showed the following weight loss pattern:

Time at 250 C, hours	Weight Loss, percent(a)
1	3.7
11	8.6
35	11.1
54	12.5
99	15.0
122	15.1

(a) Based on 0.1688-gram starting weight.

After 122 hours at 250 C, the coating was cracked slightly in the thicker areas (not surprising in view of a 15 percent weight loss after a three-dimensional structure was formed). Otherwise, the coating was still clear, colorless, nontacky, and moderately flexible.

2. Preparation of Tetraphenoxysilane/p,p'-Biphenol Resin (24288-22)

A mixture of 4.005 grams (0.0100 mole) tetraphenoxysilane and 1.862 grams (0.0100 mole) p,p'-biphenol was reacted to completion in a 350-ml capacity tube. The reaction was carried out at 250 C under nitrogen. After the mixture gelled, the evolution of phenol slowed considerably but most of the phenol was removed after 2 hours. Then the pressure was reduced to about 0.1 mm Hg and the reaction mixture was heated at 250 C for an additional 2 hours. At this point, the tube was flushed to atmospheric pressure with nitrogen and cooled. By-product phenol collected weighed 1.85 grams (98.5 percent of theory). The product was a hard, tough, horny, light-yellow resin. It was removed from the tube and broken into small fragments with some difficulty, then replaced in the tube. The product was then reheated to 250 C at 0.1 mm Hg for 24 hours to insure complete reaction. Weight loss for this heating was less than 0.1 gram. It should be noted that the weight loss realized here, in an enclosed system and a bulk sample, was essentially that predicted by theory for complete phenol removal. This is in sharp contrast to the results when a thin film of Sample 24288-23 (see above) was heated in a forced-draft oven at the same temperature. Yet the mole ratio of reactants was the same in both preparations.

3. Preparation of Tetraphenoxysilane/p,p'-Biphenol Resin (24288-25)

A preparation similar to 24288-23 was carried out except that the reactant charge was 10.012 grams (0.0250 mole) tetraphenoxysilane and 7.448 grams (0.0400 mole) p,p'-biphenol. This is sufficient biphenol to remove 80 percent of the phenoxy groups of tetraphenoxysilane if the reaction goes to completion. This reaction was prompted by the discovery that p,p'-biphenol is insoluble in resin product, Sample 24288-23. When biphenol is added to Sample 24288-23 and the mixture dissolved in THF, clear, colorless solutions result. However, when films are cast and the THF is evaporated, the biphenol precipitates yielding opaque, white coatings. Attempts to cure such coatings at temperatures ranging from 180 to 300 C resulted in opaque, cracked films which rapidly turned brown on aging at 250 C.

The present reaction proceeded much like Sample 24288-23. Gelation commenced at about the same extent of reaction (about 26 percent removal of available phenol). The product was a white, opaque, viscous resin at room temperature. Preliminary curing tests with this product indicate that coatings prepared from it are similar to Sample 24288-23.

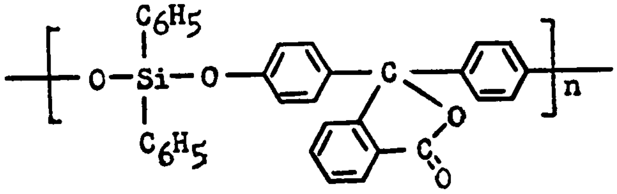
4. Condensation of Trianilinophenylsilane (TAPS) with p,p'Biphenol (Polymer No. 23563-69-1)

A mixture of 5.86 grams (0.0154 mole) TAPS and 4.18 grams (0.0231 mole) p,p'-biphenol was fused under nitrogen in a Pyrex polymerization tube heated to 150 C. After 30 minutes the temperature was raised (Wood's metal bath) to 210 C. The melt which had formed at 150 C began to evolve aniline at 200-205 C and after 5 minutes at 210 C the now-viscous melt suddenly foamed to two to three times its volume and immediately solidified. When heated to 250 C, this rigid foam did not remelt. The pressure was reduced to 0.5 mm with a vacuum pump and the foam was heated 30 minutes at 250 C. No further evidence of aniline evolution was noted, and the tube was flushed with nitrogen and cooled. The nearly-white resin product was brittle and was easily ground in a mortar to a fine powder.

