SYNTHESIS AND EVALUATION OF NEW HIGH TEMPERATURE POLYMERS FOR COATING APPLICATIONS

TECHNICAL SUMMARY REPORT
26 June 1964 - 25 September 1966

Contract No. NAS8-11338
Control No. DCN 1-4-50-01193-01 & S1 (1F)
CPB 02-1243-64

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

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

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by

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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 September 1966.

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

Approved for:

MIDWEST RESEARCH INSTITUTE

F V Morris

F. V. Morriss, Director
Chemistry Division

2 November 1966

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ABSTRACT

Experimental work is reported on the synthesis, characterization, and evaluation of organic and semiorganic polymers useful as coatings that will withstand high temperatures, high vacuum, and radiation. Poly(phenylenesiloxanes), suitable for the preparation of films, were prepared by the condensation of arylenedisilanols with cyclic siloxazanes. The polymers, which represented a variety of structures and were characterized in detail, had high molecular weights and good high- and low-temperature properties. Several were screened under high vacuum-ultraviolet irradiation conditions. High molecular weight poly(benzoxazoles) were prepared, but no satisfactory method was found for preparing poly(benzoxazole)films. Attempts to prepare titanium chelate polymers, titanoxanosiloxanes, and boroxanosiloxanes 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. Several other potentially useful polymer systems were examined briefly.

I. INTRODUCTION AND SUMMARY

The objective of this program was 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. A number of these systems were examined in the current program. In addition, developmental synthesis and evaluation work were completed on several new systems that are potentially useful in radiation resistant coating applications.

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. Vacuum-ultraviolet stability of several polymers was also studied.

The following include the polymer systems that were initially selected and the systems that were subsequently included in the scope of the work.

A. Titanoxanosiloxanes

Condensation polymerizations of a difunctional chelated titanium monomer, bis(8-oxyquinoline)diisopropoxytitanium, with diphenylsilanediol did not provide a sufficiently high molecular weight product for coating applications. Some evidence was obtained that an inherent limitation in the polymerization was the tendency to form low molecular weight cyclic compounds. Condensations of the chelated titanium monomers with p-phenylenebis(dimethylsilanol) and p-phenylenebis(diphenylsilanol) also failed to afford high molecular weight materials. A previously described condensation product of tetrakis(dimethylamino)titanium, diphenylsilanediol, and triphenylsilanol was shown to contain substantial quantities of tetrakis(triphenylsiloxy)titanium. A suitable procedure could not be found for preparing polymeric condensation products of diphenylsilanediol and chelated phthalocyanine titanium derivatives.

B. Boroxanosiloxanes, Phosphoroxanosiloxanes, and Phosphoroxanoboroxanes

A previously prepared boroxanosiloxane had a low molecular weight and was found by infrared analysis to contain siloxane linkages. A literature search revealed that phosphoroxanosiloxanes were too unstable hydrolytically to merit experimental work. Phosphoroxanoboroxanes were approached through the use of chelated boron-containing monomers, but no satisfactory polymerization procedures could be developed with model compounds.

C. Polybenzoxazoles

A satisfactory procedure for the synthesis of high molecular weight aromatic and aliphatic polybenzoxazoles was developed through the use of polyphosphoric acid as the polymerization medium. Although the polymers had good heat stability, they were highly colored and exhibited very limited solubility. No satisfactory method could be found for producing polybenzoxazole films.

D. Poly(arylenesiloxanes)

Condensation reactions of arylenedisilanols and various organosilicon monomers were studied in considerable detail, and a variety of structures with high molecular weight were prepared and characterized in detail. Polymers in this class had high heat stability, good low temperature properties, and were soluble in a variety of solvents. Solution of the polymers could be used for the preparation of coatings, and some of the coatings were screened under conditions of intense ultraviolet radiation in high vacuum.

E. Ferrocene Polyesters

An attempt to prepare ferrocene polyesters showed that aliphatic esters of ferrocene dicarboxylic acid do not undergo transesterification reactions of the type that are used to prepare polyesters from terephtalates.

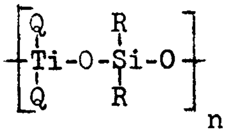
F. Other Systems

Poly(*s*-triazinyl ether) and poly(heterocyclic ethers) were examined briefly as potentially useful polymers, but satisfactory polymerization methods for these systems could not be found within the time available for evaluating their potential.

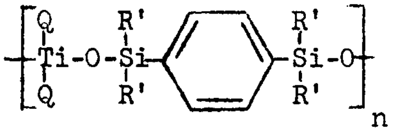
II. POLYTITANOXANOSILOXANES AND POLYBOROSILOXANES

A portion of the goal of the present work was to review experimentally a number of polymer systems containing a metal-oxygen-silicon-oxygen backbone and a system containing a phosphorus-oxygen-boron-oxygen backbone. The systems selected were those that appeared, on the basis of earlier work, to offer some potential as candidate radiation-resistant coating materials.

A. 8-Hydroxyquinoline Chelate Polymers



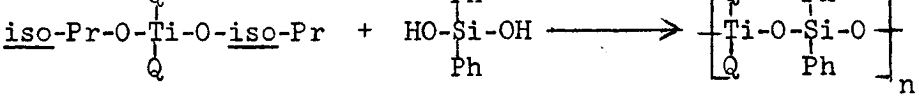
$$\left[\overset{Q}{\underset{Q}{\mathrm{Ti}}}\text{-O-}\overset{R}{\underset{R}{\mathrm{Si}}}\text{-O} \right]_n$$



Q = 8-oxyquinoline
R = phenyl
R' = methyl or phenyl

The synthesis of a low molecular weight polymer from bis(8-oxyquinoline)diisopropoxytitanium and diacetoxydiphenylsilane has been described.[1] 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.[2] 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,[3] the most promising of these methods, the condensation of titanium alkoxides with silanols, was examined. The monomer, bis(8-oxyquinoline)diisopropoxytitanium, was readily prepared by a method given in the literature.[3]

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.



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

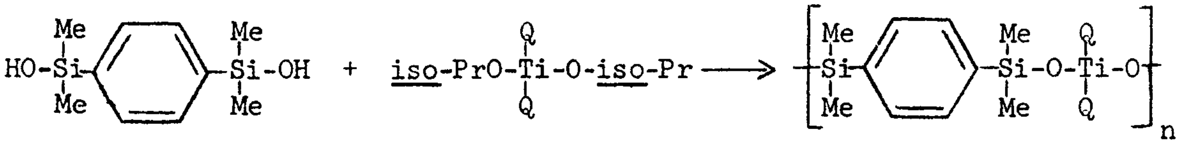
Since the molecular weight for the simple condensation product of two monomer units was 610, no significant polymerization had been achieved. The material, which was soluble in dimethylformamide and dimethyl sulfoxide, could be cast as a film from dimethylformamide, but the film did not maintain its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

Since the degree of polymerization appeared to be limited by the insolubility of low molecular weight condensation products in benzene, attempts were made to effect the polymerization in dimethyl sulfoxide, but a higher molecular weight was not obtained. In dimethylacetamide, the molecular weight was increased to 2,800. The infrared spectrum of the polymer prepared in dimethylacetamide showed a low end group (OH) concentration, and within the experimental error, the yield of the polymer was quantitative. Even with the increased molecular weight, however, the material was still not suitable for coating application. Subsequently, it was shown that a similar condensation product was at least partly soluble in xylene; therefore, solubility in aromatic solvents was probably not the factor that limited the molecular weight.

Other modes of polymerization, 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.[1] 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,[2] but the silicon-containing monomer was subsequently shown to be largely diphenylsilanediol.[4]

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.

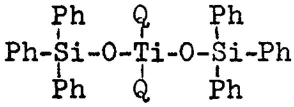


The infrared spectrum of the polymer indicated that Si-O-Ti bonds were present. A low molecular weight product was also obtained when p-phenylenebis(diphenylsilanol) was used.

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 an inherent viscosity in toluene of

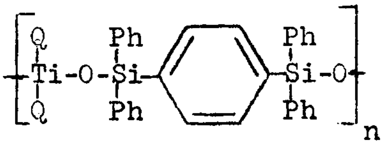
0.11. In one attempt to advance the polymerization, the prepolymer was heated with a catalytic amount of sodium hydroxide, which was added to the polymer as an aqueous solution. Under these conditions, decomposition occurred and 8-hydroxyquinoline sublimed from the mixture.

