SYNTHESIS AND EVALUATION OF NEW HIGH TEMPERATURE POLYMERS FOR COATING APPLICATIONS

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MRI Project No. 2792-C

For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

Attn: Mr. Thomas L. Perry, PR-EC

MRI

MIDWEST RESEARCH INSTITUTE
425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 1-0202

SYNTHESIS AND EVALUATION OF NEW HIGH TEMPERATURE POLYMERS FOR COATING APPLICATIONS

by

L. W. Breed
W. H. Burton
R. L. Elliott
L. M. McDonough

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PREFACE

This report was prepared by Midwest Research Institute under Contract NAS8-11338, "Synthesis and Evaluation of New High Temperature Polymers for Coating Applications," 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 Laboratory, Materials Division of the George C. Marshall Space Flight Center, with Mr. James D. Byrd acting as project manager.

This report covers work conducted from 26 June 1964 to 25 June 1965.

The work at Midwest Research Institute, designated Project 2792-C, was performed by Mr. L. W. Breed, Dr. L. M. McDonough, Mr. W. H. Burton, Mr. R. L. Elliott, and Mr. J. J. Fontanini under the administrative supervision of Dr. J. W. Barger, Assistant Director, Chemistry Division. Mr. Breed acted as project leader.

Approved for:

MIDWEST RESEARCH INSTITUTE

FVMorriss

F. V. Morriss, Director
Chemistry Division

25 June 1965

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ABSTRACT

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Experimental work is reported on the synthesis of organic and semi-organic polymers useful as coatings that will withstand high temperatures, high vacuum, and radiation. Attempts to prepare titanium chelate polymers, titanoxanosiloxanes, and borosiloxanes produced only low molecular weight products. An investigation of model systems for ferrocene polyesters and boron chelate polymers did not reveal any potentially useful methods of polymerization. High molecular weight poly(benzoxazoles) were prepared, but no satisfactory method was found for preparing poly(benzoxazole) films. A poly(phenylenesiloxane) with good film forming properties was prepared and screened under high vacuum-ultraviolet irradiation conditions. The more promising polymers were characterized by solution viscosity, elemental analysis, differential thermal analysis, thermogravimetric analysis, and solubilities.

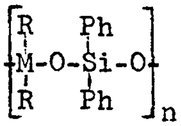
Author

I. INTRODUCTION

The objective of this program is to develop, synthesize, and evaluate new organic and semiorganic polymers with useful film-forming properties and with stability against high temperature, high vacuum, radiation, and the environment of space.

In recent years, new polymeric systems have been developed that have one or more properties that recommend their use as high temperature film-forming materials. Systems that were selected for examination in this program include the following, which have been reported to have the required heat stability:

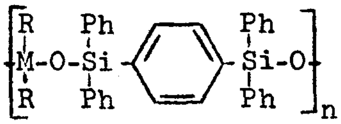
A.



$$\left[\overset{R}{\underset{R}{M}}-O-\overset{Ph}{\underset{Ph}{Si}}-O\right]_n$$

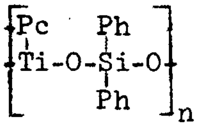
M = Ti or Zn
R = 8-Oxyquinoline

B.



M = Ti or Zr
R = 8-Oxyquinoline

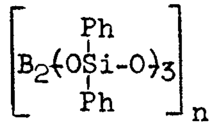
C.



$$\left[\overset{Pc}{Ti}-O-\overset{Ph}{\underset{Ph}{Si}}-O\right]_n$$

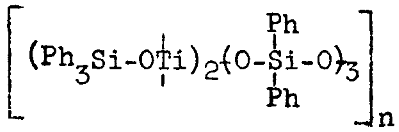
Pc = Phthalocyanine

D.



$$\left[B_2\left(O\overset{Ph}{\underset{Ph}{Si}}-O\right)_3\right]_n$$

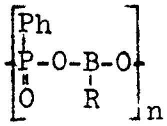
E.



$$\left[(Ph_3Si-O\overset{|}{\underset{|}{Ti}})_2\left(O-\overset{Ph}{\underset{Ph}{Si}}-O\right)_3\right]_n$$

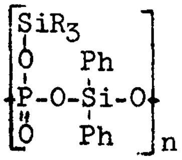
Also selected were structures related to the following new systems:

A.



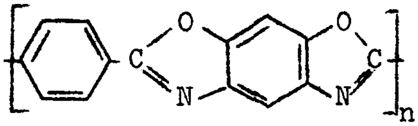
$$\left[\overset{Ph}{\underset{\overset{\|}{O}}{P}}-O-\underset{R}{B}-O\right]_n$$

B.

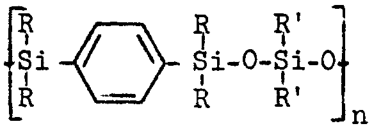


$$\left[-\underset{\overset{\|}{O}}{\overset{\overset{\displaystyle SiR_3}{|}}{\overset{O}{\underset{}{|}}}}\!\!\!\!\!\!P-O-\underset{Ph}{\overset{Ph}{Si}}-O-\right]_n$$

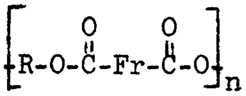
C.



D.



E.



$$\left[-R-O-\overset{\overset{\displaystyle O}{\|}}{C}-Fr-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right]_n$$

Fr = ferrocene

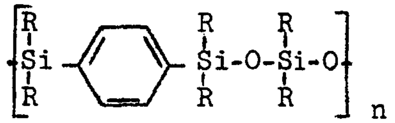
Except for the (-P-O-Si-O-) system, which the literature indicated would have a very low degree of hydrolytic stability, experimental work was carried out on the synthesis of each proposed polymer structure. The emphasis placed on the synthesis of polymers containing each structural type depended, in part, on information obtained on the systems in a survey of the literature. The following factors were considered in screening the new polymers: Thermal stability, hydrolytic stability, and film-forming ability. Some systems were abandoned because of their failure to meet these requirements. Relative molecular weights, in terms of the solution viscosities of polymers, and polymer solubilities were studied in relation to the film-forming abilities of the polymers.

As nearly as possible, systems which could be defined chemically were studied. In general, considerable attention was given to monomer purity, and monomers and polymers were characterized by ultimate analysis for elements, physical characteristics, infrared spectroscopy, and nuclear magnetic resonance spectroscopy, when applicable. In some of the work, it proved convenient to examine the properties of the polymer systems with model compounds.

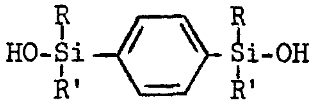
The more promising polymer systems were examined in detail including chemical and physical characterization as well as the determination of heat stability by differential thermal analyses and thermogravimetric analyses. The vacuum-ultraviolet stability of one experimental polymer was also examined.

II. DISCUSSION OF RESULTS

A. Siloxanes Containing p-Phenylene Linkages

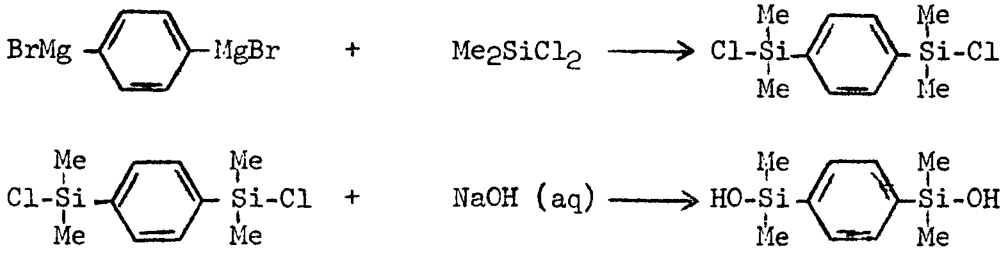


1. Monomer synthesis: The syntheses of three p-phenylenedisilane monomers were investigated: p-phenylenebis(dimethylsilanol) (I), p-phenylenebis(methylphenylsilanol) (II), and p-phenylenebis(diphenylsilanol) (III).

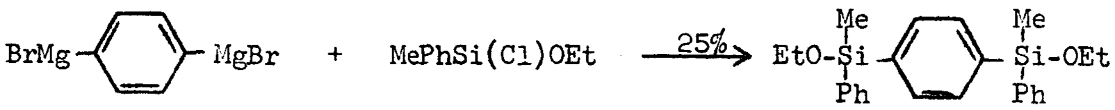


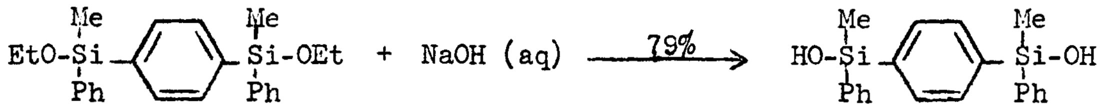
I. R = R' = Me
II. R = Me; R' = Ph
III. R = R' = Ph

p-Phenylenebis(dimethylsilanol) was readily prepared by an established procedure[1] from the intermediate, p-phenylenebis(chlorodimethylsilanol). The compound used in polymerization experiments was of equivalent purity to the compounds cited in the literature.

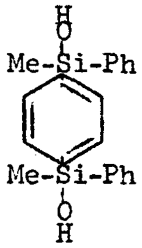


An attempt to prepare the intermediate p-phenylenebis(chloromethylphenylsilane) by a procedure similar to the preparation of p-phenylenebis-(chlorodimethylsilane) failed in each of several attempts even though the compound has been reported to be accessible by this route.[2] An alternate intermediate, p-phenylenebis(ethoxymethylphenylsilane), was successfully prepared and hydrolyzed to the required silanol.

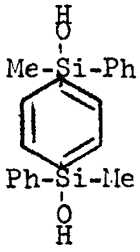




The silanol proved to be a mixture of stereoisomers. Although the compound melted over a wide range, 128-40°,* analyses for elements and the infrared spectrum were consistent with the proposed structure. With careful fractional crystallization one pure isomer melting at 156-8° was separated. An attempt was made to assign the structure of the pure isomer by NMR by shifts in the methylsilyl proton resonance, but the spectra of the two samples did not differ. The silanol melting at 128-40° was probably a mixture of isomers IIa and IIb while the silanol melting at 156-8° was one or the other of the two isomers.



II a



II b

The preparation of p-phenylenebis(diphenylsilanol) (III) offered more difficulty. The compound could not be prepared via the direct hydrolysis of the condensation product of p-dilithiobenzene and dichlorodiphenylsilane by the method described in the literature.3/ A very low yield (less than 1 per cent) of the compound was obtained by the direct hydrolysis of the condensation product of the Grignard reagent of p-dibromobenzene and dichlorodiphenylsilane.

An intermediate compound, p-phenylenebis(diphenylethoxysilane), was obtained by the method described by Noltes,4/ but the yield was only 7 per cent. The low yield of the pure product can be accounted for, at least in part, by the difficulties encountered in its purification. Whereas p-phenylenebis-(ethoxymethylphenylsilane) could be purified by distillation, this compound was not volatile below its decomposition temperature and required repeated recrystallization. Considerable losses of product were involved in the recrystallizations, and the true yield was probably considerably greater than the quantity of product isolated. This intermediate, however, could be hydrolyzed to p-phenylenebis(diphenylsilanol), m.p. 224-6°, in an 86 per cent yield.

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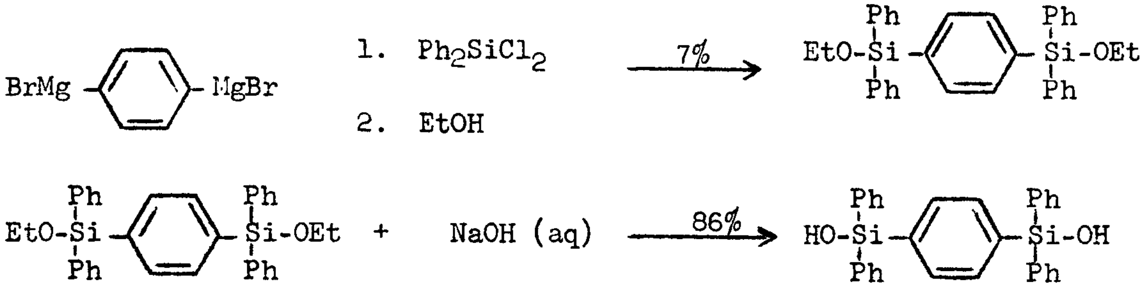
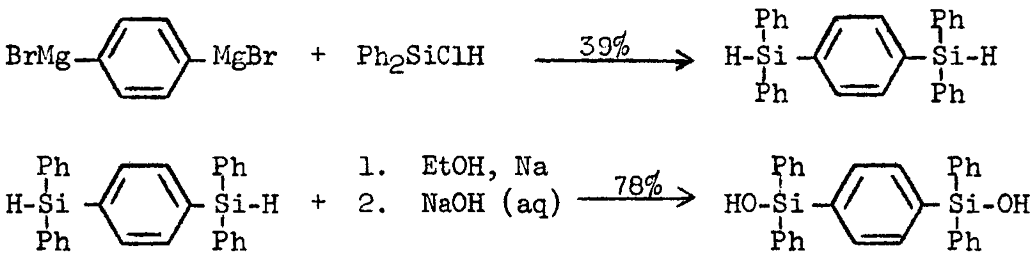
* All temperatures are given in degrees centigrade.



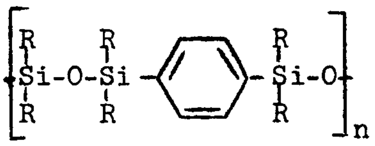
Two alternate methods were investigated for the synthesis of p-phenylenebis(diphenylsilanol); the condensation of the difunctional Grignard derivative of p-dibromobenzene with chlorodiphenylethoxysilane[5] and with chlorodiphenylsilane.[6] The latter reagent readily gave 39 per cent of p-phenylenebis(diphenylsilane) of high purity; chlorodiphenylethoxysilane gave 8 per cent of p-phenylenebis(diphenylethoxysilane), which was difficult to purify.

The p-phenylenebis(diphenylsilane) was hydrolyzed by known methods[6] to p-phenylenebis(diphenylsilanol) in a 78 per cent yield. Thus, a satisfactory synthesis route for this monomer was established.



Repetition of this experiment indicated that the melting point of p-phenylenebis(diphenylsilanol) could be significantly depressed by impurities that were difficult to remove, if the intermediate p-phenylenebis(diphenylsilane) were insufficiently purified.

2. Polymer synthesis: The three monomers, p-phenylenebis(dimethylsilanol), p-phenylenebis(methylphenylsilanol), and p-phenylenebis(diphenylsilanol) were used as representative structures that could be condensed with silazanes or silylamines to obtain polymers with the following structure:



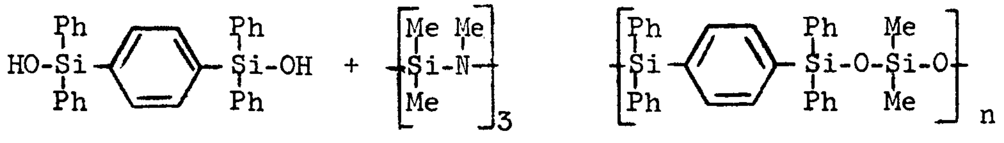
The reaction of silylamines or silazanes with silanol is the preferred route to the required structure since this reaction is known to occur rapidly and quantitatively and is not accompanied by the randomization of siloxane linkages.

Because of the availability of monomers, initial polymer synthesis were limited to the reactions of silazanes and silylamines with p-phenylenebis-(dimethylsilanol) and p-phenylenebis(diphenylsilanol). Although the purity of the p-phenylenebis(dimethylsilanol) used in the experiments was comparable to the purest material described in the literature, the infrared spectrum of the compound (Fig. 1)* contained weak siloxane absorption peaks in the 1,060 - 1,100 cm^{-1} region. Therefore, the stoichiometry of the reactions of the disilanol with the silazanes and silylamines could not be established with certainty.

The reactions of the two silanols with silazanes and silylamines were first screened in a series of experiments in which the evolution of amine was monitored as a measure of the rate of the reaction. Although the use of hydrolytically stable silazanes in the polymerization reaction would minimize difficulties in handling the monomers, the most hydrolytically stable silazanes, hexaphenyl-1,3,5-trimethylcyclotrisilazane and cis-2,4,6-triphenylhexamethylcyclotrisilazane did not react with the silanols to any appreciable extent during the 24-hr. polymerization period. The result was not entirely unexpected because relative rate of hydrolysis, alcoholysis, and silanolysis can be expected to have the same order in each of the three series.

In subsequent experiments, nonamethylcyclotrisilazane was a satisfactory reactant for introducing the $=SiMe_2$ group into the polymer chain and diphenylbis(methylamino)silane was satisfactory for introducing the $=SiPh_2$ group. Near quantitative yields of methylamine were obtained and specific viscosities indicated a reasonable degree of polymerization when these monomers were treated with p-phenylenebis(diphenylsilanol) in refluxing toluene.

Two of the polymers obtained in the preliminary experiments were examined in greater detail. The polymer from p-phenylenebis(diphenylsilanol) and nonamethylcyclotrisilazane, which was opaque and somewhat brittle, had a specific viscosity of about 0.5 in toluene.



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* All figures are found in Appendices I, II, and III, pp. 80 to 106.

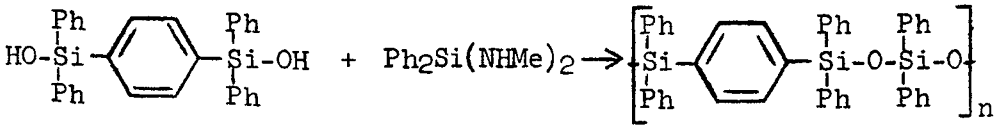
The infrared spectrum of the polymer, which is reported in Fig. 8, suggested that residual silanol, silazane, or silylamine groups were present. However, the results of the analysis for elements in this polymer agreed with the calculated values.

The procedural decomposition temperature (weight loss equals or exceeds 5%/hr) of the polymer on thermogravimetric analysis (Fig. 37) was 515°. The temperature at which decomposition occurs would seem to preclude decomposition through reorganization of siloxane linkages and the volatilization of siloxane high compounds. The TGA trace did exhibit some tailing-off beginning at about 200°, but since the polymer was not devolatilized above 150°, the small weight loss at the lower temperature could have reflected a loss of solvent or additional polymerization with the consequent loss of amine.

Although the polymer did not melt, it appeared to sinter at about 220-50°; however, differential thermal analysis of the polymer (Fig. 40) did not reveal any major phase changes up to 500°.

When a sample of this polymer was heated at 300° for 1 hr., the specific viscosity increased to 0.9, but the results of elemental analyses suggest that some decomposition had occurred by way of diphenylation.

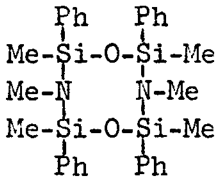
Similar results were obtained from the p-phenylenebis(diphenylsilanol)-diphenylbis(methylamino)silane polymer except that the specific viscosity was about 0.2 and the infrared spectrum of this polymer, which is reported in Fig. 9, did not show residual silanol or silylamine.



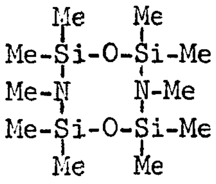
The TGA trace of this polymer is reported in Fig. 37 and the DTA trace in Fig. 40. Both suggest good heat stability. However, the polymer was brittle and not suitable for coating applications.

Because the preliminary polymers were apparently crystalline and were somewhat brittle, the silanols were subsequently condensed with siloxazanes, which could introduce additional siloxane linkages into the chain and consequently more flexibility.

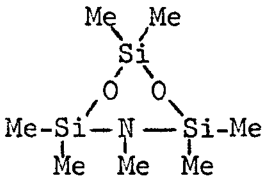
The siloxazanes that were included in the experimental work were: Hexamethyl-2,4,6,8-tetraphenyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (IV), decamethyl-1,5-diaza-3,7-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (V), and heptamethyl-1-aza-3-,5-dioxa-2,4,6-trisilacyclohexane (VI).



IV



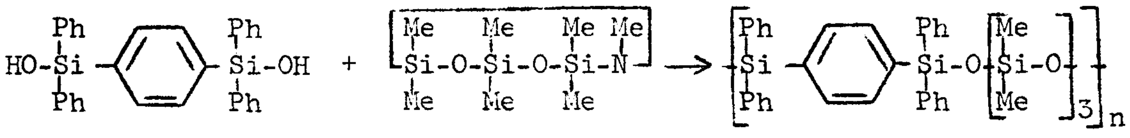
V



VI

p-Phenylenebis(diphenylsilanol) and compound IV gave a brittle material with a low specific viscosity. Polymers from p-phenylenebis(methylphenylsilanol) and compounds IV and V were, on the other hand, tacky gums.

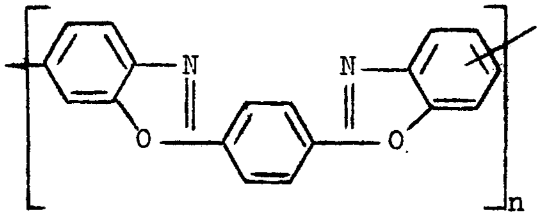
A white elastic insoluble solid was obtained from compound VI and p-phenylenebis(diphenylsilanol), when the reactants were heated in xylene at 112-15° for 24 hr., then devolatilized at 150° under reduced pressure. The polymer was examined in detail.



The infrared spectrum of the polymer (Fig. 10) was consistent with the structure and ultimate analyses for elements agreed well with the calculated values. No phase changes or melting points were observed on differential thermal analysis between 25 and 500° (Fig. 41) and the procedure decomposition temperature on the thermogravimetric analysis was 450° (Fig 39).

It had been observed that the polymer remained soluble during the initial polymerization in toluene. A soluble polymer sample was therefore prepared by heating the reactants in solvent for 5 hr. Coatings of this polymer could be sprayed on metal panels and cured at 145° to a strong elastic film. One such coated panel was exposed to ultraviolet irradiation under high vacuum and found to compare favorably with a similar panel coated with the commercial base resin used in preparing coatings for space applications. It was of particular interest that the panel coated with the experimental polymer lost no weight during the experiment. Details of the irradiation experiments are described in paragraph IV, K.

B. Polybenzoxazoles



The synthesis of three candidate bis(aminophenols) as monomers for benzoxazole preparation was first investigated. Because of the lack of stability of the bis(aminophenols) against air and light, the compounds were isolated as their hydrochloride salts. Although the syntheses of the bis-(aminophenols) are described in the literature, few of the compounds have been adequately characterized. The hydrochloride salts do not melt; therefore, the neutralization equivalents and infrared spectra were used as indexes of purity of these compounds once the identities of the products are established by elemental analyses.

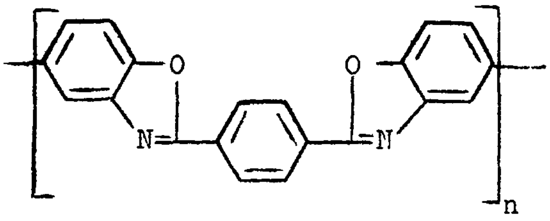
The preparation of 3,3'-dihydroxybenzidine was first reported by Burkhardt and Woods7/ and later by McCloskey,8/ who cleaved 3,3'-dimethoxybenzidine with hydriodic and hydrobromic acids, respectively. 3,3'-Dihydroxybenzidine was satisfactorily prepared and isolated as the hydrochloride salt by both procedures, but the hydrobromic acid procedure afforded better yields. An attempt to isolate and purify the free amine base resulted in decomposition of the aminophenol.

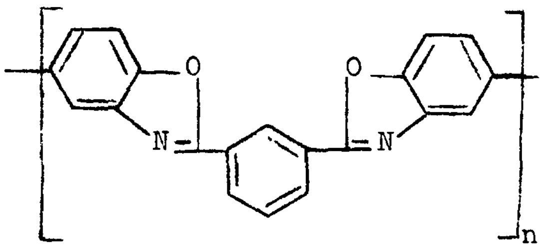
3,3'-Diamino-4,4'-biphenol was first reported by Kunze,9/ who reduced the dinitro derivative of 4,4'-biphenol with tin and hydrochloric acid. Marvel10/ later modified the procedure by the use of sodium hydrosulfite reduction. The latter method has been satisfactorily employed to prepare the dihydrochloride salt of 3,3'-diamino-3,3'-biphenol.

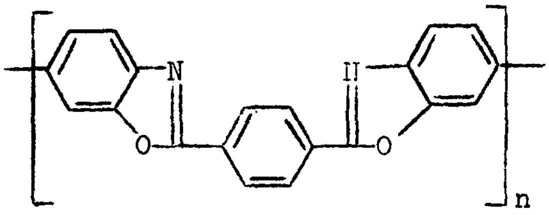
The infrared spectra of the analytical samples of the two bis(aminophenols) are recorded in Figs. 11 and 12.

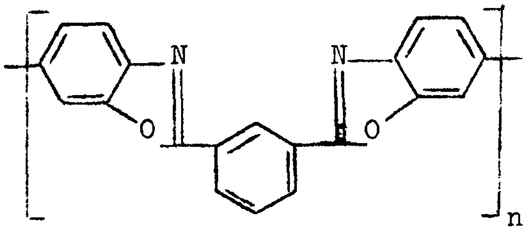
Attempts to prepare 4,6-diaminoresorcinol were less successful, but the synthesis of this monomer has not been studied in detail. Two methods had been reported for its preparation: the reduction of 4,6-bis(phenylazo)resorcinol with tin and hydrochloric acid11/ and the sequential nitration, reduction, and hydrolysis of diacetylresorcinol.12/ A repetition of the first procedure did not give a compound that could be identified as 4,6-diaminoresorcinol.

In the initial experimental work on the poly(benzoxazoles), 3,3'-dihydroxybenzidine and 3,3'-diamino-4,4'-biphenol were polymerized with isophthalamide and terephthalamide in polyphosphoric acid at 200° to obtain the



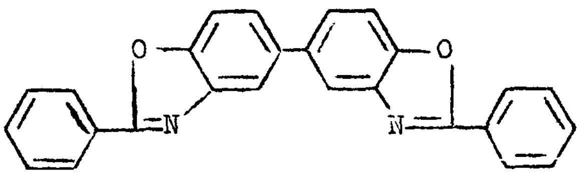


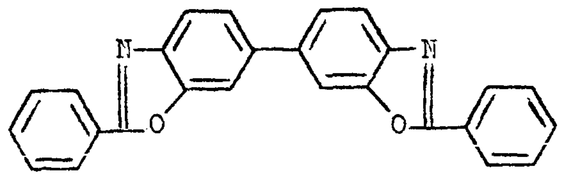




above structures. The polymer from 3,3'-diamino-4,4'-biphenol and terephthalamide had a specific viscosity in sulfuric acid of 2.54, which indicates a high degree of polymerization. Thermogravimetric analysis and differential thermal analysis traces of this polymer and the polymer from 3,3'-dihydroxybenzidine and terephthalamide (Figs. 38 and 42) showed good heat stability. Both polymers retained over 90 per cent of their weight at 500° and 60 per cent of their weight at 900° on TGA. The slight tailing-off observed at lower temperature was probably due to residual solvent since the polymers were dried at 70°.

A comparison of the infrared spectra of these two polymers (Figs. 22 and 23) with the spectra of the model compounds, 2,2'-diphenyl-5,5'-bibenzoxazole and 2,2'-diphenyl-6,6'bibenzoxazole (Figs. 13 and 14), indicated that



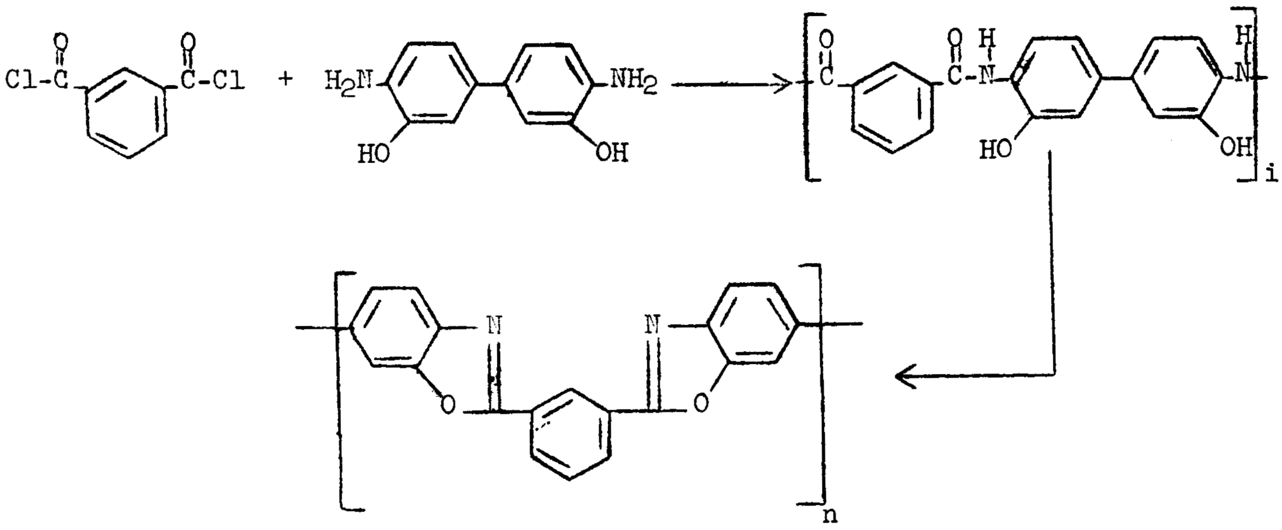


the polymer contained little or no functionality that had not cyclized to the benzoxazole structure. The polymers have not been soluble in any solvents yet examined except concentrated sulfuric acid. None of the polymers melted below 450°.

Analyses for carbon, hydrogen, and nitrogen in these two polymers did not check closely with the calculated values. No satisfactory reason for this disagreement could be found. There was no evidence in the infrared spectra that phosphate groups were incorporated in the polymers.

Since the entirely cyclized polymer is not sufficiently soluble or fusible for preparing films, attempts were made to prepare an uncyclized prepolymer which could first be cast as a film and then be cyclized or undergo a chain extension reaction. Several alternative routes to such a prepolymer were investigated.

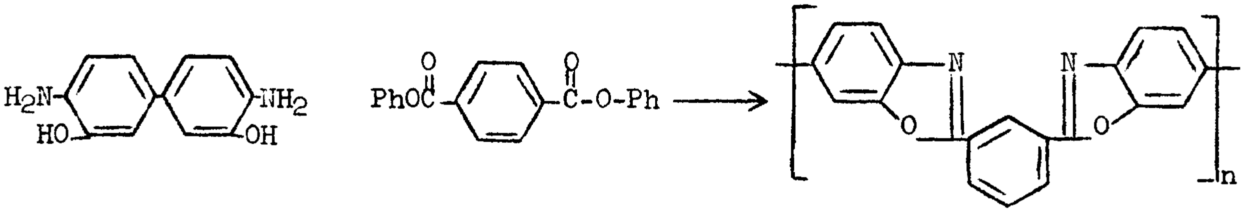
Solution polymerization of isophthalyl chloride with 3,3'-dihydroxybenzidine at -5° - 20° in a dimethylacetamide-cyclohexanone mixture has been reported to produce an uncyclized polymer with an inherent viscosity of 1.04 in sulfuric acid.13/ It is also reported that films of this polymer can be cyclized at 200° - 530°.



Attempts to reproduce the preparation of the prepolymer have not yet been successful. In a series of preparations, 3,3'-dihydroxybenzidine with either isophthalyl chloride or terephthalyl chloride gave polymers with specific viscosities of 0.12 to 0.17, and 3,3'-diamino-4,4'-diphenol gave polymers with specific viscosities of 0.07. The infrared spectra of the polymers (Figs. 20 and 21) were very similar to the spectra reported in the original publication, and to the spectra of the uncyclized model compounds, N,N'-dibenzoyl-3,3'-dihydroxybenzidine and N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenyl (Figs. 16 and 17); therefore, cyclization had not occurred. None of these polymers have been suitable for preparing films, apparently because of their low molecular weight

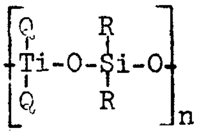
The temperature limits within which the polymerization could be carried out without effecting cyclization were examined by heating the model compounds at specified times and temperatures and determining at the end of the heating period from the infrared spectrum of the product if cyclization had occurred. When heated at 150° for 2 hr., neither compound cyclized. At 300° N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenol had cyclized to the benzoxazole, but N,N'-dibenzoyl-3,3'-dihydroxybenzidine remained unchanged. These data suggested that higher polymerization temperatures could be used in preparing the prepolymer without danger of cyclization. However, in a series of experiments, higher molecular weight prepolymers were not obtained when a polymerization temperature of 100° was used or when other acid acceptors, such as s-collidine or quinoline, were used at the higher temperature.

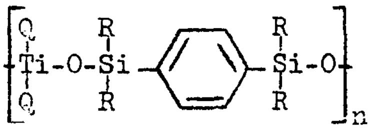
Bis(aminophenols) and phthalic acid esters of phenol have been polymerized in the melt,[14] but the products were the fully cyclized polymers.

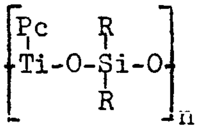


As a final approach to benzoxazole prepolymers, the monomers were polymerized in polyphosphoric acid at lower temperatures and for shorter time periods than had been used in preparing the cyclized polymers. At lower temperatures, unsatisfactory, low molecular weight products were obtained. Shorter reaction periods produced a cyclized product when a sufficiently high temperature was used to obtain a high molecular weight polymer.

C. Titanium Chelate Polymers

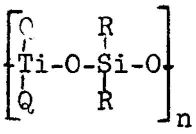

$\left[-\overset{Q}{\underset{Q}{Ti}}-O-\overset{R}{\underset{R}{Si}}-O-\right]_n$



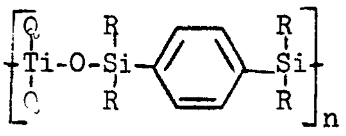

$\left[-\overset{Pc}{Ti}-O-\overset{R}{\underset{R}{Si}}-O-\right]_n$

Q = 8-oxyquinoline
Pc = phthalocyanine

1. 8-Hydroxyquinoline chelates: Difunctional chelated derivatives of titanium were required for condensation reactions with diphenylsilanediol and p-phenylenebis(diorganosilanols) to give polymers with the following structures:



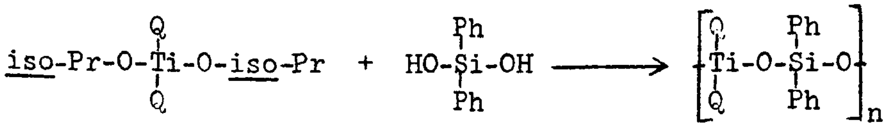
$$\left[-\overset{Q}{\underset{Q}{Ti}}-O-\overset{R}{\underset{R}{Si}}-O-\right]_n$$



Q = 8-oxyquinoline

The monomer, bis(8-oxyquinoline)diisopropoxytitanium, was readily prepared by a method given in the literature.[15] The synthesis of a low molecular weight polymer from bis(8-oxyquinoline)diisopropoxytitanium and diacetoxydiphenylsilane has been described.[16] It also has been reported that bis(dialkylamino)-bis(8-oxyquinoline)titanium and diphenylsilanediol produced a polymer that can be solvent cast as a film.[17] The molecular weight of the latter polymer was not reported. Because quantitative reactions with model compounds have been established for the synthesis of titanoxanosiloxane linkages,[15] the most promising of these methods, the condensation of titanium alkoxides with silanols, was examined.

When bis(8-oxyquinoline)diisopropoxytitanium and diphenylsilanediol were heated in benzene, a poly(bis(8-oxyquinoline)titanoxanodiphenylsiloxane) was obtained which had a molecular weight of 795 by vapor phase osmometry.



$$\underline{iso}\text{-}Pr-O-\overset{Q}{\underset{Q}{Ti}}-O-\underline{iso}\text{-}Pr \;+\; HO-\overset{Ph}{\underset{Ph}{Si}}-OH \longrightarrow \left[-\overset{Q}{\underset{Q}{Ti}}-O-\overset{Ph}{\underset{Ph}{Si}}-O-\right]_n$$

Since the molecular weight for the simple condensation product of two monomer units was 610, no significant polymerization had been achieved. The material,, which was soluble in dimethyl formamide and dimethyl sulfoxide, could be cast as a film from dimethyl formamide, but the film did not maintain its integrity when it was handled.

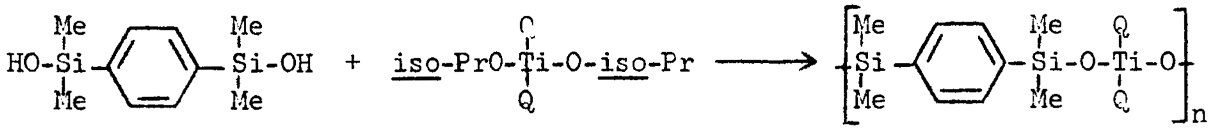
It appeared that the degree of polymerization was limited by the insolubility of low molecular weight condensation products in benzene. In an attempt to effect the polymerization in dimethyl sulfoxide, higher molecular weight was not obtained. However, with dimethyl acetamide as the polymerization solvent, the molecular weight was increased to 2,800. The infrared spectrum of the polymer prepared in dimethyl acetamide showed a low end group (OH) concentration, and within the experimental error, the yield of the polymer was quantitative.

Subsequently, a series of experiments were undertaken to determine the effect of stoichiometry on the polymerization of diphenylsilanediol and diisopropoxybis(8-oxyquinoline)titanium in dimethyl acetamide. In the procedure that was employed, difficulty was encountered in completely removing the solvent after the polymerization; therefore, polymer yields usually exceeded 100 per cent. Seven experimental levels were employed in which the ratio of silicon to titanium-containing monomers varied from 0.90 to 1.17. Although 90 per cent appeared to be the limiting yield of isopropyl alcohol and the yield varied from 70 to 90 per cent, the scatter of values was too great to make any correlation with monomer concentration. The melting points of the products also appeared to vary randomly, and there were no significant differences in the infrared spectra of the polymers. The molecular weights were not improved.