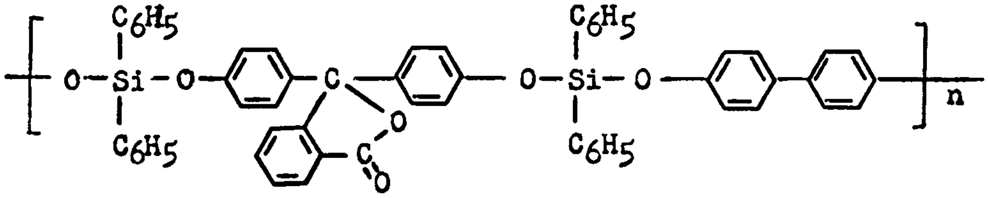
VII. POLYARYLOXYSILANES HAVING PENDENT LACTONE RINGS

A. Discussion

Two types of phenolphthalein-containing polyaryloxysilanes were successfully prepared on a laboratory scale. On such modified Polymer A structure



was obtained by condensing Monomer I with phenolphthalein, and the other



by condensing Monomer I with a mixture of phenolphthalein and p,p'-biphenol.

Both of the phenolphthalein-containing polymers were prepared with the same apparent ease as Polymer A. Although polymers having molecular weights sufficiently high to provide high mechanical strength properties were not achieved in these initial preparations, the phenolphthalein-containing polyaryloxysilanes appear to have the potential of closely matching the properties of Polymer A. Of particular interest, the TGA-indicated thermal stability (Figure 41) and softening temperature (160 C) compare favorably with those of Polymer A specimens. Thus, phenolphthalein appears to be a potential low-cost replacement for p,p'-biphenol in the Polymer A structure.