Infrared spectra of the polymers from diphenylsilanediol and diisopropoxybis(8-oxyquinoline)titanium prepared in dimethylacetamide were superimposable with the spectra of the polymers prepared in benzene, (Fig. 1). The spectra were also nearly superimposable with the spectrum of the model compound, bis(8-oxyquinoline)bis(triphenylsiloxy)titanium (Fig. 2) except for a shift of the Si-O-Ti absorption in the model compound from 905 cm^{-1} to 945 cm^{-1} in the polymer.



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

However, the spectrum of a condensation product from bis(8-oxyquinoline)diisopropoxytitanium with p-phenylenebis(diphenylsilanol) rather than diphenylsilanediol retained the absorption at the same frequency as the model compound, 905 cm^{-1} (Fig. 3).



The absence of new absorption bands in the 1000 - 1100 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 - 2,000 depending on the sample chosen for analysis.

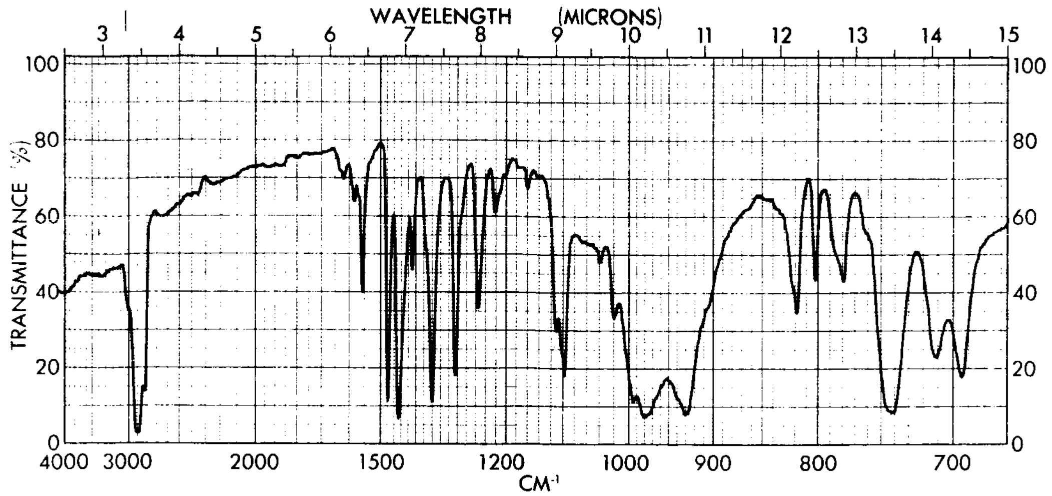


Fig. 1 - Infrared Spectrum of the Polymer from Diphenylsilanediol and Diisopropoxybis(8-oxyquinoline)titanium (Nujol)

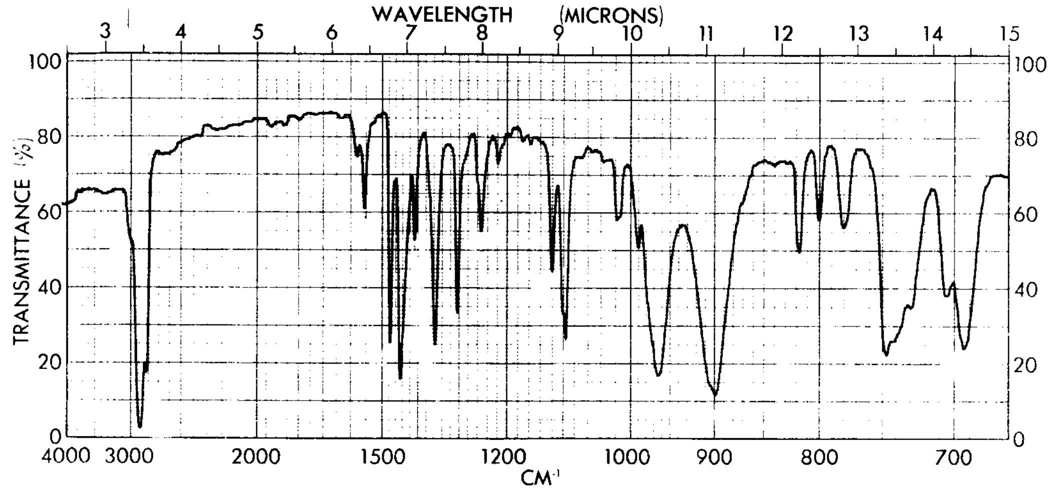


Fig. 2 - Infrared Spectrum of Bis(8-oxyquinoline)bis-(triphenylsiloxy)titanium (Nujol)

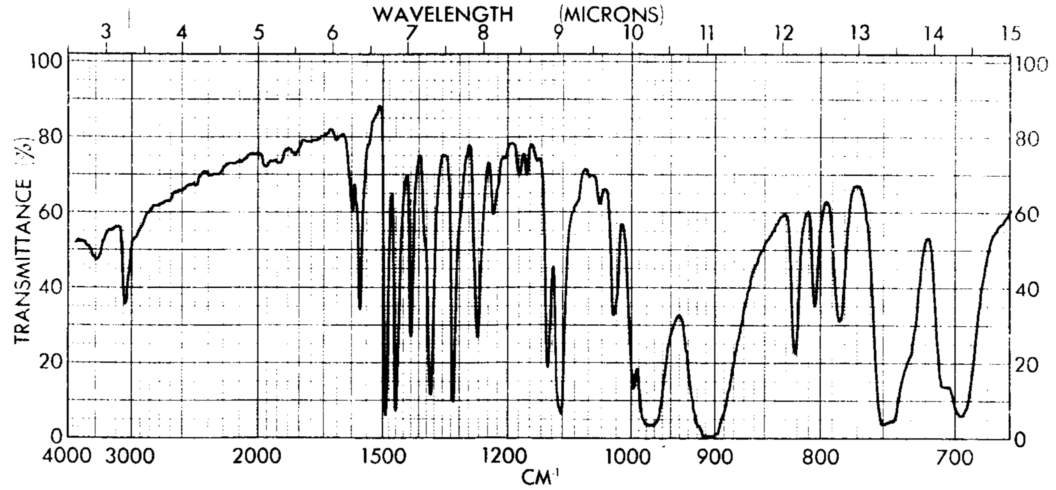
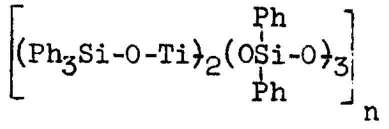


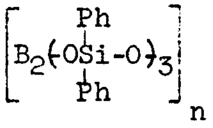
Fig. 3 - Infrared Spectrum of the Polymer from p-Phenylenebis-(diphenylsilanol) and Diisopropoxybis-(8-oxyquinoline)titanium (KBr)

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.

B. Titanoxanosiloxanes and Borosiloxanes



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



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

A polymer from tetrakis(dimethylamino)titanium, triphenylsilanol, and diphenylsilanol has been reported as a glass that can be solvent- or melt-cast as a film.[2] Repetitions of the procedure with titanium tetraisopropylate rather than tetrakis(dimethylamino)titanium gave a tan powder that melted at about 250°* and was insoluble in hot dimethylformamide.

$$2Ti(NMe_2)_4 \; + \; 2Ph_3SiOH \; + \; 2Ph_2Si(OH)_2 \longrightarrow \left[(Ph_3SiOTi)_2(OPh_2SiO)_3\right]_n + 8MeNH_2$$

Zeitler[5] 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. 4) of the tan powder from attempted resin preparation was consistent with the presence of tetrakis(triphenylsiloxy)titanium (Fig. 5).

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.[4]

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

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* All temperatures are in degrees centigrade.