Other polymerization reactions, including the melt polymerization of diphenylsilanediol and diisopropoxybis(8-oxyquinoline)titanium and the melt and solution polymerizations of diacetoxydiphenylsilane and diisopropoxybis(8-oxyquinoline)titanium, proved no more satisfactory.

A polymer has been reported as the product of treating p-phenylenebis(dimethylsilanol) with bis(8-oxyquinoline)diisopropoxytitanium in refluxing benzene.[16] The polymer, which was a brittle solid, had a molecular weight of about 1,380. The reaction of bis(8-oxyquinoline)bis(dimethylamino)titanium and p-phenylenebis(diphenylsilanol) was investigated by Tower,[17] but the silicon-containing monomer was subsequently shown to be largely diphenylsilanediol.[3]

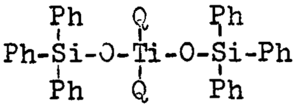
In a repetition of the first experiment, the condensation product of diisopropoxybis(8-oxyquinoline)titanium and p-phenylenebis(dimethylsilanol) was a high melting solid with a molecular weight no greater than the repeating unit. The infrared spectrum of the polymer indicated that Si-O-Ti bonds were present.



The same type of product was obtained when p-phenylenebis(diphenylsilanol) was used.

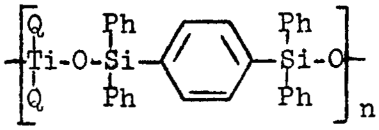
In an alternate approach, a molar excess of the siloxane was used to obtain a prepolymer with silanol end groups, which could undergo condensation in a chain extension reaction to advance the polymerization. With the excess of silanol, the materials remained soluble in benzene throughout the polymerization. The prepolymer had a specific viscosity in toluene of 0.06. In one attempt to advance the polymerization, the prepolymer was heated with a catalytic amount of sodium hydroxide which was added to the polymer as an aqueous solution. Under these conditions, decomposition occurred and 8-hydroxyquinoline sublimed from the mixture. No additional work has been carried out on this system.

Infrared spectra of the polymers from diphenylsilanediol and diisopropoxybis(8-oxyquinoline)titanium prepared in dimethylacetamide (Fig. 26) were superimposable with the spectra of the polymers prepared in benzene, (Fig. 25). The spectra were also nearly superimposable with the spectrum of the model compound, bis(8-oxyquinoline)bis(triphenylsiloxy)titanium except for a shift of the Si-O-Ti absorption in the model compound



$$\mathrm{Ph{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{Q}{\underset{Q}{Ti}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}Ph}$$

from 905 cm.$^{-1}$ to 945 cm.$^{-1}$ in the polymer. However, the spectrum of a condensation product from bis(8-oxyquinoline)diisopropoxytitanium with p-phenylenebis(dipehnylsilanol) rather than diphenylsilanediol

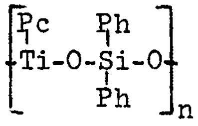


retained the absorption at the same frequency as the model compound, 905 cm.$^{-1}$ (Fig. 27).

The absence of new absorption bands in the 1,000 - 1,100 cm.$^{-1}$ region precludes siloxane formation during the polymerization, and the absence of new bands in the 800 - 860 cm.$^{-1}$ region argues against the formation of Ti-O-Ti bonds. The increase in frequency of the Ti-O-Si absorption is best explained on the basis of the probability of ring formation and the consequent damping effect of the ring. Since the acetylacetone chelate of titanium forms a dimeric oxide, which requires a cis configuration of ligands about the titanium atom, it seems reasonable to assume that 8-hydroxyquinoline derivatives of titanium may also form compounds requiring the cis titanium configuration. In the cis configuration, the chelated titanium atom could form an eight membered ring of alternating siloxy and titanoxy groups.

The chief argument against ring formation is the molecular weight data, which vary from 500 to 2,000 depending on the sample chosen for analysis. However, all molecular weights were determined on raw polymers which were not fractionated and may represent a wide range of molecular types. Evidence in favor of ring formation limiting the molecular weight of the titanoxosiloxanes is the absence of a frequency shift for the Ti-O-Si bond in the product from p-phenylenebis(diphenylsilanol) which has a structure that would make cyclization less probable. Also, data on the solubility of the condensation products in aromatic solvents indicate that insolubility may not have been a factor in limiting the molecular weights in the initial experiments.

2. Phthalocyanine chelates: A polymer from phthalocyanine titanium dichloride and triphenylsilanol, reported to have a silicon:titanium ratio of 2.8:1, was described by Towers.[17] Although the material was crystalline, the authors claimed that heat stable films could be melt- and solvent-cast. The same authors reported a second polymer from tetrakis(dimethylamino)titanium, phthalonitrile, and diphenylsilanediol that did not form a film, but was represented as containing a phthalocyanine structure.



$$\left[\overset{Pc}{\overset{|}{Ti}}-O-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{Si}}-O \right]_n$$

Pc = phthalocyanine

A repetition of the preparation by the reported method gave a black material whose thermogravimetric analysis showed a procedural decomposition temperature of 205°. This product was a mixture of at least two materials, since 51 per cent was benzene soluble.

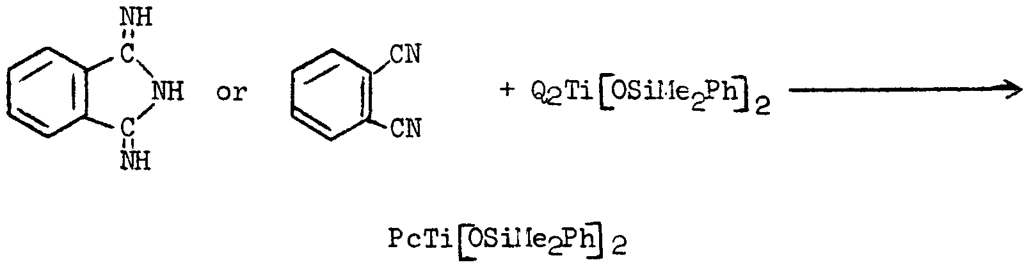
Other phthalocyanine containing polymers with degrees of polymerization less than 10 have been described in the literature, but the materials were invariably insoluble in all solvents and do not melt.[18] It can be concluded from the literature that any phthalocyanine-containing polymer with even a moderately high molecular weight cannot be used to fabricate films by the usual melt and solvent casting techniques.

Two alternate approaches to phthalocyanine-containing polymers were investigated. One approach considered the possibility of preparing a tractable polymer, which could be fabricated as a coating or film, and subsequently treated with a phthalocyanine precursor to obtain a polymer with phthalocyanine groups in the repeating units. In such a reaction, a titanium ligand in a titanoxanosiloxane could be displaced.

$$4\,P + \left[TiL_2OSiPh_2O\right]_n \longrightarrow \left[TiPcOSiPh_2O\right]_n + 2L$$

P = phthalocyanine precursor
L = ligand
Pc = phthalocyanine

A model system was chosen in which 1,3-diiminoisoindoline or phthalonitrile as the phthalocyanine precursor could displace 8-hydroxyquinoline as the ligand from bis(dimethylphenylsiloxy)(8-oxyquinoline)titanium.



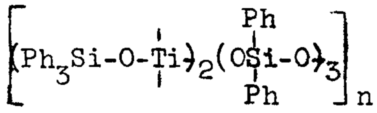
$$+\ Q_2Ti[OSiMe_2Ph]_2 \longrightarrow PcTi[OSiMe_2Ph]_2$$

Neither ligand displacement or displacement of the dimethylphenyl siloxy group occurred when the model compound was heated with either 1,3-diiminoisoindoline or phthalonitrile at 200° at atmospheric pressure or under vacuum. Higher temperatures could not be employed because the starting materials sublimed from the reaction zone at 200°.

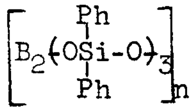
A second experimental approach to phthalocyanine-containing polymers that was considered was the condensation of phthalocyaninetitanium diisopropylate with diphenylsilanediol. However, attempts to prepare the monomer from a mixture of solid phthalocyanine and titanium tetraisopropylate failed.

$$PcTi(O\text{-}\underline{iso}\text{-}Pr)_2 + Ph_2Si(OH)_2 \longrightarrow \{PcTiOSiPh_2O\}_n$$

D. Titanoxanosiloxanes and Borosiloxanes



$$\left[(Ph_3Si\text{-}O\text{-}\overset{|}{\underset{|}{Ti}})_2(O\overset{Ph}{\underset{Ph}{Si}}\text{-}O)_3\right]_n$$



$$\left[B_2(O\overset{Ph}{\underset{Ph}{Si}}\text{-}O)_3\right]_n$$

A polymer from tetrakis(dimethylamino)titanium, triphenylsilanol, and diphenylsilanol has been reported as a glass which can be solvent- or melt-cast as a film.[17] Repetitions of that procedure with titanium tetraisopropylate rather than tetrakis(dimethylamino)titanium gave a tan powder that

$$2Ti(NMe_2)_4 + 2Ph_3SiOH + 2Ph_2Si(OH)_2 \longrightarrow [(Ph_3SiOTi)_2(OPh_2SiO)_3]_n + 8MeNH$$

melted at about 250° and was insoluble in hot dimethyl formamide.

Zeitler[19] has shown that the reaction of titanium tetrabutylate with triphenylsilanol gave tetrakis(triphenylsiloxy)titanium quantitatively regardless of the mole ratio of reactants. An infrared spectrum (Fig. 24) of the tan powder from attempted resin preparation was consistent with the presence of tetrakis(triphenylsiloxy)titanium.

Because failure to obtain a resin may have been a result of the different starting materials, the preparation was repeated with tetrakis-(dimethylamino)titanium in place of titanium tetraisopropylate. A tan powder, insoluble in dimethylformamide, was obtained which had an infrared spectrum identical to the other sample.

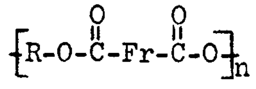
It has been reported that a borosiloxane polymer, which was an amber glass-like material, was obtained by treating two molar equivalents of trimethylborate with three molar equivalents of diphenylsilanediol.[3]

$$2B(OMe)_3 + 3Ph_2Si(OH)_2 \longrightarrow \left[B_2(Ph_2SiO)_3\right]_n + 6MeOh$$

Recalculation of the molar quantities from the gram quantities used in the experiments showed that the molar ratio was 1:1.91 rather than 1:1.5.

Borosiloxanes were prepared from mixtures containing both molar ratios of tributylborate and diphenylsilanediol. The product from the 1:1.91 molar ratio was a glass at room temperature that became brittle after 1 hr. at 450°. The molecular weight of the polymer, which had a Si:B ratio of 1.94:1, was 597 compared with 652 for the repeating unit. The polymer prepared from a 1:1.5 molar ratio was a glass at room temperature and softened at 85°. The presence of siloxane in the infrared spectrum of the polymer (Fig. 35) is consistent with Anderson's observation that the product from dibutoxymethylboron and diphenylsilanediol did not contain B-O-Si bonds.[20]

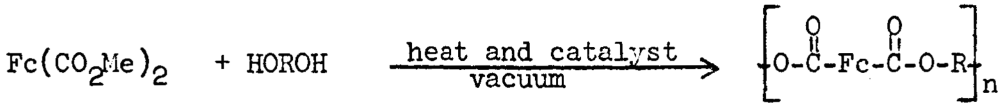
E. <u>Ferrocene Polyesters</u>



$$\left[R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Fr\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_n$$

Fr = ferrocene

Two approaches to the polymerization of ferrocene-containing monomers by transesterifaction were considered as potential routes to ferrocene polyesters. In the first method, dimethyl ferrocenedicarboxylate was heated with a slight excess of a diol in the presence of a suitable transesterification catalyst. The procedure is commonly used for the preparation of more conventional polyesters.

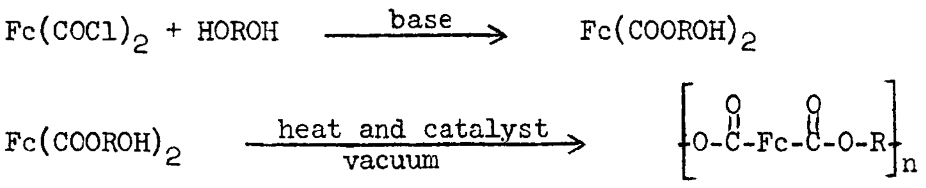


$$\mathrm{Fc(CO_2Me)_2} + \mathrm{HOROH} \xrightarrow[\text{vacuum}]{\text{heat and catalyst}} \left[\mathrm{O-\overset{\overset{O}{\|}}{C}-Fc-\overset{\overset{O}{\|}}{C}-O-R}\right]_n$$

The required monomer, 1,1'-dimethyl ferrocenedicarboxylate, was most satisfactorily prepared via the hypochlorite oxidation of 1,1'-diacetylferrocene[21,22] and the subsequent esterification of the ferrocene dicarboxylic acid with methanol in the presence of sulfuric acid. An alternate method involving the lithiation of ferrocene[23] produced mixtures of mono- and disubstituted ferrocene carboxylic acid esters, which required a chromatographic separation that was not suitable for larger quantities.

In attempts to effect transesterification of 1,1'-dimethyl ferrocenedicarboxylate with 2,2,4,4-tetramethyl-1,3-cyclobutanediol or 2,2'-dimethyl-1,3-propanediol, the ferrocene methyl ester was usually recovered from the reaction mixtures unchanged. Temperatures of 150° were employed and catalysts used included zinc acetate dihydrate, sulfuric acid, sodium, and titanium tetraisopropylate. Difficulties in effecting the reaction were complicated by the ease with which the reactants sublimed and by the decomposition of the ferrocene esters when air was not rigorously excluded from the mixtures.

A second approach to the synthesis of ferrocene polyesters involved the preparation of an intermediate diol ester, which could be used in a polymerization reaction.



$$\mathrm{Fc(COCl)_2} + \mathrm{HOROH} \xrightarrow{\text{base}} \mathrm{Fc(COOROH)_2}$$

$$\mathrm{Fc(COOROH)_2} \xrightarrow[\text{vacuum}]{\text{heat and catalyst}} \left[\mathrm{O-\overset{\overset{O}{\|}}{C}-Fc-\overset{\overset{O}{\|}}{C}-O-R}\right]_n$$

The acid chloride, which was prepared according to the method described by Knoblock[22] by the action of oxalyl chloride on 1,1'-ferrocenedicarboxylic acid, was treated with ethylene glycol in the presence of pyridine to obtain pure 1,1'-bis(2-hydroxyethoxycarbonyl)ferrocene. Although this compound was not the preferred monomer, its preparation established a synthetic method for the esters needed in the polymerization reactions.

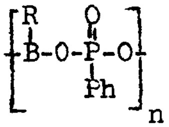
A suitable ester was prepared by the same method from 1,1'-ferrocenedicarbonyl chloride and 2,2-dimethyl-1,3-propanediol and isolated as a crude residue, which was chiefly 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene.

$$Fc(COCl)_2 \; + \; HOCH_2CMe_2CH_2OH \longrightarrow Fc(COOCH_2CMe_2CH_2OH)_2$$

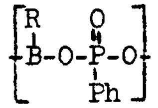
The identification was based on the preparative route and verified by a comparison of the infrared spectrum of 1,1'-bis(2-hydroxyethoxycarbonyl)ferrocene (Fig. 28) and the spectrum of the residue (Fig. 29).

This monomer, however, appeared to be equally resistant to transesterification reactions. Under the same conditions that bis(2-hydroxyethyl)terephthalate formed a high polymer, 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene failed to show any sign of reaction.

F. Boron Chelate Polymers



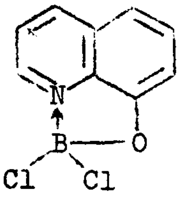
$$\left[-\overset{R}{B}-O-\underset{Ph}{\overset{\overset{O}{\|}}{P}}-O- \right]_n$$

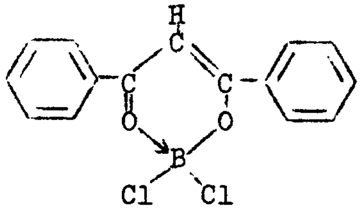
In considering candidate monomers for polymers containing the structural unit,  $\left[-\overset{R}{B}-O-\underset{Ph}{\overset{\overset{O}{\|}}{P}}-O- \right]$, chelated boron compounds were selected because they offered improved oxidative, hydrolytic, and chemical stability. It is well known that boron-substituted alkyl and aryl groups in certain compounds are unstable with respect to oxidation and disproportionation and that the BO bond is hydrolytically unstable. The chelate derivatives of boron are more hydrolytically stable than other boron-containing compounds, presumably because the filling of the vacant orbital on boron blocks the normal route by which hydrolysis occurs.

Although chelate derivatives of boron were first reported by Dilthey in 1906,[24] little is known of their chemistry. Very recently, a method for preparing a difunctional monomer, dichloro(8-oxyquinoline)boron, was reported in the literature.[25] This procedure was satisfactorily repeated to obtain

$$QH + BCl_3 \longrightarrow QBCl_2 \qquad QH = \text{8-hydroxyquinoline}$$

the 8-hydroxyquinoline and the dibenzoylmethane chelate derivatives of boron trichloride. An attempt to extend the reaction to chelate derivatives of boron tribromide failed. The boron trichloride derivatives gave a satisfactory elementary analysis for the structures:

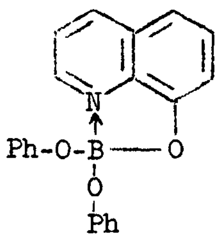


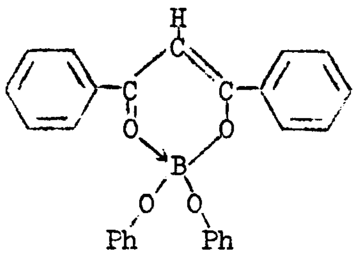


Although these compounds were difunctional monomers, condensation reactions with phenylphosphonic acid to produce a polymer would split out hydrogen chloride as a small molecule. The polymerization reaction would be considerably more useful if a less reactive compound were formed. Therefore, an attempt was made to prepare the corresponding alkoxy and phenoxy derivatives.

When isopropyl borate was heated with 8-hydroxyquinoline in refluxing toluene, isopropyl alcohol was displaced and an insoluble chelated derivative was isolated, but the product could not be characterized by elemental analyses as diisopropoxy-8-oxyquinolineboron. The compound contained a ratio of about two boron atoms per 8-hydroxyquinoline group and no residual isopropoxy groups. Isopropyl borate did not react with dibenzoylmethane.

Treatment of triphenylborate with 8-hydroxyquinoline at a lower temperature afforded a good yield of diphenoxy-8-oxyquinolineboron. The corresponding dibenzoylmethane derivative was also prepared. These compounds gave satisfactory elementary analyses for the following structures. The same





compounds could also be prepared from the chelated boron chlorides and phenol.

A model of the polymerization reaction suitable for preparing boron and phosphorus-containing polymers from these monomers was examined. When diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron was treated with diphenylphosphinic acid in refluxing chlorobenzene, no evidence for a reaction could be detected. Because of the failure of the model reaction to occur in the expected manner and because of the apparent lack of hydrolytic stability of the chelated boron compounds, no additional work was carried out on this system.

III. ANTICIPATED WORK

During the next contract period, it is planned that the following experimental approaches to high temperature, high vacuum, and radiation resistant polymers suitable for space environment will be followed:

1. Poly(benzoxazoles): New bis(aminophenols), which can possibly impart solubility and flexibility in high molecular weight poly(benzoxazoles) will be prepared and incorporated in new polymer systems. New monomers may include bis(3-amino-4-hydroxyphenyl)methane, 2,2-bis(3-amino-4-hydroxyphenyl) propane, bis(3-amino-4-hydroxyphenyl)sulfone, and bis(3-amino-4-hydroxyphenyl) ether. Polyphosphoric acid will be used as a medium for these polymerizations.

2. Polysilylaromatics: New phenylene-linked solixanes will be prepared by the condensation of p-phenylenedisilanols with siloxanes, silazanes, or siloxazanes. Structures will be selected which provide improved physical properties, and the effects of structural changes will be correlated with high vacuum-ultraviolet stability. New disilanols that may be screened include those that incorporate the m-phenylene,p,p'-bis(phenylene)oxy, and the 1,2,4,5-tetrafluorophenylene groups.

3. Poly(porphrinosiloxanes): The porphyrino group will be considered as a chelating ligand for preparing titanoxanosiloxanes.

4. Chelated boron-organic diol polymers: The polymeric products that can be derived from the condensation of 8-oxyquinolinediphenoxyboron and related compounds with organic diols will be prepared and screened.

5. Poly(s-triazinylethers): Condensation products of dichloro-s-triazines or dichloropyridazines with organic diols will be prepared and screened.

6. Poly(5-vinyl-8-hydroxyquinoline): Poly(5-vinyl-8-hydroxyquinoline) and its chelate derivatives will be prepared and screened.

7. Poly(heterocyclic ethers): Polymer derived from such compounds as the copper salts of 4-bromo-6-hydroxypyrimidine or 3-bromo-6-hydroxypyridazine will be prepared and screened.

8. Phenyltrichlorosilane-p-phenylenebis(chlorophenylsilane) cohydrolysates: Largely phenylated cohydrolysates containing at least a small portion of a phenylenedisilane, which can serve at a crosslinking agent, will be prepared and screened.

IV. EXPERIMENTAL PART

Reactions involving organometallic reagents, silicon halides, titanium alkoxides, zirconium alkoxides, boron alkoxides or halides, and other moisture sensitive compounds were carried out in glassware which was flamed out under nitrogen prior to use. These reactions were protected from atmospheric moisture either with drying tubes containing calcium sulfate (Drierite) or a flow of dry nitrogen.

Solvents were reagent grade and were anhydrous when moisture sensitive compounds were used.

Phenylmagnesium bromide was used as a 3 *M* solution in ether from Arapahoe Chemical Company, and *n*-butyllithium was used as a 15 per cent solution in hexane from Foote Mineral Company.

Analyses for elements were performed by Spang Microanalytical Laboratory, Box 1111, Ann Arbor, Michigan. Molecular weight determinations by vapor pressure osmometry were performed by Crobaugh Laboratories, Box 4078, Charleston, West Virginia.

All temperatures are reported in degrees centigrade.

A. *p*-Phenylenedisilane Monomers and Intermediates

1. *p*-Phenylenebis(chlorodimethylsilane): (Method: Reference 1) A solution of 100 g. (0.423 mole) of *p*-dibromobenzene and 164 g. (1.27 moles) of freshly distilled dichlorodimethylsilane in 275 ml. of ether was added dropwise to 31.0 g. (1.27 g. atoms) of magnesium. The magnesium was activated with iodine after about 50 ml. of the solution had been added, and the remaining solution was added at a rate that maintained reflux. The product was heated and stirred 18 hr., cooled, filtered, and the salts were washed with ether. After the combined filtrate and washings were evaporated, distillation gave 44 g. (25 per cent) of *p*-phenylenebis(chlorodimethylsilane) b.p. 113-117° (0.4 mm.), m.p. 79-81° (reported, 87°).[1]

2. *p*-Phenylenebis(dimethylsilanol): (Method: Reference 1) A solution of 21.0 g. (0.08 mole) of *p*-phenylenebis(chlorodimethylsilane) in 300 ml. of ether was added during 15 min. to a solution of 6.5 g. (0.16 mole) of sodium hydroxide in 108 ml. of water, which was stirred and maintained at 0° during the addition. The ether layer was separated, combined with a 150 ml. ether washing of the aqueous phase, and dried over sodium carbonate. Upon

evaporation of the solvent, 7.5 g. (41 per cent) of p-phenylenebis(dimethylsilanol), m.p. 133.5-134.5° (reported, 135°)[1] was obtained. Two repetitions of the procedure afforded the same product in yields of 44 and 57 per cent. The infrared spectrum of this compound is shown in Fig. 1.

3. p-Phenylenebis(chloromethylphenylsilane)(attempted): An attempt was made to prepare this compound by the procedure described by Popeleva.[2] A mixture of 36.5 g. (1.5 g. atoms) of magnesium, 7.0 g. of p-dibromobenzene and 50 ml. of ether was activated with iodine and treated with a solution containing 111 g. (total, 0.50 mole) of p-dibromobenzene, 210 g. (1.10 moles) of dichloromethylphenylsilane, and 350 ml. of ether over a 2-hr. period. The mixture was stirred and heated at reflux for 18 hr., filtered, and the filtrate was evaporated. Additional filtration was required to remove the salts that precipitated during the evaporation. After a preliminary rapid distillation, the product was fractionally distilled, and the following fractions were separated: 12.1 g., b.p. 95-113° (0.07 mm.), n_D^{24} 1.5718; 3.1 g., b.p. 114-128° (0.07 mm.), n_D^{24} 1.5646; 4.2 g., b.p. 129-150° (0.07 mm.), n_D^{24} 1.5600; 5.7 g., b.p. 151-175° (0.07 mm.), n_D^{24} 1.5701; 23.2 g., b.p. 177-188° (0.07 mm.), n_D^{24} 1.5898 (reported, 187-196° (1-2 mm.), n_D^{20} 1.6072); 260-274° (12 mm.).[2]

In a repetition of this experiment, tetrahydrofuran was used as a solvent rather than ether. Distillation of the product obtained from 118 g. (0.50 mole) of p-dibromobenzene, 36.5 g. (1.5 g. atoms) of magnesium, and 287 g. (1.5 moles) of dichloromethylphenylsilane, gave the following fractions: 10 g., b.p. 117-130° (0.3 mm.), n_D^{25} 1.5349; 3.5 g., b.p. 136-152° (0.3 mm.), n_D^{25} 1.5363; 20.9 g., b.p. 154-200° (0.3 mm.), n_D^{25} 1.5399.

4. Chloroethoxymethylphenylsilane: (Method: Reference 26) To a stirred solution of 95.6 g. (0.50 mole) of dichloromethylphenylsilane in 200 ml. ether was added dropwise during 40 min. a mixture of 23.0 g. (0.50 mole) of anhydrous ethanol and 39.6 g. (0.50 mole) of pyridine. The mixture was stirred for an additional hour, and 58.5 g. of pyridine hydrochloride (calcd. 57.8 g.) was separated by filtration and washed with ether. The combined filtrate and washings were devolatilized at 60° (20 mm.), added to the crude product from a separate 0.25-mole experiment and fractionally distilled through a 30-cm. vacuum-jacketed column packed with Berl saddles. The fraction which boiled at 111-112.5° (28-30 mm.), n_D^{25} 1.4876 was identified as chloroethoxymethylphenylsilane (reported, 101° (20 mm.); n_D^{25} 1.4820).[26] The yield was 85 per cent.

5. p-Phenylenebis(ethoxymethylphenylsilane): A mixture of 13.5 g. (0.55 g. atoms) of magnesium (activated with iodine), 4.0 g. of p-dibromobenzene, and 40 ml. of tetrahydrofuran was treated with a solution of 55.0 g. (total, 0.25 mole) of p-dibromobenzene, 110.4 g. (0.55 mole) chloroethoxymethylphenylsilane, and 110 ml. of tetrahydrofuran over a 1-hr. period. The

mixture was stirred and heated at reflux for 3 hr., filtered, and the filtrate evaporated. Devolatilization of the residue under reduced pressure gave 7.2 g. of a liquid, boiling at 45-105° (2 mm.).

When the residue was refluxed with 600 ml. of anhydrous ethanol and cooled, an oil separated. The solvents were evaporated from the mixture, and the residue was extracted twice with 100-ml. portions of hot toluene. The toluene-soluble fraction was devolatilized at 130° (0.1 mm.) and fractionally distilled twice to yield 25.2 g. (25 per cent) of *p*-phenylenebis(ethoxymethylphenylsilane), b.p. 173-183° (0.02 mm.), n_D^{25} 1.5541, d_{25} 1.0566. The infrared spectrum (Fig. 2) was consistent with the structure.

Anal. Calcd. for $C_{24}H_{30}O_2Si_2$: C, 70.88; H, 7.44; MR_D 123.11.[27] Found: C, 70.81; H, 7.43; MR_D 123.16.

6. *p-Phenylenebis(methylphenylsilanol)*: A solution of 1.2 g. (0.030 mole) of sodium hydroxide in 7 ml. of methanol and 1 ml. of water was mixed with a solution of 4.1 g. (0.010 mole) of *p*-phenylenebis(ethoxymethylphenylsilane) in 2.5 ml. of anhydrous ethanol. After 5 min., a solution of 1.2 g. (0.030 mole) in 8 ml. water was added with swirling. An hour later, the mixture was poured into an ice-cold solution of 10.3 g. of potassium dihydrogen phosphate in 75 ml. water. After four days, the crystalline precipitate was filtered to give 2.8 g. (80 per cent) of crude material, m.p. 92-96°. Three recrystallizations from a 50-50 mixture of toluene-petroleum ether (b.p. 60-90°) gave 1.0 g. (29 per cent) of *p*-phenylenebis(methylphenylsilanol), m.p. 128-140°C.

Anal. Calcd. for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.33; Si, 16.03. Found: C, 68.36; H, 6.23; Si, 16.09.

Repetition of the procedure using 17.4 g. (0.0428 mole) of *p*-phenylenebis(ethoxymethylphenylsilane) gave 11.8 g. (79 per cent) of crude material. Repeated recrystallization of the sample from 50-50 mixtures of toluene and petroleum ether (b.p. 60-90°) afforded 1.2 g. of a pure isomer melting at 156-158°.

Anal. Calcd. for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.33; Si, 16.03. Found: C, 68.38; H, 6.53; Si, 15.96.

From the filtrates, 4.3 g. of a compound melting at 127-141° was recovered. The infrared spectra of the two compounds are shown in Figs. 3 and 4. The two spectra differed only in the presence of a band at 780 $cm.^{-1}$ in the lower melting isomer. The NMR spectra of the two compounds did not differ except for the sharpness of the SiOH proton peak, which was more diffuse in the higher melting compound. The following chemical shifts and relative peak intensities were observed: SiMe, $\delta = 0.40$; SiOH, $\delta = 6.40$; SiPh, $\delta = 7.19 - 7.62$; peak intensity ratio, 6:2:14.

7. p-Phenylenebis(diphenylsilanol) (via the direct hydrolysis of the condensation product of p-phenylenebis(magnesium bromide) and dichlorodiphenylsilane): A mixture containing 26.7 g. (1.1 g. atoms) of magnesium (activated with iodine), 7.0 g. of p-dibromobenzene, and 50 ml. of tetrahydrofuran was treated with a solution of 111 g. (total, 0.50 mole) of p-dibromobenzene, and 253 g. (1.0 mole) of dichlorodiphenylsilane in 175 ml. of tetrahydrofuran. The addition required 1.5 hr. Heating was continued while toluene was added and tetrahydrofuran was distilled out of the mixture until the reflux temperature reached 109°, which required 5 hr. After the product was filtered and devolatilized, an attempt to distill the residue at 170° (0.1 mm.) was unsuccessful because of decomposition. The intermediate, p-phenylenebis(chlorodiphenylsilane), did not crystallize when the residue was cooled; therefore, the following attempts were made to hydrolyze the impure material directly to the silanol:

(a) About 15 g. of the residue was stirred 2 hr. with 40 ml. of 5 per cent hydrochloric acid and 40 ml. of ether. The ether phase was separated, washed with water and 10 per cent sodium carbonate, and dried over sodium sulfate. Addition of petroleum ether (b.p. 35-60°) gave 1.0 g. of a solid, m.p. 187-191°.

(b) About 20 g. of the residue was stirred 1 hr. with 100 ml. of concentrated ammonium hydroxide and 100 ml. of ether. When the ether layer was separated, washed with water, dried over sodium sulfate, and evaporated, an oil was obtained that crystallized from a benzene-petroleum ether (b.p. 35-60°) mixture. Recrystallization gave 0.6 g. of p-phenylenebis(diphenylsilanol), m.p. 216-217.5° (reported, 225.5-227.0°).3/ The infrared spectrum of the product was identical to the spectrum reported by Towers for p-phenylenebis(diphenylsilanol).17/

8. p-Phenylenebis(diphenylsilanol) (attempted via the direct hydrolysis of the condensation product of p-dilithiobenzene and dichlorodiphenylsilane: (Method: Reference 17) p-Dilithiobenzene (prepared by heating 11.8 g. (0.05 mole) of p-dibromobenzene in 100 ml. of petroleum ether (b.p. 35-60°) and 65 ml. of 1.68 M n-butyllithium in hexane for 24 hr.) was added dropwise to a stirred solution of 25.3 g. (0.10 mole) of dichlorodiphenylsilane in 100 ml. of petroleum ether (b.p. 35-60°). After the addition was complete, the petroleum ether was distilled out while an equal volume of toluene was added, and the product was refluxed 3 hr. Filtration gave 11.5 g. (calcd. 4.2 g.) of

salts. The filtrate was devolatilized to 250° and the residue was mixed with 100 ml. of 5 *M* ammonium hydroxide in a Waring Blendor. After the aqueous phase was decanted, the remaining oil was crystallized from benzene to give 2.5 g. of a material, m.p. 185-186°. The spectrum of this material was not similar to an authentic sample.

9. *Chlorodiphenylethoxysilane*: A mixture of 25.3 g. (0.55 mole) of anhydrous ethanol and 43.5 g. (0.55 mole) of pyridine was added dropwise during 1.5 hr. to a stirred solution of 139 g. (0.55 mole) of dichlorodiphenylsilane in 260 ml. ether. The mixture was stirred for an additional 30 min. and the salts were filtered off and washed with ether. The combined filtrate and washings were devolatilized at 60° (15 mm.) and fractionally distilled through a 30-cm. vacuum-jacketed column to give 116 g. (81 per cent) of chlorodiphenylethoxysilane, b.p. 116-119° (0.7 mm.).

Anal. Calcd. for $C_{14}H_{15}ClOSi$: C, 63.98; H, 5.75; Cl, 13.49; Eq. wt., 262.8. Found: C, 63.91; H, 5.80; Cl, 13.70; Eq. wt., 264 and 267 (by titration).

10. *p-Phenylenebis(ethoxydiphenylsilane)*: (Method: Reference 4) To a mixture of 31.0 g. (1.27 g. atoms) of magnesium (activated with iodine), 7.0 g. of *p*-dibromobenzene and 50 ml. of tetrahydrofuran was added a solution of 93.0 g. (total 0.423 mole) of *p*-dibromobenzene, 321 g. (1.27 moles) of dichlorodiphenylsilane, and 150 ml. of tetrahydrofuran over a period of 45 min. When the addition was complete, the mixture was refluxed 3 hr., the tetrahydrofuran was replaced by toluene, and refluxing was continued at 110° for 3.5 hr. After the product was filtered and the salts were washed with toluene, the combined filtrate and washings were evaporated. The residue was boiled 1 hr. in 2 liters of anhydrous ethanol and a small amount of material that remained insoluble was filtered off. From the cooled ethanol solution precipitated 58.0 g. of the crude product, m.p. 120-132°. Numerous attempts to purify the material by recrystallization from ethanol failed, but in these attempts, considerable high melting solids and oily products were separated. The remaining 20.5 g., m.p. 147.5-151.5°, upon recrystallization from toluene, gave 13.6 g. (6.7 per cent) of *p*-phenylenebis(diphenylethoxysilane), m.p. 158-161° (reported, 158-160°).[4] The infrared spectrum (Fig. 5) is consistent with the structure.

A mixture of 9.7 g. (0.40 g. atoms) of magnesium (activated with iodine), 4.0 g. of *p*-dibromobenzene, and 40 ml. of tetrahydrofuran was treated with a solution of 39.0 g. (total, 0.182 mole) of *p*-dibromobenzene and 105 g. (0.40 mole) of chlorodiphenylethoxysilane in 75 ml. of tetrahydrofuran during 1 hr. The mixture was stirred and heated at reflux for 3 hr., filtered, and the salts were washed with toluene. The filtrate was heated to reflux, and the tetrahydrofuran was replaced with toluene. Additional salts precipitated and were filtered off and washed with toluene. A viscous, yellow oil separated from the filtrate. The supernatant liquid was decanted and after devolatilization at 60° (0.05 mm.), the residue was dissolved in 50 ml. hot toluene and filtered. Cooling and filtration gave 16.4 g. of tan solids, m.p. 133-136.5°C. The filtrate was again devolatilized and the residue was recrystallized from 25 ml. toluene to give 19.0 g., m.p. 136-139.5°. One additional crop of 3.5 g., m.p. 145-154°, was obtained from the residue. When the combined crops were recrystallized from toluene, 26.5 g. (28 per cent) of impure p-phenylenebis(diphenylethoxysilane) which melted at 150-155° was obtained. An additional recrystallization from tetrahydrofuran gave 7.3 g. (8 per cent) of the purified product melting at 156-161° (reported 158-160°). The remaining material recovered from the recrystallization melted at 110-115°.

11. p-Phenylenebis(diphenylsilanol) (via the hydrolysis of p-phenylenebis(ethoxydiphenylsilane)): A solution of 1.2 g. (0.030 mole) of sodium hydroxide, 7 ml. of methyl alcohol and 1 ml. of water was added to a refluxing solution of 5.3 g. (0.010 mole) of p-phenylenebis(diphenylethoxysilane) in 10 ml. of tetrahydrofuran. The mixture was allowed to cool for 5 min., and a solution of 1.2 g. (0.030 mole) of sodium hydroxide in 8 ml. of water was added and swirled at 5-min. intervals for 30 min. This mixture was added to an ice-cold solution of 10.3 g. of potassium dihydrogen phosphate in 75 ml. of water and dried to give 4.0 g. (85 per cent) of crude p-phenylenebis(diphenylsilanol), m.p. 206-209°. The infrared band at 1,030 cm.$^{-1}$ (SiOEt) was no longer present. The crude product was combined with the product from the hydrolysis of p-phenylenebis(diphenylsilane) for purification. Hydrolysis of several combined samples of p-phenylenebis(ethoxydiphenylsilane), which melted within the range of 156-161° gave 86 per cent of p-phenylenebis(diphenylsilanol), m.p. 224-226° (reported, 225.5-227.0°).[3]

12. Chlorodiphenylsilane: (Method: Reference 28) A solution of 1.69 moles of phenylmagnesium bromide in 560 ml. of ether was added dropwise to a stirred solution of 101.6 g. (0.75 mole) of trichlorosilane in 125 ml. ether which was cooled to 5°. The addition required 2 hr. After the mixture was refluxed for 3.5 hr., cooled, and filtered, the filtrate and washings were devolatilized to 60° (15 mm.). Filtration and flash distillation gave 119 g. (76 per cent) of crude product, b.p. 108-152° (2-4 mm.). Redistillation through a 30-cm. vacuum-jacketed column packed with Berl saddles gave 83.6 g. (54 per cent) of chlorodiphenylsilane, b.p. 115-122° (1.5-2.0 mm.) (reported, 140-145° (7 mm.)).[28]

Two repetitions of the procedure afforded 51, 46, and 38 per cent yields of chlorodiphenylsilane, b.p. 146-152° (10.5 mm.), 116-122° (7 mm.), and 152-158° (9 mm.), respectively.