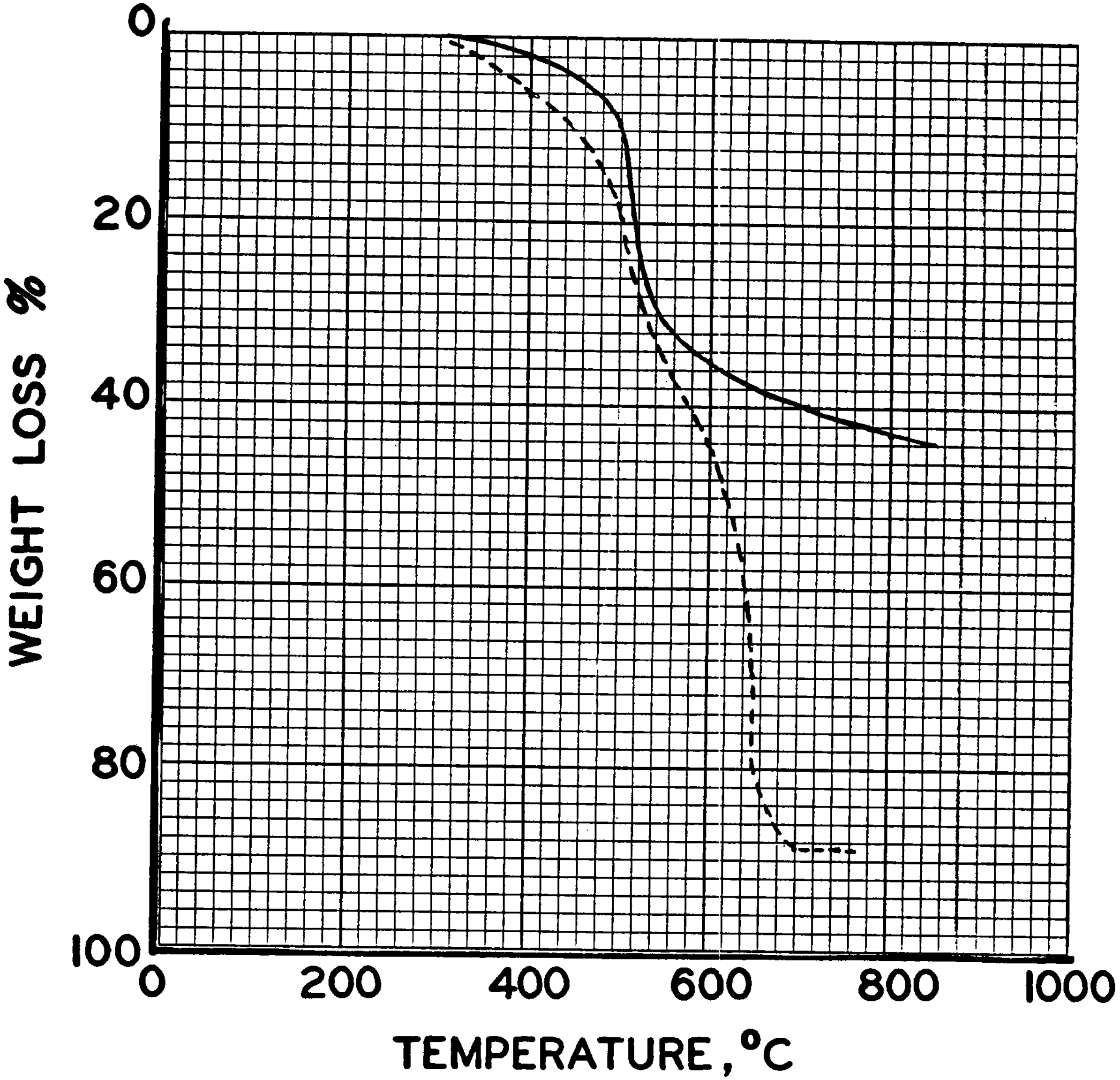


Figure 41. Thermogravimetric Analyses Under Air (----) and Nitrogen (——) for Polymer (No. 23448-3-B) Obtained by Condensing Dianilinodiphenylsilane with Phenolphthalein

The infrared spectrum of phenolphthalein-containing polyaryloxysilane No. 23448-3-B (Figure 42) included bands at 720 and 690 cm^{-1} arising from the aromatic rings attached to silicon, a sharp band at 1429 cm^{-1} and a broad band at 1125 cm^{-1} attributed to the $Si\text{-}C_6H_5$ linkages, absorptions between 824 and 835 cm^{-1} contributed by the 1,4-phenylene units in the chain, bands between 1200 and 1300 cm^{-1} from the Si-O linkages, and a strong absorption at about 1770 cm^{-1} contributed by the lactone ring of the phenolphthalein chain component. The spectrum shows no indication that the lactone ring was opened during the polymerization reaction.

As would be expected from its structure, the infrared spectrum (Figure 43) of polyaryloxysilane No. 23448-4-A was very similar to that (Figure 42) of Polymer 23448-3-B that contained phenolphthalein, but no copolymerized p,p'-biphenol.

Thermogravimetric analyses of Polymer 23448-3-B in air and nitrogen (Figure 41) indicated the material to have good resistance to heat. The polymer experienced negligible weight loss up to 400 C and losses of only 18.5 percent (in air) and 9.5 percent (in nitrogen) up to 500 C. The final weight loss of 88.2 percent for the sample heated under air corresponds closely with the calculated value of 87.7 percent for the polymer being reduced to SiO_2.

Thermogravimetric analyses (Figure 44) of Polymer No. 23448-4-A similarly indicated good resistance to heat in either air or nitrogen. The thermograms showed negligible weight losses up to about 400 C, and 11.4 and 16.8 percent weight losses at 500 C under nitrogen and air, respectively. The total weight loss of 87 percent for the specimen heated to 900 C in air corresponds closely with a total conversion of the polymer to a SiO_2 residue.

Attempts were made to crosslink the phenolphthalein-containing polymers by fusing them at 200 C (2 hours) with a variety of reagents including hexamethylenetetraamine, benzidine, triethylene tetraamine, ammonium chloride, pentaerythritol, terephthalic acid, oxamide, pyromellitic dianhydride, pyromellitic acid, hydrazine dihydrochloride, ethylenediamine dihydrochloride, 1,4-benzenedimethanol, and anhydrous