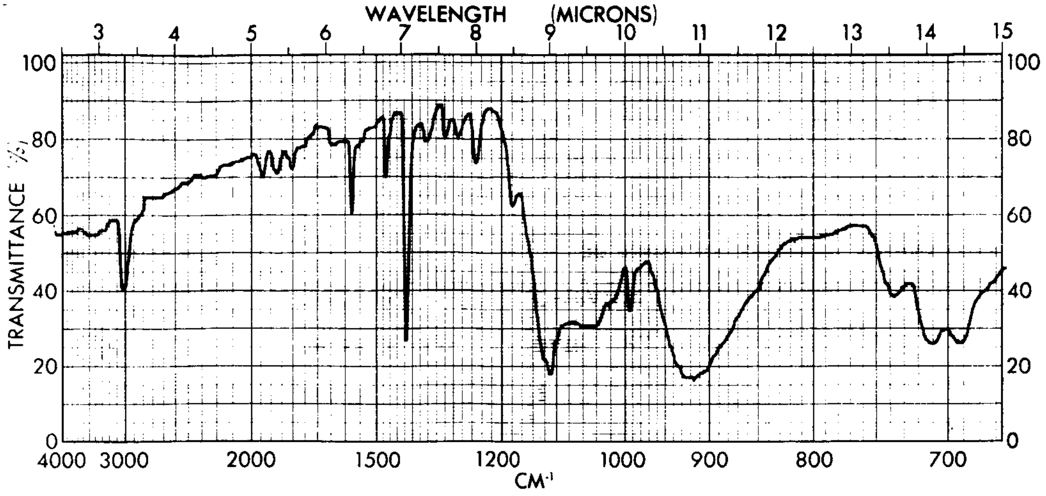


Fig. 4 - Infrared Spectrum of the Polymer from Tetraisopropoxytitanium, Diphenylsilanol, and Triphenylsilanol (KBr)

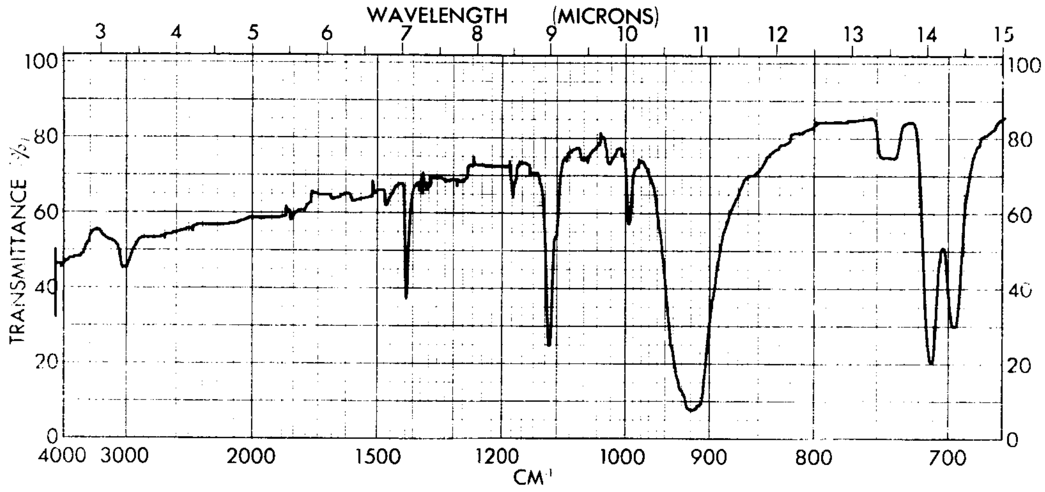


Fig. 5 - Infrared Spectrum of Tetrakis(triphenylsiloxy)titanium (KBr)

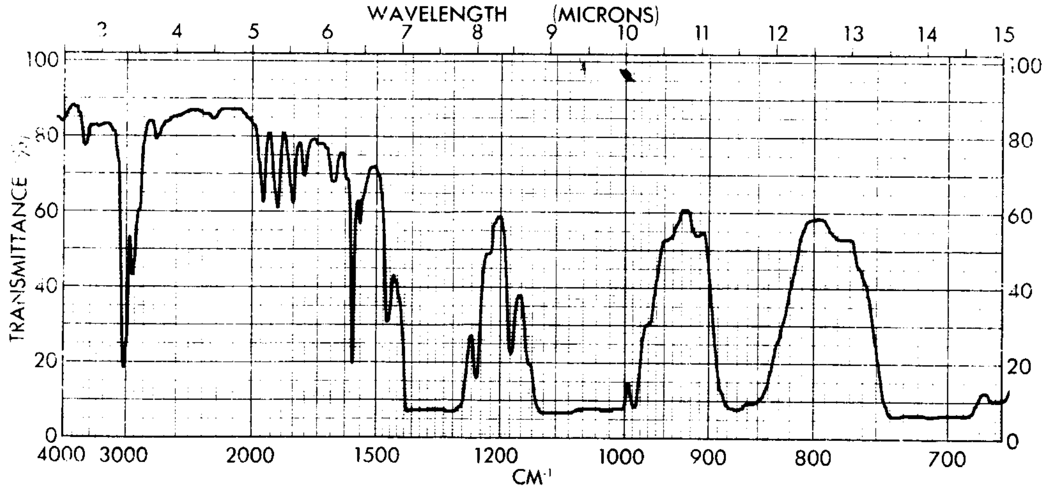


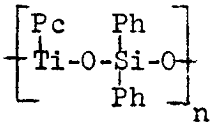
Fig. 6 - Infrared Spectrum of the Polymer from n-Butylborate and Diphenylsilanediol (Smear)

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. 6) is consistent with Anderson's observation that the product from dibutoxymethylboron and diphenylsilanediol did not contain B-O-Si bonds.[6]

C. 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.[2] 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.



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

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.

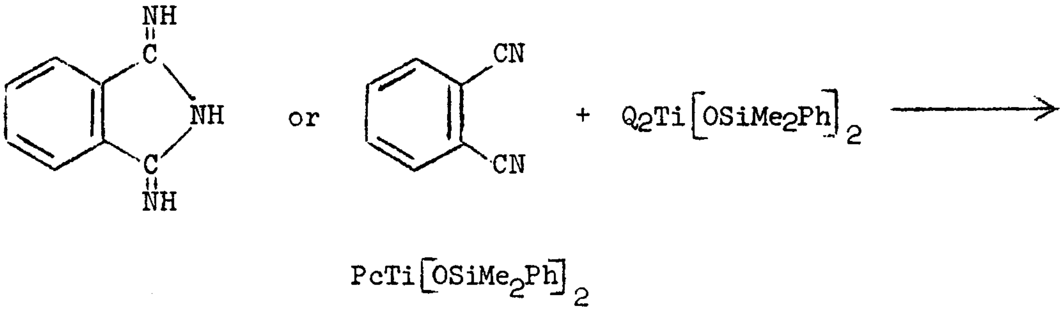
Other phthalocyanine-containing polymers with degrees of polymerization less than 10 have been described in the literature, but the materials were invariably insoluble in all solvents and did not melt.[7] It can be concluded from the literature that any phthalocyanine-containing polymer with even a moderately 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.



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.

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

D. Experimental

Throughout this report, reactions involving organometallic reagents, silicon halides, titanium alkoxides, zirconium halides, boron alkoxides or halides, or other moisture sensitive compounds were carried out in glassware which was flamed out under nitrogen prior to use. The reactions were protected from atmospheric moisture either with drying tubes packed with Drierite or with a positive nitrogen atmosphere.

Solvents were reagent grade and were anhydrous when moisture sensitive compounds were used. Phenylmagnesium bromide and methylmagnesium bromide were used as 3M solutions 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, or by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Molecular weight determinations by vapor pressure osmometry were performed by Crobaugh Laboratories, Box 4078, Charleston, West Virginia, and light scattering experiments and gel permeation chromatography by Arro Laboratories, Joliet, Illinois.

1. 8-Hydroxyquinoline Chelate Polymers

a. Bis(8-oxyquinoline)diisopropoxytitanium: (Method: Reference 3) 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°,[3] 172 - 173°,[8] 166 - 171°)[9] was not changed after recrystallization from toluene.

Anal. Calcd. for $C_{24}H_{26}N_2O_4Ti$: C, 63.44; H, 5.77; N, 16.6. Found: C, 63.49; H, 5.87; N, 6.24.

b. 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[10] 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.

c. Tetrakis(dimethylamino)titanium: (Method: Reference 11) 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° (0.30 - 0.50 mm.) (reported, 50° (0.05 mm.)).[11]

d. Polymer from tetraisopropoxytitanium, diphenylsilanediol, and triphenylsilanol: In this experiment, the procedure described by Towers[2] 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. 4) was similar, but not identical, to the spectrum of an authentic sample of tetrakis(triphenylsiloxy)titanium (Fig. 5), differing mainly in the presence of Si_2O absorption in the 1075 - 1025 cm^{-1} region. In a thermogravimetric analysis (Fig. 7), the material lost weight continuously above 150°.