13. Dichlorophenylsilane: (Method: Reference 28) A solution of 1.0 mole (334 ml. of 3 M solution) of phenylmagnesium bromide in ether was added during 1.5 hr. to a stirred solution of 136 g. (1.0 mole) of trichlorosilane in 500 ml. of ether, which was maintained at 5° during the addition. The mixture was stirred 1 hr. at 5° and for two additional hours at room temperature. After the salts were filtered off and the filtrate was evaporated and fractionally distilled through a 30 cm. vacuum-jacketed column packed with Berl saddles, 81.0 g. (46 per cent) of dichlorophenylsilane, b.p. 115-118° (102 mm.) was obtained (reported, 65° (10 mm.)).[28]

A repetition of the experiment gave 36 per cent of diphenylchlorosilane boiling at 103° (52 mm.).

14. Chloromethylphenylsilane: (Method: Reference 29) A solution of 0.356 mole (119 ml. of 3 M solution) of methylmagnesium iodide in ether was added during 2 hr. to a stirred solution containing 63.1 g. (0.356 mole) of dichlorophenylsilane in 300 ml. of ether while the mixture was maintained at 0-5°. After the mixture was stirred for 1 hr. at 5°, ether was distilled out over a 3-hr. period, and petroleum ether (b.p. 60-90°) was added to the mixture to maintain a constant volume. The salts were filtered off, the solvents were evaporated, and the residue was fractionally distilled through a 20 cm. vacuum-jacketed column packed with glass helices to obtain 6.1 g. (11 per cent) of chloromethylphenylsilane, boiling at 114-115° (103 mm.) (reported, 115°(100 mm.)).[29]

15. p-Phenylenebis(diphenylsilane): (Method: Reference 6) A mixture of 8.4 g. (0.346 g. atoms) of magnesium (activated with iodine) and 30 ml. of tetrahydrofuran was treated with a solution of 40.8 g. (0.173 mole) of p-dibromobenzene, 79.2 g. (0.38 mole) of chlorodiphenylsilane, and 100 ml. of tetrahydrofuran during 1 hr. After the mixture was stirred and heated at reflux for 1.5 hr., the thick, gray mass was poured onto cracked ice. After 15 min., the aqueous phase was decanted and the thick precipitate was treated with 250 ml. of petroleum ether (b.p. 60-90°). This mixture was washed with two 250-ml. portions of water, filtered, and the filtrate evaporated to give 72 g. (94 per cent) of crude product, m.p. 84-90°. The crude material after three recrystallizations from petroleum ether (b.p. 60-90°) afforded 29.5 g. (39 per cent) of p-phenylenebis(diphenylsilane), m.p. 102-105° (reported 105-107°).[6] The infrared spectrum of this compound is reported in Fig. 6.

Anal. Calcd. for $C_{30}H_{26}Si_2$: C, 81.39; H, 5.92; Si, 12.69. Found: C, 81.37; H, 6.00; Si, 12.74.

One repetition of the experiment gave a 77 per cent yield of a semisolid product that was not purified, but was used directly in an hydrolysis experiment.

In a second repetition, 171.4 g. (85 per cent) of crude *p*-phenylenebis(diphenylsilane) was obtained. A portion of the material (50 g.) which was insoluble in hot petroleum ether (b.p. 60-90°) melted 155-165°. Two recrystallizations afforded 3.8 g. of a material melting at 199-200°. Elemental analyses for the compound correspond to the calculated percentages of elements in *p*-phenylenebis(diphenylsilane) or bis(*p*-diphenylsilylphenyl)diphenylsilane. The compound was insoluble in carbon tetrachloride, chloroform, dimethylsulfoxide, dimethylacetamide, and acetone.

Anal. Calcd. for $C_{30}H_{26}Si_2$: C, 81.39; H, 5.92; Si, 12.69; Calcd. for $C_{48}H_{40}Si_3$: C, 82.22; H, 5.75; Si, 12.02. Found: C, 81.81; H, 5.77; Si, 12.31.

The compound melting at 199-200° was too insoluble for obtaining a NMR spectrum, but the spectrum of the compound melting at 102-105° was consistent with the structure of *p*-phenylenebis(diphenylsilane). The following resonance peaks were observed: SiPh, δ = 7.28-7.80; SiH, δ = 5.49. The relative intensities of the peaks were 26:2.

Crystallization of the petroleum ether-soluble portion gave 39 g. of crude *p*-phenylenebis(diphenylsilane), m.p. 100-103°. A soluble oil (82 g.) was also recovered.

16. *p-Phenylenebis(diphenylsilanol) (via the hydrolysis of p-phenylenebis(diphenylsilane))*: About 25 mg. of sodium was added to a refluxing solution of 28.0 g. (0.0633 mole) of *p*-phenylenebis(diphenylsilane) in 18 ml. of anhydrous ethanol and 20 ml. of tetrahydrofuran. After refluxing for 5 hr. and cooling overnight, the mixture solidified to a white mass. The solid was heated to reflux to redissolve the solid, and a solution of 7.6 g. (0.19 mole) of sodium hydroxide in 6.3 ml. of methanol was added. After 5 min., a solution of 7.6 g. (0.19 mole) of sodium hydroxide in 50 ml. of water was added. The solution was stored 30 min. and poured into an ice-cold solution of 65 g. of potassium dihydrogen phosphate in 475 ml. of water. The white precipitate was filtered off and dried *in vacuo* to give 34.7 g. (115 per cent) of a white solid, m.p. 191-196° dec. Recrystallization from 1,300 ml. toluene gave 23.5 g. (78 per cent) of *p*-phenylenebis(diphenylsilanol), m.p. 224-226° (reported, 225.5 - 227.0°).[3] The infrared spectrum of the compound was consistent with its structure (Fig. 7).

Anal. Calcd. for $C_{30}H_{26}O_2Si_2$: C, 75.90; H, 5.52; Si, 11.83. Found: C, 76.87: H, 5.77; Si, 10.62.

Hydrolysis of the crude semi-solid p-phenylenebis(diphenylsilane) afforded, after one recrystallization from toluene, 37 g. (41 per cent) of p-phenylenebis(diphenylsilanol). Additional recrystallizations from toluene gave 29 g. of the silanol, which melted at 216-217°. The infrared spectrum of the sample was superimposable with the spectrum of the compound melting at 224-226°. Further recrystallizations of a portion of the material increased the melting point to 220-222°.

Hydrolysis of p-phenylenebis(diphenylsilane) that melted at 100-103° by the same procedure, after three recrystallizations from toluene, gave 74 per cent of p-phenylenebis(diphenylsilanol), m.p. 216-217°. The melting point did not change after additional recrystallizations.

Anal. Calcd. for $C_{30}H_{26}O_2Si_2$: C, 75.90; H, 5.52; Si, 11.83. Found: C, 76.19; H, 5.82; Si, 11.58.

The infrared spectra of the compounds melting at 216-217° and 224-226° did not differ. The NMR spectra of the two compounds were superimposable, but difficult to correlate with the structure of the compound. Resonance peaks were observed in the following regions: SiPh, δ = 7.18-7.62; SiOH, δ = 7.0; and Me (in toluene), δ = 2.08. The relative intensities of these peaks were 24:4.4:1.5.

B. Aminosilane and Silazane Monomers

1. Nonamethylcyclotrisilazane: Nonamethylcyclotrisilazane was redistilled and the fraction collected boiled at 122.5-126.0° (43 mm.) (reported, 96-97° (10 mm.)).[30]

2. Bis(methylamino)methylphenylsilane: (Method: Reference 30) Methylamine was introduced above the surface of a stirred solution of 76.4 g. (0.40 mole) of dichloromethylphenylsilane in 500 ml. of petroleum ether (b.p. 60-90°) which was maintained at 5°. When the methylamine began to reflux in a Dry Ice condenser connected to the system, the addition was stopped and the mixture was refluxed 1 hr. After the amine hydrochloride salts were filtered off, the solvent was removed from the filtrate and the residue was distilled through a 30-cm., vacuum-jacketed column. Bis(methylamino)methylphenylsilane (34.2 g., 48 per cent) was collected as a fraction boiling at 95-96° (7 mm.); n_D^{20} 1.5116 (reported, 95-96° (6 mm.); n_D^{25} 1.5090).[30]

3. Bis(methylamino)diphenylsilane: (Method: Reference 14) A flow of methylamine was introduced above a cooled and stirred solution of 61 g. (0.25 mole) of dichlorodiphenylsilane in 1.8 liters of petroleum ether (b.p. 60-90°). The flow of amine was adjusted so that the temperature of the solution

did not exceed 15°. When the addition was complete, the mixture was heated at reflux for 1 hr., cooled, and filtered. After the solvent was distilled off, fractional distillation of the residue gave 48 g. (82 per cent) of bis(methylamino)diphenylsilane, b.p. 105-108° (0.1 mm.); n_D^{28} 1.5693 (reported, 108-112° (0.1 mm.); n_D^{27} 1.5690).[30]

4. Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: (Method: Reference 31) Excess methyl amine was added to a solution of 38.0 g. (0.137 mole) of 1,5-dichlorohexamethyltrisiloxane in 300 ml. of petroleum ether (b.p. 60-90°) at 25°. After the addition was completed (1-1/2 hr.), the reaction mixture was filtered, stripped of solvent, and distilled to give 15.5 g. (48.3 per cent) of the trisilacyclohexane boiling at 64-70° (21 mm.), n_D^{27} 1.4062 (reported, 65-70 (21 mm.); n_D^{27} 1.4059[31] and 5.3 g. (14.5 per cent) of 1,5-bismethylaminohexamethyltrisiloxane boiling at 93-95° (20 mm.), n_D^{27} 1.4108, (reported, 97-98 (20 mm.), n_D^{27} 1.4070).[31]

C. Poly(p-phenylenesiloxanes)

1. Polymerization of p-Phenylenedisilanols and Cyclotrisilazanes or Silylamines: Preliminary Experiments: In typical experiments, the following procedure was used: A mixture of 0.436 g. (0.00166 mole) of nonamethylcyclotrisilazane, 2.374 g. (0.00500 mole) of p-phenylenebis(diphenylsilanol), and 10 ml. of toluene was heated at 100-115° for 24 hr., and the methylamine evolved during the reaction was swept into a standard acid solution with a slow stream of dry nitrogen. The rate of polymerization was measured by back-titrating the standard acid solution at periodic intervals: 0.5 hr., 0.5 per cent; 1.0 hr., 5.3 per cent; 2 hr., 27.1 per cent; 4 hr., 35.5 per cent; and 24 hr., 51.6 per cent. When the toluene was distilled off and the residue was devolatilized at 150° for 1 hr., 2.40 g. (91 per cent) of the polymer was obtained. The polymer sintered at 220-245°, and the specific viscosity of a 0.5 per cent solution of the polymer in toluene was 0.54 at 30°. Its infrared spectrum is reported in Fig. 8.

Anal. Calcd. for $(C_{32}H_{30}O_2Si_3)_n$: C, 72.40; H, 5.70; Si, 15.88. Found: C, 72.03; H, 5.89; Si, 16.07.

When the polymer was heated at 300° for 1 hr. under reduced pressure, the specific viscosity increased to 0.87.

Anal. Calcd. for $(C_{32}H_{30}O_2Si_3)_n$: C, 72.40; H, 5.70; Si, 15.88. Found: C, 70.30; H 5.90; Si, 15.65.

A polymer, similarly prepared from equimolar quantities of p-phenylenebis(diphenylsilanol) and diphenylbis(methylamino)silane, had a specific viscosity (c = 0.5 per cent in toluene at 30°) of 0.2. The infrared spectrum of the polymer is reported in Fig. 9.

Anal. Calcd. for $C_{42}H_{34}O_2Si_3$: C, 77.02; H, 5.23; Si, 12.87. Found: C, 75.40; H, 5.35; Si, 14.75.

This polymer, heated at 280° for 1 hr. under reduced pressure, became partly insoluble in toluene. Data relating to a series of similar experiments is reported in Table I.

Thermogravimetric analyses of these two polymers are reported in Fig. 37 and differential thermal analyses in Fig. 40.

2. Polymers from p-phenylenedisilanols and silazanes, silylamines, or siloxazanes:

Procedure A: A solution of 1.422 g. (0.003 mole) of p-phenylenebis-(diphenylsilanol) and 0.8565 g. (0.0015 mole) of hexamethyl-2,4,6,8-tetraphenyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane in 1 ml. of xylene was heated at 150-175° for 3 hr., then devolatilized at 150° (0.1 mm.) for 1 hr. The polymer, 2.114 g. (97 per cent), was a light colored, brittle solid, and had a specific viscosity of 0.30 in a 0.5 per cent solution in toluene at 30°. A film prepared from a toluene solution was hard and brittle.

Procedure B: A mixture of 1.130 g. (0.005 mole) of p-phenylenebis-(dimethylsilanol) and 1.21 g. (0.005 mole) bis(methylamino)diphenylsilane was heated without solvent at 160-195° for 4 hr., then at 200° (0.1 mm.) for 1 hr. The polymer, 2.06 g. (103 per cent), was a clear, slightly tacky, elastic solid, and a 0.5 per cent solution in toluene had a specific viscosity of 0.63 at 30°. A soft, elastic film was prepared from a toluene solution. The film, after being heated at 125° overnight in an oven, was harder and still elastic.

Data relating to similar experiments are reported in Tables II and III. Unless stated otherwise, all polymers were devolatilized by heating 1 hr. at 150° (0.1 mm.).

One of the polymers was characterized in detail. A solution of 1.422 g. (0.003 mole) of p-phenylenebis(diphenylsilanol) and 0.705 g. (0.003 mole) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane in 5 ml. of toluene was heated at 112-115° for 24 hr. The solvent was stripped off and the residue was heated at 150° (0.1 mm.) for 1 hr. The polymer, a white, elastic solid, was insoluble in toluene and dimethylacetamide.

Anal. Calcd. for $(C_{36}H_{42}O_4Si_5)_n$: C, 63.66; H, 6.24; Si, 20.68. Found: C, 63.44; H, 6.27; Si, 20.52.

TABLE I

POLYMERIZATION OF p-PHENYLENEDISILANES WITH SILAZANES AND SILYLAMINES: PRELIMINARY EXPERIMENTS

Reactants		Per Cent Amine Evolved After					Polymer Yield	Softening Point	Specific Viscosity in Toluene
Silanol	Silazane or Silylamine	0.5 Hr.	1 Hr.	2 Hr.	4 Hr.	24 Hr.	(%)	(°C)	(c = 0.5%)
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Nonamethylcyclotrisilazane (0.00166 mole)	0.5	5.3	27.1	35.5	51.6	91	Sinters 220-45°	0.54
		8.0	20.0	43.5	66.3	91.0	93	Sinters 225-35°	0.48
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Nonamethylcyclotrisilazane (0.00200 mole)	12.0	27.3	49.0	80.0	99.5	92	Sinters 135-50°	0.18
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Hexaphenyl-1,3,5-trimethyl-cyclotrisilazane (0.00166 mole)	0.0	0.0	1.3	1.3	3.6	-	-	-
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Hexaphenyl-1,3,5-trimethyl-cyclotrisilazane (0.00166 mole)	0.6	1.3	1.3	1.3	-	-	-	0.05
p-Phenylenebis-(dimethylsilanol) (0.0100 mole)	Nonamethylcyclotrisilazane (0.00333 mole)	7.2	13.3	25.0	50.5	85.0	99	-	-
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	cis-2,4,6-Triphenylhexa-methylcyclotrisilazane (0.00166 mole)	0.6	0.6	0.6	-	1.9	-	-	0.02
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Diphenylbis(methylamino)-silane (0.00500 mole)	35.4	38.7	40.0	41.2	43.5	96	-	0.02
		75.0	80.2	83.0	87.0	91.0	93	Some shrinkage at 200°	0.19
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Phenylmethylbis(methyl-amino)silane (0.00500 mole)	88.2	93.1	96.7	96.7	98.7	95	-	0.04

TABLE II

POLYMERS FROM p-PHENYLENEDISILANOLS AND SILOXAZANES

	Silanol	Siloxazane	Procedure (solvent) (°C/hr)	Amine Evolved (%)	Polymer Yield (%)	Specific Viscosity (toluene, 30°) (C = 0.5%)	Polymer Description	Film Description
1.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	$(SiMePhOSiMePhNMe)_2$ (0.0025 mole)	A Toluene 112-125°/30 hr	53	93	0.083	Light colored, brittle solid	Hard, brittle
2.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$(SiMePhOSiMePhNMe)_2$ (0.0015 mole)	A Xylene 150-175°/3 hr	-	97	0.30	Light colored, brittle	Hard, brittle
3.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMePhOSiMePhNMe)_2$ (0.001425 mole)	A Xylene 150°/6 hr	63	103	0.13 Some insoluble	Light colored, elastic solid	Soft, slightly tacky
4.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMe_2OSiMe_2NMe)_2$ (0.001425 mole)	A Xylene 144-150°/8 hr	69	100	0.07	Light colored, tacky gum	Tacky gum
5.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMe_2OSiMe_2NMe)_2$ (0.001425 mole)	A Xylene 135°/17 hr	86	100	0.09	Light colored, tacky gum	Tacky gum
6.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$\overline{SiMe_2OSiMe_2OSiMe_2N}Me$ (0.003 mole)	A Toluene 112-115°/24 hr	89	-	Insoluble	A white elastic solid	-
7.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$\overline{SiMe_2OSiMe_2OSiMe_2N}Me$ (0.003 mole)	A Xylene 130-5°/5.5 hr	-	-	-	Clear, viscous solution	Tacky, rubbery film cured in air oven at 145°/24 hr to a strong, elastic film
8.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$\overline{SiMe_2OSiMe_2OSiMe_2N}Me$ (0.003 mole)	A Xylene 130-5°/5.5 hr	-	-	0.07	White, elastic gum	Cured in air oven at 145°/48 hr to a strong, elastic film

TABLE III

POLYMERS FROM p-PHENYLENEDISILANOLS AND SILAZANES OR SILYLAMINES

	Silanol	Silazane or Silylamine	Procedure (solvent) (°C/hr)	Amine Evolved (%)	Polymer Yield (%)	Specific Viscosity (toluene, 30°) (C = 0.5%)	Polymer Description	Film Description
1.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	A Toluene 110°/24 hr 160°/19 hr	36.2	107	0.014	Light colored, elastic gum	Soft, tacky, then became hard and brittle
2.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	B 160-195°/4 hr 200°(0.1 mm)/1 hr	77.3 95.0	102 102	0.63 0.32	Clear, slightly tacky elastic solid	Light colored, soft, elastic. After 18 hr., 125°, harder, but still elastic.
3.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Dimethyldianilinosilane (0.005 mole)	B 165°/0.5 hr 200°/0.1 mm)/5 hr	-	91	0.33	Violet colored, soft tacky gum	Soft, tacky
4.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Dimethyldianilinosilane (0.005 mole)	B 200°/1 hr 200-220°(0.1 mm)/2.5 hr	-	87	0.31	Violet colored, tacky gum	Soft, tacky
5.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	B 120-225°/5 hr 220°(0.1 mm)/1 hr	75	89	Insoluble	Clear, brittle solid	-
6.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	Dimethyldianilinosilane (0.003 mole)	B 180°/2 hr 210°(0.1 mm)/4.5 hr	-	87	Insoluble	Dark colored, brittle solid	-
7	p-Phenylenebis(diphenylsilanol) (0.003 mole)	1,3-Dianilinotetramethyldisiloxane (0.003 mole)	B 170°/1 hr 200°(0.1 mm)/4 hr	-	93	Insoluble	Dark colored, slightly elastic solid	-
8.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	Nonamethylcyclotrisilazane (0.00166 mole)	A Toluene 112-120°/24 hr	70	96	Insoluble	White, hard solid	White powder from dimethylacetamide
9.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	1,3-Dianilinotetramethyldisiloxane (0.003 mole)	A Toluene 125°/6 hr	-	-	0.11	Brown, hard solid	Tough, flexible
10.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	Dimethyldianilinosilane (0.00285 mole)	B 180°/1 hr 200°(0.1 mm)/4 hr	-	96	Insoluble	Dark colored, elastic solid	-

Differential thermal analysis of the polymer revealed no major phase changes or melting points from 25-500° (Fig. 41). The procedural decomposition temperature (weight ≥ 5 per cent/hr) on thermogravimetric analysis was 450° (Fig. 39).

Similar monomer compositions remained soluble throughout the polymerization in solvent, and one of these solutions (Table II, No. 7) containing a low molecular weight polymer was cast as a film. The infrared spectrum of one of the soluble polymers is reported in Fig. 10. The vacuum-ultraviolet evaluation of such a film is described in Section IV. K. of this report.

D. Benzoxazole Monomers, Intermediates, and Model Compounds

1. 3,3'-Dihydroxybenzidine: (Method: Reference 8) A mixture of 30.0 g. (0.123 mole) of 3,3'-dimethoxybenzidine and 500 ml. of 48 per cent hydrobromic acid was refluxed for 24 hr., cooled and neutralized with 300 ml. of saturated sodium acetate. The grey precipitate was filtered off, washed twice with hot ethanol and dried under vacuum to give 22.9 g. (86 per cent) of 3,3'-dihydroxybenzidine, m.p. 283-285° (reported, 292°).[7] The product could not be recrystallized from aqueous pyridine by the procedure described in the literature.[32]

2. 3,3'-Dihydroxybenzidine dihydrochloride:

a. Via the hydriodic acid cleavage of 3,3'-dimethoxybenzidine: (Method: Reference 7) After a mixture of 24.4 g. (0.10 mole) of 3,3'-dimethoxybenzidine and 240 ml. of 57 per cent hydriodic acid was refluxed 24 hr. under an atmosphere of nitrogen, the excess hydriodic acid was removed under reduced pressure. The residue, dissolved in 600 ml. of boiling water, was filtered, treated with 15 g. of sodium bisulfite to remove iodine, refiltered with charcoal, and the filtrate was neutralized with 250 ml. of saturated sodium acetate solution. The precipitated 3,3'-dihydroxybenzidine was boiled in hot ethanol then dissolved in 250 ml. of water by the addition of concentrated hydrochloric acid until the pH of the solution was 2. After the solution was filtered with charcoal, the hydrochloride salt was precipitated by the addition of concentrated hydrochloric acid. When the salt was collected by filtration, washed with 6 N hydrochloric acid, and dried in vacuum over potassium hydroxide, 10.9 g. (38 per cent) of 3,3'-dihydroxybenzidine dihydrochloride was obtained. The infrared spectrum is reported in Fig. 11.

Anal. Calcd. for $C_{12}H_{14}Cl_2N_2O_2$: C, 49.84; H, 4.88; N, 9.69; Neut. Equiv., 145. Found: C, 50.06; H, 4.92; N, 9.55; Neut. Equiv., 141.

b. Via the hydrobromic acid cleavage of 3,3'-dimethoxybenzidine: After a mixture of 30.0 g. (0.123 mole) of 3,3'-dimethoxybenzidine and 500 ml. of 48 per cent hydrobromic acid was refluxed 24 hr., the insoluble portion was collected by filtration, dissolved in 600 ml. of hot water, and neutralized with 300 ml. of saturated sodium acetate solution. The insoluble portion was again collected by filtration, washed with water, slurried in 150 ml. of hot ethanol, collected by filtration, and washed with hot ethanol. When the product was purified by the same procedure used in the hydriodic acid cleavage, 20.1 g. (56 per cent) of 3,3'-dihydroxybenzidine dihydrochloride with a neutralization equivalent of 146 was obtained. A repetition of the experiment gave 59 per cent of the hydrochloride with a neutralization equivalent of 146.

3. 2,2'-Dinitro-*p*,*p*'-biphenol: (Method: Reference 8) To a stirred suspension of 84.3 g. (0.453 mole) of *p*,*p*'-biphenol in 1,000 ml. of glacial acetic acid at 10-20° was slowly added 300 ml. of nitric acid during 45 min. The mixture was stirred without cooling for 45 min., then poured into 2 liters of ice water. The orange-brown solid was filtered off, slurried in ethanol, refiltered, washed with ethanol and ether, and dried to give 117 g. (94 per cent) of 2,2'-dinitro-*p*,*p*'-biphenol, m.p. 274-276°C (reported, 286°).[10]

Repetition of the experiment gave 120 g. (96 per cent) of crude material which melted at 270-275°. Recrystallization of 30 g. of the crude product from 4.5 liters of xylene afforded 18.2 g. of 2,2'-dinitro-*p*,*p*'-biphenol, m.p. 279-281°. In a subsequent experiment, the crude product was recrystallized from a 30:70 mixture of cyclohexane-xylene to obtain 47 per cent of purified 2,2'-dinitro-*p*,*p*'-biphenol, m.p. 277-279°C.

4. 2,2'-Diamino-*p*,*p*'-biphenol dihydrochloride: Sodium hydrosulfite (115 g., 0.66 mole) was added in portions over a 1-hr. period to a stirred mixture of 28.0 g. (0.101 mole) of 2,2'-dinitro-*p*,*p*'-biphenol in 1,600 ml. of concentrated ammonium hydroxide at 35°. Filtration gave a peach-colored solid which was added immediately to 500 ml. of stirred 6 N hydrochloric acid. The yellow solid was collected by filtration and dissolved in 500 ml. of water.

After the solution was filtered with charcoal and treated with 400 ml. of concentrated hydrochloric acid, 14.9 g. (51 per cent) of 2,2'-diamino-*p*,*p*'-biphenol dihydrochloride precipitated. The product was collected by filtration, washed with 6 N hydrochloric acid, and dried under vacuum. The infrared spectrum is reported in Fig. 12.

Anal. Calcd. for $C_{21}H_{41}Cl_2N_2O_2$: C, 49.84; H, 4.88; N, 9.60; Neut. Equiv., 145. Found: C, 49.29; H, 4.62; N, 9.62, Neut Equiv., 138.

Four repetitions of the experiment gave 78, 77, 60 and 48 per cent yields of the same product with a neutralization equivalent of 144.

5. 4,6-Diaminoresorcinol dihydrochloride (attempted): A solution of 35.0 g. (0.411 mole) of potassium nitrite in 50 ml. of water was added to a stirred mixture of 37.2 g. (0.40 mole) of aniline in 100 ml. of concentrated hydrochloric acid and 400 g. of ice. After 10 min., a solution of 22.0 g. (0.20 mole) of resorcinol in 100 ml. of water was added, and the mixture was poured into a solution of 48 g. (1.2 mole) of sodium hydroxide in 800 ml. of water and 800 g. of ice. The mixture was stirred 1 hr., then the diazo compound was collected by filtration, washed with two 350-ml. portions of saturated sodium chloride solution, and pressed with a rubber dam.

To a stirred mixture of about three-fourths of the diazo compound, 30 g. (0.252 g. atom) of tin, and 3 liters of water, which was heated at 50°, was added 500 ml. of concentrated hydrochloric acid over a period of 1 hr. Stirring and heating was continued 3 hr. when the filtrate of samples taken from the mixture became yellow-brown. The mixture was filtered and the filtrate was treated with hydrogen sulfide until tin sulfide no longer precipitated. After the sulfide was removed by filtration and the filtrate was evaporated, the residue was treated twice with a mixture of 60 ml. of water, 30 ml. of concentrated hydrochloric acid, and 30 ml. of alcohol. Purification of the 36.6 g. of crude material was effected by precipitation of the hydrochloride salt from an aqueous solution with concentrated hydrochloric acid. The purified product, which weighed 13.0 g., was not identified as 4,6-diaminoresorcinol hydrochloride.

Anal. Calcd. for $C_6H_{10}Cl_2N_2O_2$: C, 33.82; H, 4.73; N, 13.15. Found: C, 0.0; H, 0.0; N, 0.0.

6. Isophthalamide: A stirred solution of 40.6 g. (0.20 mole) of isophthalyl chloride in 500 ml. of ether was treated with 55 ml. of concentrated ammonium hydroxide during 30 min. After the mixture was stirred an additional 30 min. and filtered, 40.0 g. of crude product was obtained. Recrystallization from 2,500 ml. of water gave 22.2 g. (72 per cent) of isophthalamide, m.p. 268-271° (reported, 280°).[33]

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.44; H, 4.69; N, 15.55.

When the procedure was repeated using recrystallized isophthalyl chloride (m.p. 43.5-45.0°), 20.4 g. (66 per cent) of isophthalamide, m.p. 270-272° (from water), was obtained.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.62; H, 4.72; N, 15.69, 15.76.

7. Terephthalamide: To a stirred solution of 40.6 g. (0.20 mole) of terephthalyl chloride in 700 ml. of ether was added 60 ml. of concentrated ammonium hydroxide over a 30-min. period. After the mixture was stirred an additional 30 min. and filtered, 55.6 g. of a crude material was obtained, which was boiled with 5 liters of water. Upon filtration, 18.0 g. of insoluble material which melted at 323-326° was obtained. Terephthalamide, m.p. 325-327°, crystallized from the filtrate. The infrared spectra of the two compounds were very similar, and the combined yield of the two fractions was 95 per cent.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H. 4.91; N, 17.07. Found: C, 58.66; H, 4.78; N, 13.98, 13.89.

8. Diphenyl terephthalate: A stirred mixture of 20.3 g. (0.10 mole) of terephthalyl chloride and 18.8 g. (0.20 mole) of phenol was heated at 90-110°C under nitrogen for 30 min. Subsequently, the solid mass was boiled in 800 ml. of ethanol. When the mixture was cooled, filtered, and the insoluble portion recrystallized from tetrahydrofuran, 19.0 g. (60 per cent) of diphenyl terephthalate was obtained, m.p. 196-198° (reported, 191°).[34]

9. Diphenyl isophthalate: When a mixture of 20.3 g. (0.10 mole) of isophthalyl chloride and 18.8 g. (0.20 mole) of phenol was heated at 100° for an hour, hydrochloric acid was evolved. The liquid was cooled, added to 400 ml. of ethanol, and the heavy white precipitate was filtered off to give 12.7 g. (40 per cent) of crude product. Recrystallization from ethanol afforded 7.0 g. (22 per cent) of diphenyl isophthalate, m.p. 136-137.5° (reported, m.p. 120°).[34]

10. 2,2'-Diphenyl-5,5'-bibenzoxazole: After a mixture of 1.446 g. (0.00500 mole) of 2,2'-diamino-p,p'-biphenol dihydrochloride and 60.0 g. of 116 per cent polyphosphoric acid was heated and stirred for 2.4 hr. under a flow of dry nitrogen, 1.221 g. (0.0100 mole) of benzoic acid was added and the mixture was heated at 200° for 19 hr. The hot, dark brown solution was poured into 300 ml. of water, and the precipitated material was collected by filtration, washed with water, and methanol, and dried under reduced pressure at 70°. The crude product (1.89 g., 96 per cent), m.p. 230-240°, gave 0.96 g. (50 per cent) of the purified 2,2'-diphenyl-5,5'-bibenzoxazole, m.p. 239-244° after recrystallization from dimethylformamide. A second recrystallization from dimethylformamide increased the melting point to 244-245.5°. The infrared spectrum is reported in Fig. 13.

Anal. Calcd. for $C_{26}H_{16}N_2O_2$: C, 80.39; H, 4.15; N, 7.21. Found: C, 80.25; H, 4.29; N, 7.25.

11. 2,2'-Diphenyl-6,6'-bibenzoxazole: A procedure similar to the method described in paragraph 14. D. 10. was employed to convert 1.446 g. (0.00500

mole) of 3,3'-dihydroxybenzidine dihydrochloride to 1.61 g. (83 per cent) of crude 2,2'-diphenyl-6,6'-bibenzoxazole, m.p. 238-242°. Recrystallization of the crude material from dimethylformamide gave 0.69 g. (36 per cent) of the purified product which melted at 243-246° (reported, 249-250°).35/ The infrared spectrum is reported in Fig. 14.

Anal. Calcd. for $C_{26}H_{16}N_2O_2$: C, 80.39; H, 4.15; N, 7.21. Found; C, 79.90; H, 4.19; N, 7.13.

12. N,N'-Dibenzoyl-3,3'-dihydroxybenzidine: A solution of 2.809 g. (0.0200 mole) of benzoyl chloride in 6.7 ml. of cyclohexanone was added dropwise during 30 min. to a stirred solution of 2.892 (0.0100 mole) of 3,3'-dihydroxybenzidine dihydrochloride in 23 ml. of dimethylacetamide and 7.1 ml. of pyridine at 0°. A yellow-orange precipitate formed near the end of the addition. The mixture was stirred for an additional 3 hr. at 0°, allowed to warm to 25°, and poured into 200 ml. of water. When the precipitated material was collected by filtration, washed with water and methanol, and dried at 70° in vacuum, 4.2 g. (98 per cent) of crude product, m.p. 322-326°, was obtained. Recrystallization from 100 ml. of dimethylformamide afforded 2.5 g. (58 per cent) of N,N'-dibenzoyl-3,3'-dihydroxybenzidine, m.p. 323-327°.

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.17, 73.02; H, 4.98, 5.11; N, 6.86, 6.84.

In a repetition of the experiment, 4.0 g. (94 per cent) of the crude product was obtained. The infrared spectra, Fig. 15, of the crude and recrystallized products were superimposable.

13. N,N'-Dibenzoyl-2,2'-diamino-p,p'-biphenol: When 2.892 g. (0.0100 mole) of 2,2'-diamino-p,p'-biphenol hydrochloride was treated with 2.809 (0.0200 mole) of benzoyl chloride by the procedure described in paragraph IV. D. 12., 3.7 g. (87 per cent) of crude N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenol, which melted at 319-321°, was obtained. Recrystallization from a dimethylformamide-ethanol mixture afforded 2.5 g. (59 per cent) of the purified product, m.p. 322-326°. The infrared spectra of the compound, Fig. 16, did not change after recrystallization.

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.15; N, 6.60. Found: C, 72.77, 72.93; H, 4.88, 4.96; N, 6.92, 6.87.

A repetition of the experiment gave 93 per cent yield of the crude material.

14. N,N'-Dibenzoyl-3,3'-dimethoxybenzidine: A solution of 5.6 g. (0.040 mole) of benzoyl chloride in 50 ml. of benzene was added slowly to a stirred solution of 4.9 g. (0.020 mole) of 3,3'-dimethoxybenzidine in 50 ml. of pyridine. When the precipitated material was collected by filtration, washed sequentially with benzene, ethanol, water, and ethanol, and dried, 6.5 g. (77 per cent) of crude N,N'-dibenzoyl-3,3'-dimethoxybenzidine was obtained. One recrystallization from dimethylformamide gave 5.7 g. (63 per cent) of the purified compound, m.p. 245-247° (reported, 236°).36/ The infrared spectrum is reported in Fig. 17.

15. Thermal decomposition of N,N'-dibenzoyl-3,3'-dihydroxybenzidine: The infrared spectrum of a small quantity of the compound, heated under nitrogen at 150° for 2 hr., did not change. When the compound was heated for 2 hr. at 300° under nitrogen, the color turned gray and the material which became partly fused, melted at 219-224°. An infrared spectrum of the product (Fig. 18) was similar to the closed ring analog, 2,2'-diphenyl-6,6'-dibenzoxazole (Fig. 14) (reported, m.p. 249-250°).35/

When 1.273 g. of N,N'-dibenzoyl-3,3'-dihydroxybenzidine was heated at 100° for 3 hr. in a mixture of 7 ml. of dimethylacetamide, 2.2 ml. of cyclohexanone, and 2.4 ml. of pyridine, most of the compound dissolved. The product was poured into water and the precipitate was collected by filtration, washed with water and methanol, and dried under reduced pressure. A total of 1.14 g. (90 per cent) of N,N'-dibenzoyl-3,3'-dihydroxybenzidine, m.p. 314-320°, was recovered.

16. Thermal decomposition of N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenol: The infrared spectra of samples of this compound did not change significantly when the samples were heated at 150° and 300° for 2 hr. under nitrogen. The spectrum of the material heated at 300° is reported in Fig. 19.

When 1.273 g. of N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenol was heated 3 hr. at 100° in solution with pyridine, dimethylacetamide, and cyclohexanone in the manner described in paragraph IV. D. 15, 1.10 g. (86 per cent) of the compound was recovered. The infrared spectrum of the product was the same as that of the starting material.

17. Thermal decomposition of N,N'-dibenzoyl-3,3'-dimethoxybenzidine: The compound, heated in a differential thermal analyzer at 15°/min under nitrogen showed no evidence of decomposition below its melting point. A melting endotherm at about 325° was observed as well as a decomposition exotherm, which showed a peak at about 440°. The infrared spectrum of a sample heated to 325° under these conditions and cooled rapidly showed a loss of the amide II absorption band at 1520 cm.$^{-1}$.

When 0.37 g. of the compound was heated at 325° for 2 hr. under nitrogen, a drop of a liquid, which was identified as methyl benzoate by its infrared spectrum, distilled. The infrared spectrum of the residue indicates the presence of residual ester, and the NH absorption at 3,350 $cm.^{-1}$ had shifted to 3,450 $cm.^{-1}$, indicating a decrease in hydrogen bonding.