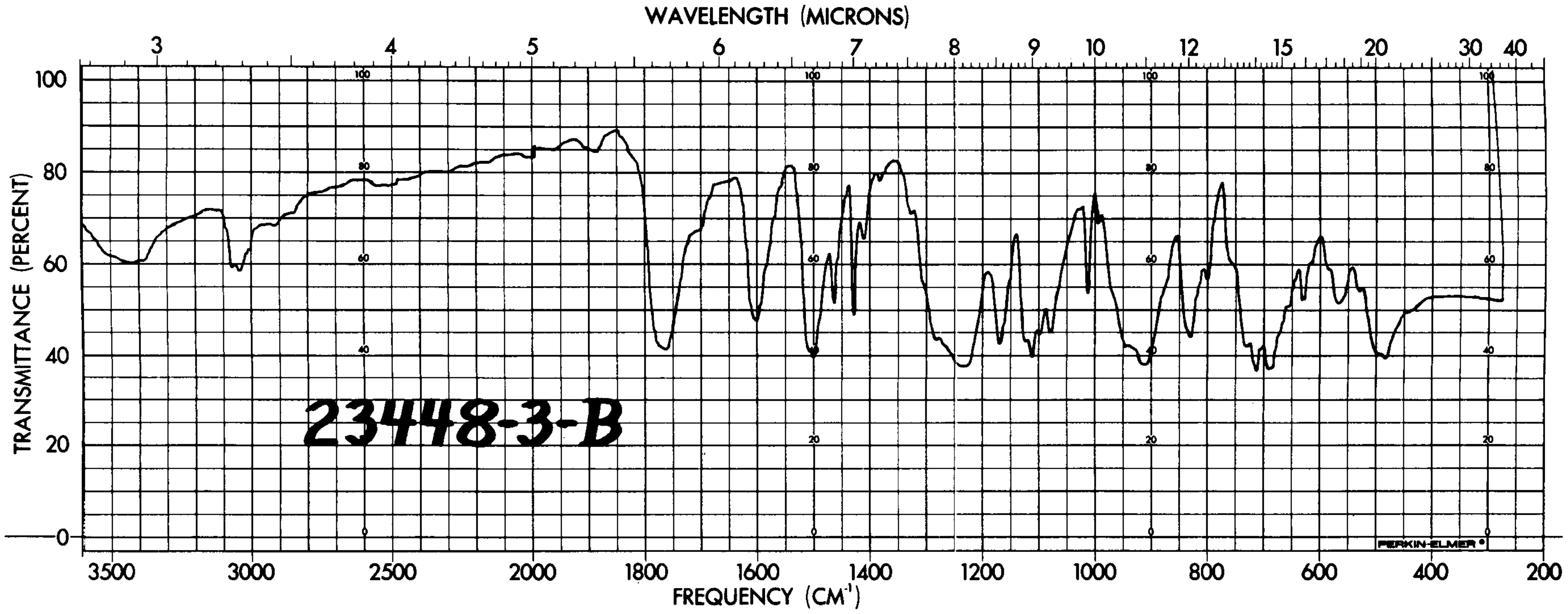


Figure 42. Infrared Spectrum of Polyaryloxysilane from Dianilinodiphenylsilane and Phenolphthalein