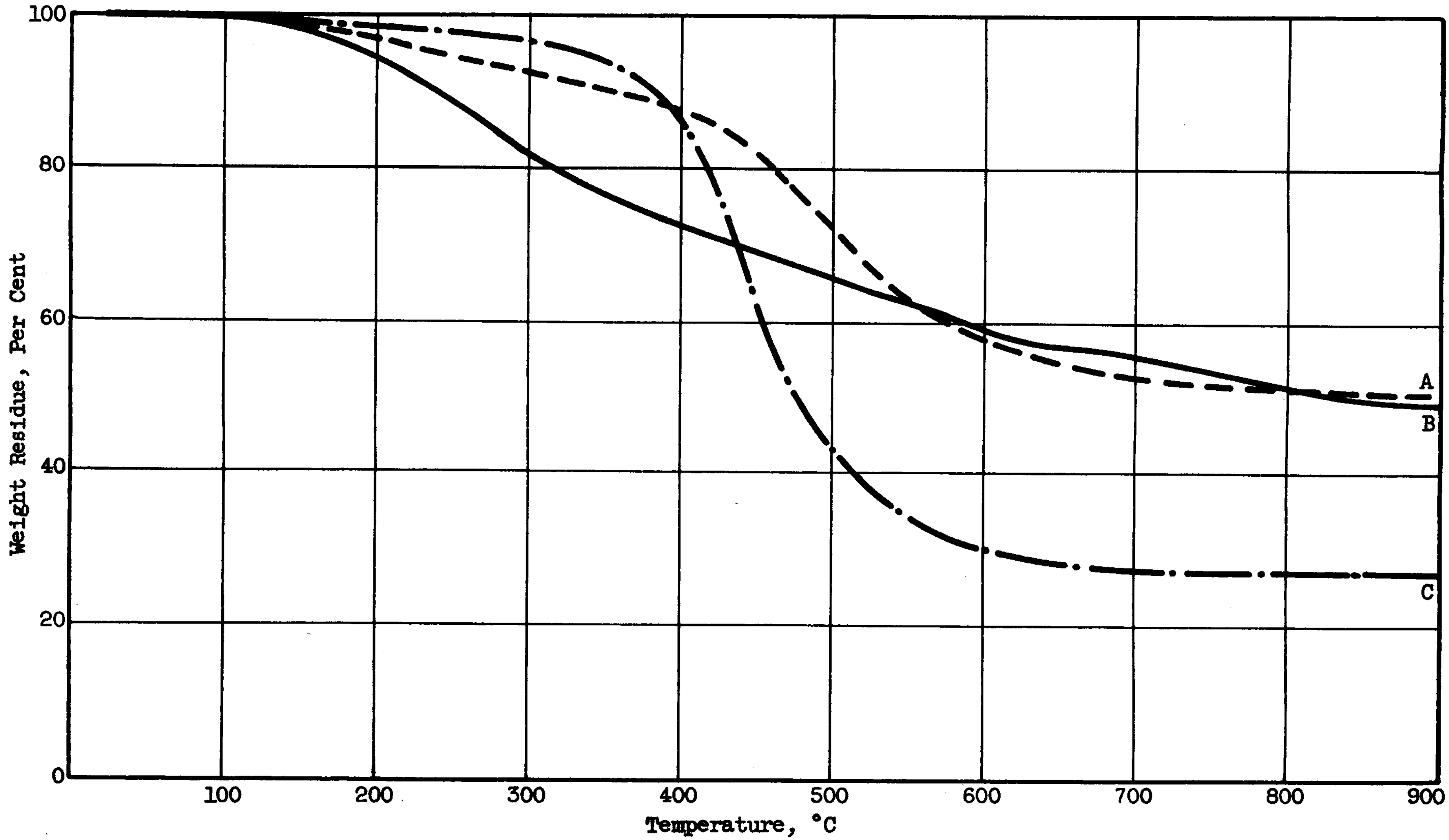


Fig. 7 - Thermogravimetric Analyses - Heating Rate = 3°/Min; N_2 Atmosphere

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

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°).

e. Polymer from tetrakis(dimethylamino)titanium, triphenylsilanol and diphenylsilanediol: (Method: Reference 2) 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.2/ The latter polymer contained a much stronger band at 3400 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.

f. 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.1/ The same polymer has been prepared by Thomas from bis(8-oxyquinoline)bis(diethylamino)titanium.10/ 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 dimethyl sulfoxide, but insoluble in most other common organic solvents.

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.

g. 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 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.

h. Polymer from diphenylsilanediol and bis(8-oxyquinoline)diisopropoxytitanium (prepared in dimethyl sulfoxide): 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 dimethyl sulfoxide 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°).

i. 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 dimethyl sulfoxide.

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 materials were similar.

j. 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 dry 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 3400 cm^{-1}, but was otherwise identical to the spectra of the polymers obtained from the same materials in benzene and in dimethyl sulfoxide.

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°).

k. Diacetoxydiphenylsilane: (Method: Reference 1) 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).1/

l. 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.1/ 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.

m. Polymer from diacetoxydiphenylsilane and bis(8-oxyquinoline)diisopropoxytitanium (melt): (Method: Reference 1) 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}.

n. Polymer from p-phenylenebis(dimethylsilanol) and bis(8-oxyquinoline)diisopropoxytitanium (in benzene): (Method: Reference 1) 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_{inh} (toluene) = 0.11 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.

o. 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).

2. Polymer Containing Boron and Silicon

Towers prepared a similar polymer with the proposed structure $[B_2(OPh_2SiO)_3]_n$;[2] 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. 7, p. 15.

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.).

Anal. Calcd. for $(C_{36}H_{30}B_2O_6Si_3)_n$: B, 3.31; Si, 12.92; Mol. Wt. for 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.

3. Phthalocyanine Derivatives

a. 1,3-Diiminoisoindoline: (Method: Reference 12) 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°12/ and 193°13/).

b. Sodium phthalocyanine: (Method: Reference 4) 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 the residue was dried in air overnight, 4.1 g. (38 per cent) of sodium phthalocyanine was obtained.

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.

c. Phthalocyanine: (Method: Reference 14) 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.

d. 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.

e. Chlorodimethylphenylsilane: (Method: Reference 1) 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°),1/ was obtained.

f. Dimethylphenylsilanol: 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. The infrared spectrum of the residue indicated that both siloxane and silanol groups were present and the unpurified material was used in subsequent experiments.

g. Bis(dimethylphenylsiloxy)bis(8-oxyquinoline)titanium: (Method: Reference 1) 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 refractive 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°)1/ was obtained.

h. 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. flask 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 Wood's 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 3200 cm^{-1} (NH or OH) and 1720 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.

i. 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 was 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°.

j. Product from tetrakis(dimethylamino)titanium, phthalonitrile, and diphenylsilanediol: (Method: Reference 1) 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. 7, p.15) showed a procedural decomposition temperature of 205° (weight loss $\geq$ 5 per cent/hr).

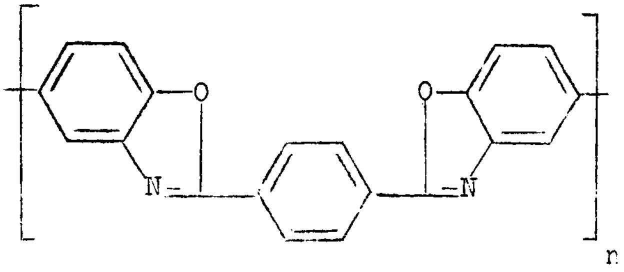
III. POLYBENZOXAZOLES

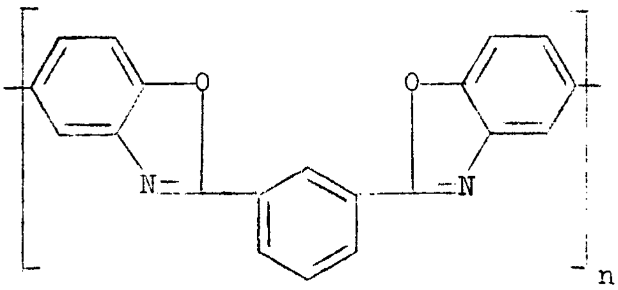
At the beginning of the work on polybenzoxazoles, little had been reported on the synthesis of this class of polymers, although other polyaromatic systems had been studied in detail. Aliphatic polybenzoxazoles had been prepared by Brinker in a melt polymerization of 3,3'-dihydroxybenzidine and mixed aliphatic dibasic acids.[15/] Subsequently, fully aromatic polybenzoxazoles were reported by Kubota as the product of thermal ring closure of a polyamide derived from isophthalyl chloride and 3,3'-dihydroxybenzidine.[16/] A melt polymerization technique had also been used by Moyer to prepare aromatic polybenzoxazoles from 3,3'-dihydroxybenzidine and diphenyl phthalates.[17/] In the course of this work, Imai published the results of polymerizing 3,3'-dihydroxybenzidine and 2,2'-diamino-p,p'-biphenol with terephthalic, isophthalic, and sebacic acids.[18,19/] Other recent disclosures of polybenzoxazole syntheses include a publication by Korshak[20/] and a series of patents,[21/] which employ methods described by ubota and Moyer. More recently Stacy reported melt homo condensation of 3-amino-4-hydroxybenzonitrile and cocondensation of 3,3'-dihydroxybenzidine with isophthalamide to obtain polybenzoxazoles.[22/]