E. Poly(benzoxazoles)

1. Polymers from bis(aminophenols) and phthalyl chlorides: 3,3'-Dihydroxybenzidine dihydrochloride or 2,2'-diamino-p,p'-biphenol dihydrochloride was polymerized with isophthalyl or terephthalyl chloride by the method reported by Kubota.[13] The results are summarized in Table IV. The infrared spectra of the polymers from isophthalyl chloride and 2,2'-diamino-p,p'-biphenol and 3,3'-dihydroxybenzidine are shown in Figs. 20 and 21. The following is a typical example of the procedure that was employed. A solution of 4.337 g. (0.015 mole) of 3,3'-dihydroxybenzidine dihydrochloride in 33 ml. of dimethylacetamide and 5.2 ml. of pyridine was added dropwise during 30 min. to a stirred mixture of 3.045 g. (0.015 mole) of tetraphthalyl chloride in 10 ml. of cyclohexanone at 0°. A yellow precipitate formed immediately and the mixture was stirred at room temperature for 3 hr. and let stand overnight. The mixture was poured into 250 ml. of water and the yellow-orange precipitate was filtered off, washed with water and methanol and dried under reduced pressure at 70° to give 4.28 g. (82 per cent) of a yellow-green powder which did not melt at 380°. The specific viscosity of the polymer ($c = 0.5$ per cent in sulfuric acid at 30°) was 0.13.

2. Polymer from 3,3'-dihydroxybenzidine and terephthalamide in polyphosphoric acid: A mixture of 60.0 g. of 116 per cent polyphosphoric acid and 1.446 g. (0.00500 mole) of 3,3'-dihyroxybenzidine dihydrochloride was heated and stirred for 2.5 hr. at 150° under a flow of dry nitrogen. Terephthalamide (0.821 g., 0.00500 mole) was added and heating was continued at 200° for 19 hr. The polymer was isolated by pouring the hot solution into water, washing the precipitated mass with water, first by decantation and then in a Waring Blendor, and storing the product in 10 per cent sodium bicarbonate overnight. Subsequent filtration, washings with water and methanol, and drying under vacuum at 70° afforded 1.57 g. (101 per cent) of the polybenzoxazole which did not melt below 450°. The specific viscosity of a 0.5 per cent solution in sulfuric acid at 30° was 0.22. Its infrared spectrum is reported in Fig. 22. DTA and TGA data are presented in Figs. 38 and 42.

Anal. Calcd. for $(C_{20}H_{10}N_2O_2)_n$: C, 77.41; H, 3.25; N, 9.03. Found: C, 73.86; H, 3.76; N, 6.68.

TABLE IV

POLYMERIZATION OF PHTHALYL CHLORIDES WITH BIS(AMINOPHENOLS)

	Acid Chloride	Mode of Addition	Base	Final Temp. (°C)	Yield (%)	Specific Viscosity (sulfuric acid, 30°) (C = 0.5%)	Physical Appearance
3,3'-Dihydroxybenzidine Dihydrochloride with:							
1.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Pyridine	25	94	0.14	Olive green powder
2.	Isophthalyl chloride[a]	Acid chloride to aminophenol[c]	Pyridine	25	110	0.12	Olive green powder[d]
3.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	Pyridine	25	107	0.17	Olive green powder[f]
4.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c,g]	Pyridine	25	100	0.09[h]	Brown powder
5.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	Pyridine	100	94	0.11	Light green powder
6.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	s-Collidine	100	99	0.13	Green powder
7.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	Quinoline	100	104	0.18	Green powder
8.	Terephthalyl chloride[b,i]	Aminophenol to acid chloride[c]	Pyridine	25	82	0.13	Yellow green powder
2,2'-Diamino-p,p'-biphenol Dihydrochloride with:							
9.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Pyridine	25	96	0.07	Olive green powder
10.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	Pyridine	25	104	0.07	Tan powder
11.	Isophthalyl chloride[e]	Acid chloride to aminophenol[c]	Pyridine	100	94	0.07	Gray powder
12.	Terephthalyl chloride[b,i]	Aminophenol to acid chloride[c]	Pyridine	25	84	0.07	Yellow green powder

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a/ Melted partially at 42-4°.
b/ Did not form a homogeneous solution.
c/ Dissolved in freshly distilled cyclohexanone and dimethylacetamide.
d/ A 5 per cent solution of the polymer in dimethylacetamide evaporated under a heat lamp in air, produced a dark brown, brittle film. The polymer was soluble in hexamethylphosphoramide to the extent of 4.8 g. in 100 ml.
e/ Melting point 43.5-45° after one recrystallization from heptane.
f/ When a 5 per cent solution of the polymer in dimethylacetamide was evaporated at 200°, a brittle film was obtained. The powder film, heated 30 min. at 250-300° (0.1 mm.), became insoluble in cold dimethylacetamide. The specific viscosity of the resulting material was 0.15 (0.5 per cent in sulfuric acid).
g/ The reactants were maintained at -20° during the addition and a 100 per cent molar excess of pyridine was used.
h/ After the polymer was heated at 150° for 2 hr. under nitrogen, the specific viscosity was 0.11 (C = 0.5 per cent in sulfuric acid).
i/ Melting point 81-6°.

3. Polymer from 2,2'-diamino-p,p'-biphenol and terephthalamide in polyphosphoric acid: In a procedure similar to paragraph IV. E. 2, 1.446 g. (0.00500 mole) of 2,2'-diamino-p,p'-biphenol and 0.821 g. (0.00500 mole) of terephthalamide in 60.0 g. of polyphosphoric acid gave 1.62 g. (104 per cent) of the polybenzoxazole. The polymer did not melt below 450° and had a specific viscosity in toluene at 30° (c = 0.5 per cent) of 2.54. The infrared spectrum of the polymer is reported in Fig. 23. The polymer (0.05 g. in 10 ml. of solvent) was insoluble in boiling dimethylacetamide, chlorobenzene, 90 per cent formic acid, trifluoroacetic acid, 6 N sodium hydroxide, and methylpyrolidone. The polymer was also insoluble in m-cresol and 5 per cent lithium chloride in dimethylacetamide at room temperature. DTA and TGA data are presented in Figs. 38 and 42.

Anal. Calcd. for $(C_{20}H_{10}N_2O_2)_n$: C, 77.41; H, 3.25; N, 9.03. Found: C, 71.17; H, 3.51; N, 6.42.

When the procedure was repeated with 6.506 g. (0.0225 mole) of 2,2'-diamino-p,p'-biphenol dihydrochloride and 3.694 g. (0.0225 mole) of terephthalamide in 270 g. of polyphosphoric acid, the mixture gelled after 18 hr. The polymer, blended with water, treated with 10 per cent sodium bicarbonate solution, and washed with water and methanol, gave 7.1 g. (101 per cent) of the polybenzoxazole, η_{sp} = 1.17 and 3.98 (c = 0.1 and 0.2 per cent in sulfuric acid at 30°, respectively.

4. Other polymers from bis(aminophenols) and phthalamides in polyphosphoric acid: The polymers described in Table V were prepared by the procedure described in paragraphs IV. E.2. and IV. E.3.

5. Polymer from isophthalyl chloride and 2,2'-diamino-p,p'-biphenol in polyphosphoric acid (attempted): A mixture of 60.0 g. of 116 per cent polyphosphoric acid and 1.446 g. (0.00500 mole) of 3,3'-diamino-4,4'-biphenol dihydrochloride was stirred and heated for 3 hr. at 150° under a flow of dry nitrogen. Isophthalyl chloride (0.821 g., 0.00500 mole) was added and the mixture was heated at 200° for 19 hr. Some of the isophthalyl chloride sublimed out of the reaction mixture; therefore, the experiment was discontinued.

6. Polymer from 2,2'-diamino-p,p'-biphenol and isophthalyl chloride (by interfacial polycondensation): A solution of 1.72 g. (0.043 mole) of sodium hydroxide in 10 ml. of water and 2.892 g. (0.0100 mole) of 2,2'-diamino-p,p'-biphenol dihydrochloride in 50 ml. of water was mixed in a Waring Blendor with a solution of 2.030 g. (0.0100 mole) of isophthalyl chloride in 50 ml. chloroform. After a few seconds the mixture became homogeneous and gelled. Fifty milliliters of water and 50 ml. of chloroform was added and mixing was continued for another 15 sec. After the contents were heated on a steam bath

TABLE V

POLYMERIZATION OF BIS(AMINOPHENOLS) AND PHTHALAMIDES IN POLYPHOSPHORIC ACID

	Amide	Aminophenol (as the Hydrochloride)	Mantle Temp.	Reaction Time (hr.)	Yield	Specific Viscosity (Sulfuric Acid, 30°) (c = 0.5%)	Physical Appearance
1.	Isophthalamide[a]	2,2'-Dihydroxy-benzidine	200	19.0	95	0.15[b]	Green powder
2.	Isophthalamide[a]	2,2'-Diamino-p,p'-biphenol	200	19.0	-	-	[c]
3.	Terephthalamide	2,2'-Diamino-p,p'-biphenol	210-220	19.0[d]	101	1.69[e]	Green powder
4.	Terephthalamide	2,2'-Diamino-p,p'-biphenol	150	19.0	39	0.04[b]	Green powder
5.	Terephthalamide	2,2'-Diamino-p,p'-biphenol	210-220	2.5[d]	97	5.77[b]	Green powder
6.	Terephthalamide	2,2'-Diamino-p,p'-biphenol	200	3.0	-	-	[c]

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[a] m.p. 270° - 272°; prepared from recrystallized isophthalyl chloride.

[b] 0.5 per cent in sulfuric acid.

[c] Polymer precipitated upon addition of water as a finely divided solid that could not be separated by filtration.

[d] Gelation occurred.

[e] 0.2 per cent in sulfuric acid.

for 2 hr., the polymer was filtered off, washed with water and methanol, and dried under vacuum at 70°. A brownish-black polymer, 2.46 g. (79 per cent), was obtained. The polymer did not melt below 400° and had a specific viscosity (0.5 per cent in sulfuric acid) of 0.07 at 30°.

7. Polymer from 3,3'-dihydroxybenzidine and terephthalyl chloride (by interfacial polycondensation): In a procedure similar to paragraph IV. E. 6., 2.892 g. (0.0100 mole) of 3,3'-dihydroxybenzidine dihydrochloride, 1.68 g. (0.042 mole) of sodium hydroxide, and 2.030 g. (0.0100 mole) of terephthalyl chloride gave 3.0 g. (96 per cent) of brown-black polymer which did not melt below 400°.

8. Polymerization of 3,3'-dihydroxybenzidine dihydrochloride and diphenyl terephthalate (attempted in benzene): A mixture of 1.446 g. (0.00500 mole of 3,3'-dihydroxybenzidine dihydrochloride, 1,592 g. (0.00500 mole) of diphenyl terephthalate, 0.9 ml. of pyridine, and 50 ml. of benzene was refluxed for 1.5 hr. An insoluble solid was present throughout the reaction. When the mixture was cooled, unchanged diphenyl terephthalate precipitated.

9. Melt polymerization of 2,2'-diamino-p,p'-biphenol and diphenylterephthalate (attempted): (Method: Reference 14) After a solution of 1.446 g. (0.005 mole) of 2,2'-diamino-p,p'-biphenol dihydrochloride in 50 ml. of water was neutralized with aqueous sodium hydroxide, the free amine was filtered off, washed with water, and dried under reduced pressure. A mixture of the free amine and 1.592 g. (0.00500 mole) of diphenyl terephthalate was heated under nitrogen in a Wood's metal bath from 65 to 215° over a 1-hr. period. The mixture shrank and darkened, but did not melt. A small amount of liquid condensed in the neck which was identified by its odor as phenol. The gray product (2.6 g., 167 per cent) was partly soluble in acetone, but left a black, insoluble residue.

10. Polymerization of 3,3'-dihydroxybenzidine dihydrochloride and diphenyl isophthalate (attempted in xylene): When a mixture of 1.446 g. (0.00500 mole) of 3,3'-dihydroxybenzidine dihydrochloride, 1,592 g. (0.00500 mole) of diphenyl isophthalate, 0.9 ml. of pyridine and 50 ml. of benzene was heated at reflux, a portion of the reactants was not soluble. Fifty milliliters of xylene were added, the benzene was distilled off, and the mixture was refluxed for 1 hr. The same material remained insoluble. No solid precipitated when the mixture was cooled.

F. Titanium and Zirconium-Containing Monomers, Intermediates, and Polymers

1. *Bis(8-oxyquinoline)diisopropoxytitanium*: (Method: Reference 15) A solution of 256 g. (1.76 moles) of 8-hydroxyquinoline in 800 ml. of toluene was added to 251 g. (0.88 mole) of freshly distilled tetraisopropoxytitanium in 400 ml. of toluene over a 2.5-hr. period. Stirring was continued for an hour after the addition was complete, then 800 ml. of toluene was distilled out. When the product was cooled, 301 g. (75 per cent) of bis(8-oxyquinoline)-diisopropoxytitanium separated and was collected by filtration. The melting point 184-186° (reported, 174-176°,[15] 172-173°,[37] 166-171°)[38] was not changed after recrystallization from toluene.

Anal. Calcd. for $C_{24}H_{26}N_2O_4Ti$: C, 63.44; H, 5.77; N, 6.16. Found: C, 63.49; H, 5.87; N, 6.24.

2. *Bis(8-oxyquinoline)diisopropoxyzirconium (attempted)*: To a stirred mixture of 32.8 g. (0.10 mole) of tetraisopropoxyzirconium in 125 ml. of toluene was added a solution of 29.0 g. (0.20 mole) of 8-hydroxyquinoline in 220 ml. of toluene. The product, which separated upon addition of the 8-hydroxyquinoline, was stirred 2 hr. at room temperature and collected by filtration. There was obtained 23.1 g. (92 per cent conversion based on 8-hydroxyquinoline) of tetra(8-oxyquinoline)zirconium, which did not melt at 325°. The infrared spectrum of the product was identical to the spectrum reported by Thomas[39] for the tetrasubstituted derivative.

Anal. Calcd. for $C_{36}H_{24}N_4O_4Zr$: C, 64.74; H, 3.62; N, 8.39. Found: C, 64.55; H, 3.76; N, 8.34.

In a second experiment, reverse addition of the reactants gave similar results.

3. *Tetrakis(dimethylamino)titanium*: (Method: Reference 40) A stirred solution of 64 g. (1.0 mole) of *n*-butyllithium in 625 ml. hexane at -10° was treated with 45 g. (1.0 mole) of dimethylamine, which was added as a gas above the surface of the liquid. The temperature of the reaction mixture was maintained at -10° with a Dry Ice-acetone bath during the addition, which required 1.5 hr. The white, turbid mixture was stirred an additional 15 min., then allowed to warm to 25°. Titanium tetrachloride (42.7 g., 0.225 mole) was added dropwise during 30 min. to the stirred mixture at 5-10°. The yellow-orange liquid was refluxed at 60° for 2 hr. to remove the excess dimethylamine and butane. The mixture was filtered and the filtrate evaporated at 60° (0.05 mm.). Subsequent distillation through a 30-cm. vacuum-jacketed column gave 21.6 g. (44 per cent) of tetrakis(dimethylamino)titanium, b.p. 56-68°C (0.30 - 0.50 mm.) (reported, 50° (0.05 mm.)).[40]

4. Polymer from tetraisopropoxytitanium, diphenylsilanediol, and triphenylsilanol: In this experiment, the procedure described by Towers[17] for preparing the polymer, $[(Ph_3SiOTi)_2(OSiPh_2O)_3]_n$, was repeated, but tetraisopropoxytitanium was used in place of tetrakis(dimethylamino)titanium.

To 8.5 g. (0.030 mole) of freshly distilled tetraisopropoxytitanium dissolved in 100 ml. of benzene was added 8.3 g. (0.030 mole) of triphenylsilanol in 45 ml. of ether during 30 min. The mixture was stirred during the addition and for 1 hr. after the addition was complete. Subsequently, 9.7 g. (0.045 mole) of solid diphenylsilanediol was added. During the latter addition, which required 1 hr., a heavy white precipitate formed. After the mixture was refluxed 2 hr., the solvents were distilled out and a thick gum was obtained that became brittle and powdery at room temperature. Upon devolatilization at 210° (0.8 mm.), the residue darkened slightly. The product began to soften at 250° and melted at 344-358° (Al block). It was soluble in chloroform, but insoluble in hot benzene and hot dimethylformamide. The infrared spectrum (Fig. 24) was similar, but not identical, to the spectrum of an authentic sample of tetrakis(triphenylsiloxy)titanium, differing mainly in the presence of Si_2O absorption in the 1,075-1,025 $cm.^{-1}$ region. In a thermogravimetric analysis (Fig. 36), the material lost weight continuously above 150°.

Anal. Calcd. for $(C_{72}H_{60}O_8Si_5Ti_2)_n$: Si, 10.89; Mol. Wt. for repeating unit, 1,289. Found: Si, 8.50; Mol. Wt. 1,159 (by VPO in chloroform at 37°).

5. Polymer from tetrakis(dimethylamino)titanium, triphenylsilanol and dimethylsilanediol. (Method: Reference 17) A solution of 8.734 g. (0.0316 mole) of triphenylsilanol in 45 ml. ether was added dropwise during 45 min. to a stirred solution of 7.084 g. (0.0316 mole) of tetrakis(dimethylamino)titanium of 100 ml. of benzene. After the mixture was stirred an additional hour, 10.253 g. (0.0474 mole) of solid diphenylsilanediol was added. During this addition, which required 1 hr., the color changed from orange to light yellow and a thick precipitate formed. The mixture was stirred and refluxed 2 hr., the solvents were distilled off, and the residue was dried at 130° (0.05 mm.) to give 20.8 g. (calcd. 14.9 g.) of a brittle tan solid. An infrared spectrum of this material was identical to the spectrum obtained from the polymer from tetraisopropoxytitanium and was very similar to the spectrum reported by Towers.[17] The latter polymer contained a much stronger band at 3,400 $cm.^{-1}$. When the product was further dried at 210° (0.7-1.0 mm.) for 30 min., the infrared spectrum of the light brown, brittle solid, m.p. 317-330°, had not changed.

6. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium (prepared in benzene): The experiment described in the literature for the preparation of $[Ph_2SiO(C_9H_6NO)_2TiO]_n$, was repeated.[16] The same

polymer has been prepared by Thomas from bis(8-oxyquinoline)bis(diethylamino)-titanium.[8] A mixture of 13.0 g. (0.060 mole) of diphenylsilanediol, 27.2 g. (0.060 mole) of bis(8-oxyquinoline)diisopropoxytitanium, and 270 ml. of benzene was stirred and heated until the azeotrope, which distilled out of the mixture, contained no more isopropyl alcohol. During the heating, sufficient benzene was added to the mixture to maintain a constant volume. When the product was collected by filtration, washed with benzene, and dried under reduced pressure, 34.8 g. (calcd. 33.2) of a bright yellow powder was obtained which melted at 343-347°. The product was soluble in cold dimethylformamide, dimethylacetamide, and dimethylsulfoxide, but insoluble in most other common organic solvents. Its infrared spectrum is shown in Fig. 25.

Anal. Calcd. for $(C_{30}H_{22}N_4OSiTi)_n$: N, 5.09; Mol. Wt. for the repeating unit, 551. Found: N, 5.20; Mol. Wt. 795 (by VPO in dimethylformamide at 100°).

Ten grams of the polymer was heated in 200 ml. of boiling xylene overnight and filtered. Evaporation of the solvent gave 0.9 g. of xylene-soluble material, which melted at 261-265°. The infrared spectrum of the soluble portion was identical to the spectrum of the whole polymer.

7. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium (powder polymerization): Five grams of a polymer prepared from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium in benzene (see paragraph IV. F. 6) was heated and stirred under 0.5 mm. of nitrogen at 100° for 20 min., 180° for 1 hr., and 250° for 5 hr. The product, which was cooled under 0.5 mm. of nitrogen and stored under nitrogen, melted at 330-336°. A thin layer of reddish powder on the inside surface of the flask (m.p. 360-373°)was partly soluble in hot dimethylformamide. A film cast from the soluble portion was powdery.

8. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium (prepared in dimethylsulfoxide): A mixture of 8.7 g. (0.40 mole) of diphenylsilanediol, 18.2 g. (0.040 mole) of bis(8-oxyquinoline)diisopropoxytitanium and 250 ml. of dimethylsulfoxide was heated slowly (1.5 hr.) to 180°. An orange precipitate, which formed at 90°, dissolved at 156° to give a bright red solution. A distillate from the mixture, which was collected at 130-180°, contained about 6 g. of isopropyl alcohol (by VPC using a column packed with 20 per cent Carbowax on 60-80 mesh white Chromosorb; calcd. 4.8 g.). The solvent was distilled off at 0.2 mm., and 26.4 g. (calcd. 22.1 g.) of a foamed, brittle solid was obtained. The infrared spectrum of this polymer was similar to the spectrum of the polymer obtained from the same materials in benzene.

Anal. Found: Mol. Wt., 671 (by VPO in dimethylformamide at 100°).

9. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium (melt): A mixture of 4.326 g. (0.0200 mole) of diphenylsilanediol and 9.088 g. (0.0200 mole) of bis(8-oxyquinoline)diisopropoxytitanium was stirred and heated to 160° (0.5 mm.) under nitrogen. Within a few minutes, a trace of a white sublimed solid appeared in the glass outlet tube. At 180°, the reaction mixture melted and bubbling was observed. The dark orange melt was heated to 210°, stirred for 30 min., and cooled under nitrogen. An infrared spectrum of the sublimed solid (m.p. 130-135°) was identical to the spectrum of diphenylsilanediol. The residue (10.5 g., 95 per cent) was a dark orange powder, m.p. 220-231°. The infrared spectrum was very similar to the spectra of polymers made from the same materials in benzene and dimethylsulfoxide.

A similar experiment in which the reactants were not stirred until the mixture had melted also produced some sublimed diphenylsilanediol. The dark orange residue weighed 11.6 g. (calcd. 11.0 g.), m.p. 146-182°. The infrared spectra of both polymers were similar.

10. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium in dimethylacetamide: A mixture of 8.7 g. (0.040 mole) of diphenylsilanediol, 18.2 g. (0.040 mole) of bis(8-oxyquinoline)diisopropoxytitanium, and 180 ml. of dimethylacetamide was heated slowly to 168° during 1.5 hr. An insoluble precipitate dissolved at 100°. A distillate from the mixture, which was collected at 130-162°, contained 4.9 g. (calcd. 4.8 g.) of isopropyl alcohol by VPC using a 2.7-meter column packed with 20 per cent PEG 4,000 on 60-80 mesh Chromosorb.

The solvent was distilled at 75° (20 mm.), then at 140° (0.5 mm.), and 22.5 g. (calcd. 22.1 g.) of an orange solid was obtained, m.p. 242-246°. The infrared spectrum of this material contained no -OH peak at 3,400 cm.$^{-1}$, but was otherwise identical to the spectra of the polymers obtained from the same materials in benzene and in dimethylsulfoxide.

Anal. Calcd. for $(C_{30}H_{22}N_4O)_n$: Molecular weight for the repeating unit, 551. Found: 2,800 (by VPO in dimethylformamide at 100°).

The effect of stoichiometry on the reaction of the subject compounds in dimethylacetamide was examined in a series of experiments and the results are reported in Table VI. All reactions were carried out under an atmosphere of nitrogen, and all apparatus was dried with a free flame and flushed with nitrogen before the reactants were introduced. The following is a typical experiment. After 135 ml. of dry dimethylacetamide was distilled from phosphorus pentoxide into a 250-ml., round-bottom flask containing 6.489 g. (0.0300 mole) of diphenylsilanediol and 13.632 g. (0.0300 mole) of diisopropoxybis(8-oxyquinoline)titanium, the mixture was heated at atmospheric pressure and the

TABLE VI

CONDENSATION OF DIPHENYLSILANEDIOL WITH DIISOPROPOXYBIS(8-OXYQUINOLINE)TITANIUM IN DIMETHYLACETAMIDE

Reactants (moles)		Yields (%)		Molecular Weight	M.P. (°C)
Diphenylsilanediol	Diisopropoxybis-(8-oxyquinoline)titanium	Isopropyl Alcchol	Polymer		
0.0270	0.0300	74.3	164	-	297-307
0.0285	0.0300	76.8	165	-	307-321
0.0300	0.0300[a]	80.1	109	-	288-301
0.0315	0.0300[b]	84.5	101[c]	2,129	288-296
0.0330	0.0300	89.7	157	-	278-297
0.0340	0.0300	77.1	115	-	81-96
0.0349	0.0300	87.5	116	-	275-295

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[a] In a duplicate experiment, a 83 per cent yield of isopropyl alcohol was obtained and the polymer was recovered as 17.6 g. (106 per cent) of an orange powder, m.p. 301-308°.

[b] In a duplicate experiment, a 75 per cent yield of isopropyl alcohol was obtained and 112 per cent of the polymer, m.p. 220-35° was obtained.

[c] When this polymer was heated under vacuum at 145° to a constant weight, the corrected yield was 96 per cent. No change was observed in the infrared spectrum except for the disappearance of the amide carbonyl absorption at 1,640 cm^{-1}

solvent was allowed to distill until the product precipitated. About 15 ml. of residue remained. The remaining solvent was distilled at reduced pressure. The distillates were combined, and aliquots were analyzed by VPC to determine the quantitiy of isopropyl alcohol obtained in the reaction. Calculations were based on the comparison of peak area ratios of isopropyl alcohol to *n*-butanol, which was used as an internal standard in the analyses, with peak area ratios of the same alcohols in standard solutions. A typical infrared spectrum is reported in Fig. 26.

11. Polymer from diacetoxydiphenylsilane and bis(8-oxyquinoline)diisopropoxytitanium (in benzene): The experiment described in the literature for the preparation of $[Ph_2SiO(C_9H_6NO)_2TiO]_n$, was repeated.[16] A mixture of 9.011 g. (0.0300 mole) of diacetoxydiphenylsilane, 13.631 g. (0.0300 mole) of bis(8-oxyquinoline)diisopropoxytitanium, and 150 ml. of benzene was heated to reflux for 2 hr. A small amount of insoluble material was filtered off and the clear, orange filtrate was devolatilized to 150° (0.05 mm.) to give 21.4 g. (calcd. 16.5 g.) of a red, viscous liquid. Analysis of the distillate by VPC showed no isopropyl acetate.

12. Polymer from diacetoxydiphenylsilane and bis(8-oxyquinoline)-diisopropoxytitanium (melt): (Method: Reference 16) A mixture of 6.008 g. (0.020 mole) of diacetoxydiphenylsilane and 9.087 g. (0.020 mole) of bis(8-oxyquinoline)diisopropoxytitanium was heated at 175° under nitrogen for 16 hr. A distillate (3.15 g., calcd. 4.1 g.) from the mixture was 95 per cent pure isopropyl acetate (by VPC). The red viscous residue was heated to 100° (0.03 mm.) to give 11.9 g. (calcd. 11.1 g.) of a foamed orange solid, m.p. 184-190°. The infrared spectrum showed a weak Si-O-Ti band at 940 $cm.^{-1}$.

13. Diacetoxydiphenylsilane: (Method: Reference 16) A solution of 120 g. (2.00 moles) of glacial acetic acid in 100 ml. of ether was added dropwise over 2 hr. to a stirred mixture of 253 g. (1.00 mole) of dichlorodiphenylsilane, 166 g. (2.10 moles) of pyridine, and 650 ml. of ether. The thick mixture was filtered and the pyridine hydrochloride salts were washed with ether. Evaporation of the combined filtrate and washings and subsequent distillation gave 208 g. (70 per cent) of diacetoxydiphenylsilane, b.p. 138-140° (0.06 mm.); n_D^{27} 1.5357 (reported, 158-162° (0.17 mm.), n_D^{20} 1.5372).[7]

14. Polymer from *p*-phenylenebis(dimethylsilanol) and bis(8-oxyquinoline)diisopropoxytitanium (in benzene): (Method: Reference 16) A mixture of 5.560 g. (0.0250 mole) of *p*-phenylenebis(dimethylhydroxysilane), 11.360 g. (0.0250 mole) of bis(8-oxyquinoline)diisopropoxytitanium, and 130 ml. benzene was stirred and heated until the azeotrope, which distilled out of the mixture, contained no more isopropyl alcohol. A total of 2.12 g. (71 per cent) isopropyl alcohol was found in the distillate (by VPC). During the heating, benzene

was added to maintain constant volume. After the solvent was distilled under reduced pressure and the residue was heated to 60° (0.05 mm.), 14.4 g. (calcd. 14.1 g.) of a polymer was obtained, m.p. 273-278°. The infrared spectrum indicated an Si-O-Ti band at 910-920 cm.$^{-1}$.

Anal. Calcd. for $(C_{28}H_{30}N_2O_4Si_2Ti)_n$: Molecular weight for the repeating unit,563. Found: Molecular Weight 502 (by VPO in dimethylformamide at 100°).

A similar experiment, in which a 25 per cent mole excess of the diol and 550 ml. of benzene was used, gave 2.12 g. (89 per cent) of isopropyl alcohol (by VPC) and 13.2 g. (calcd. 12.3 g.) of a yellow powder, m.p. 118-157°; η_{sp} (toluene) = 0.06 at 30°. The reactants remained soluble throughout the polymerization.

Four grams of the polymer was wet with 4 ml. of 0.02 per cent sodium hydroxide then devolatilized at 100° (10 mm.). Further heating at 250° under nitrogen for 36 hr. and cooling under vacuum gave a trace of sublimed 8-hydroxyquinoline, m.p. 75-76.5°. The infrared spectrum of the residue was similar to that of the starting material.

15. Polymer from p-phenylenebis(diphenylsilanol) and bis(8-oxyquinoline)diisopropoxytitanium (in toluene): A mixture of 4.74 g. (0.0100 mole) of (p-phenylenebis(diphenylsilanol), 4.544 g. (0.0100 mole) of bis(8-oxyquinoline)diisopropoxytitanium, and 200 ml. of toluene was stirred and heated to reflux over a period of 1 hr. All the reactants were soluble at the reflux temperature. Heating was continued for 2.5 hr., and most of the solvent distilled off. Filtration gave 7.2 g. (89 per cent) of a dark yellow solid which melted at 340-375°. Evaporation of the filtrate gave an additional 1.8 g. of a red powder which melted at 247-287°. The infrared spectra of the two products were similar and nearly superimposable with the spectrum of the model compound, bis(8-oxyquinoline)bis(triphenylsiloxy)titanium. The specific viscosity of the main fraction in chloroform was 0.014 (0.5 per cent solution). The infrared spectrum of the polymer is shown in Fig. 27.

G. Phthalocyanine Intermediates, Monomers, and Model Compounds

1. 1,3-Diiminoisoindoline: (Method: Reference 41) An autoclave was charged with 50.0 g. (0.39 mole) of phthalonitrile (m.p. 142-144°) and 300 ml. of methanol. Liquid ammonia (100 ml.) was added slowly while the mixture was stirred. After the autoclave was sealed, the mixture was heated without stirring at 90-125° for 4 hr. then stored at room temperature for 70 hr. When the contents of the autoclave were filtered and evaporated, the blue solid residue that was obtained was redissolved in a minimum amount of methanol and

treated with charcoal. The product was precipitated from the resulting yellow solution with ether, and two fractions were obtained: a pink solid, m.p. 179-181°, and a tan solid, m.p. 182-184°. An additional amount of a tan solid, m.p. 181-183° was obtained when the solvent was evaporated. An attempt to chromatograph the solid melting at 179-181° indicated that at least four components were present. Recrystallization of the combined material from ether-methanol cooled with a Dry Ice-acetone bath gave 0.7 g. (0.1 per cent) of 1,3-diiminoisoindoline, m.p. 189-192° (reported, 196°[41] and 193°[42]).

2. *Sodium phthalocyanine*: (Method: Reference 3) A mixture of 10 g. (0.078 mole) of phthalonitrile, 1.8 g. (0.078 g. atom) of sodium and 100 ml. of *n*-amyl alcohol was refluxed 15 min. The hot mixture was filtered and washed with ether until the washings were colorless. After drying in air overnight, there was obtained 4.1 g. (38 per cent) of sodium phthalocyanine.

In a second experiment, phthalonitrile was dissolved in boiling *n*-amyl alcohol and subsequently treated with sodium. From 22 g. of phthalonitrile was obtained 6.4 g. (27 per cent) of sodium phthalocyanine. Additional colored impurities could be removed from both products by trituration with acetone.

3. *Phthalocyanine*: (Method: Reference 43) A flask which had been washed with concentrated hydrochloric acid and distilled water was charged with 10.5 g. (19 mmoles) of sodium phthalocyanine and about 150 ml. of distilled water. The mixture was heated at 90° for four days, filtered, and the residue was dried in air. Phthalocyanine containing some sodium phthalocyanine was obtained.

Anal. Calcd. for $C_{32}H_{18}N_8$: C, 74.69; H, 3.53; N, 21.8; Na, 0.00. Calcd. for the sodium salt: Na, 8.25. Found: C, 74.8; H, 3.55; N, 21.2; Na, 2.50.

4. *Phthalocyaninediisopropoxytitanium (attempted)*: A mixture prepared by adding 2.2 g. (0.0043 mole) of phthalocyanine to a solution of 10.4 g. (0.035 mole) of freshly distilled tetraisopropoxytitanium in 100 ml. of toluene was heated at 95° for five days. The solid product, which was collected by filtration and washed with benzene until no more color was removed, was not identified.

Anal. Calcd. for $C_{38}H_{30}O_2N_8Ti$: Ti, 7.07. Found Ti, 1.87.

5. *Chlorodimethylphenylsilane*: (Method: Reference 16) Two hundred milliliters of a 3 *M* solution of phenylmagnesium bromide in ether (0.6 mole) was added dropwise over a period of 65 min. to a stirred solution of 155 g. (1.2

moles) of freshly distilled dichlorodimethylsilane in 250 ml. of ether. The next day the mixture was filtered and distilled, and 65 g. (60 per cent) of chlorodimethylphenylsilane, b.p. 190-196° (reported, 191-194°)[16], was obtained.

6. Dimethylphenylsilanol: (Method: Reference 5) A solution of 62 g. (0.36 mole) of chlorodimethylphenylsilane in 450 ml. of ether was added dropwise to 60 g. (0.72 mole) of sodium bicarbonate in 500 ml. of water and 100 ml. of ether, which was stirred and maintained below 20° during the addition. The addition required 70 min. The ether layer was separated, dried over sodium carbonate, and evaporated. During an attempted distillation through a 15 in. column packed with Berl saddles, water distilled at a pot temperature of 120° (14 mm.). The infrared spectrum of the residue showed that the siloxane had formed.

After 36 g. (0.13 mole) of 1,3-diphenyltetramethyldisiloxane was added dropwise over a period of 1 hr. to a stirred solution of 10.2 g. (0.26 mole) of sodium hydroxide in 100 ml. of isopropyl alcohol, the solution was stirred 16 hr. at 70-80°. Removal of the solvents at reduced pressure gave a viscous liquid which was dissolved in 175 ml. of dry ether and added dropwise over a period of 3 hr. to a mixture of 180 ml. of ether, 365 ml. of water, and 17.2 g. (0.29 mole) of acetic acid. After the mixture was stirred an additional 2 hr., the ether layer was separated, washed twice with distilled water, and dried over sodium sulfate. Distillation gave about 0.5 ml. of a cloudy fraction, b.p. 105-155° (14 mm.) (reported, for dimethylphenylsilanol 101-102° (14 mm.)),[44] and 10.5 g. of the siloxane, b.p. 155-157° (14 mm.), (reported, 158-160° (14.7 mm.),[45] 161° (15 mm.)[46]).

In a repetition of the experiment, the product was not distilled. The infrared spectrum of the residue indicated that both siloxane and silanol groups were present; therefore, the unpurified material was used in subsequent experiments.

7. Bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium: (Method: Reference 16) A solution of 10 g. (0.066 mole) of the impure dimethylphenylsilanol in 50 ml. of benzene was added dropwise to a nearly boiling solution of 10.0 g. (0.022 mole) of bis(8-oxyquinoline)diisopropoxytitanium in 100 ml. of benzene. After the addition was complete, additional benzene was added to maintain a constant volume while the isopropyl alcohol-benzene azeotrope was allowed to distill. A total of 150 ml. was collected before the refactive index of the distillate equaled the refractive index of benzene. Evaporation of the solvent gave a viscous liquid that crystallized when it was stored overnight under petroleum ether. When the crude product, m.p. 112-116°, was recrystallized from benzene-cyclohexane, 3.2 g. (23 per cent) of bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium, m.p. 134-137° (reported, 137-138°)[16] was obtained.

8. Product from 1,3-diiminoisoindoline and bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium: A mixture of 0.204 g. (0.346 mmole) of bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium and 0.200 g. (1.48 mmole) of 1,3-diiminoisoindoline was added to a 15-ml. flasked equipped with a distilling head containing a thermometer and a 15-ml. receiving flask. The reactants, which were thoroughly mixed prior to heating, were heated at 180-200° for 2 hr. in a Woods metal bath. During the heating, about 20 mg. of a colorless crystalline solid, which melted at 204-208°, collected in the distilling head. The infrared spectrum contained bands at 3,200 cm.$^{-1}$ (NH or OH) and 1,720 cm.$^{-1}$ (C:O or C:N). The solid was neither a starting material, dimethylphenylsilanol nor 8-hydroxyquinoline.

In a second experiment, the reactants were heated at 1 mm., and during the first hour about 5 mg. of bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium collected in the distilling head. Neither dimethylphenylsilanol nor 8-hydroxyquinoline distilled when the residue was heated 18 hr.

9. Product from phthalonitrile and bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium: When a mixture of 0.200 g. (0.345 mmole) of bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium, 0.174 g. (1.48 mmole)of phthalonitrile (m.p. 142-144°), and 0.0150 g. of ammonium molybdate were mixed and heated 6 hr. at 200° (1 mm.), the only material that distilled was 50 mg. (34 per cent recovery) of phthalonitrile, m.p. 134-138°.