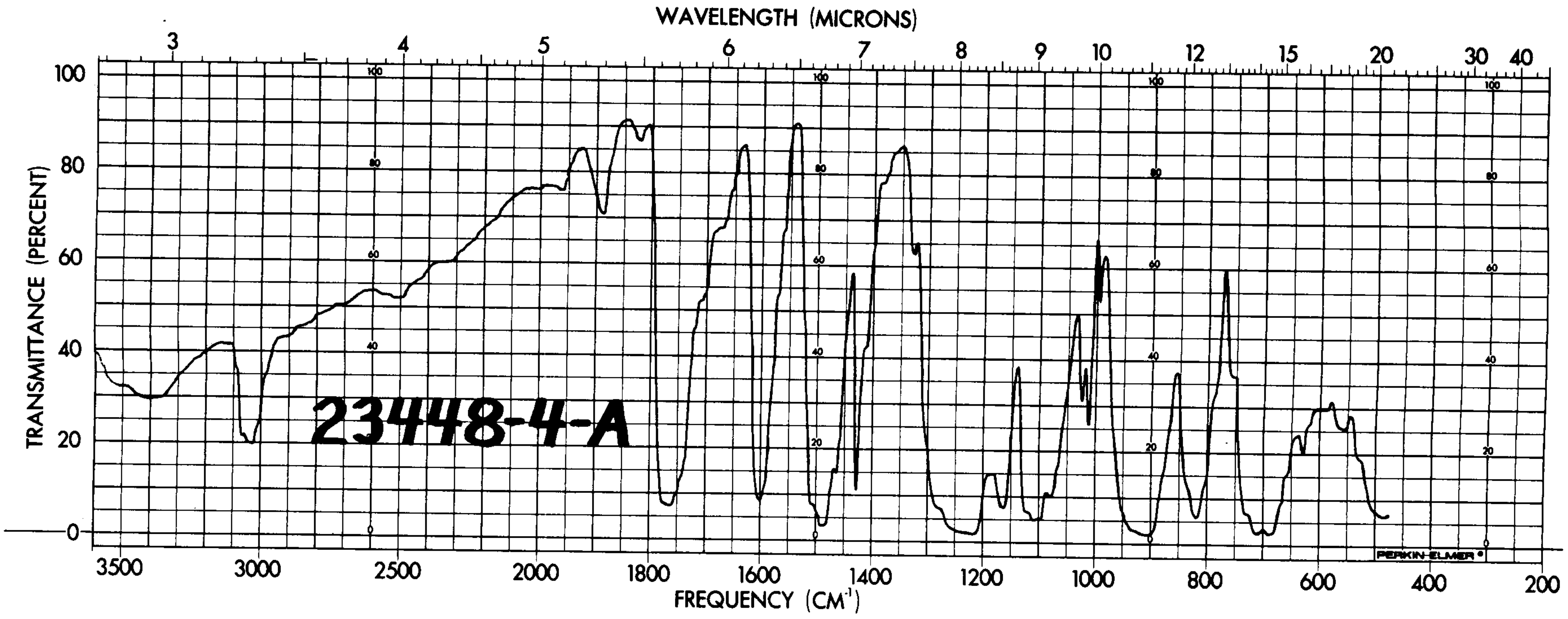


Figure 43. Infrared Spectrum of Polyaryloxysilane from Dianilinodiphenylsilane, Phenolphthalein, and p,p'-Biphenol