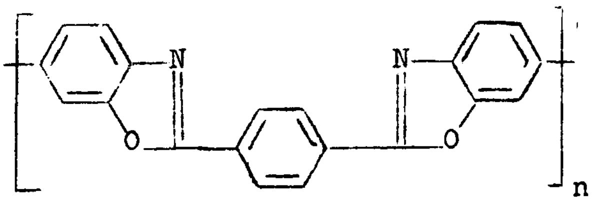
A. Aromatic Polybenzoxazoles

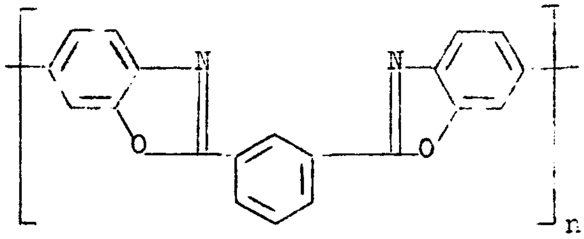
Although monomers and model compounds were prepared by established procedures, many of the compounds had not been adequately characterized in the earlier literature. The aminophenol monomers were characterized by elemental analyses, and compounds of equivalent purity to the analytical samples were used in the polymerizations. The aminophenols were isolated and stored as the more stable hydrochloride salts.

Polyphosphoric acid (116 per cent) has been demonstrated to be effective as a polymerization medium in obtaining high molecular weight polymers directly in other polyaromatic systems.[23 - 25/] 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 illustrated structures.



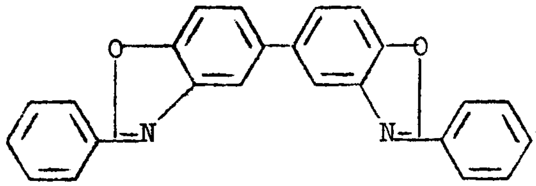


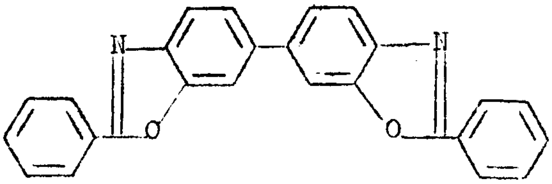




The polymer from 2,2'-diamino-*p*,*p*'-biphenol and terephthalamide had an inherent viscosity in sulfuric acid of 3.33, which indicates a high degree of polymerization. Thermogravimetric analysis and differential thermal analysis traces of this polymer and the polymer from 3,3'-dihydroxybenzidine and terephthalamide (Figs. 8 - 11) 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 trailing-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. 12 and 14) with the spectra of the model compounds, 2,2'-diphenyl-5,5'-bibenzoxazole and 2,2'-diphenyl-6,6'bibenzoxazole (Figs. 13 and 16), indicated that





the polymer contained little or no functionality that had not cyclized to the benzoxazole structure. The spectrum of the polymer from isophthalamide and 3,3'-dihydroxybenzidine is also shown in Fig. 15. The polymers were not soluble in any solvents examined except concentrated sulfuric acid. None of the polymers melted below 450°.

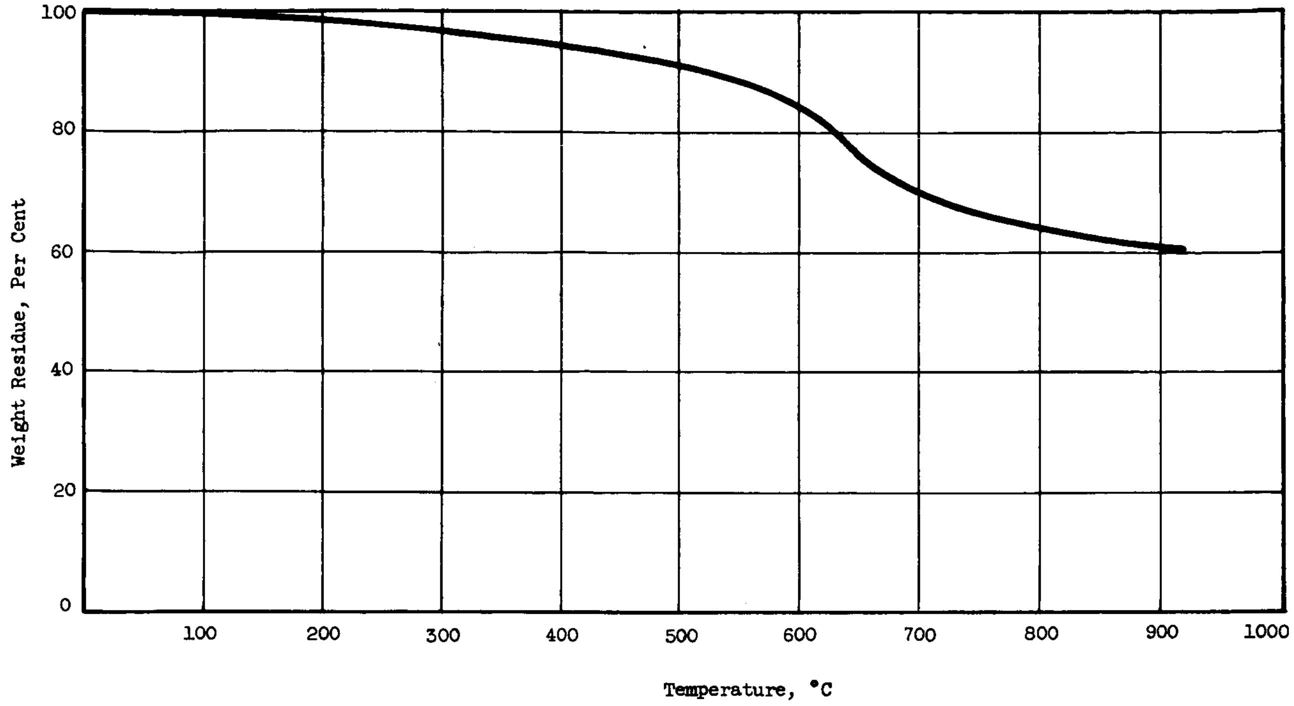


Fig. 8 - Thermogravimetric Analysis of a Poly(benzoxazole) Prepared from Terephthalamide and 3,3'-Dihydroxybenzidine in Polyphosphoric Acid - Heating Rate = 3°/Min, N_2 Atmosphere