10. Product from tetrakis(dimethylamino)titanium, phthalonitrile, and diphenylsilanediol: (Method: Reference 16) A mixture of 3.00 g. (0.0134 mole) of tetrakis(dimethylamino)titanium and 6.86 g. (0.0535 mole) of phthalonitrile in 150 ml. of pyridine was refluxed for 6 hr., and 2.90 g. (0.0134 mole) of diphenylsilanediol was added. Refluxing for an additional 6 hr., distillation of the solvent, and drying at 200° (1 mm.) afforded 9.6 g. of a black residue. Extraction of the residue with two 100-ml. portions of benzene gave, after evaporation under vacuum, two soluble portions that weighed 4.4 g. and 0.5 g., respectively. The benzene-insoluble residue weighed 4.7 g. A thermogravimetric analysis of the residue before extraction (Fig. 36) showed a procedural decomposition temperature of 205° (weight loss ≥ 5 per cent/hr).

H. Polymer Containing Boron and Silicon

1. Polymer from Tri(n-butoxy)boron and diphenylsilanediol: Towers prepared a similar polymer with the proposed structure $[B_2(OPh_2SiO)_3]_n$;[17] however, the calculated quantities of reactants shown by this author do not agree with the required molar ratio. Therefore, two experiments, one with the

reported gram quantities and one with the calculated gram quantities, were carried out.

A solution of 16.1 g. (0.07 mole) of tri(n-butoxy)boron in 100 ml. of heptane was mixed with 22.7 g. (0.105 mole) of diphenylsilanediol and 50 ml. of benzene. After the mixture was heated at the reflux temperature for 6 hr., the solvents were distilled out and the residue was devolatilized at 200° (1 mm.). Additional heating of the slightly viscous liquid residue to 350° (1 mm.) gave 4.8 g. of liquid distillate, b.p. 100-130° (1 mm.), n_D^{24} 1.4339 and 1 g. of crystal that sublimed during the distillation, m.p. 185-187° (from benzene-petroleum ether, b.p. 35-60°).

Anal. Found: B, 2.96; Si, 11.68; Mol. Wt., 509 (by VPO in benzene at 37°).

About 20 g. of a glassy polymeric residue, which softened at about 85°, was obtained. The thermogravimetric analysis of this residue is reported in Fig. 36.

A similar experiment in which 16.1 g. (0.07 mole) of tri(n-butoxy)-boron, 29.0 g. (0.134 mole) of diphenylsilanediol, 100 ml. of heptane, and 50 ml. of benzene were employed gave 27.4 g. (calcd. 22.8 g.) of a glassy solid after the product was devolatilized at 300° (1 mm.). The infrared spectrum is reported in Fig. 35.

Anal. Calcd. for $(C_{36}H_{30}B_2O_6Si_3)_n$: B, 3.31; Si, 12.92; Mol. Wt. for the repeating unit, 652. Found: B, 2.59; Si, 13.00; Mol. Wt. 594 (by VPO in benzene at 37°).

When the polymer was heated at 450° for 1 hr., a brittle, brown solid was obtained which had lost 36 per cent of its weight.

I. Ferrocene-Containing Monomers

1. Dimethyl 1,1'-ferrocenedicarboxylate (from the lithium intermediate): (Method: Reference 23)

a. 1,1'-Ferrocenedicarboxylic acid: A solution of 64 g. (1.00 mole) of n-butyllithium in 625 ml. of hexane was added dropwise during 2.5 hr. to 36.8 g. (0.20 mole) of ferrocene in 600 ml. of tetrahydrofuran at 0° under nitrogen. The mixture was stirred at 0° for 6 hr., allowed to warm to room temperature overnight, cooled to -70°, and slowly added to a slurry of ether and Dry Ice. After the ether had evaporated, the residue was extracted with water and the aqueous extract was filtered and acidified. Filtration, washing with water, and drying over phosphorus pentoxide afforded 51.4 g. of a mixture of ferrocenoic acid and 1,1'-ferrocenedicarboxylic acid.

b. Dimethyl 1,1'-ferrocenedicarboxylate: The mixed acids were added to 500 ml. of methanol containing 11 ml. of sulfuric acid and the resulting mixture was refluxed overnight, cooled, and poured onto 1,000 g. of ice. The mixed esters were extracted with ether, and the ether solution was washed with 6 per cent sodium bicarbonate until the color of aqueous layer did not change. After the ether solution was dried with sodium sulfate, evaporation of the ether under vacuum gave 38 g. of crude mixed esters. The mixed esters were dissolved in benzene and chromatographed in 1.5 lb. of alumina with petroleum ether-benzene (1:1, 1:2, 1:3, 1:4), benzene, and ether. There were obtained 13.0 g. (26.6 per cent) of methyl ferrocenoate, m.p. 64-74° (reported, 70-71°),[47] and 9.9 g. (16.4 per cent) of dimethyl 1,1'-ferrocenedicarboxylate, m.p. 110-115° (reported, 114-115°).[48] After one recrystallization from heptane, 8.8 g. of diester, m.p. 112.5-113.5°, was obtained.

2. Dimethyl 1,1'-ferrocenedicarboxylate (from the acetyl intermediate):

a. 1,1'-Diacetylferrocene: (Method: Reference 21) To a stirred mixture of 59.6 g. (0.45 mole) of aluminum chloride and 175 ml. of methylene chloride under nitrogen, 35.4 g. (0.45 mole) of acetyl chloride was added dropwise. After the aluminum chloride dissolved, a solution of 32.6 g. (0.175 mole) of ferrocene in 175 ml. of methylene chloride was added dropwise during 1 hr. The purple reaction mixture was stirred for 70 hr., poured onto 250 g. of ice, and the phases were separated. Washing the methylene chloride solution with water to remove hydrogen chloride, drying the same solution with sodium sulfate, and removing the methylene chloride under vacuum afforded, after recrystallization, 21.2 g. (45 per cent) of 1,1'-diacetylferrocene, m.p. 125-128° (from cyclohexane), (reported, 127.0-127.5°).[21]

In a repetition of the experiment, 108 g. (74 per cent) of crude 1,1'-diacetylferrocene was obtained.

b. 1,1'-Ferrocenedicarboxylic acid: (Method: Reference 22) A mixture of 21.2 g. (0.079 mole) of 1,1'-diacetylferrocene and 500 ml. of commerical 5.25 per cent sodium hypochlorite was protected from light and stirred at 50°. At 1.5-hr. intervals, three additional 250-ml. portions of sodium hypochlorite were added. When the mixture was stirred overnight at 50° and filtered, 5.3 g. of an unidentified precipitate (m.p. 317-326°), which was insoluble in methylene chloride, was obtained. After the filtrate was treated with sodium bisulfite and acidified with hydrochloric acid, the resulting precipitate was dissolved in ether, from which it was extracted with sodium bicarbonate and reprecipitated by the addition of hydrochloric acid. The yield of 1,1'-ferrocenedicarboxylic acid was 7.8 g. (36 per cent).

An alternate procedure, described by Yamakawas[49] in which methanol was employed as the solvent, gave no acidic product.

c. Dimethyl 1,1'-ferrocenedicarboxylate: 1,1'-Ferrocenedicarboxylic acid was esterified by the procedure described in paragraph IV.G.1.c. From 7.8 g. (0.0285 mole) of 1,1'-ferrocenedicarboxylic acid was obtained 8.3 g. (95 per cent) of crude dimethyl 1,1'-ferrocenedicarboxylate, m.p. 106-108°. After the crude product was recrystallized from heptane, 4.8 g. of the diester was obtained, m.p. 112.5-113.5° (reported, 114-115°).[48]

3. 1,1'-Bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene (attempted): A mixture of 4.5 g. (14.9 mmoles) of dimethyl 1,1'-ferrocenedicarboxylate, 3.3 g. (29.8 mmoles) of 2,2-dimethyl-1,3-propanediol, and 0.008 g. of zinc acetate dihydrate was heated at 150° under nitrogen for 1 hr. Appreciable diol was collected as a solid distillate; 10 g. more of diol was added, and the mixture was heated for 3 hr. The reaction mixture was cooled and ground to a fine powder. Chromatography of a portion of the powder on alumina with petroleum ether-benzene gave two ferrocene-containing compounds: 0.26 g. (82 per cent) of dimethyl 1,1'-ferrocenedicarboxylate (m.p. 112.5-113.5°) and 0.057 g. (18 per cent) of a compound (m.p. 91.5-93.0°) whose infrared spectrum was consistent with the structure of 1-methoxycarbonyl-1'-(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene; however, this structural assignment was not verified by elemental analyses.

Anal. Calcd. for $C_{18}H_{22}O_5Fe$: C, 57.75; H, 5.88. Found: C, 56.75; H, 6.35.

The remaining powder, 40 g. of 2,2-dimethyl-1,3-propanediol, and 2.5 g. of sulfuric acid were heated under nitrogen at 150° for 18 hr. The viscous liquid, which was obtained by cooling the reaction mixture, was poured onto 300 g. of ice and extracted with benzene. The benzene and water layers were separated and each was extracted, the benzene layer with water and the water layer with benzene, until the color of the extracts did not change. A red oil was salted out when the remaining water solution was treated with sodium chloride. An infrared spectrum of the oil showed the absence of the ester carbonyl (1,710 cm.$^{-1}$), a weak CC stretch characteristic of ferrocene derivatives, (1,460 cm.$^{-1}$), and the presence of an olefin (1,635 cm.$^{-1}$). Upon standing, the benzene solution of the products remaining after extraction gave crystalline 2,2-dimethyl-1,3-propanediol, which was removed by filtration. After the solution was passed over a short column of alumina to remove any remaining diol, evaporation of the benzene under vacuum gave 3.8 g. of crude dimethyl 1,1'-ferrocenedicarboxylate (m.p. 110-114°).

4. *Transesterification of dimethyl 1,1'-ferrocenedicarboxylate with 2,2,4,4-tetramethyl-1,3-cyclobutanediol (attempted)*: A mixture of 3.00 g. (9.94 mmoles) of dimethyl 1,1'-ferrocenedicarboxylate, 1.58 g. (11.0 mmoles) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and 0.004 g. of zinc acetate dihydrate was heated to 140° under nitrogen in a 50-ml. flask connected to a rotary evaporator which in turn was connected to a vacuum line. During the first hour of heating, diol sublimed. The pressure was slowly reduced to 0.1 mm. After 2 hr., no increase in melt viscosity had been observed.

The flask containing the mixture was connected to a distillation apparatus and 3.0 g. of 2,2,4,4-tetramethyl-1,3-cyclobutanediol and ca. 0.025 g. of tetraisopropyl titanate was added. The mixture was protected from atmospheric moisture with a tube containing Drierite, but was not blanketed with nitrogen. While the mixture was heated for 3 hr. at 150-220° in Wood's metal bath, 4.4 g. of a colorless liquid distilled (b.p. 65°). Vapor phase chromatography showed four constituents of which one was about 50 per cent of the total. An infrared spectrum of the distillate was consistent with the structure of cyclopentadiene carboxylic acid methyl ester.

5. *Transesterification of dimethyl 1,1'-ferrocenedicarboxylate and 2,2-dimethyl-1,3-propanediol (attempted)*: A mixture of 8.0 g. (26.5 mmoles) of dimethyl ferrocenedicarboxylate, 41 g. (400 mmoles) of 2,2-dimethyl-1,3-propanediol, and 0.012 g. (0.53 mmoles) of sodium was heated at 150° under nitrogen for 5 hr. After the mixture was cooled, added to water, and extracted with ether, the ether solution was dried over sodium sulfate and the ether was removed under reduced pressure. The residue dissolved in benzene was passed over alumina. After the benzene was evaporated, 9.5 g. of a red solid was obtained which melted at 103-109°. Chromatography of a portion of the solid gave a single ferrocene-containing compound which melted at 112.5-113.5° (melting point of an authentic sample of dimethyl 1,1'-ferrocenedicarboxylate, 112.5-113.5°).

6. *1,1'-Bis(3-hydroxy-2,2,4,4-tetramethyl-1-cyclobutoxycarbonyl)-ferrocene (attempted)*: A mixture of 4.63 g.(15.3 mmoles) of dimethyl 1,1'-ferrocenedicarboxylate, 4.96 g. (36.8 mmoles) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 0.005 g. of zinc acetate dihydrate and 0.025 g. of tetraisopropyl titanate was heated at 150° under nitrogen with stirring. During 1 hr., extensive sublimation of a white solid occurred, m.p. 126-133°. After the addition of 3 g. more of the diol and two more hours of heating, no distillation of liquid material had been observed. The residue melted at 96-101.5°. A portion of the residue was chromatographed on alumina with petroleum ether-benzene solutions. Only one colored ferrocene-containing band developed. The melting point of the solid, from this band, was 114-115° (m.p. of dimethyl 1,1'-ferrocenedicarboxylate, 114-115°).

7. 1,1'-Ferrocenedicarbonyl chloride: (Method: Reference 50) When a mixture of 15.0 g. (54.7 mmoles) of 1,1'-ferrocenedicarboxylic acid, 25.0 g. (197 mmoles) of oxalyl chloride, 10 drops of pyridine, and 200 ml. of methylene chloride was refluxed 6 hr., the acid dissolved. Evaporation of the solvent under reduced pressure left a residue which upon recrystallization from heptane gave 11.5 g. (70 per cent) of 1,1'-ferrocenedicarbonyl chloride melting at 97-98° (reported, 98-100°).[50]

In a repetition of the experiment, the mixture was stirred 20 hr. at room temperature and refluxed 6 hr. A total of 12.2 g. (74 per cent) of 1,1'-ferrocenedicarbonyl chloride was obtained.

8. 1,1'-Bis(2-hydroxyethoxycarbonyl)ferrocene: A solution of 1.0 g. (3.22 mmoles) of 1,1'-ferrocenedicarbonyl chloride in 15 ml. of methylene chloride was added to a solution of 0.15 g. of pyridine in 33.6 g. (54.2 mmoles) of glycol, and the mixture was stirred at room temperature for 18 hr. Evaporation of the solvent and excess glycol at 90° (1 mm.) gave a liquid residue which was insoluble in heptane, but soluble in water. Hydroxyl (3,400 cm.$^{-1}$) and carbonyl (1,710 cm.$^{-1}$) were present in the infrared spectrum of the residue. Attempts to derivatize a total of 1.2 g. of the residue with 3,5-dinitrobenzoyl chloride failed. The remaining crude material was chromatographed on alumina with methylene chloride. An orange band was eluted, but three additional bands remained on the column. Evaporation of the methylene chloride from the eluate afforded a red liquid which partially crystallized after 76 hr. Trituration of the residue left an orange powder, m.p. 56-60°, which after recrystallization from cyclohexane gave 0.4 g. of 1,1'-bis(2-hydroxyethoxycarbonyl)ferrocene melting at 66-67°. The infrared spectrum is reported in Fig. 28.

Anal. Calcd. for $C_{16}H_{18}FeO_6$: C, 53.06; H, 5.01. Found: C, 52.98; H, 5.04.

9. 1,1'-Bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene: A solution of 12.2 g. (39.1 mmoles) of 1,1'-ferrocenedicarbonyl chloride, 8.15 g. (78.2 mmoles) of 2,2-dimethyl-1,3-propanediol, 10 drops of pyridine, and 50 ml. of methylene chloride was refluxed and stirred under nitrogen for 22 hr. When the methylene chloride was removed under reduced pressure and the residue was heated for 3 hr. at 85° (0.1 mm.) and for another 3 hr. at 125° (0.1 mm.), 1.5 g. of 2,2-dimethylpropanediol (identified by its infrared spectrum) sublimed. An ether solution of the residue was extracted with water, and 0.15 g. of a red oil, which was chiefly, 2,2-dimethyl-1,3-propanediol, was salted from the aqueous extract. Upon evaporation of the ether solution, a residue was obtained which was redissolved in a 50/50 mixture of benzene and chloroform and chromatographed on alumina. After the mixture was developed and the major fraction was eluted from the column with chloroform, evaporation of the solvent at 60° (0.1 mm.) gave 13.4 g. (77 per cent) of a residue tentatively identified

as crude 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene, which may contain oligomers. The infrared spectrum is reported in Fig. 29.

10. Bis(2-hydroxyethyl)terephthalate: (Method: Reference 51) A mixture of 50 g. (0.258 moles) of dimethyl terephthalate, 294 g. (5.16 moles) of ethylene glycol and 0.010 g. of zinc acetate dihydrate was heated and distillate was collected between 70° and 188°. After 30 ml. had distilled, the residue was cooled to room temperature and poured into 1 liter of cold water. Additional product was precipitated with sodium chloride. Recrystallization of the dried precipitate from ethanol gave 23 g. (35 per cent) of bis-(2-hydroxyethyl)terephthalate m.p. 107-110° (reported, 109°).[51]

11. Poly(ethylene terephthalate): A mixture of 15 g. of bis(2-hydroxyethyl)terephthalate and about 0.015 g. of tetraisopropyltitanate in a 50-ml. flask was connected to a rotary evaporator. The pressure was reduced to 1 mm. and the rotated flask was heated at 270-280° in a Wood's metal bath. After 15 min. glycol ceased to distill and after 30 min. a viscous polymer had formed from which a fiber could be drawn.

12. Polymer from 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)-ferrocene (attempted): A mixture of 13.4 g. of 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene and about 0.015 g. of tetraisopropyltitanate were treated according to the procedure for the preparation of polyethylene terephthalate. After 2 hr. at 25° (1 mm.), no neopentyl glycol had distilled.

J. Boron- and Phosphorus-Containing Monomers, Intermediates, and Model Compounds

1. Diisopropoxy-8-oxyquinolineboron (attempted): A solution of 36.2 g. (0.25 mole) of 8-hydroxyquinoline in 170 ml. of toluene was added rapidly to a stirred solution of 47.0 g. (0.25 mole) of isopropylborate in 30 ml. of toluene. After the mixture was refluxed 3 hr., distillation through a packed column gave an isopropyl alcohol-toluene mixture boiling at 78-108°. A yellow solid precipitated from the cooled solution and was collected by filtration. The solid, which weighed 12.9 g., melted at 138° to above 210°. When the solid was washed with hot toluene, the melting point was raised to 355-357°.

Anal. Calcd. for $C_{37}H_{28}B_7N_4$: C, 59.38; H, 3.77; B, 10.12; N, 7.49. Found: C, 59.44; H, 3.80; B, 10.24; N, 7.57.

A similar experiment with 0.1 molar quantities afforded 6.7 g. of the unidentified yellow solid melting at 355-357°. The infrared spectrum (Fig. 30) of the compound showed -OH absorption at 3,400 cm.$^{-1}$.

2. Dihydroxy-8-oxyquinolineboron (attempted): When a mixture of 15.5 g. (0.25 mole) of boric acid and 36.2 g. (0.25 mole) of 8-hydroxyquinoline in 200 ml. of toluene was refluxed for 3 hr., a heavy precipitate formed and 8.25 ml. of water was collected in a Dean-Stark trap. The solid, 30.9 g., collected by filtration and dried in a vacuum desiccator, melted at 355-359°. The infrared spectrum was similar to the material obtained from isopropylborate and 8-hydroxyquinoline.

3. (1-Oxy-1-propene-1,3-diphenyl-3-one)dihydroxyboron (attempted): When a mixture of 1.03 g. (0.0166 mole) of boric acid and 11.2 g. (0.0500 mole) of dibenzoylmethane was refluxed in 50 ml. of toluene, 0.8 ml. of water had collected in a Dean-Stark trap after 8 hr. The yellow solid, which precipitated when the solution was cooled, was filtered off. Evaporation of the filtrate gave 7.1 g. (63.4 per cent) of unchanged dibenzoylmethane, melting point 74-77°. The solid, 3.0 g., after precipitation from hot chloroform with toluene melted at 403-406° with decomposition.

A repetition of the experiment with 0.98 g. (0.158 mole) of boric acid and 7.1 g. (0.0317 mole) of dibenzoylmethane gave 1.9 g. of an unidentified material melting at 286-316° and 5.1 g. (71.8 per cent) of recovered dibenzoylmethane, melting point 74-77°.

4. (1-Oxy-1-propene-1,3-diphenyl-3-one)diisopropoxyboron (attempted): After 20 g. (0.12 mole) of isopropylborate in 100 ml of benzene was added dropwise to 24.3 g. (0.12 mole) of dibenzoylmethane in 200 ml. of benzene, additional benzene was added to the mixture to maintain a constant volume while 200 ml. of solvent was distilled out. Upon evaporation of the solvent and trituration of the residue with ether, 17 g. (70 per cent recovery) of the dibenzoylmethane was recovered.

When the experiment was repeated with twice the amount of isopropylborate, isopropyl alcohol could not be identified (by VPC) in the distillate from the reaction mixture. Addition of 50 ml. of the solution to an equal volume of ether containing 3 drops of sulfuric acid gave a precipitate, which was collected by filtration, washed with ether, and dried. There was obtained 1.5 g. of a product which melted at 341-345° and did not show isopropyl proton resonance in the NMR spectrum.

In a third experiment, 2.4 g. (0.012 mole) of dibenzoylmethane, 20 g. (0.12 mole) of isopropylborate, 30 ml. of benzene, and 30 ml. of ether containing 3 drops of sulfuric acid were mixed. The crystalline solid which separated was collected by filtration, washed with ether, and dried. The product (1.04 g., 43 per cent) melted at 359-363°. The infrared spectra and the NMR spectra of the compounds melting at 341-345° and 359-363°, mixed m.p. (50/50) 343-347°, were superimposable.

A solution of 1.0 g. of sulfuric acid in 20 ml. of ether was added to a solution of 4.45 g. (0.020 mole) of dibenzyolmethane and 1.25 g. (0.0665 mole) of triisopropylborate in 70 ml. of ether. After the yellow solid precipitated, filtration and drying afforded 1.6 g. of a compound that melted at 350-352°.

Anal. Calcd. for $C_{29}H_{21}B_2O_{11}$: C, 61.41; H, 3.37; B, 3.82. Found: C, 61.88; H, 3.72; B, 3.81.

5. Dichloro(8-oxyquinoline)boron: (Method: Reference 25) A yellow precipitate formed immediately upon the addition of 6.54 g. (0.045 mole) of 8-hydroxyquinoline to 100 ml. of partially frozen chloroform containing 11.7 g. (0.10 mole) of boron trichloride. The mixture, which was allowed to warm to room temperature, was stirred overnight and filtered. When the yellow solid product was triturated with chloroform and dried under vacuum, 7.3 g. (65 per cent) of dichloro(8-oxyquinoline)boron, m.p. 259-261° (reported, 265°),[25] was obtained. The infrared spectrum is shown in Fig. 31. An attempt to purify a similar prepration by vacuum sublimation at 230° resulted in decomposition.

6. Dichloro(1-oxy-1-propene-1,3-diphenyl-3-one)boron: In a manner similar to the preparation of dichloro(8-oxyquinoline)boron, 11.7 g. (0.10 mole) of boron trichloride in 100 ml. of chloroform and 11.0 g. (0.049 mole) of dibenzoylmethane gave 8.8 g. (59 per cent) of dichloro(1-oxy-1-propene-1,3-diphenyl-3-one), m.p. 232-234° (from benzene). The infrared spectrum is reported in Fig. 32.

Anal. Calcd. for $C_{15}H_{11}BCl_2O_2$: C, 59.07; H, 3.64; B, 3.55. Found: C, 59.11; H, 3.64; B, 3.56.

Repetition of the procedure gave 9.1 g. (61 per cent) of dichloro-(1-oxy-1-propene-1,3-diphenyl-3-one)boron, m.p. 233-234° (from benzene).

7. Dichloro(α-picolino)boron (attempted): When 6.15 g. (0.050 mole) of α-picolinic acid, m.p. 130-133°, was added to 11.7 g. (0.10 mole) of boron trichloride in 160 ml. of partially frozen chloroform, no precipitate formed. Evaporation of the mixture gave 8.5 g. (138 per cent) of recovered α-picolinic acid, m.p. 130-133°.

8. Dibromo(8-oxyquinoline)boron (attempted): A solution of 2.18 g. (15.1 mmoles) of 8-hydroxyquinoline in 25 ml. of chloroform was added slowly to a stirred solution of 3.78 g. (15.1 mmoles) of boron tribromide in 25 ml. of chloroform. Both solutions were cooled to -70°. After the mixture had warmed to room temperature, it was stirred an additional hour and the liquid was decanted. The remaining solvent was removed under reduced pressure to give 3.8 g. of an unidentified compound, m.p. 250-252°.

Anal. Calcd. for $C_9H_6BBr_2NO$: C, 34.34; H, 1.92; B, 3.44; N, 4.45. Found: C, 37.47; H, 2.53; B, 4.18; N, 4.89.

9. Dibromo(1-oxy-1-propene-1,3-diphenyl-3-one)boron (attempted): A solution of 3.81 g. (17.0 mmoles) of dibenzoylmethane in 20 ml. of methylene chloride was added to a stirred solution of 4.26 g. (17.0 mmoles) of boron tribromide in 15 ml. of methylene chloride. Both solutions were cooled to -70°. After the solution had warmed to room temperature, petroleum ether (b.p. 30-60°) was added dropwise. A methylene chloride-insoluble precipitate formed which was collected by filtration, washed with petroleum ether, and dried at 79° (0.1 mm.) over phosphorus pentoxide for 24 hr. There was obtained 6.7 g. of an unidentified compound which melted at 259-260°.

Anal. Calcd. for $C_{15}H_{11}BBr_2O_2$: C, 45.73; H, 2.82; B, 2.75. Found: C, 50.42; H, 4.89; B, 2.28.

10. Triphenylborate: (Method: Reference 52) A solution of 11.7 g. (0.10 mole) of boron trichloride in 25 ml. of methylene chloride was slowly added to a solution of 25.4 g. (0.30 mole) of phenol in 100 ml. of chloroform. The mixture was allowed to warm to room temperature and the solvent and hydrogen chloride were removed under reduced pressure. Distillation gave 19.4 g. (75 per cent) of triphenylborate which boiled at 158-159° (0.1 mm.) (reported, 157-158° (0.05 mm.)).[52/]

An attempt to prepare triphenylborate by an alternate procedure gave a low melting product. A mixture of 12.0 g. (0.19 mole) of boric acid and 94 g. (1.0 mole) of phenol was heated until the phenol-water azeotrope ceased to distill. After the excess phenol was distilled off at reduced pressure, triphenylborate was collected at 195-205° (2 mm.) Recrystallization from methylene chloride-petroleum ether (b.p. 30-60°) gave 42 g. (77 per cent) of triphenylborate, m.p. 72-75° (reported, 92-93°).[52/]

11. Diphenoxy(8-oxyquinoline)boron: By the procedure described in paragraph IV.12., 2.56 g. (8.83 mmoles) of triphenylborate and 1.28 g. (8.83 mmoles) of 8-hydroxyquinoline gave 1.10 g. (113 per cent) of phenol. The crude product was dissolved in a minimum of methylene chloride (ca. 30 ml.), and 10 per cent additional solvent was added. When an equal volume of petroleum ether (b.p. 30-60°) was added, the resulting solution stayed clear for several minutes before crystals formed. After 2 hr., 30 ml. more of petroleum ether was added and the solution was stored overnight. The solvent phase was decanted and the crystals were dried in a vacuum desiccator containing Drierite. The yield was 2.66 g. (88 per cent) of diphenoxy(8-oxyquinoline)boron, m.p. 155-158°. The infrared spectrum is reported in Fig. 33.

<u>Anal</u>. Calcd. for $C_{21}H_{16}O_3NB$: C, 73.92; H, 4.73; B, 3.17; N, 4.11. Found: C, 73.82; H, 4.81; B, 3.35; N, 4.13.

In a previous experiment, diphenoxy(8-oxyquinoline)boron was recrystallized from methylene chloride and obtained as a fine powder which immediately liquefied and turned brown upon exposure to air.

12. <u>Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (from triphenyl borate and dibenzoylmethane)</u>: Methylene chloride was distilled from phosphorus pentoxide into a flask containing 6.1 g. (0.021 mole) of triphenylborate and 4.2 g. (0.021 mole) of dibenzoylmethane until the reactants just dissolved (ca. 30 ml.). The methylene chloride was removed from the yellow solution under vacuum at room temperature and phenol (1.97 g., 97 per cent) was removed at 55° (1 mm.). A portion (0.9 g.) of the crude product (m.p. 122-146°) was recrystallized from methylene chloride, giving 0.5 g. (56 per cent) of diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron, m.p. 171-173°. The product, m.p. 171-173°, could also be obtained by adding petroleum ether (b.p. 30-60°) to a solution of the crude product in methylene chloride. The infrared spectrum of the pure material is reported in Fig. 34.

<u>Anal</u>. Calcd. for $C_{27}H_{21}BO_4$: C, 77.15;H, 5.04; B, 2.57. Found: C, 76.96; H, 5.08; B, 2.61.

13. <u>Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (from dichloro-(1-oxy-1-propene-1,3-diphenyl-3-one)boron and phenol)</u>: After a mixture of 1.5 g. (4.92 mmoles) of dichloro(1-oxy-1-propene-1,3-diphenyl-3-one)boron, 0.93 g. (9.84 mmoles) of phenol,and about 20 ml. of methylene chloride was stirred at room temperature for 22 hr., most of the boron-containing material remained undissolved. An additional 1.95 g. (20.8 mmoles) of phenol was added, and the mixture was refluxed for 1.5 hr. Upon evaporation of the resulting solution and distillation of the excess phenol at 80° (0.1 mm.), 1.9 g. (92 per cent) of crude diphenoxy(1-oxy-1-propene-3-one)boron was obtained as a residue. Recrystallization of the residue from a methylene chloride-petroleum ether (b.p. 30-60°) gave 1.2 g. of the purified compound which melted at 169-171°. The infrared spectrum of the compound was the same as the spectrum of an authentic sample except for spurious weak bands below 1,400 $cm.^{-1}$ and a medium intensity band at 950 $cm.^{-1}$

14. <u>Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (attempted from dibromo(1-oxy-1-propene-1,3-diphenyl-3-one)boron and phenol)</u>: When a mixture of 1.5 g. (3.8 mmoles) of the compound that was tentatively identified as dibromo(1-oxy-1-propene-1,3-diphenyl-3-one)boron, 2.8 g. (30 mmoles) of phenol, and 30 ml. of dimethylacetamide was stirred 5 hr., the borate dissolved. Stirring was continued 15 hr., then the mixture was devolatilized at

50° (0.1 mm.). The semisolid residue was partly soluble in 25 ml. of methylene chloride. When the methylene chloride solution was decanted and the residue was devolatilized at 0.1 mm., the insoluble yellow precipitate gave 0.80 g. of a brown oil. Slow addition of petroleum ether to the solution also precipitated a brown oil.

A repetition of the experiment with 1.11 g. (2.82 mmoles) of the dibromo(1-oxy-1-propene-1,3-diphenyl-3-one)boron and 0.53 g. (5.64 mmoles) of phenol afforded 0.95 g. of a yellow compound, m.p. 350-352°, which was not identified. The compound gave a positive Beilstein test and was soluble in methylene chloride.

Anal. Calcd. for $C_{65}H_{51}B_3Br_2O_8$: C, 67.73; H, 4.46; B, 2.82; Br, 13.87. Found: C, 67.46; H, 4.47; B, 2.93; Br, 13.8.

15. Phenylphosphonic acid: (Method: Reference 53) A mixture of 50 g. (0.26 mole) of phenylphosphonic dichloride and 100 ml. of water was swirled until the dichloride dissolved. The resulting hot solution was cooled in an ice bath and the crude phenylphosphonic acid was collected by filtration, redissolved in water at about 70°, allowed to stand at room temperature, and then in an ice bath. The mixture was filtered and the solid product, which melted at 162-163.5° (reported, 161-163°),[53] was dried in a vacuum desiccator over Drierite for 24 hr. The yield was 33 g. (81 per cent).

16. Benzenephosphonic diisopropoxide (attempted): When 30 g. (0.15 mole) of benzenephosphonic dichloride was dissolved in 60 ml. of isopropyl alcohol, the solution became hot and hydrochloric acid was evolved. The residue that was obtained after the isopropyl alcohol was distilled and the remaining material was devolatilized at 200° (1 mm.) melted at 160-165° and had an infrared spectrum identical to benzenephosphonic acid.

17. Diphenylphosphonic acid: (Method: Reference 54) A solution of 0.200 mole of phenylmagnesium bromide in 667 ml. of ether, which was prepared by diluting commercial 3 M phenylmagnesium bromide in diethylether, was added dropwise during 2.5 hr. to a stirred solution of 30.6 g. (0.200 mole) of phosphorus oxychloride in 500 ml. of ether. After the mixture was stored overnight and the ether was decanted, the residue was hydrolyzed with 200 ml. of water and sufficient solid sodium hydroxide was added to bring the pH to 10-11. The insoluble triphenylphosphine oxide was filtered off, and the filtrate was acidified with concentrated hydrochloric acid to precipitate the phosphinic acid. Filtration and drying gave 10.1 g. (49 per cent) of diphenylphosphinic acid which melted at 185-186° after recrystallization from a petroleum ether-benzene mixture(reported, m.p. 190-192°).[54]

18. Bis(diphenylphosphinico)(1-oxy-1-propene-1,3-diphenyl-3-one)-boron (attempted): A solution of 1.0 g. (2.94 mmoles) of diphenoxy(1-oxy-1 propene-1,3-diphenyl-3-one)boron, 1.22 g. (5.88 mmoles) of diphenylphosphinic acid, and 30 ml. of chlorobenzene was refluxed in an atmosphere of nitrogen for 22 hr. When the solvent was distilled to 90° (0.1 mm.), no phenol could be detected in the distillate. An infrared spectrum of the residue was similar to an equimolar mixture of the reactants with the exception of the very weak phosphinic acid OH absorption at 2,650 cm.$^{-1}$ and spurious peaks of low intensity at 1,060 cm.$^{-1}$ and in the 700-800 cm.$^{-1}$ region.

19. Tris(diphenylphosphinico)boron (attempted): When a solution of 1.6 g. (13.6 mmoles) of boron trichloride in 15 ml. of methylene chloride was added to a mixture of 8.5 g. (40.9 mmoles) of diphenylphosphinic acid and 15 ml. of methylene chloride, the acid immediately dissolved. After the solution was stored 18 hr. at room temperature, the product was devolatilized to 50° (0.1 mm.), and 8.6 g. of a white residue which melted at 89-92° was obtained. When 1.0 g. of the residue was extracted with benzene, 0.15 g. remained undissolved. An infrared spectrum of the benzene-insoluble fraction (m.p. 156-165°) was consistent with its identification as boric acid; the infrared spectrum of the benzene-soluble fraction (m.p. 177-182°) was identical with an authentic spectrum of diphenylphosphinic acid.

K. Ultraviolet-Vacuum Film Study

Initial studies of the effect of simulated solar ultraviolet radiation in space on the reflectance of potential protective coatings are reported.

1. Apparatus: Specimen total reflectance and diffuse reflectance curves from 0.24 to 2.2 μ were recorded before and after exposure with a Beckman DK-1 double-beam spectrophotometer and reflectance attachment. Freshly prepared magnesium oxide was used as the reflectance reference material.

The irradiation chamber, which is shown in Figs. 43, 44, and 45, was a short cylinder constructed so that 14 pairs of reflector specimens mounted in isolated pie-shaped compartments could be simultaneously subjected to UV in a simulated space environment. The entire inner surface of the chamber was coated with a black potassium silicate and graphite mixture. The specimens were mounted around the inside rim of the chamber so that the reflected energy was absorbed by the black chamber walls. The outer surface of the chamber was water-cooled.

The UV irradiation source was an air-cooled mercury vapor lamp (General Electric B-H6) located at the vortex of the compartments so that all specimens were equally exposed.

The irradiation chamber was evacuated in the bell jar of a CEC Model LCI-14B Vacuum Coating Unit. The vacuum in the system was determined by means of a CEC Model 6P-140 Pirani Gage and a CVC Model 6 PH-100A Discharge Gage. A pressure-regulated switch in the power circuit protected the UV lamp against a cooling line failure.

2. Irradiation: Five ceramic-coated metal plates (supplied by NASA) were coated by a Paaschs VL airbrush with a protective coating (see Table I). Plates 1, 2 (duplicates), 4, and 5 (duplicates), were cured at 25° for 48 hr., and plate 3 was cured in an air oven at 145° for 48 hr. The plates were irradiated for 48 hr., at a pressure of 2×10^{-5} to 9.2×10^{-6} mm. Hg. Weight losses of the films during irradiation are shown in Table VII.

TABLE VII

ULTRAVIOLET IRRADIATION

Plate	Coating	Thickness (mils)	Initial Wt. (g.)	Final Wt. (g.)	Wt. Loss (g.) - (%)
1	LTV-602	1.7	0.1064	0.1010	0.0054 - 5.4
2	LTV-602	1.9	0.1212	0.1117	0.0095 - 8.5
3	S 716 11[a]	2.0	0.1202	0.1262	0.0060 - 0.0
4	S-13	6.7	0.6836	0.6776	0.0060 - 0.89
5	S-13	6.2	0.6334	0.6275	0.0059 - 0.94

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[a] A polymer prepared from p-phenylenebis(diphenylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

Initially, all plates were clear and shiny, but after irradiation plates 1,2, and 3 were light brown in color. No change in appearance was observed in plates 5 and 6. Plate 3 was the only one that did not lose weight during exposure.

Although the total and diffuse reflectance from 0.24 to 2.2 μ were determined before and after irradiation, the regions from 0.24 to 0.36 μ and 0.70 to 2.20 μ showed very little change; consequently, the data are not included. The per cent reflectance from 0.40 to 0.70 μ is shown in Table VIII. The reflections were predominantly diffusely scattered with only a few per cent of the incident energy being specular.