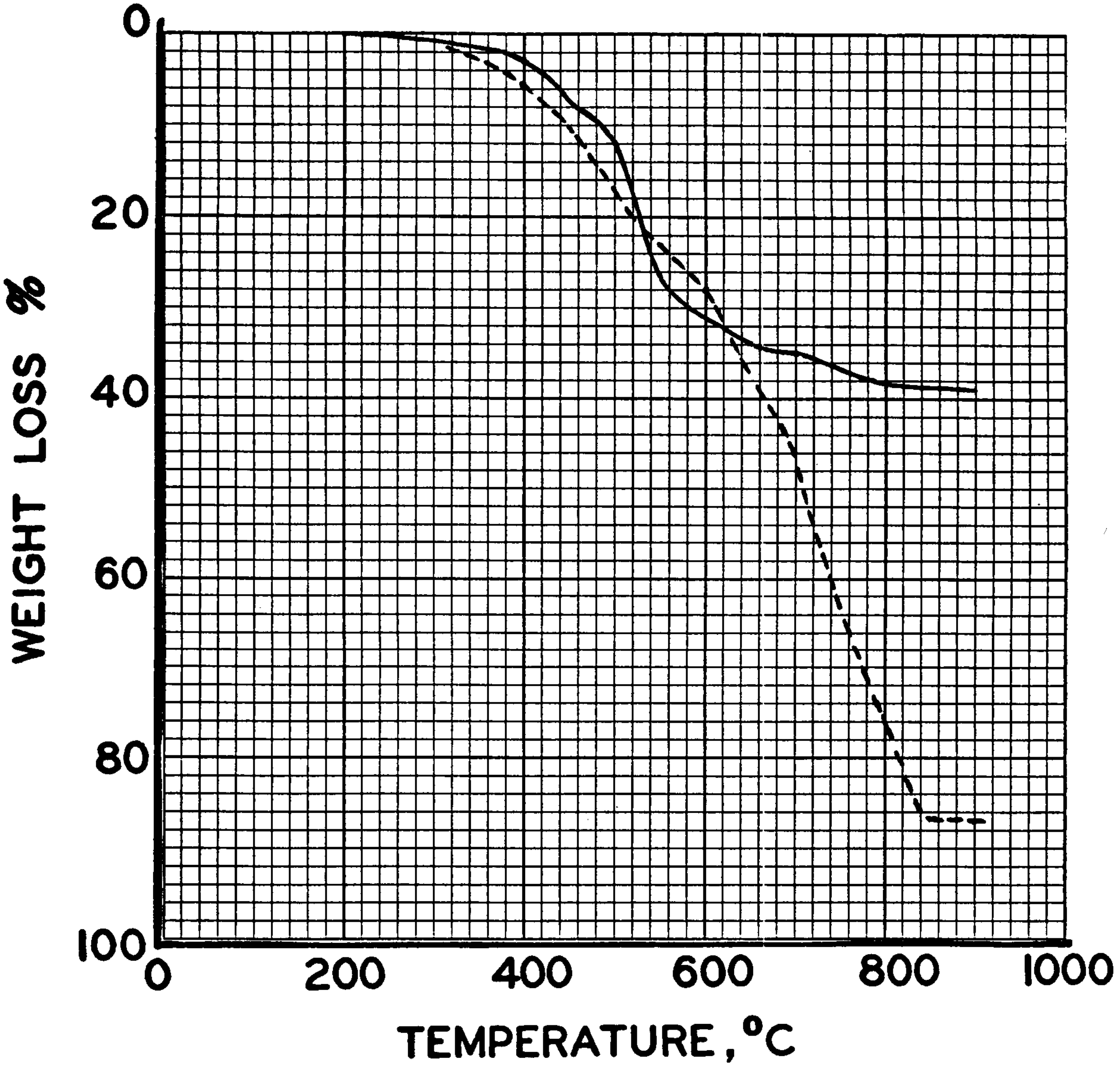


Figure 44. Thermogravimetric Analyses Under Air (----) and Nitrogen (——) of Polymer (No. 23448-4-A) Obtained by Condensing Dianilinodiphenylsilane with Phenolphthalein and p,p'-Biphenol

phloroglucinol. In none of these cases was there evidence of gelation indicating that crosslinking had occurred.

B. Experimental

1. Polycondensation of Dianilinodiphenylsilane and Phenolphthalein

a. A mixture of 7.32 grams (0.02 mole) of dianilinodiphenylsilane (m.p. 164-166 C) and 6.36 grams (0.02 mole) of phenolphthalein (Baker's reagent grade) was placed in a 250-ml round-bottomed flask. A slow stream of nitrogen was passed over the reactants as the flask was heated by a Wood's metal bath that had been preheated to 225 C. Within 10 minutes a homogeneous melt was obtained and polymerization occurred as evidenced by refluxing of the condensation side product, aniline. A vacuum was applied to the flask and the polymerization mixture was heated at 225 C under a vacuum for 30 minutes to produce a high-viscosity melt from which low-strength fibers could be drawn. The cooled polymer (Sample 23448-1-A) was transparent, light green, brittle glass.

Analysis for $C_{32}H_{22}SiO_4$		
	Calculated:	C, 77.08; H, 4.44; Si, 5.62
	Found:	C, 76.51; H, 4.77; Si, 5.83

b. A similar polymerization was carried out in which 14.64 grams (0.04 mole) of dianilinodiphenylsilane and 12.72 grams (0.04 mole) of phenolphthalein were fused under nitrogen and then heated for 1 hour at 250 C under a vacuum. An additional 1.0 gram of dianilinodiphenylsilane was then added under a protective nitrogen atmosphere to this viscous melt and polymerization under vacuum at 250 C was continued for one additional hour. Low-strength fibers could be drawn from the resulting high-viscosity melt. The cooled polymer (Sample 23448-3-B) was very light yellow, but transparent and somewhat brittle. Samples of the product were compression molded between aluminum foil at 160 C in a laboratory press to produce highly transparent, but brittle film. The softening temperature of the polymer, as determined on a

Fisher-Johns melting point block heated at the rate of 4 C/minute was 150-155 C. This softening temperature corresponds closely with those of Polymer A samples investigated earlier in this program(1).