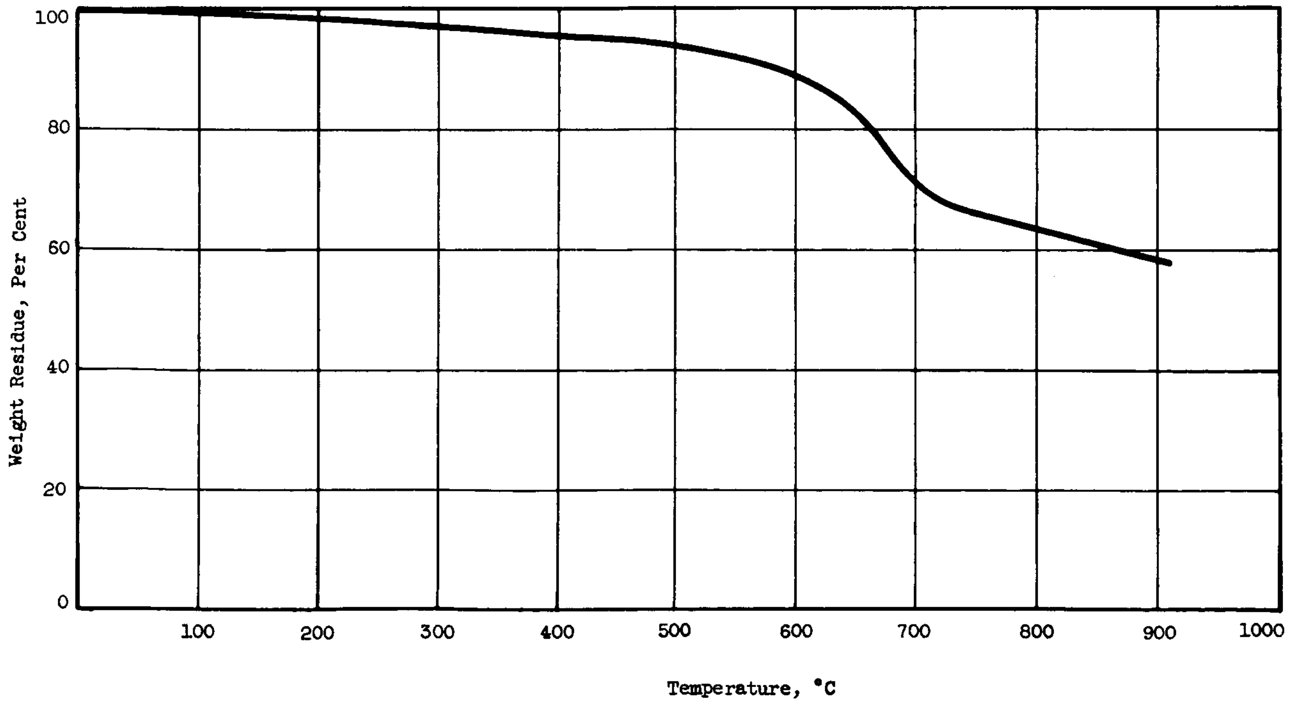


Fig. 9 - Thermogravimetric Analysis of a Poly(benzoxazole) Prepared from Terephthalamide and 2,2'-Diamino-p,p'-biphenol in Polyphosphoric Acid - Heating Rate = 3°/Min, N_2 Atmosphere

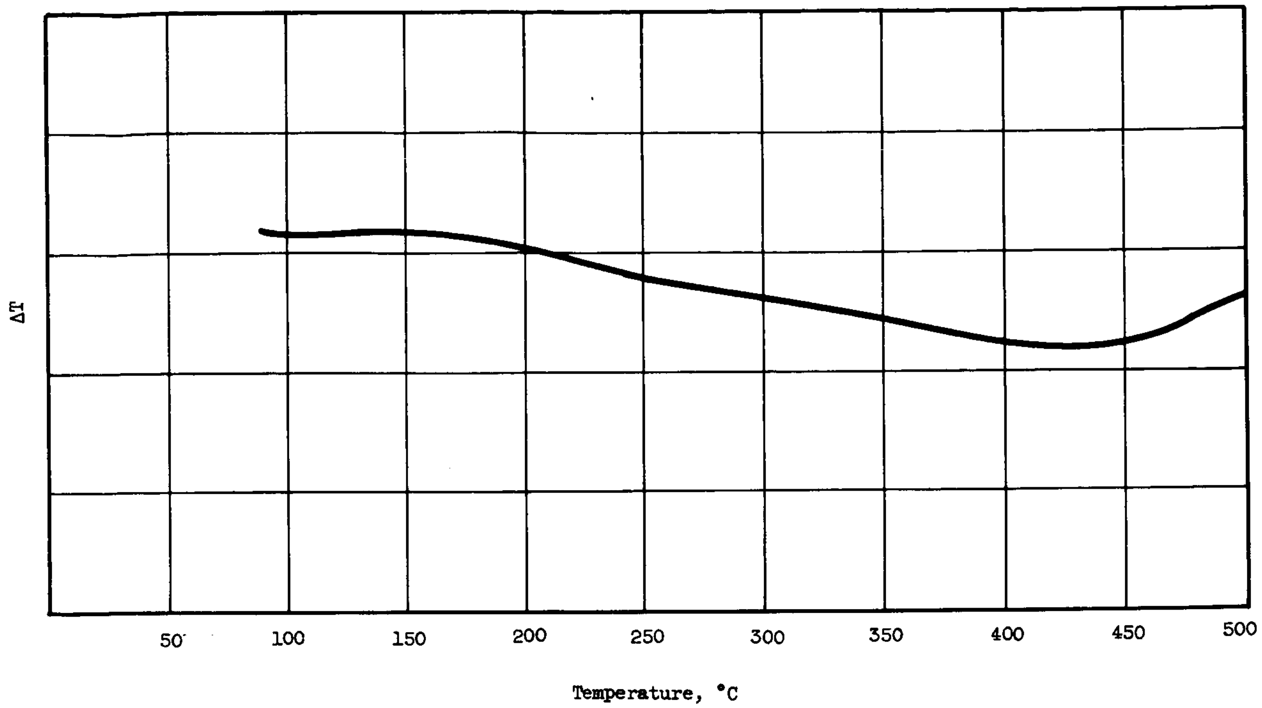


Fig. 10 - Differential Thermal Analysis of a Poly(benzoxazole) from Terephthalamide and 3,3'-Dihydroxybenzidine in Polyphosphoric Acid - Heating Rate = 15°/Min, N_2 Atmosphere

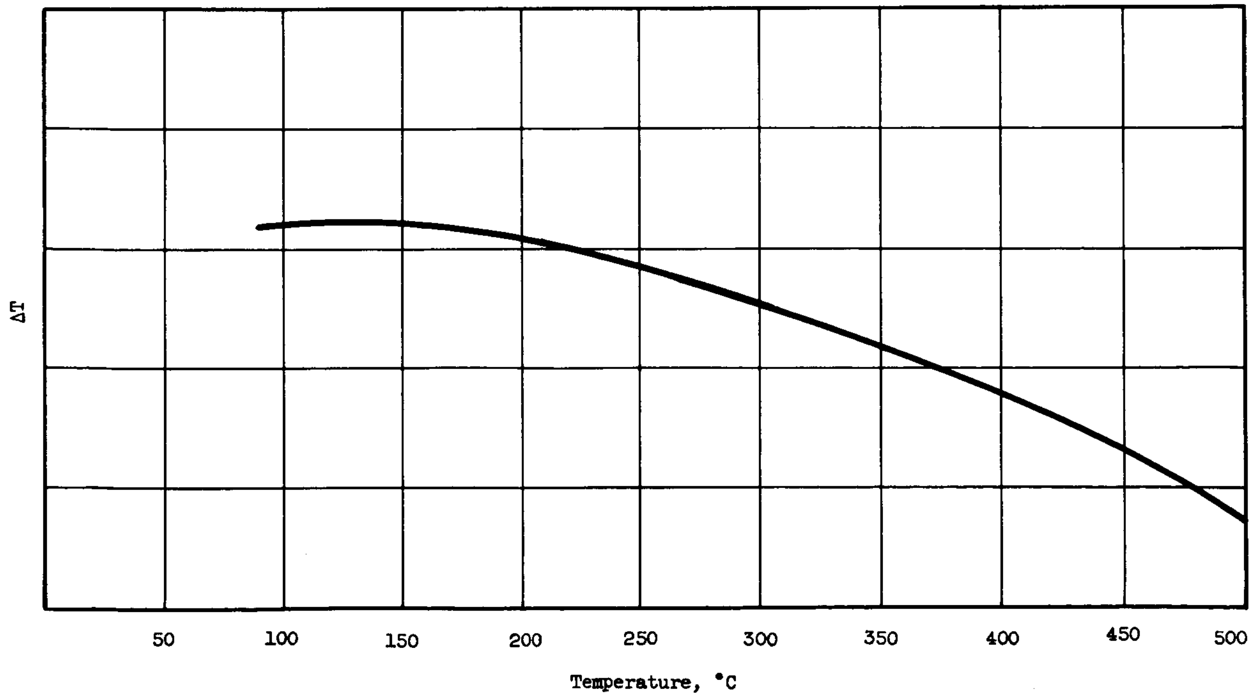


Fig. 11 - Differential Thermal Analysis of a Poly(benzoxazole) from Terephthalamide and 2,2'-Diamino-p,p'-biphenol in Polyphosphoric Acid - Heating Rate = 15°/Min, N_2 Atmosphere