TABLE VIII

ULTRAVIOLET RADIATION (400-700 mμ)

Wave-length (mμ)	Total Reflectance (%)									
	No. 1		No. 2		No. 3		No. 4		No. 5	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
400	68.0	18.0	53.0	16.5	65.0	5.5	86.0	79.0	87.0	80.0
425	82.5	28.0	75.0	24.5	80.5	8.5	94.0	88.0	95.0	90.0
450	84.5	33.5	77.5	30.0	84.5	15.5	96.0	92.0	96.0	92.5
475	86.5	39.0	81.0	37.0	86.0	22.0	95.5	93.5	95.5	93.5
500	89.5	45.5	82.5	42.5	88.0	31.0	95.5	93.5	94.5	94.5
550	89.0	56.5	85.0	52.5	89.5	50.5	94.5	94.5	94.5	95.0
600	91.5	66.0	88.5	63.0	91.5	70.0	97.5	97.5	98.0	99.0
650	91.5	72.0	88.5	69.5	92.0	80.0	98.0	99.5	98.5	100.0
700	91.5	75.0	88.0	72.5	90.5	84.0	97.5	98.0	98.0	99.5
	Diffuse Reflectance (%)									
400	65.0	16.0	65.0	12.5	64.0	1.0	86.0	77.0	84.0	76.0
425	80.0	24.0	72.5	21.0	77.5	3.0	94.0	86.0	94.0	86.0
450	82.0	31.0	75.0	26.5	79.5	8.0	94.5	89.0	95.0	89.0
475	84.0	36.5	77.5	33.0	82.0	16.0	95.0	90.5	95.5	90.0
500	85.5	41.5	79.0	38.0	83.0	24.0	94.5	91.0	94.5	90.0
550	87.0	52.0	82.5	48.5	85.0	44.0	88.0	91.0	93.5	91.5
600	88.5	62.0	85.0	58.5	87.0	62.0	91.5	95.0	97.0	95.0
650	90.0	69.5	86.5	66.0	87.5	74.0	97.5	96.5	97.5	96.5
700	87.5	72.0	85.0	68.5	86.0	78.0	96.0	94.0	97.0	95.0

Plots of wavelength (400-700 μ) versus per cent total reflectance for plates 1, 3, and 5 are shown in Figs. 46, 47, and 48, respectively. The per cent reflectance of plates 1 and 3 was much less after irradiation, but the change in reflectance of plate 5 was very slight.

V. NEW COMPOUNDS AND POLYMERS

New compounds and polymers prepared during this report period are listed in Table IX. Compounds which had been reported but were not previously characterized are also included. Only the polymers that were characterized are reported.

TABLE IX

NEW COMPOUNDS AND POLYMERS

Compound or Polymer	Reference Paragraph
p-Phenylenebis(ethoxymethylphenylsilane)	IV.A.5.
p-Phenylenebis(methylphenylsilanol)	IV.A.6.
Chlorodiphenylethoxysilane	IV.A.8.
Polymer from nonamethylcyclotrisilazane and p-phenylenebis(diphenylsilanol)	IV.C.1.
Polymer from diphenylbis(methylamino)silane and p-phenylenebis(diphenylsilanol)	IV.C.1.
Polymer from heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane and p-phenylenebis(diphenylsilanol)	IV.C.2.
3,3'-Dihydroxybenzidine hydrochloride	IV.D.2.
2,2'-Diamino-p,p'-biphenol hydrochloride	IV.D.4.
2,2'-diphenyl-5,5'-bibenzoxazole	IV.D.10.
2,2'-Diphenyl-6,6'-bibenzoxazole	IV.D.11.
N,N'-Dibenzoyl-3,3'-dihydroxybenzidine	IV.D.12.
N,N'-dibenzoyl-2,2'-diamino-p,p'-biphenol	IV.D.13.
Polymer from 3,3'-dihydroxybenzidine and terephthalamide	IV.E.2.

TABLE IX (Concluded)

Compound or Polymer	Reference Paragraph
Polymer from 2,2'-diamino-*p*,*p*'-biphenol and terephthalamide	IV.E.3
1,1'-Bis(3-hydroxyethoxycarbonyl)ferrocene	IV.I.8.
Dichloro(1-oxy-1-propene-1,3-diphenyl-3-one)boron	IV.J.6.
Diphenoxy-8-oxyquinolineboron	IV.J.11
Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron	IV.J.12.

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APPENDIX I

INFRARED SPECTRA OF COMPOUNDS AND POLYMER

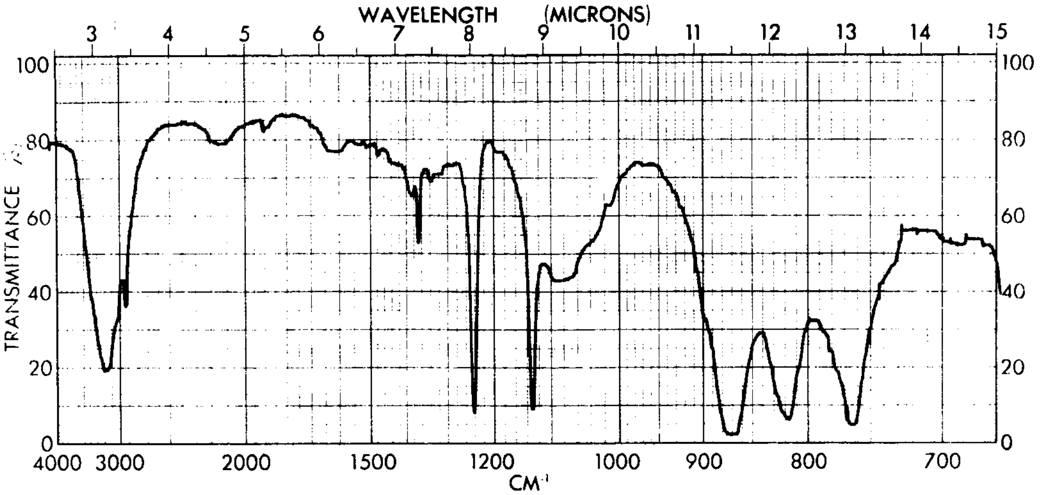

Fig. 1 - Infrared Spectrum of p-Phenylenebis(dimethylsilanol) (KBr)

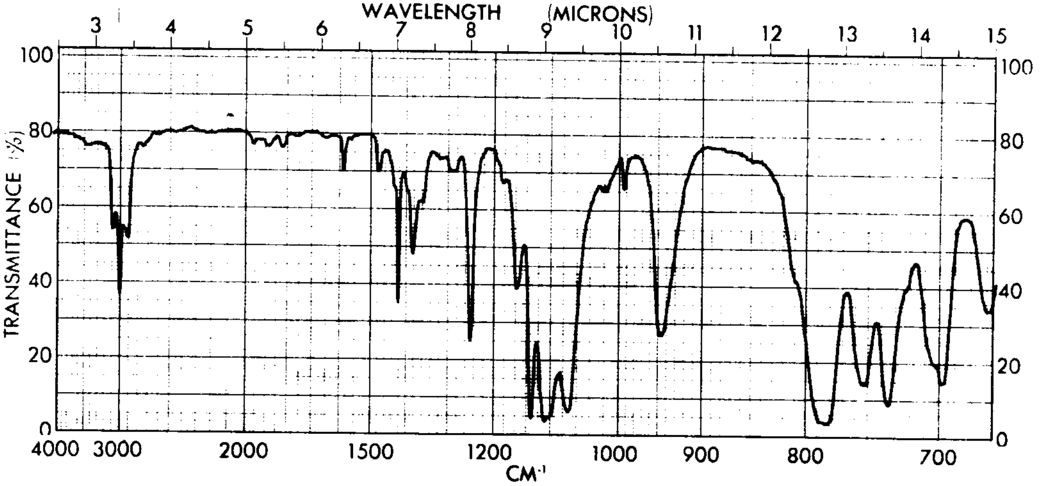

Fig. 2 - Infrared Spectrum of p-Phenylenebis(methylphenylethoxysilane) (Smear)

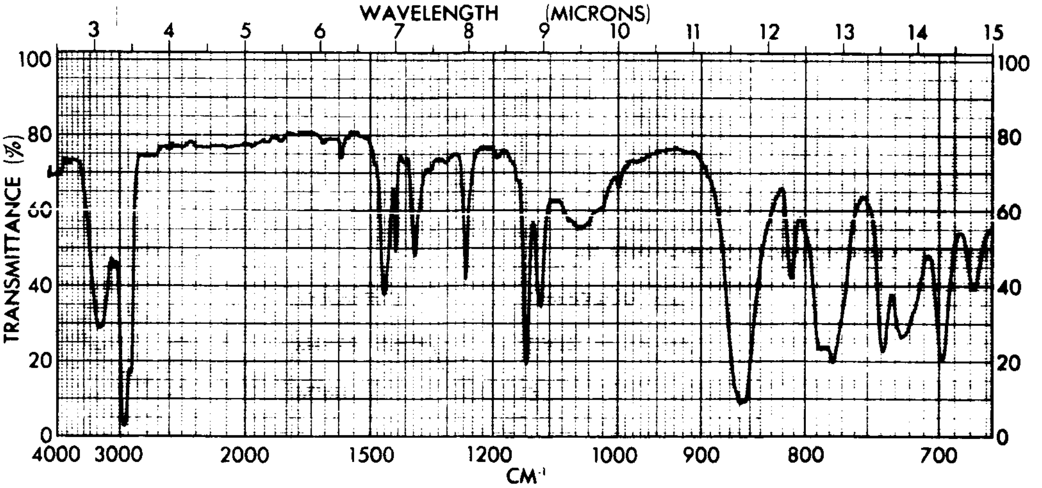

Fig. 3 - Infrared Spectrum of p-Phenylenebis(methylphenylsilanol), m.p. 127-140° (Nujol)

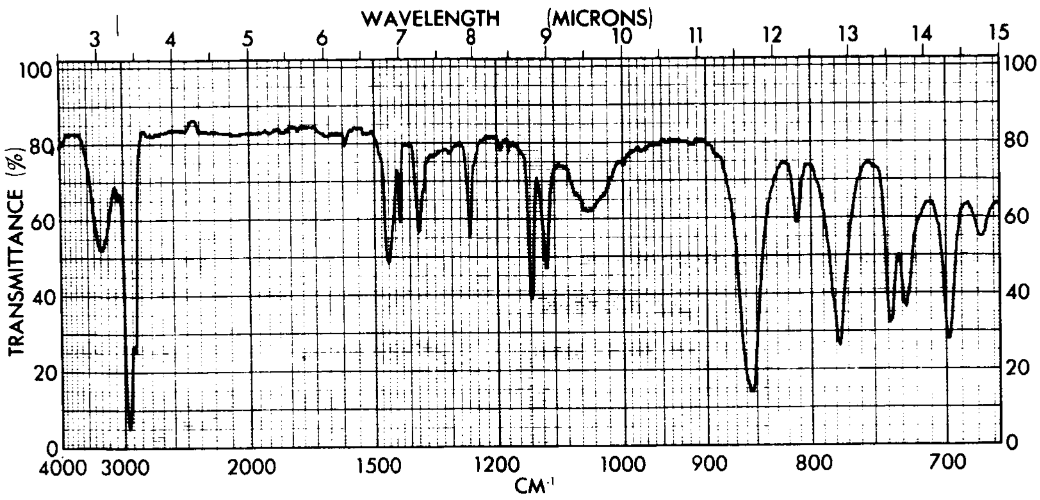

Fig. 4 - Infrared Spectrum of p-Phenylenebis(methylphenylsilanol), m.p. 156-158° (Nujol)

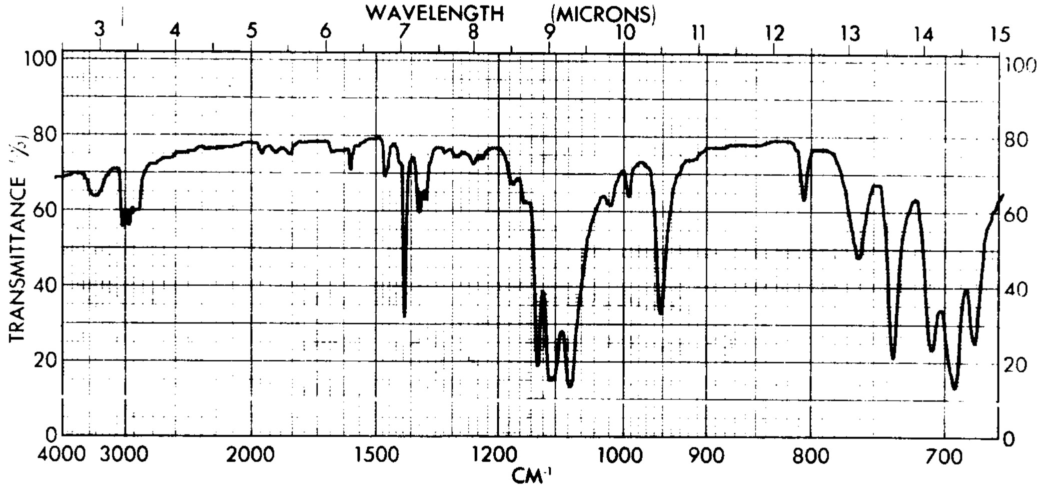

Fig. 5 - Infrared Spectrum of p-Phenylenebis(diphenylethoxysilane) (KBr)

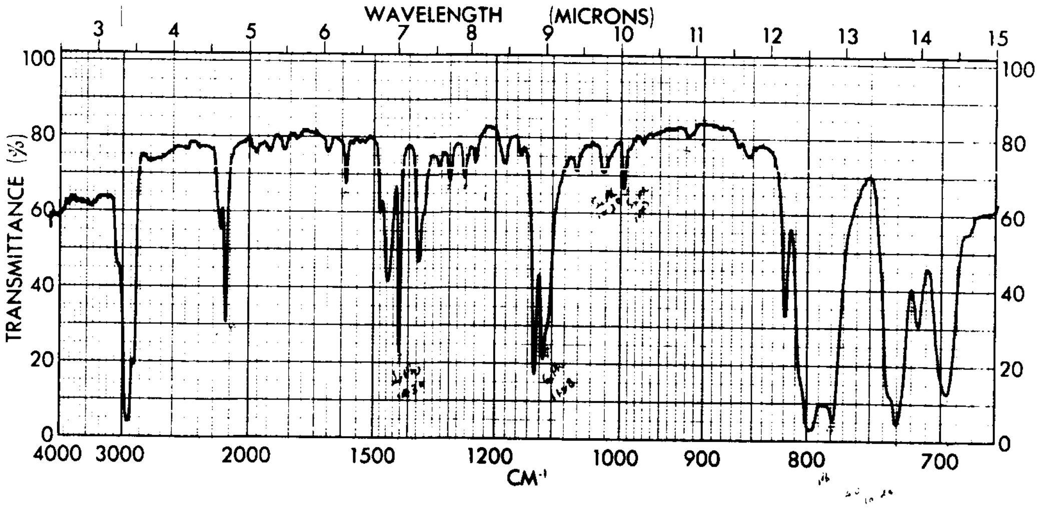

Fig. 6 - Infrared Spectrum of p-Phenylenebis(diphenylsilane) (Nujol)

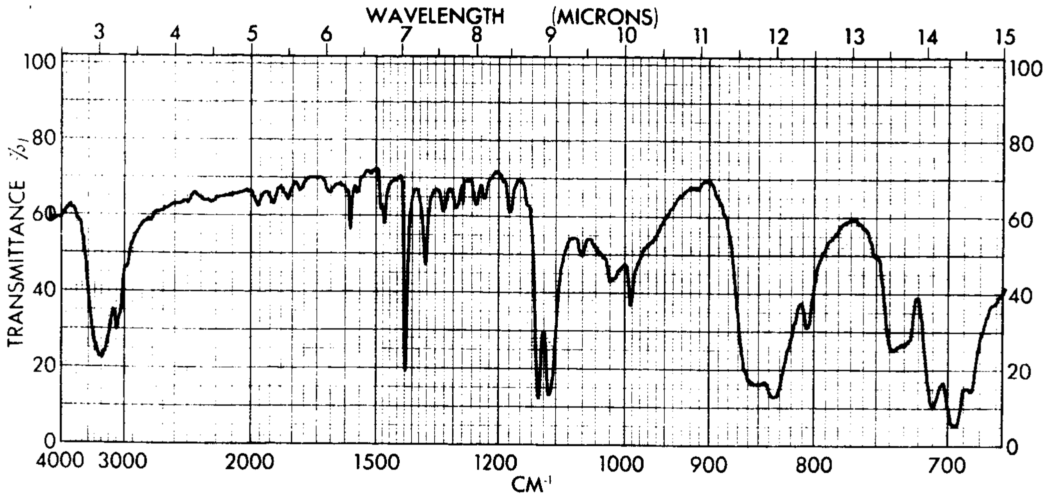

Fig. 7 - Infrared Spectrum of p-Phenylenebis(diphenylsilanol), m.p. 224-226° (KBr)

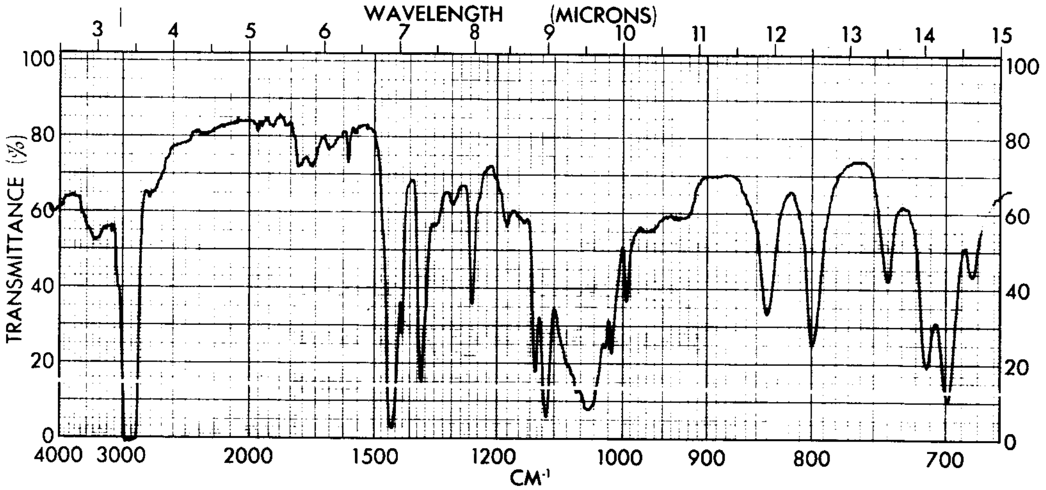

Fig. 8 - Infrared Spectrum of the Polymer from Nonamethylcyclotrisilazane and p-Phenylenebis(diphenylsilanol), η_{sp} 0.54 (Nujol)

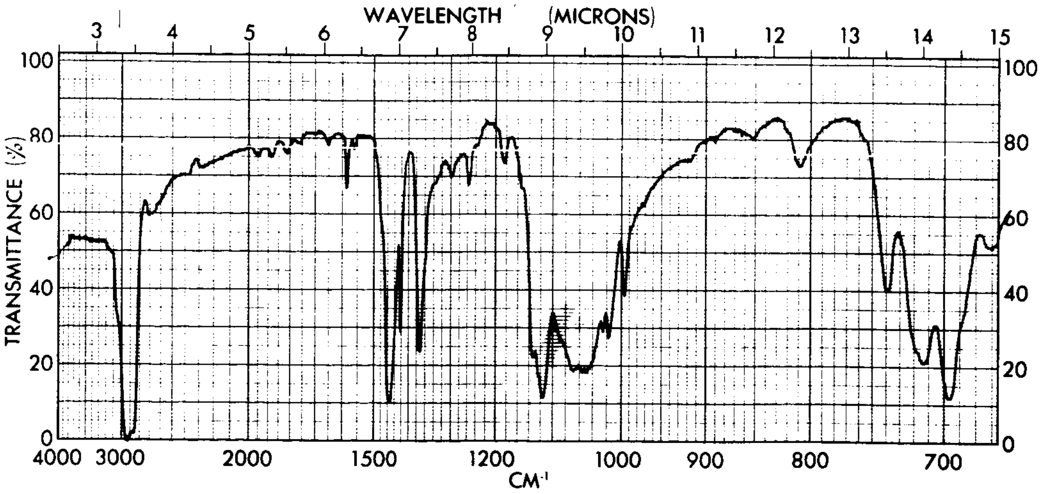

Fig. 9 - Infrared Spectrum of the Polymer from Bis(methylamino)diphenylsilane and p-Phenylenebis(diphenylsilanol), η_{sp} 0.20 (Nujol)

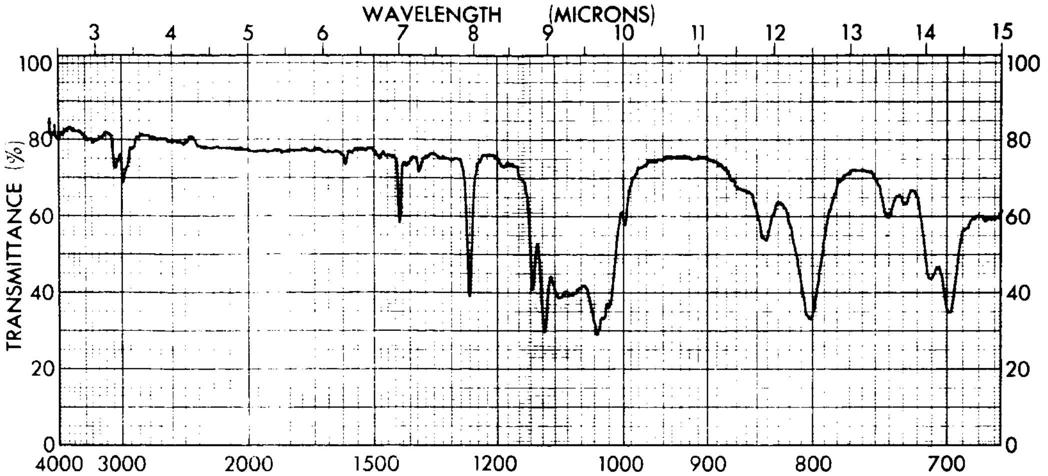

Fig. 10 - Infrared Spectrum of the Polymer from Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane and p-Phenylene-bis(diphenylsilanol), η_{sp} 0.07 (Film)

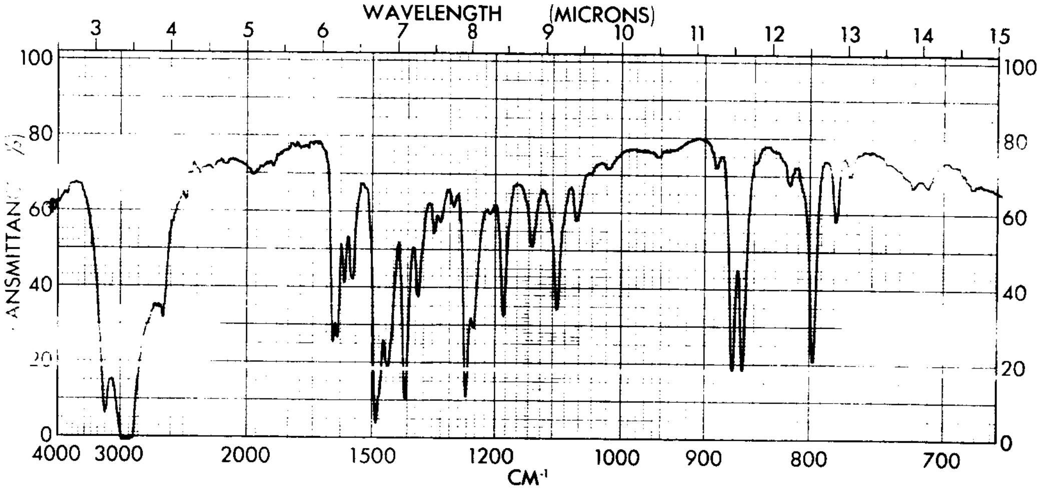

Fig. 11 - Infrared Spectrum of 3,3'-Dihydroxybenzidine Hydrochloride (Nujol)

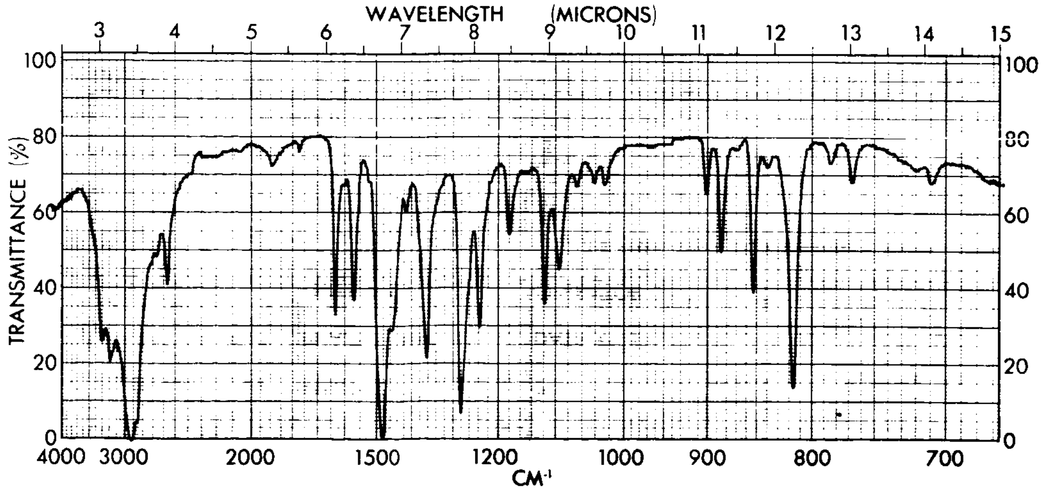

Fig. 12 - Infrared Spectrum of 2,2'-Diamino-p,p'-biphenol Hydrochloride (Nujol)

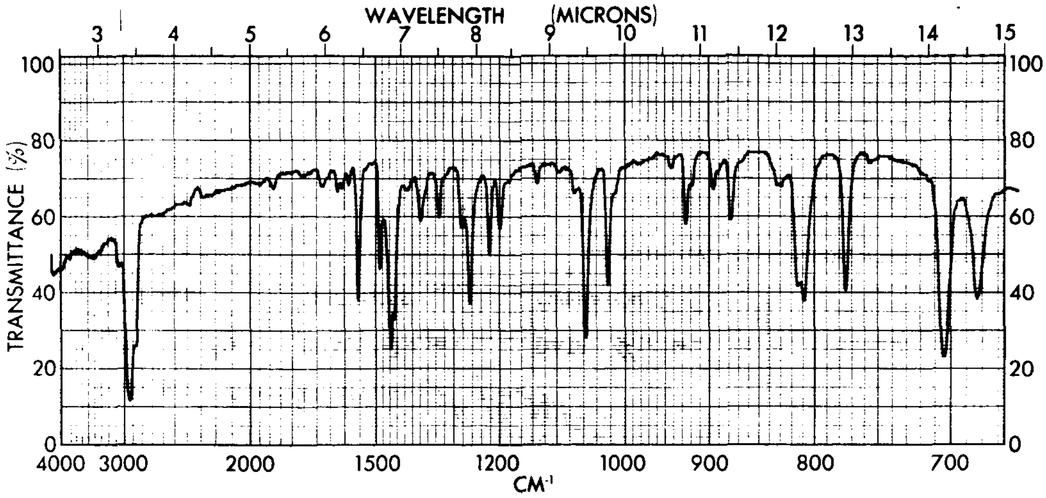

Fig. 13 - Infrared Spectrum of 2,2'-Diphenyl-5,5'-bibenzoxazole (Nujol)

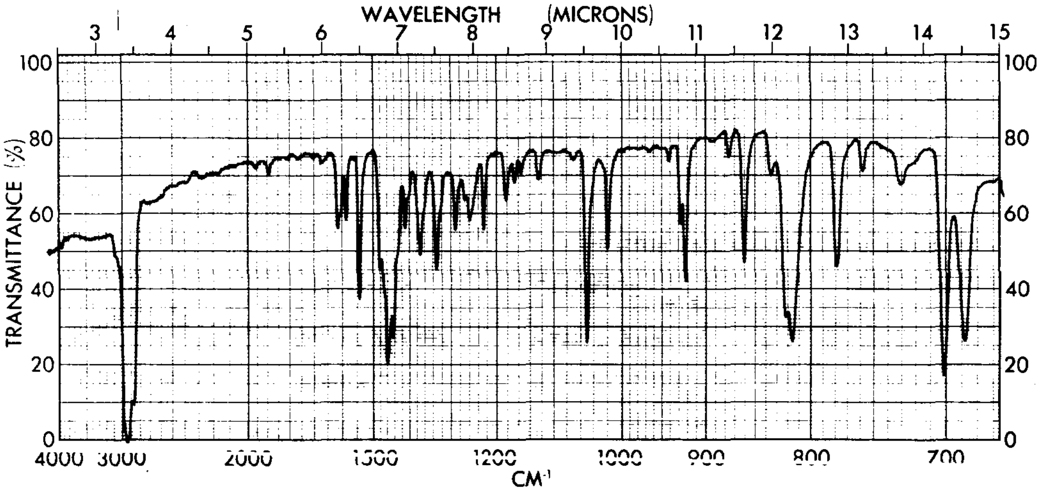

Fig. 14 - Infrared Spectrum of 2,2'-Diphenyl-6,6'-bibenzoxazole (Nujol)

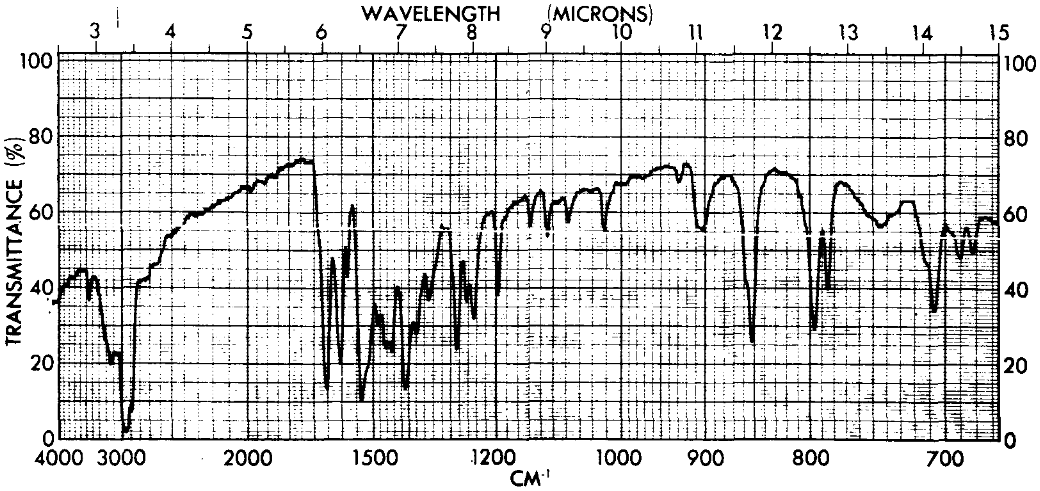

Fig. 15 - Infrared Spectrum of N,N'-Dibenzoyl-3,3'-dihydroxybenzidine (Nujol)

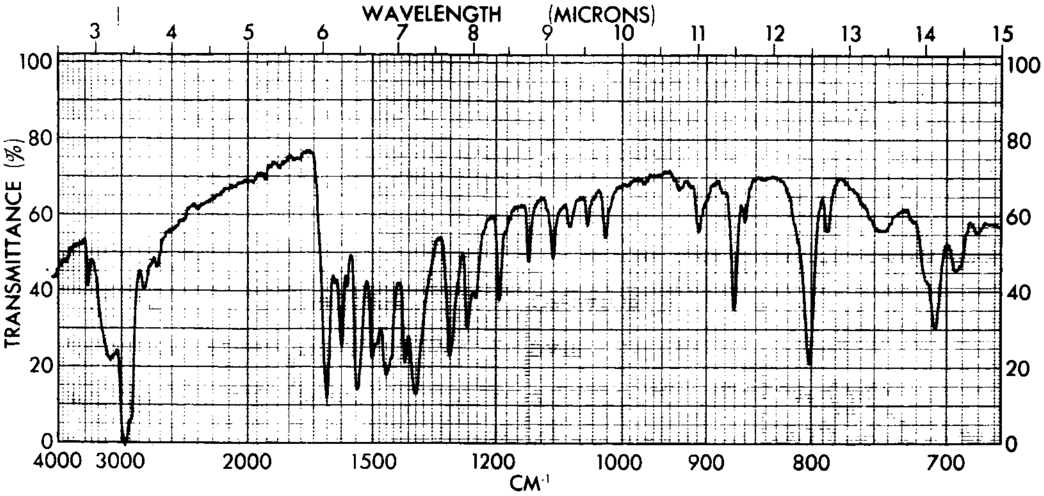

Fig. 16 - Infrared Spectrum of N,N'-Dibenzoyl-2,2'-diamino-p,p'-biphenol (Nujol)

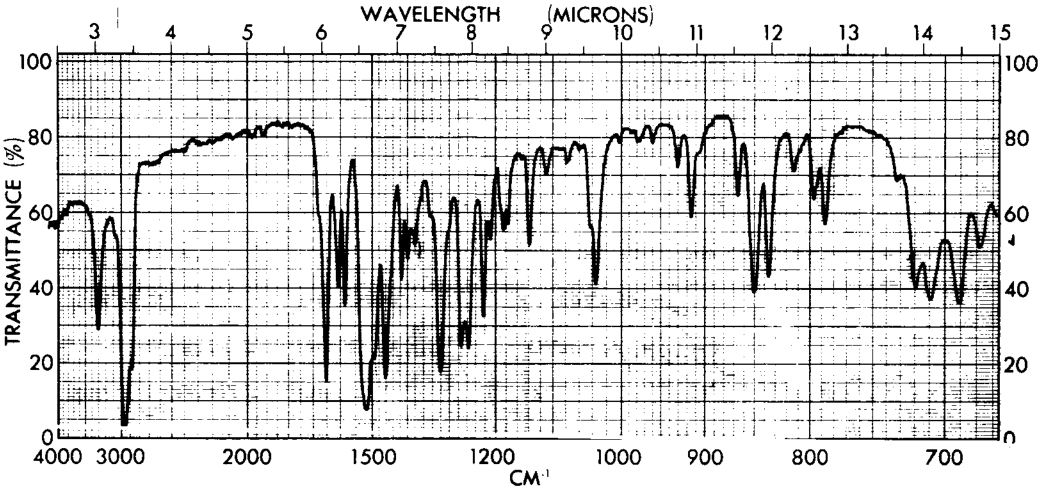

Fig. 17 - Infrared Spectrum of N,N'-Dibenzoyl-3,3'-dimethoxybenzidine (Nujol)

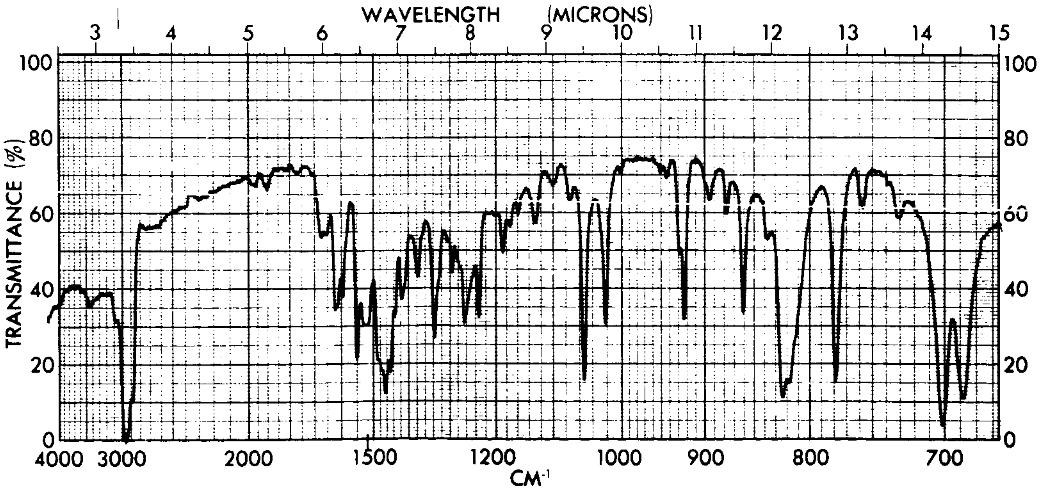

Fig. 18 - Infrared Spectrum of N,N'-Dibenzoyl-3,3'-dihydroxybenzidine Heated 2 Hr. at 300°

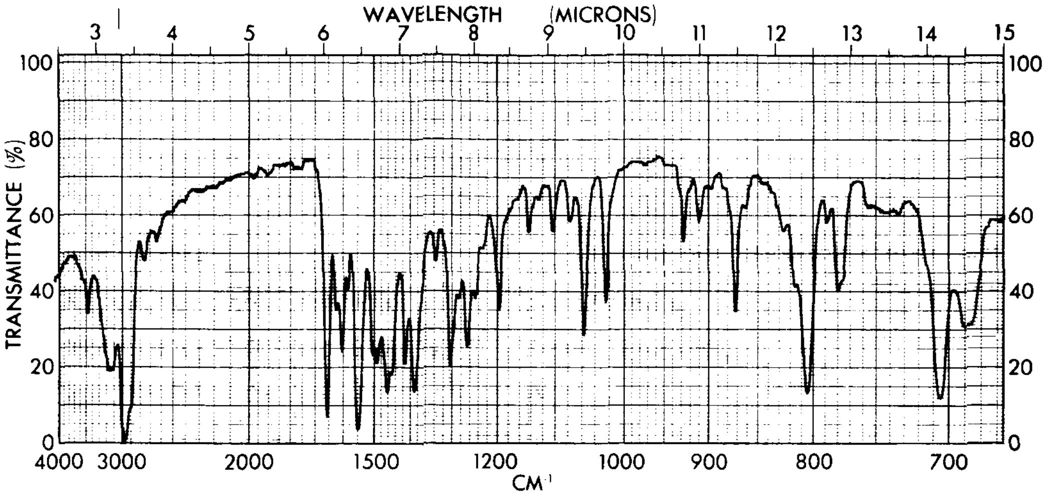

Fig. 19 - Infrared Spectrum of N,N'-Dibenzoyl-2,2'-diamino-p,p'-biphenol Heated 2 Hr. at 300° (Nujol)