Analysis for $C_{32}H_{22}SiO_4$ Calculated: C, 77.08; H, 4.44; Si, 5.62
Found: C, 76.60; H, 4.58; Si, 5.98

2. Polycondensation of Dianilinodiphenylsilane, Phenolphthalein, and p,p'-Biphenol

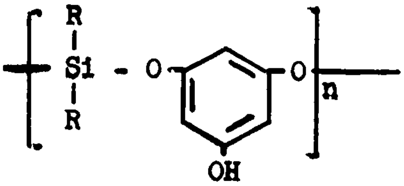
A mixture of 7.32 grams (0.02 mole) of dianilinodiphenylsilane, 3.18 grams (0.01 mole) of phenolphthalein, and 1.86 grams (0.01 mole) of p,p'-biphenol was heated under nitrogen at 230 C until fusion had occurred and polymerization had started as evidenced by refluxing of the condensation side product, aniline. The melt was then heated for 90 minutes under a vacuum (about 1 mm pressure), and then cooled to room temperature. The product polymer (Sample 23448-4-A) was transparent, amber in color, and brittle. Fibers could be drawn from its melt, and it could be converted to film by pressing it between sheets of aluminum foil in a laboratory press at 160 C. The softening temperature of the polymer, as determined on a Fisher-Johns melting point block heated at a rate of 4 C/minute, was 160 C.

Analysis for $C_{55}H_{40}Si_2O_6$ Calculated: C, 77.43; H, 4.72; Si, 6.57
Found: C, 77.27; H, 4.95; Si, 6.72

VIII. CONDENSATION OF DIANILINOSILANE MONOMERS WITH PHLOROGLUCINOL AND RESORCINOL

A. Discussion

Condensation of dianilinosilanes with phloroglucinol could conceivably lead to three-dimensional polyaryloxysilanes if each of the three phloroglucinol OH groups participate in the condensation, or to linear polyaryloxysilanes having pendent OH groups



if two of the OH groups participate in the condensation reactions more readily than the third. The latter type polymer would be structurally similar to a novolak and would be expected to cure readily if heated with hexamethylenetetraamine.

Condensations of dianilinodimethylsilane and dianilinodiphenylsilane with anhydrous phloroglucinol, and dianilinodiphenylsilane with a mixture of phloroglucinol and p,p'-biphenol were carried out. These polymer syntheses were accomplished as unagitated melt condensations in polymerization tubes and were characterized by the rapid formation of apparently lighly crosslinked products or mixtures of crosslinked and noncrosslinked polymers. While the products of these polymerizations were not thoroughly characterized, a specimen of crosslinked material was observed to fail to melt when heated to 300 C.

Several small-scale condensations of dianilinodimethylsilane and dianilinomethylvinylsilane with resorcinol were also carried out. These reaction products were obtained as viscous liquid polymers. In one case, a molecular weight (Mw) of only about 9,000 was obtained. Cursory examination of these low molecular weight polymers suggests that their growth may be limited by the formation of cyclic polyaryloxysilane structures. Both phloroglucinol and resorcinol appear to behave somewhat abnormally in polyaryloxysilane syntheses, so that their potentials as useful monomers in future polyaryloxysilane development seem questionable.

B. Experimental

1. Condensation of Dianilinodiphenylsilane with Phloroglucinol and p,p'-Biphenol

A mixture of 7.33 grams (0.02 mole) of dianilinodiphenylsilane, 0.63 gram (0.005 mole) of anhydrous phloroglucinol, and 2.79 grams (0.015 mole) of p,p'-biphenol was fused at 200 C under a nitrogen sweep in a 40-ml polymerization tube. Aniline was evolved and the reactive mixture foamed and hardened within several minutes. The resin was then heated at 200 C under a vacuum for 40 minutes. A heterogeneous resinous product was obtained consisting of two types of polymer: (1) a foamed, at least partially crosslinked, material that could be pressed into a semibrittle sheet at 250 C by a laboratory press and which softened, but failed to melt, when heated above 300 C in air in an aluminum weighing dish; and (2) a material (Sample No. 23448-24-1) that melted readily at about 160 C. The latter material was quickly converted to a black, nonfusible resin when it was heated at 160 C with a small amount of hexamethylenetetraamine.

2. Condensation of Dianilinodimethylsilane with Phloroglucinol and p,p'-Biphenol

A mixture of 4.2 grams (0.017 mole) of dimethyldianilinosilane, 0.97 gram (0.008 mole) of anhydrous phloroglucinol, and 1.48 grams (0.008 mole) of vacuum-dried p,p'-biphenol was fused under a nitrogen sweep in a 40-ml capacity polymerization tube heated to 215 C by means of a Wood's metal bath. Aniline was rapidly evolved from the reaction mixture and was allowed to reflux for 10 minutes. A vacuum was then applied and the melt was heated for an additional 30 minutes. The product was a yellow-orange resin consisting of two parts: (1) an upper, apparently crosslinked, layer that was rubbery at 215 C; and (2) a lower uncrosslinked layer that was entirely fluid at 215 C.