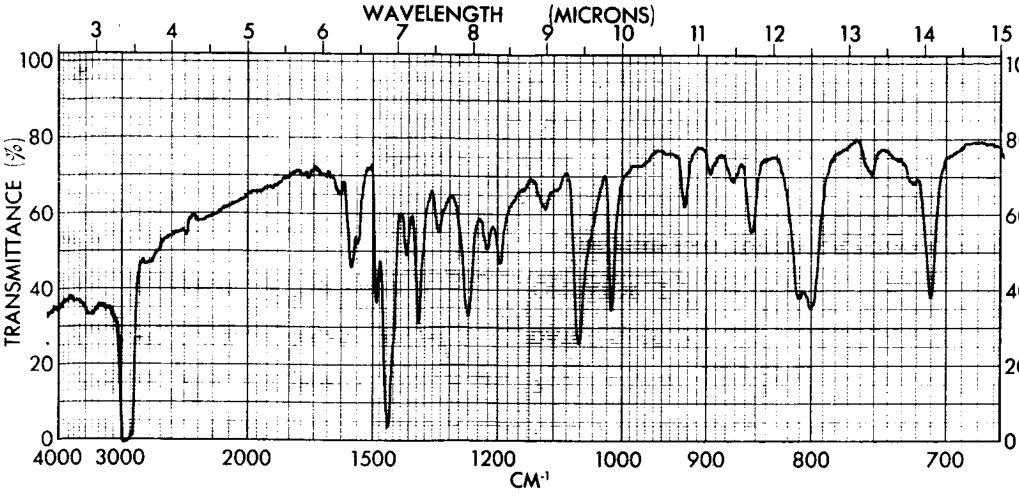


Fig. 12 - Infrared Spectrum of the Polymer from 2,2'-Diamino-p,p'-biphenol and Terephthalimide in Polyphosphoric Acid (Nujol)

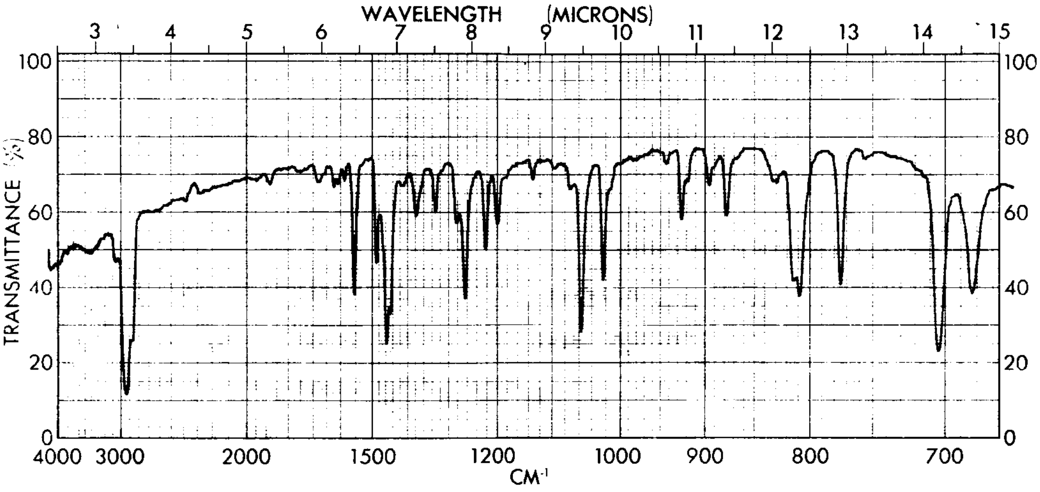


Fig. 13 - Infrared Spectrum of 2,2'-Diphenyl-5,5'-bibenzoxazole (Nujol)

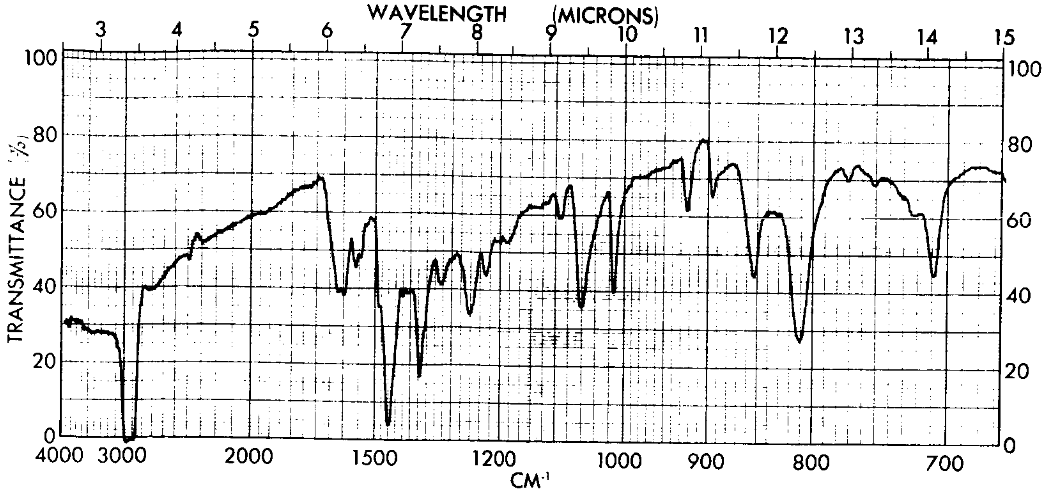


Fig. 14 - Infrared Spectrum of the Polymer from 3,3'-Dihydroxybenzidine and Terephthalimide in Polyphosphoric Acid (Nujol)

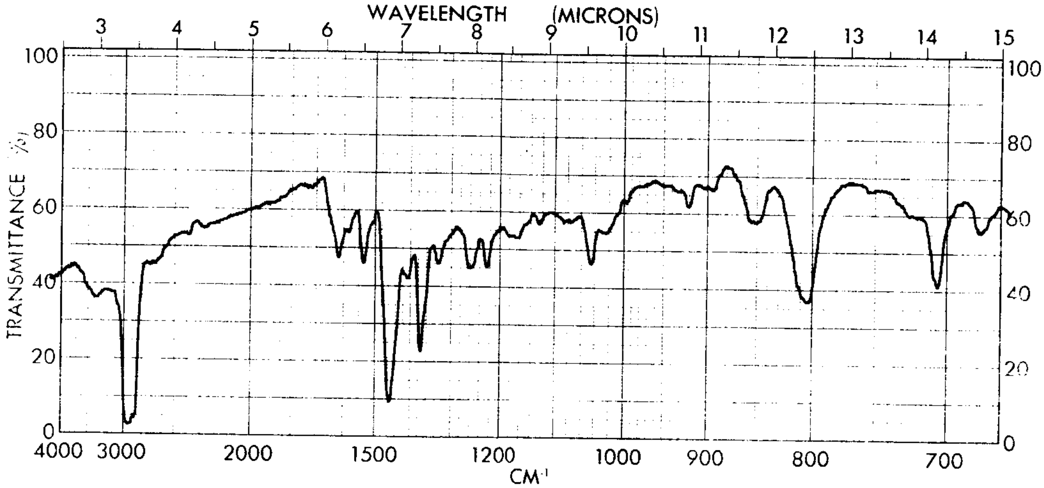


Fig. 15 - Infrared Spectrum of the Polymer from 3,3'-Dihydroxybenzidine and Isophthalimide in Polyphosphoric Acid (Nujol)