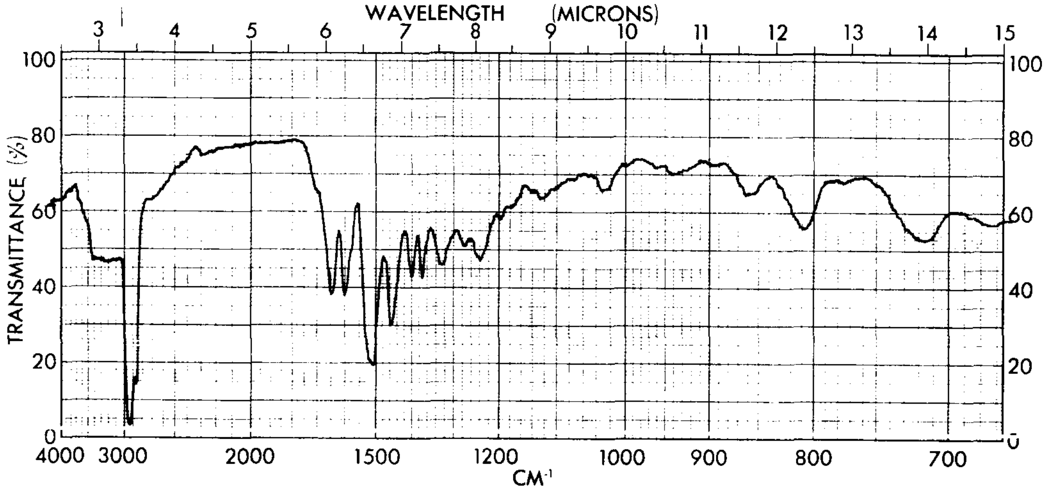

Fig. 20 - Infrared Spectrum of the Polymer from 3,3'-Dihydroxybenzidine and Isophthalyl Chloride in Dimethylacetamide-Cyclohexanone (Nujol)

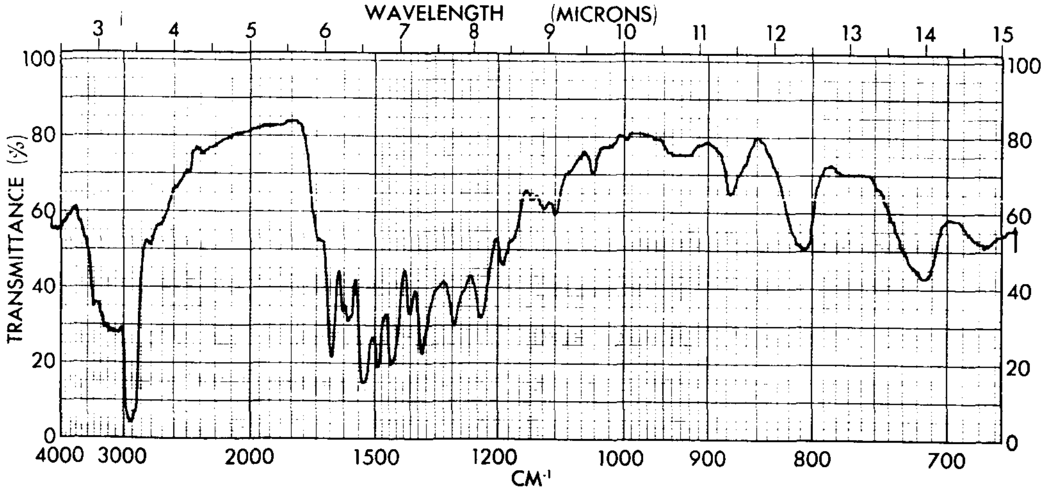

Fig. 21 - Infrared Spectrum of the Polymer from 2,2'-Diamino-p,p'-biphenol and Isophthalyl Chloride in Dimethylacetamide-Cyclohexanone (Nujol)

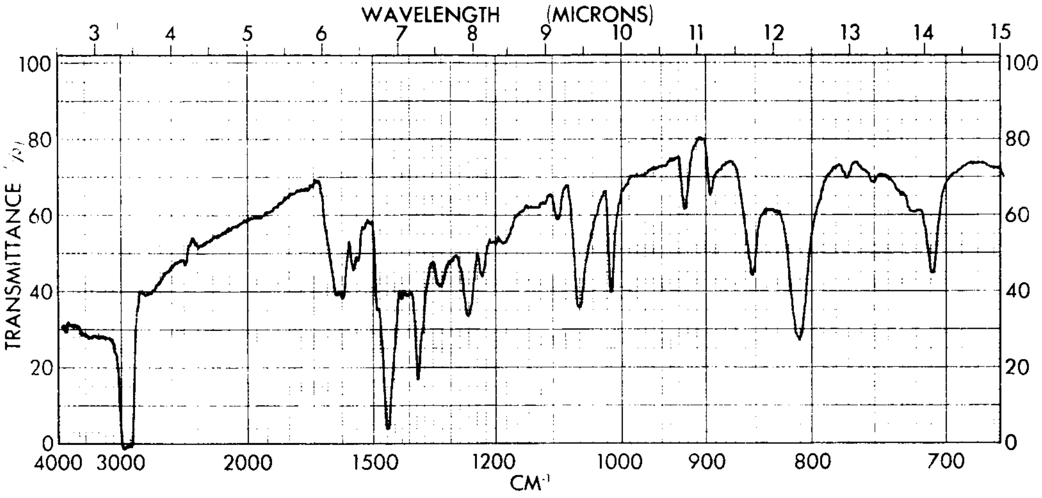

Fig. 22 - Infrared Spectrum of the Polymer from 3,3'-Dihydroxybenzidine and Terephthalimide in Polyphosphoric Acid, η_{sp} 0.22 (Nujol)

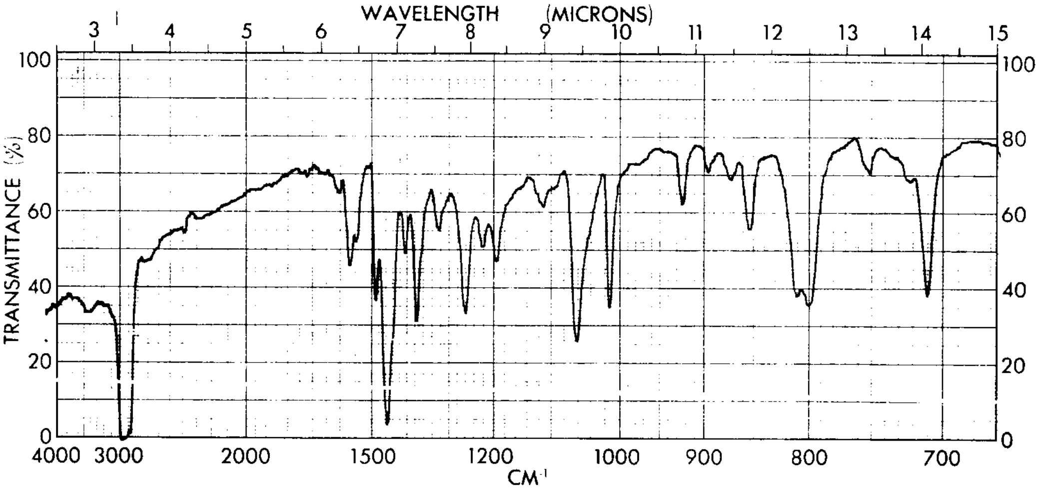

Fig. 23 - Infrared Spectrum of the Polymer from 2,2'-Diamino-p,p'-biphenol and Terephthalimide in Polyphosphoric Acid, η_{sp} 2.54 (Nujol)

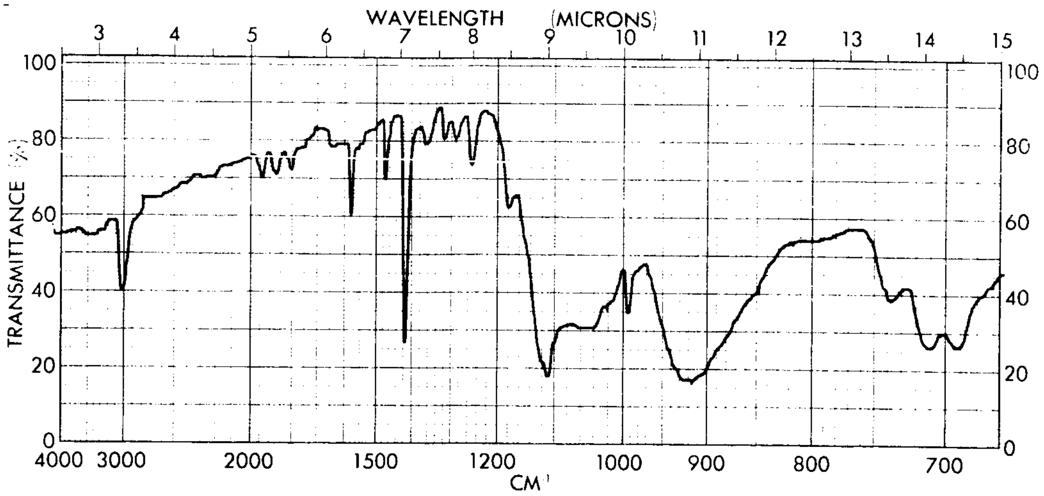

Fig. 24 - Infrared Spectrum of the Polymer from Tetraisopropoxytitanium, Diphenylsilanol, and Triphenylsilanol (KBr)

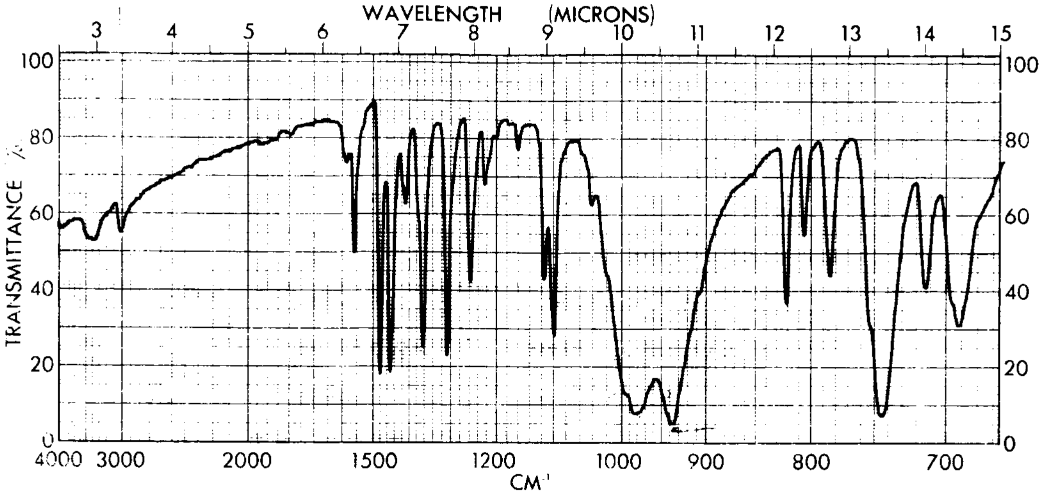

Fig. 25 - Infrared Spectrum of the Polymer from p-Phenylenebis(diphenylsilanol) and Diisopropoxybis(8-oxyquinoline)titanium (KBr)

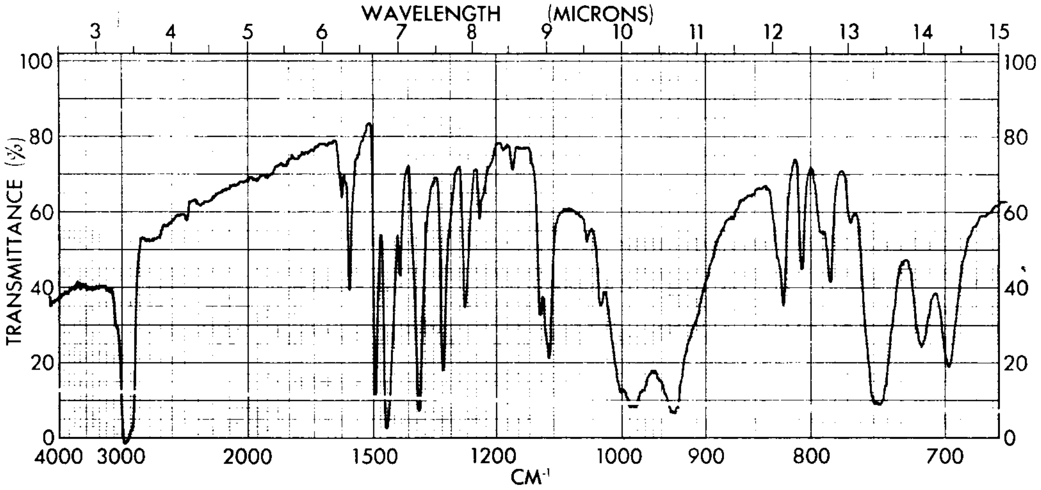

Fig. 26 - Infrared Spectrum of 1,1'-Bis(2-hydroxyethoxycarbonyl)ferrocene (Smear)

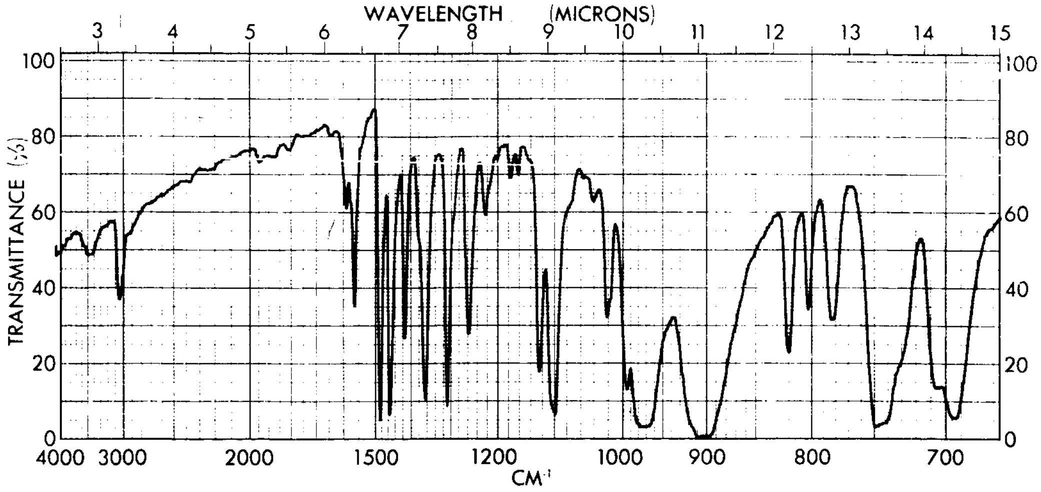

Fig. 27 - Infrared Spectrum of 1,1'-Bis(3-hydroxy-2,2'-dimethyl-1-propoxycarbonyl)ferrocene (Smear)

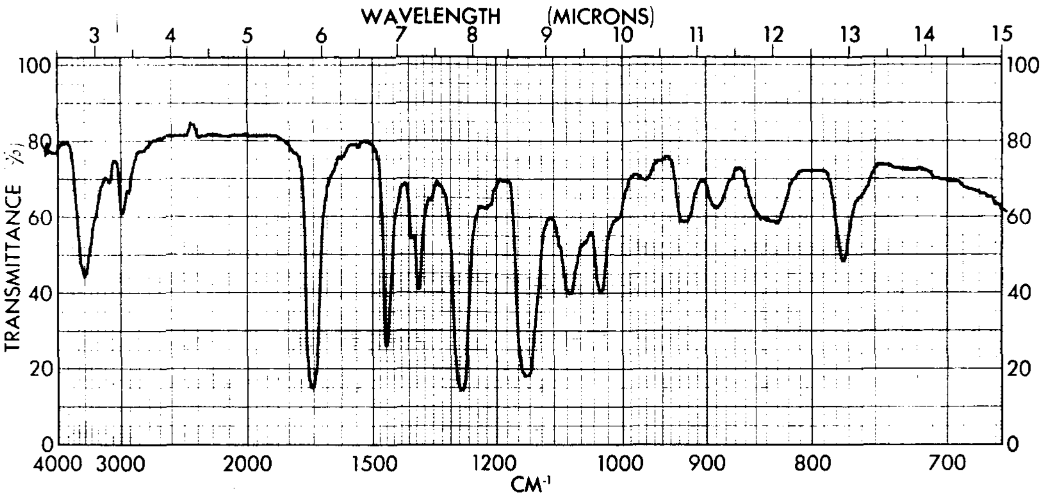

Fig. 28 - Infrared Spectrum of 1,1'-Bis(2-hydroxyethoxycarbonyl)ferrocene (Smear)

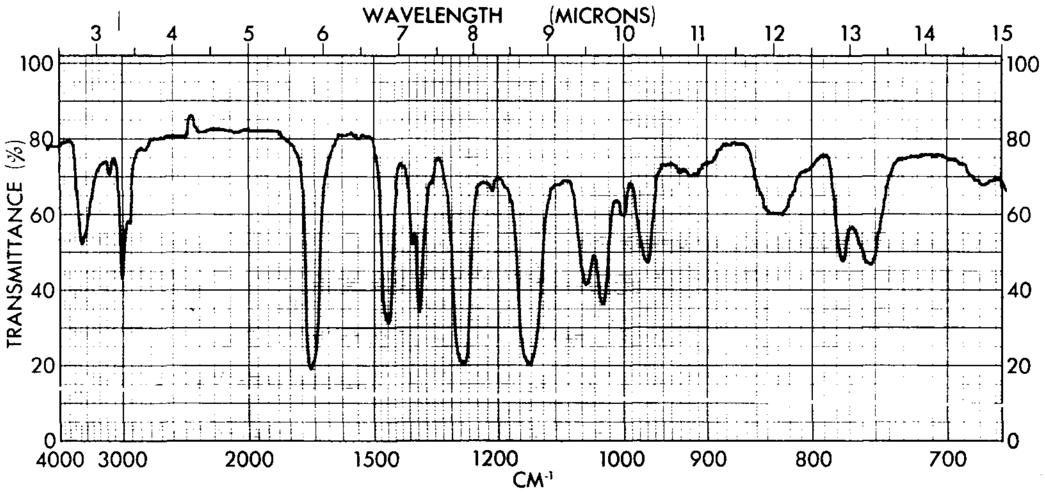

Fig. 29 - Infrared Spectrum of 1,1'-Bis(3-hydroxy-2,2'-dimethyl-1-propoxycarbonyl)ferrocene (Smear)

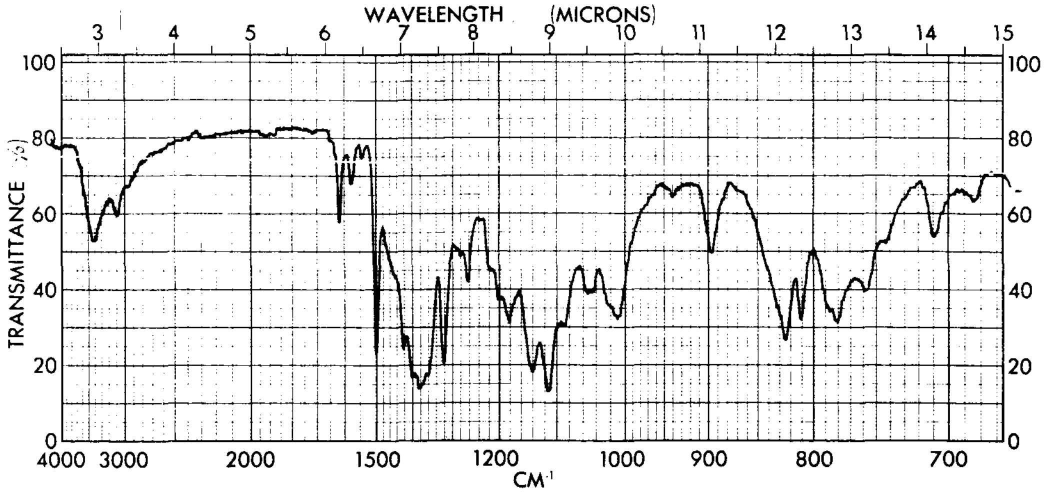

Fig. 30 - Infrared Spectrum of the Product from 8-Hydroxyquinoline and Isopropylborate (KBr)

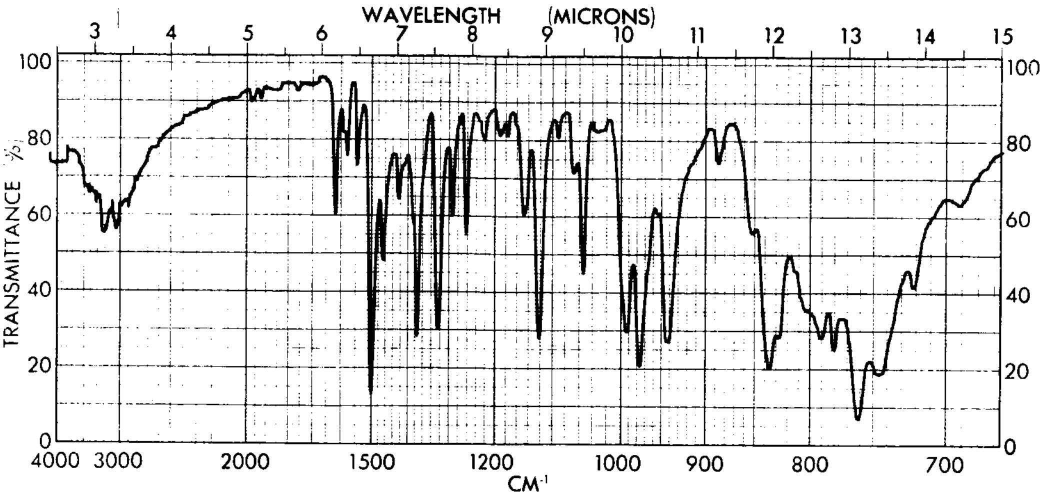

Fig. 31 - Infrared Spectrum of Dichloro(8-oxyquinoline)boron (KBr)

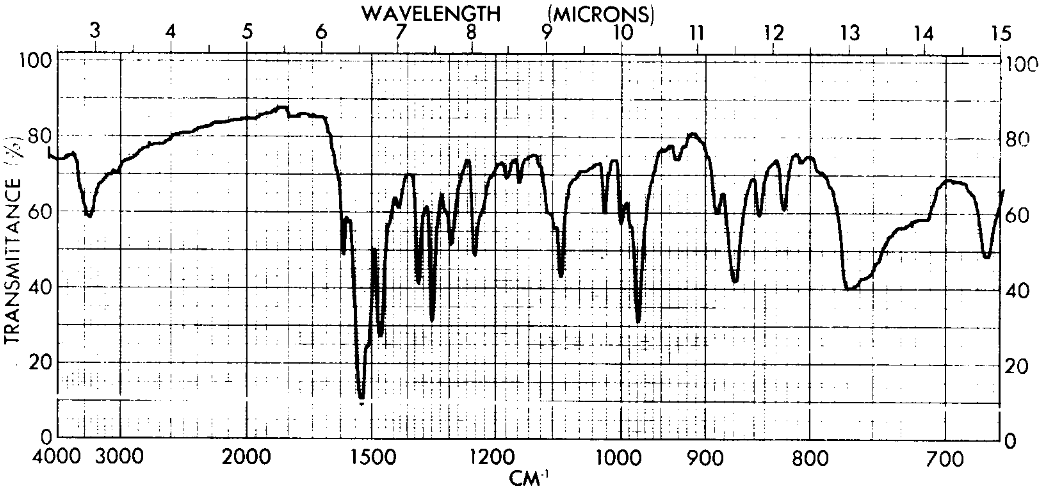

Fig. 32 - Infrared Spectrum of Dichloro(1-oxy-1-propene-1,3-diphenyl-3-one)boron (KBr)

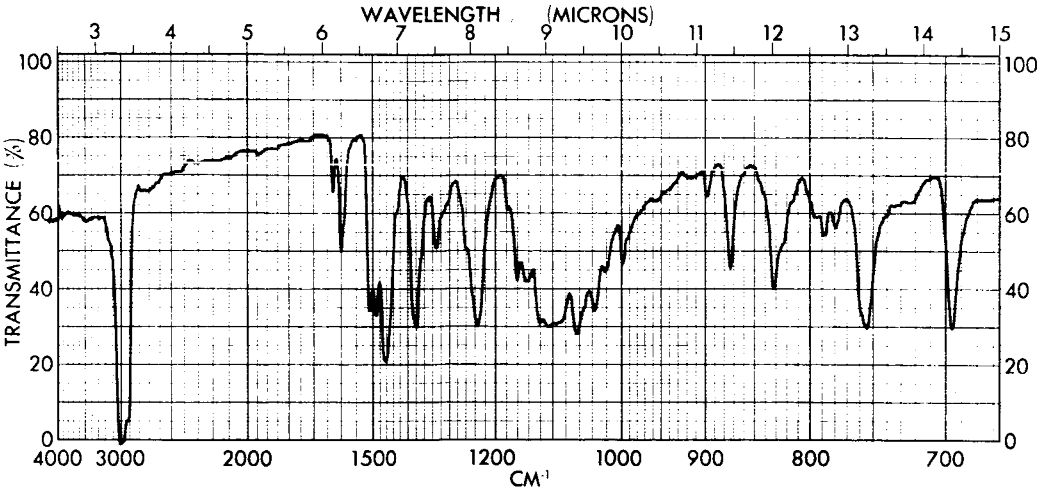

Fig. 33 - Infrared Spectrum of Diphenoxy(8-oxyquinoline)boron (Nujol)

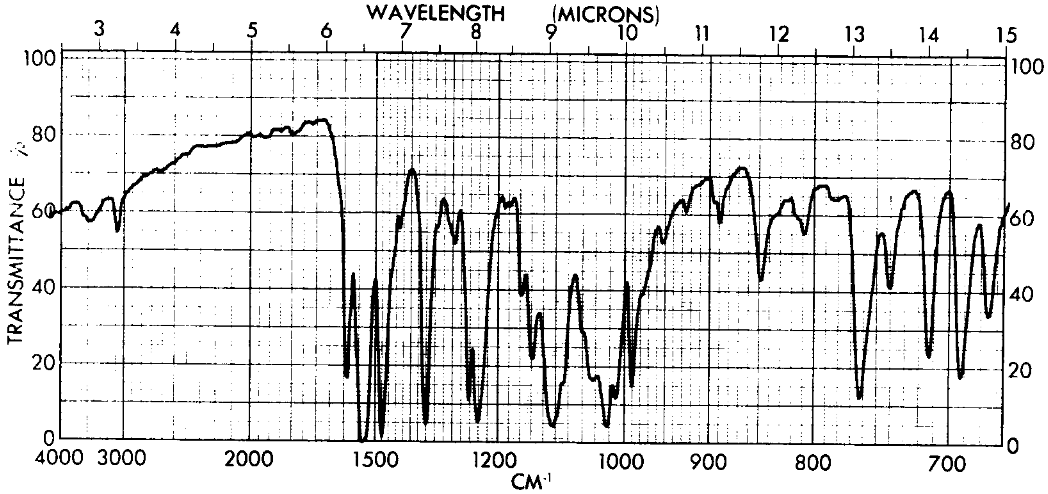

Fig. 34 - Infrared Spectrum of Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (KBr)

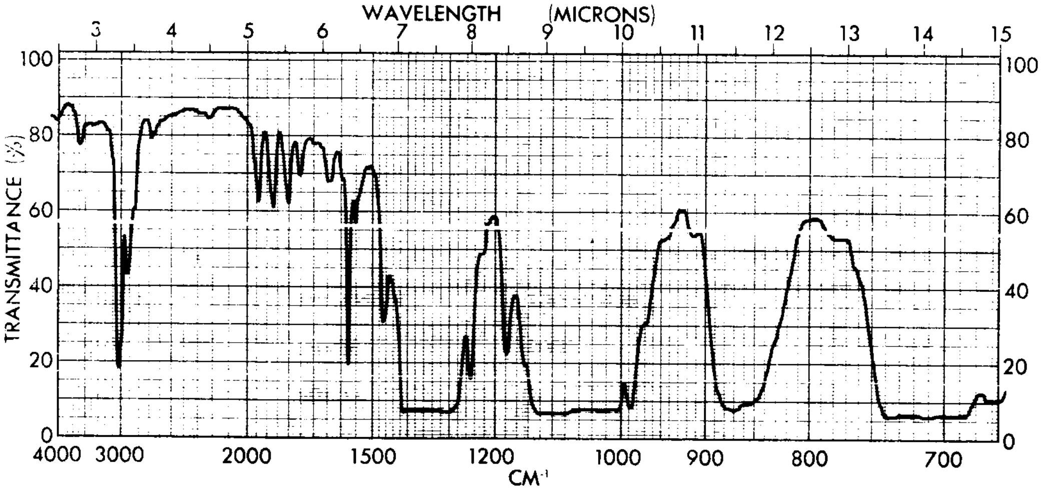

Fig. 35 - Infrared Spectrum of the Polymer from n-Butylborate and Diphenylsilanediol (Smear)

APPENDIX II

DIFFERENTIAL THERMAL ANALYSES AND THERMOGRAVIMETRIC ANALYSES

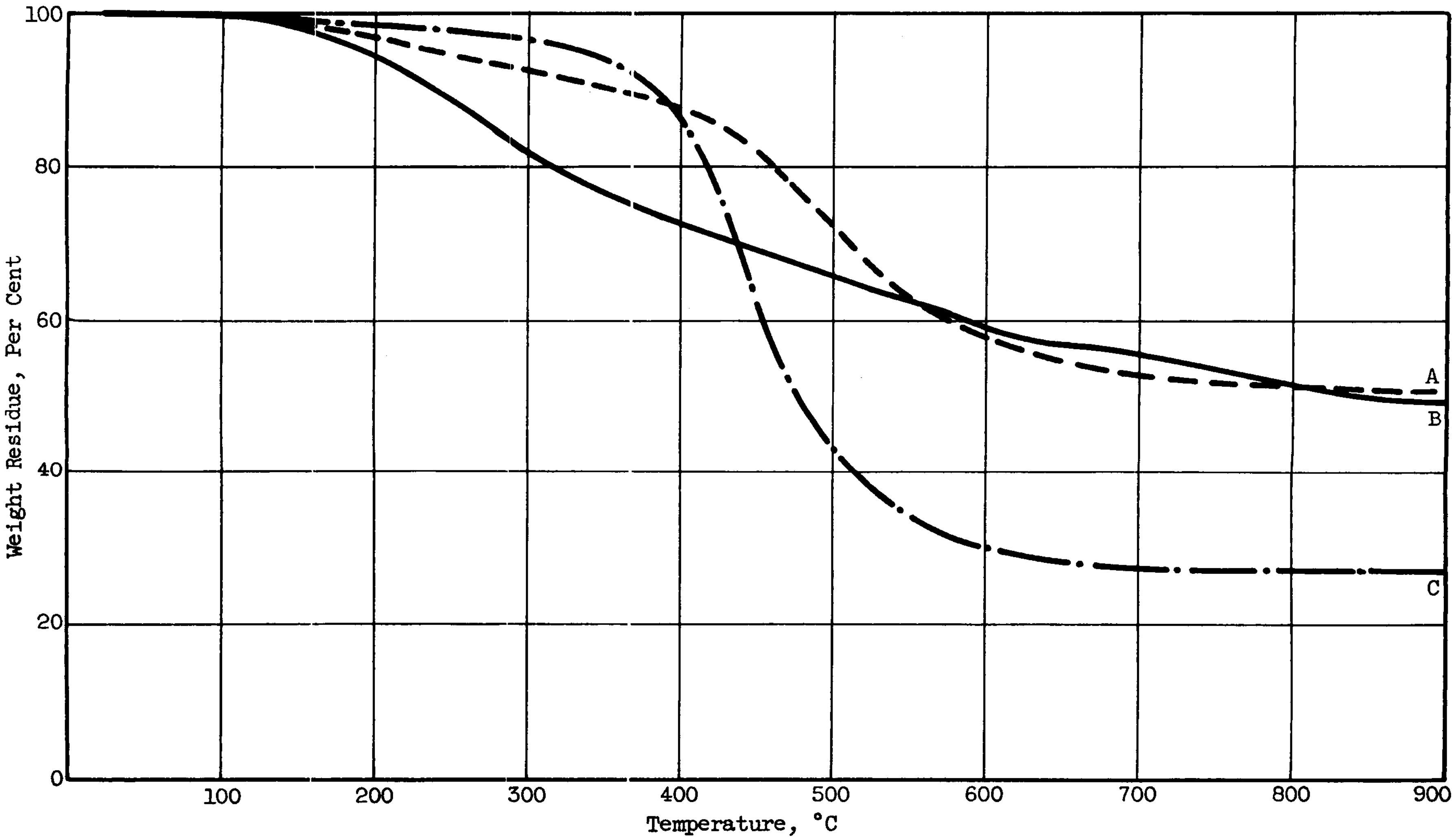

Fig. 36 - Thermogravimetric Analyses - Heating Rate = 3°/Min; N_2 Atmosphere

A. Product from Diphenylsilanediol, Triphenylsilanol, and Tetraisopropoxytitanium
B. Product from Tetrakis(dimethylamino)titanium, Phthalonitrile, and Diphenylsilanediol
C. Product from Diphenylsilanediol and n-Butylborate

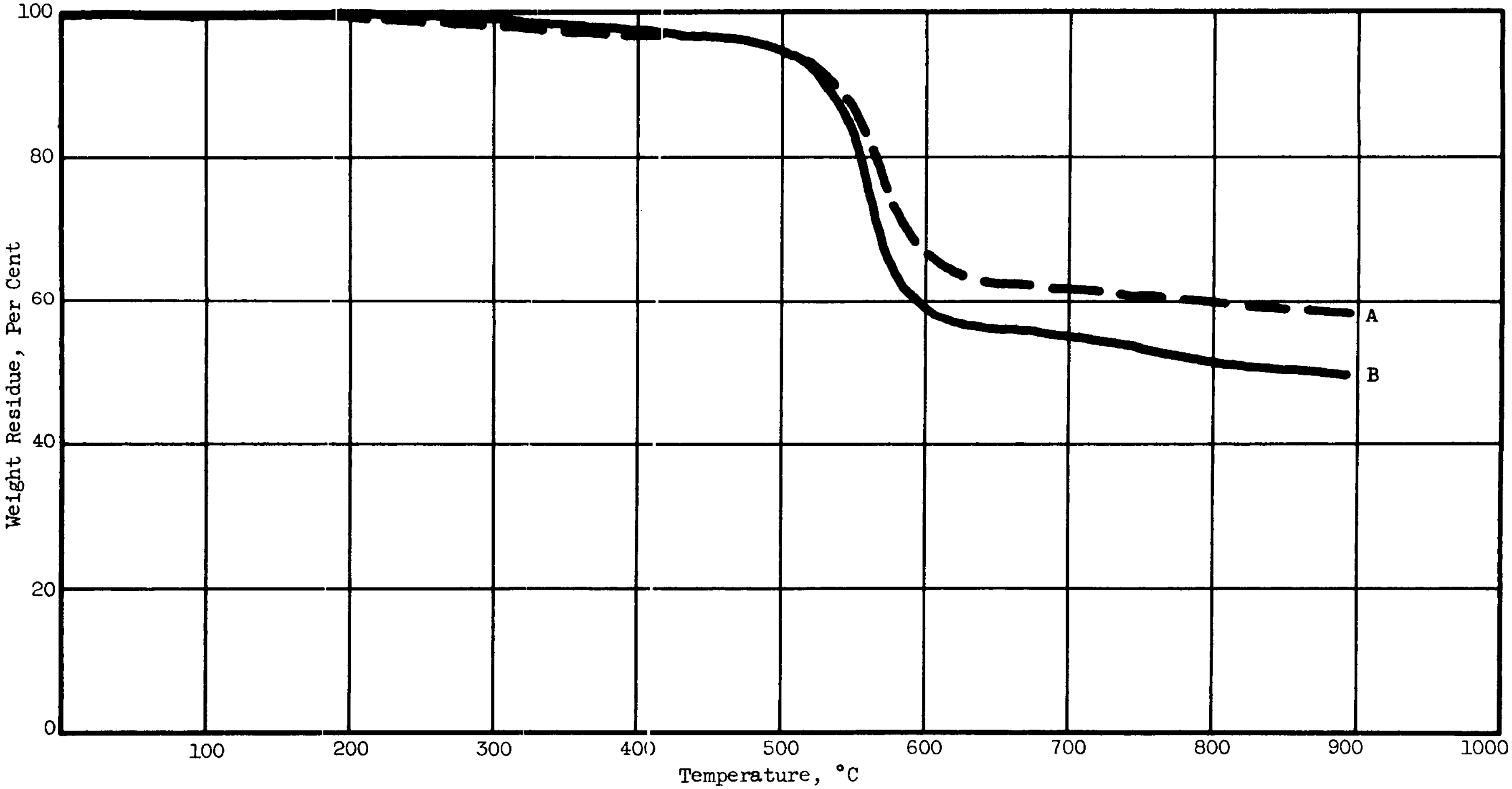

Fig. 37 - Thermogravimetric Analyses of Poly(p-phenylenesiloxanes) - Heating Rate = 3°/Min; N_2 Atmosphere

A. Polymer from p-Phenylenebis(diphenylsilanol) and Bis(methylamino)diphenylsilane
B. Polymer from p-Phenylenebis(diphenylsilanol) and Nonamethylcyclotrisilazane