3. Condensation of Dianilinodiphenylsilane with Phloroglucinol

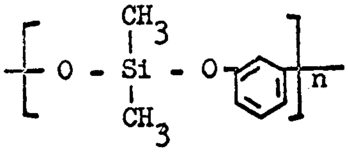
An intimate mixture of 1.26 grams (0.01 mole) of anhydrous phloroglucinol and 5.49 grams (0.015 mole) of dianilinodiphenylsilane was heated under a nitrogen atmosphere at 200-225 C for 10 minutes. During this time, fusion of the reactions occurred and a vigorous evolution of aniline was observed. The reaction mixture was then heated at 225 C under a vacuum for 1.5 hours. The resinous product was soft and gummy at 225 C, suggesting a low degree of crosslinking, and cooled to provide a glossy, brittle, amber-colored solid.

4. Polycondensation of Dianilinodimethylsilane with Resorcinol (Polymer No. 23753-22)

A mixture of 40.73 grams (0.1680 mole) of dianilinodimethylsilane and 18.50 grams (0.1680 mole) of resorcinol (reagent grade, sublimed *in vacuo*) was fused under nitrogen in a single-neck, 250-ml, round-bottomed flask heated to 195 C in a Wood's metal bath. Vigorous reaction started almost immediately. Aniline was allowed to reflux at atmospheric pressure for 15 minutes, then the temperature was gradually raised to 250 C and aniline distilled off rapidly. The pressure was reduced over a 1-hour period to 0.40 mm. After 1 hour and 20 minutes at this pressure, no further distillation was observed, yet the product was a fairly thin melt. The vessel was flushed to atmospheric pressure with nitrogen. By-product aniline was recovered from the cold trap in 31.5-gram (100.8 percent) yield. The product was a clear, light-tan colored, extremely viscous liquid.

Analysis for $C_8H_{10}O_2Si$		
	Calculated:	C, 57.80; H, 6.06; N, 0
	Found:	C, 57.55; H, 5.99; N, 0.06

GPC indicated an Mw of approximately 9,000. There was also a peak on the GPC chromatogram corresponding to an appreciably lower molecular weight material (less than 1000). Subsequent treatment of the viscous liquid product at high temperature (300 C) *in vacuo* (0.8 mm) yielded a small amount (approximately 1 percent) of a white sublimate. This sublimate, which melted at 110-120 C, was investigated with infrared and high resolution mass spectrometry. It is tentatively concluded that the sublimate consisted of resorcinol and a mixture of cyclic structures with the repeat unit



where n = 2 through at least 8, with the trimer (n = 3, Mw = 498) predominating . This latter compound would be hexamethylcyclotri[-1,3-benzo]siloxane.

5. Polycondensation of Dianilinomethylvinylsilane with Resorcinol (Polymer No. 23753-32)

A mixture of 7.441 grams (0.02920 mole) of dianilinomethylvinylsilane and 3.215 grams (.02920 mole) of resorcinol (reagent grade, sublimed *in vacuo*) was fused under nitrogen in a Pyrex tube (capacity approximately 40 cc). A Wood's metal bath heated to 210 C was used as the heat source. Reaction started immediately at 210 C and was continued at that temperature and atmospheric pressure for 30 minutes. The temperature was then raised to 225 C and aniline began to distill. The pressure was reduced over a 30-minute period to 0.4 mm and heating continued at that temperature for 15 minutes. No evidence of reaction was detected at this time (no aniline distilling, no bubbling of the thin melt) so the tube was flushed with nitrogen and cooled. By-product aniline amounting to 5.5 grams (101 percent) yield was recovered. The product was a light-yellow, viscous liquid. Addition of approximately 5 percent t-butyl perbenzoate to a small portion of this liquid, followed by heating to about 150 C for approximately 15 minutes, resulted in the formation of a weak, elastomeric gum.

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Cincinnati, Ohio 45215

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Nonmetallic Materials Division
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