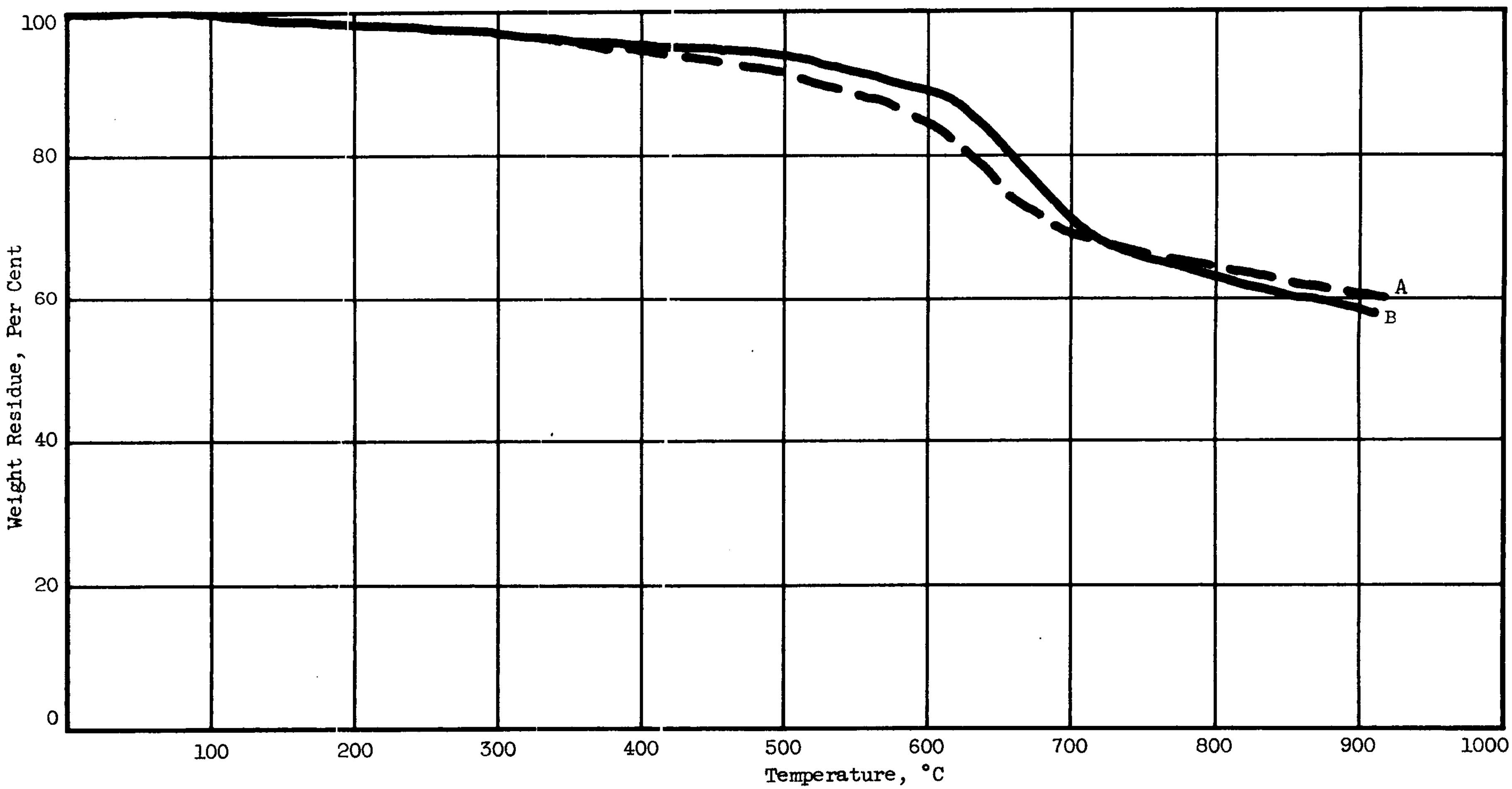

Fig. 38 - Thermogravimetric Analyses of Poly(benzoxazoles) - Heating Rate = 3°/Min; N_2 Atmosphere

A. Polymer from Terephthalamide and 3,3'-Dihydroxybenzidine in Polyphosphoric Acid
B. Polymer from Terephthalamide and 2,2'-Diamino-p,p'-biphenol in Polyphosphoric Acid

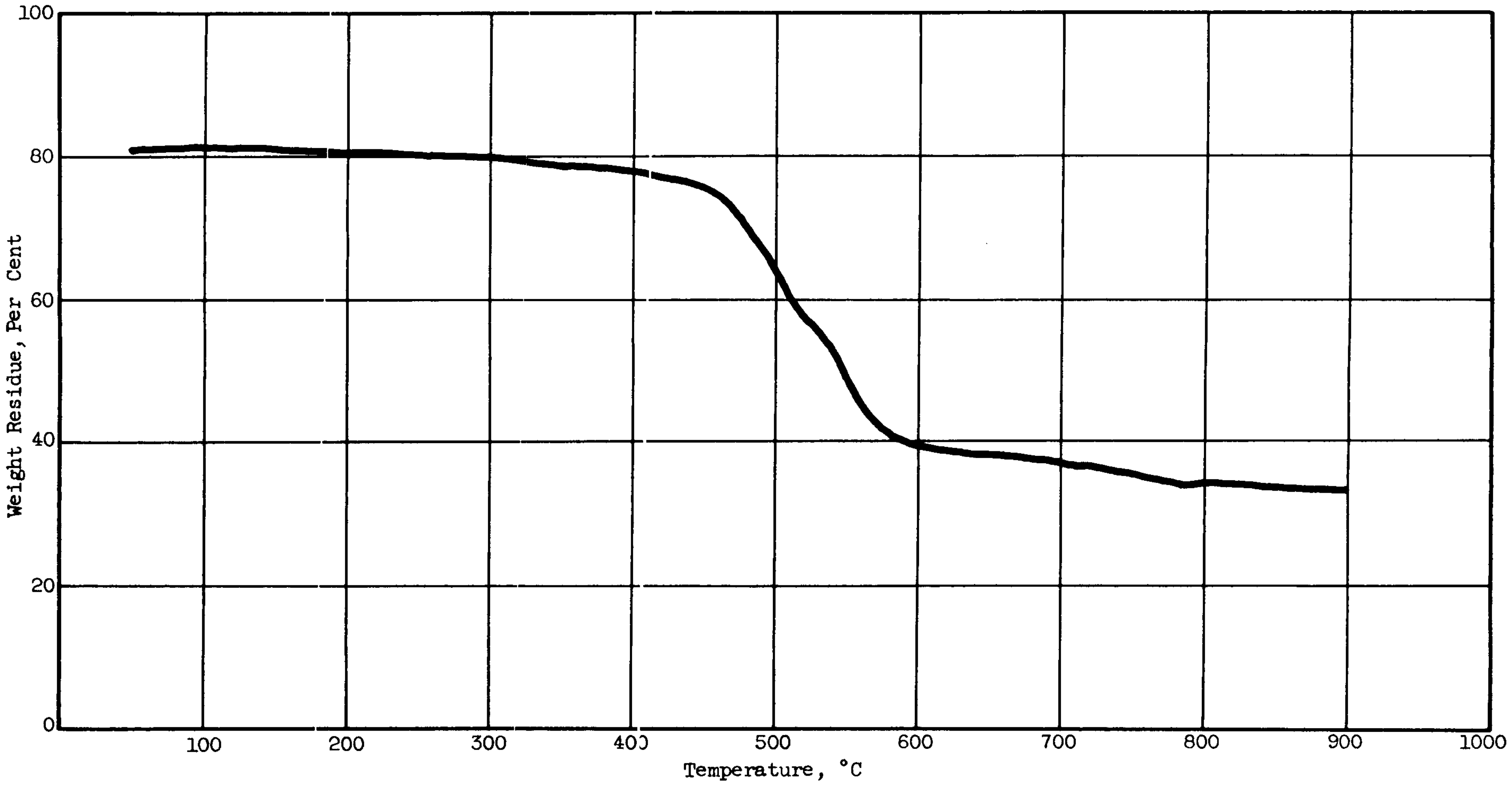

Fig. 39 - Thermogravimetric Analysis of a Polymer from p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane - Heating Rate = 3°/Min; N_2 Atmosphere

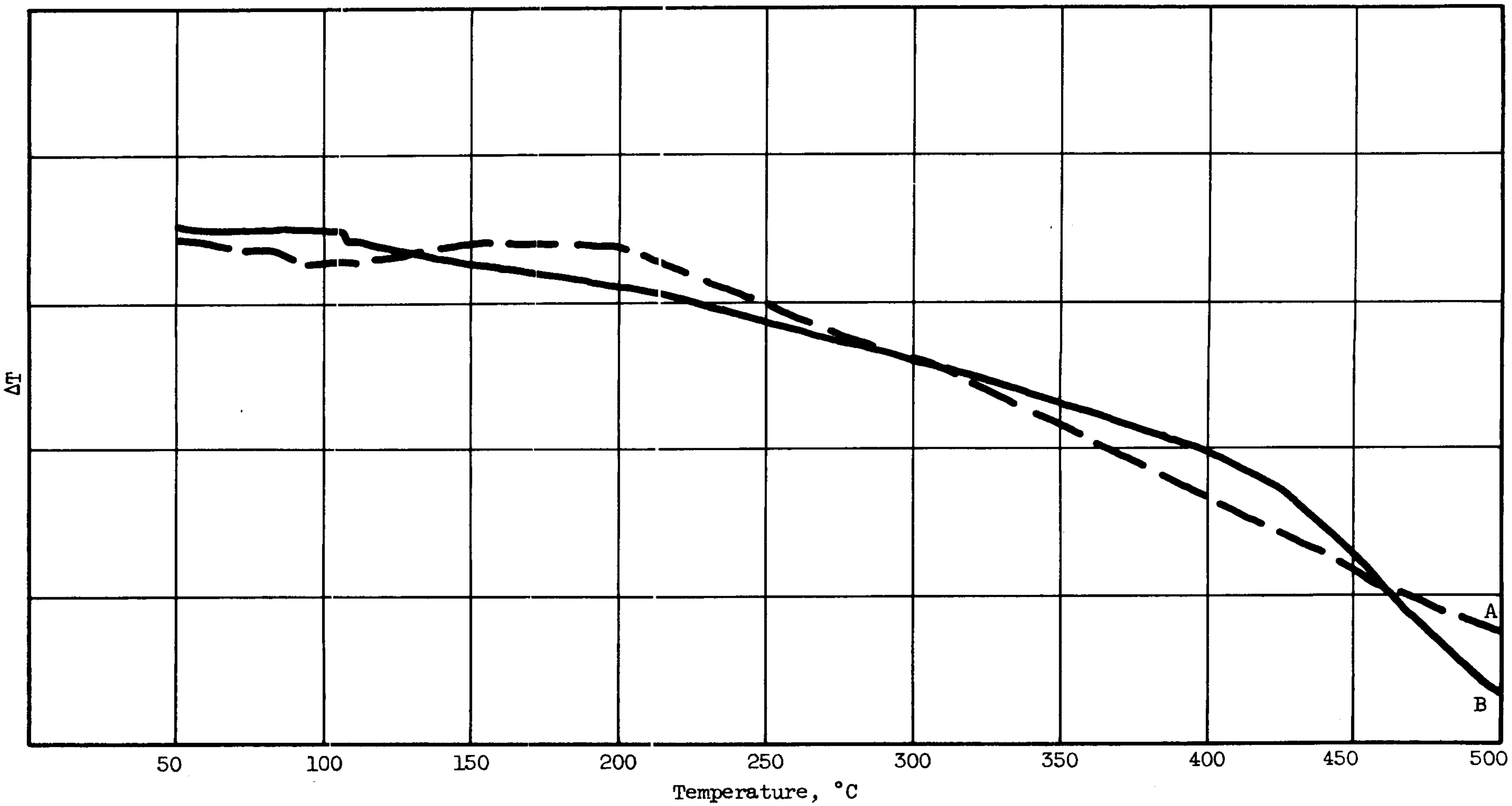

Fig. 40 - Differential Thermal Analyses of Poly(p-phenylenesiloxane) - Heating Rate = 15°/Min

A. Polymer from p-Phenylenebis(diphenylsilanol) and Bis(methylamino)diphenylsilane
B. Polymer from p-Phenylenebis(diphenylsilanol) and Nonamethylcyclotrisilazane

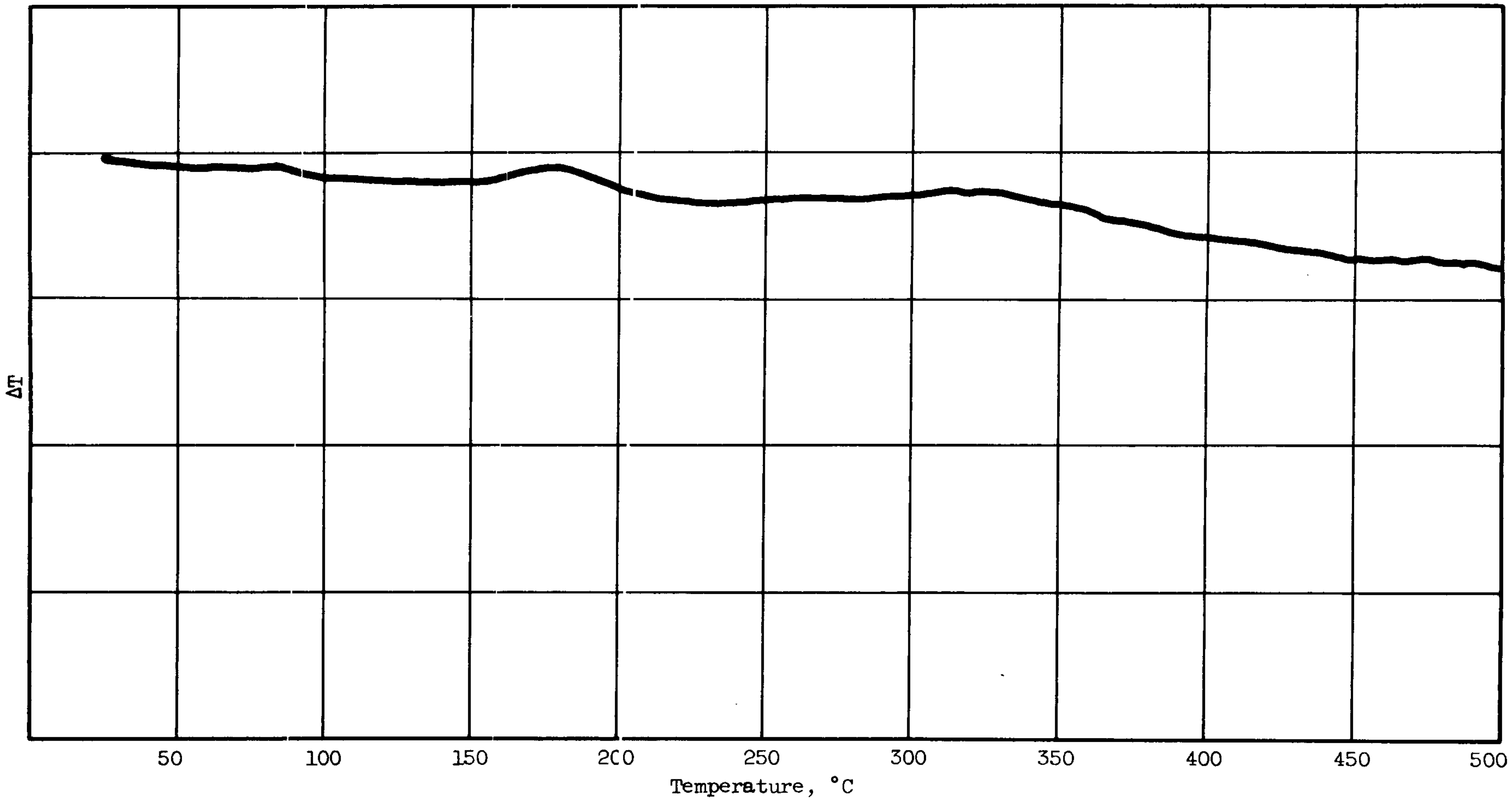

Fig. 41 - Differential Thermal Analysis of a Polymer from p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane - Heating Rate = 15°/Min

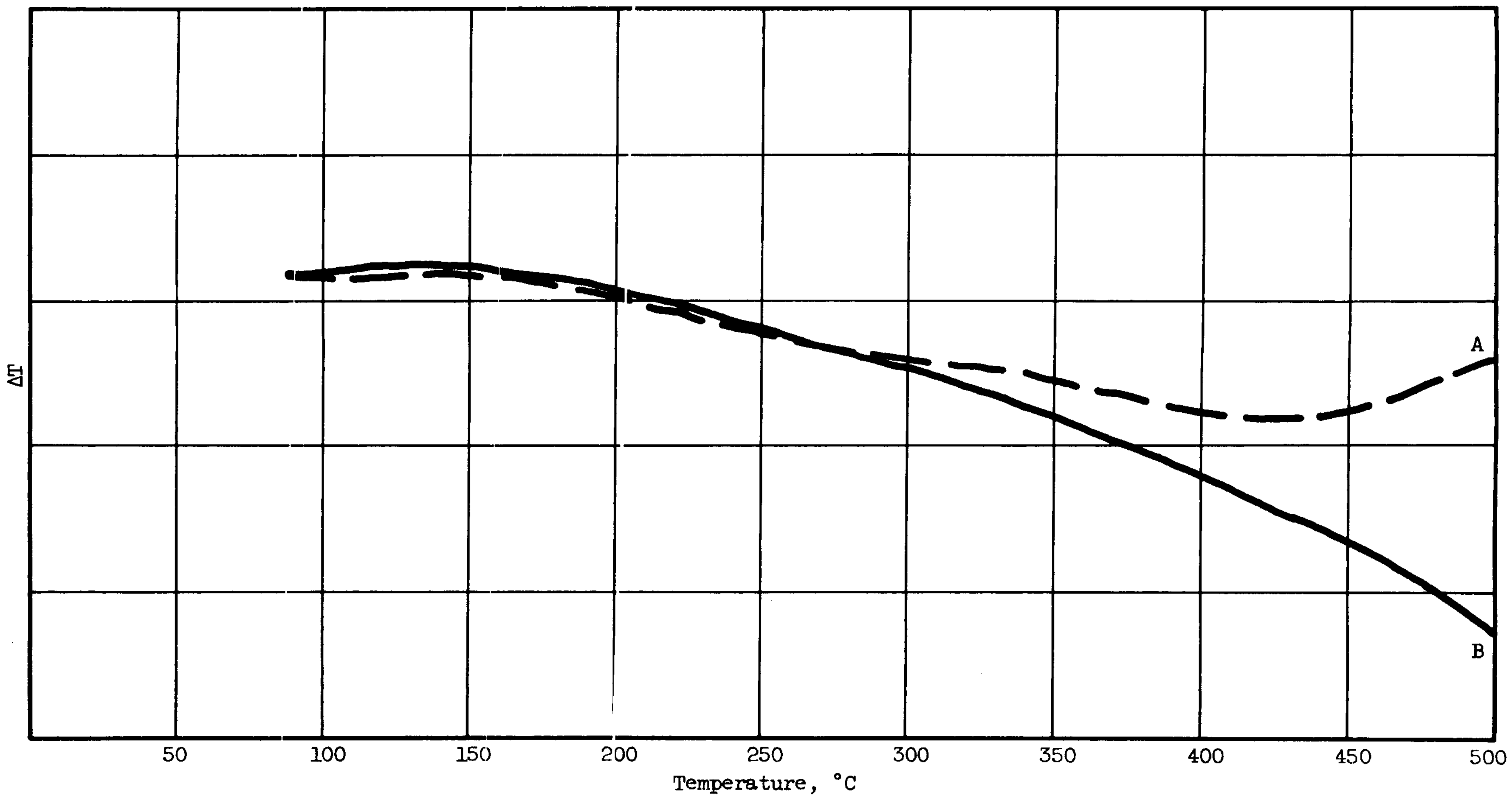

Fig. 42 - Differential Thermal Analyses of Poly(benzoxazoles) - Heating Rate = 15°/Min

A. Polymer from Terephthalamide and 3,3'-Dihydroxybenzidine in Polyphosphoric Acid
B. Polymer from Terephthalamide and 2,2'-Diamino-p,p'-biphenol in Polyphosphoric Acid

APPENDIX III

SOLAR SIMULATOR SYSTEM AND REFLECTANCE DATA

Fig. 43 - Solar Simulator System

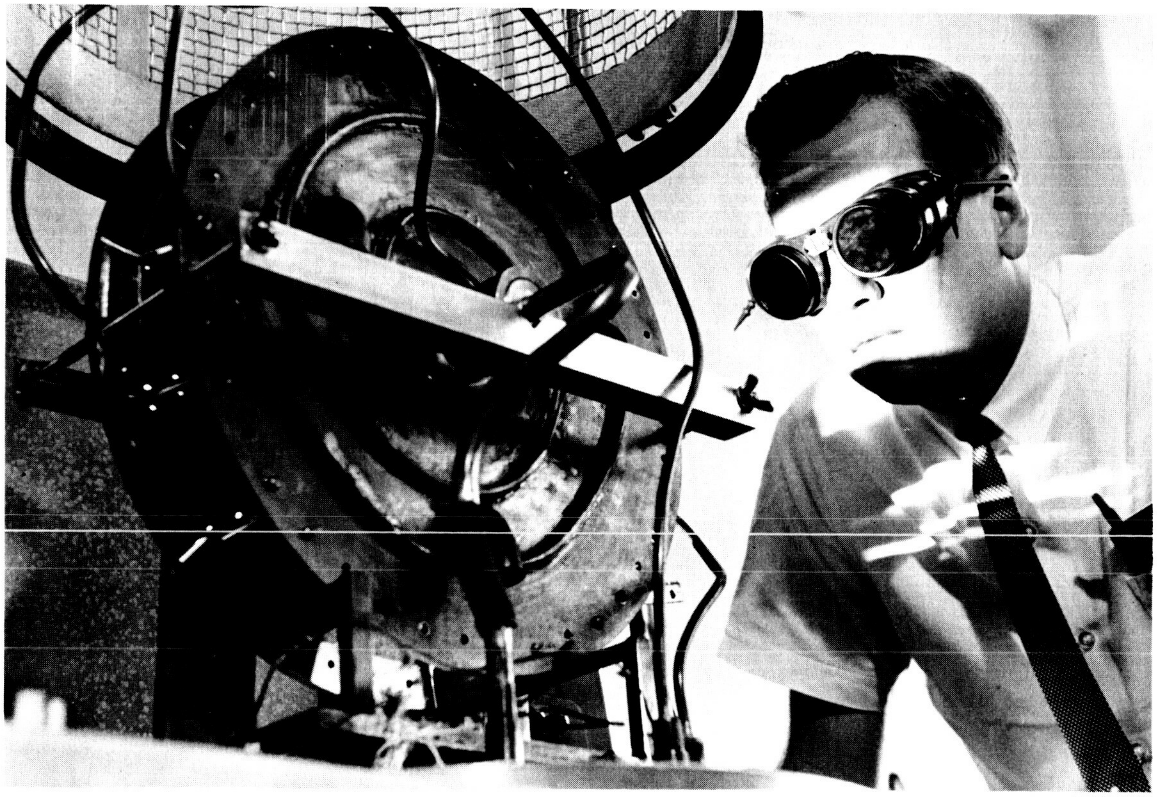

Fig. 44 - Lamp During Operation

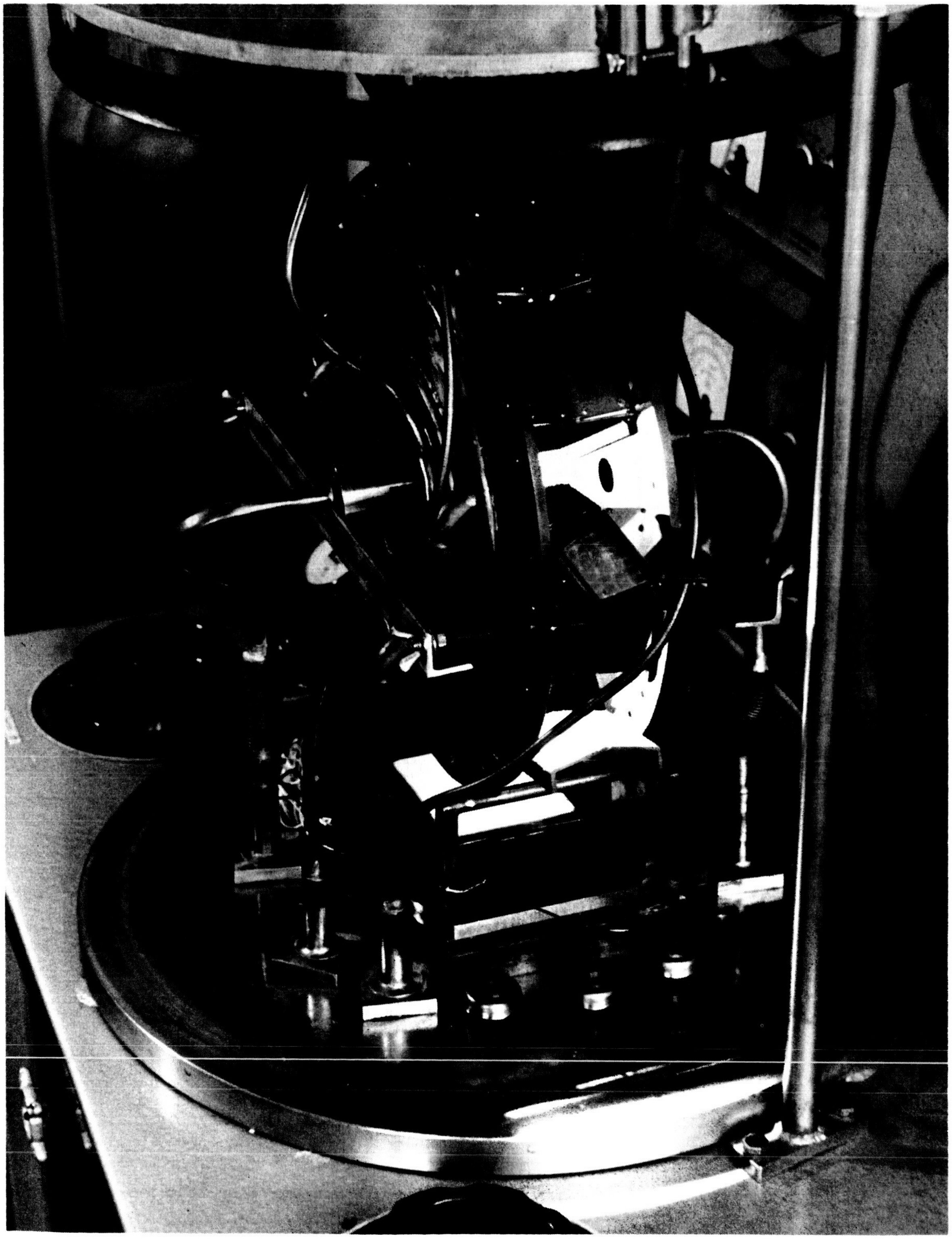

Fig. 45 - Irradiation Chamber

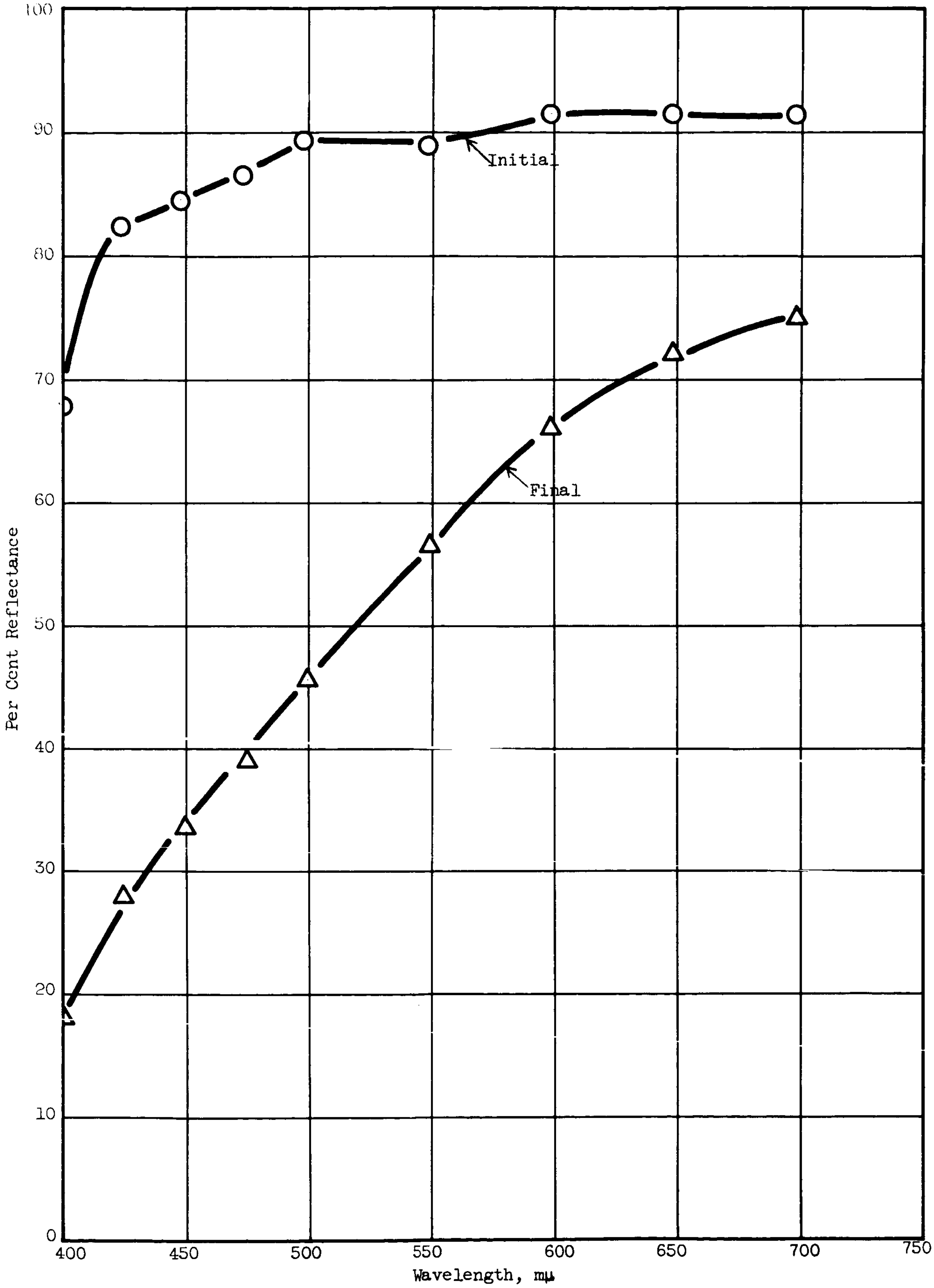

Fig. 46 - Reflectance of Plate 1 (LTV-602)

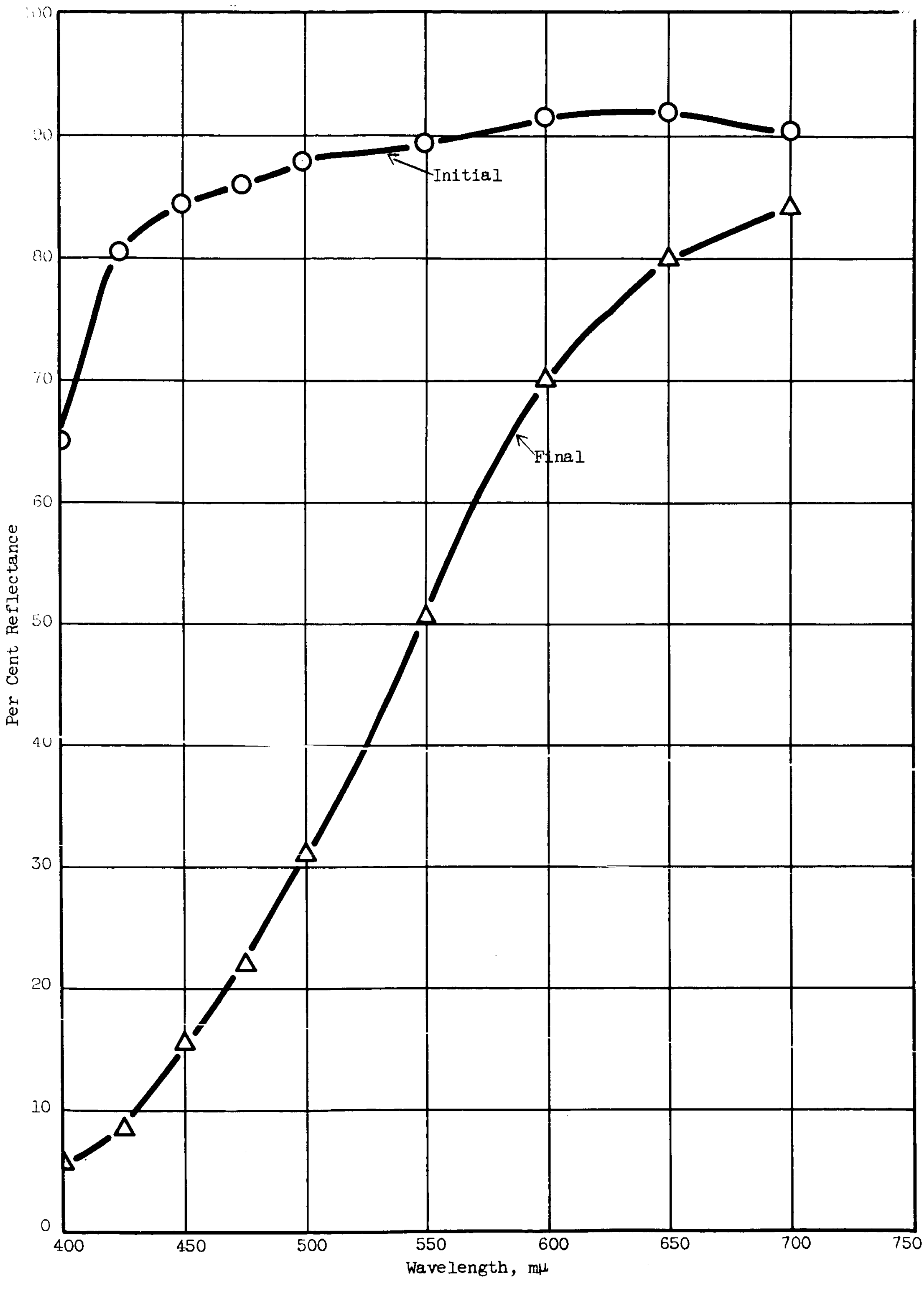

Fig. 47 - Reflectance of Plate 3 (Experimental Poly-p-phenylenesiloxane, see Table VIII, p. 73)

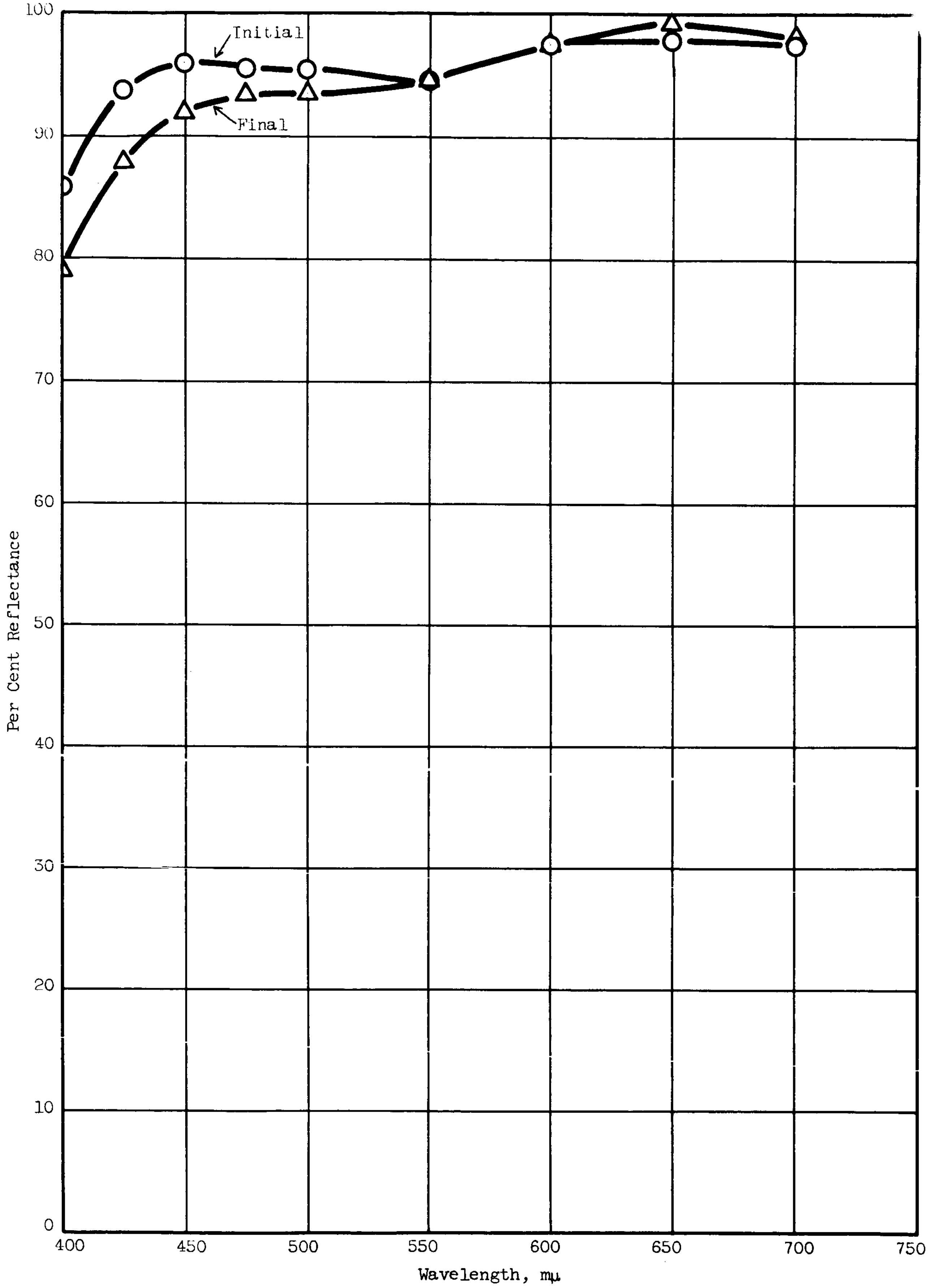

Fig. 48 - Reflectance of Plate 4 (S-13)

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