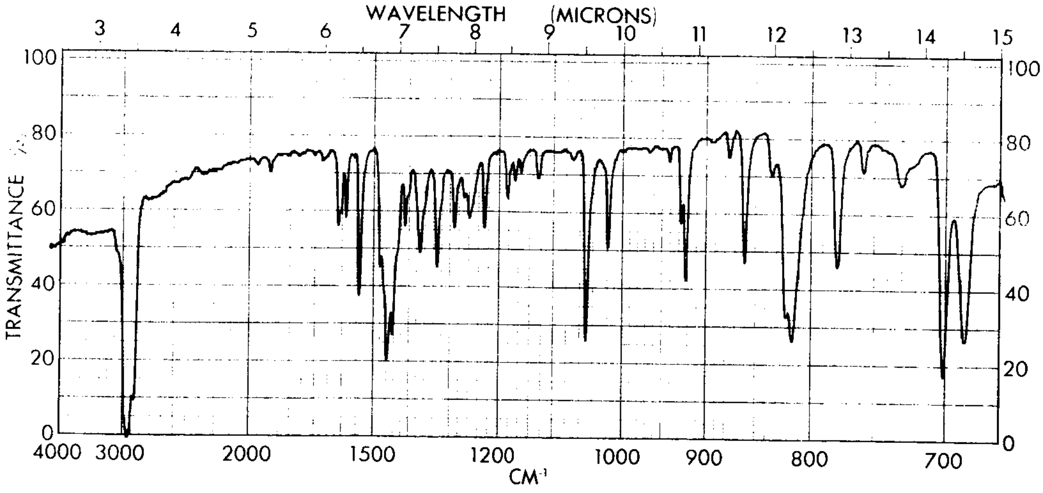
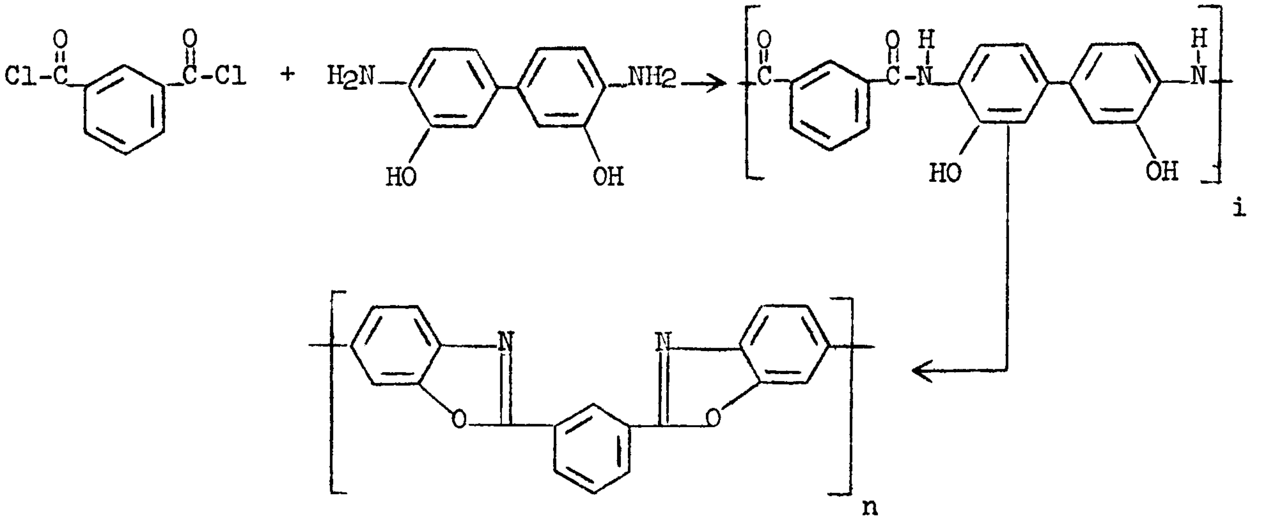


Fig. 16 - Infrared Spectrum of 2,2'-Diphenyl-6,6'-bibenzoxazole (Nujol)

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. Solution polymerization of isophthalyl chloride with 3,3'-dihydroxybenzidine at -5° - 20° in a dimethylacetamide-cyclohexanone mixture had been reported to produce an uncyclized polymer with an inherent viscosity of 1.04 in sulfuric acid.[16] It was also reported that films of this polymer could be cyclized at 200° - 530°.



Attempts to reproduce the preparation of the prepolymer were not successful. In a series of preparations, 3,3'-dihydroxybenzidine with either isophthalyl chloride or terephthalyl chloride gave polymers with inherent viscosities of 0.33 - 0.24, and 3,3'-diamino-4,4'-diphenol gave polymers with inherent viscosities of 0.14. The infrared spectra of the polymers (Figs. 17 and 19) 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. 18 and 20); therefore, cyclization had not occurred. None of these polymers were suitable for preparing films, apparently because of their low molecular weights.

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 (Fig. 21), but N,N'-dibenzoyl-3,3'-dihydroxybenzidine remained unchanged (Fig. 22). These data suggested that higher polymerization temperatures could be used in preparing the prepolymer without danger of cyclization.

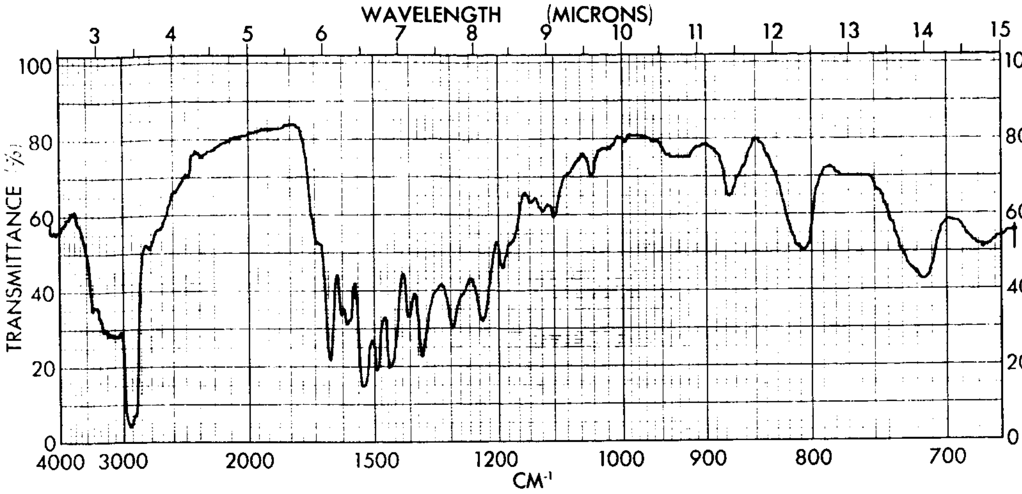


Fig. 17 - Infrared Spectrum of the Polymer from 2,2'-Diamino-p,p'-biphenol and Isophthalyl Chloride in Dimethylacetamide-Cyclohexanone (Nujol)

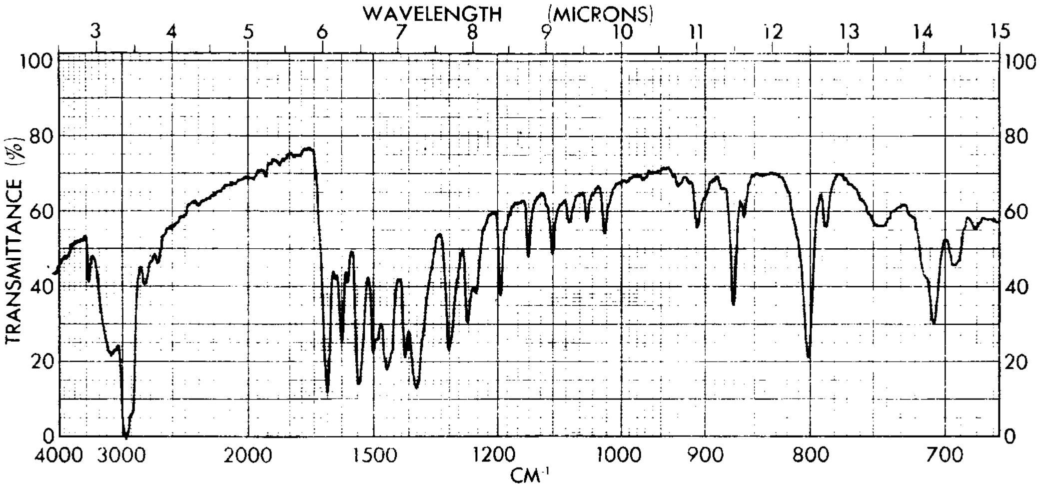


Fig. 18 - Infrared Spectrum of N,N'-Dibenzoyl-2,2'-diamino-p,p'-biphenol (Nujol)

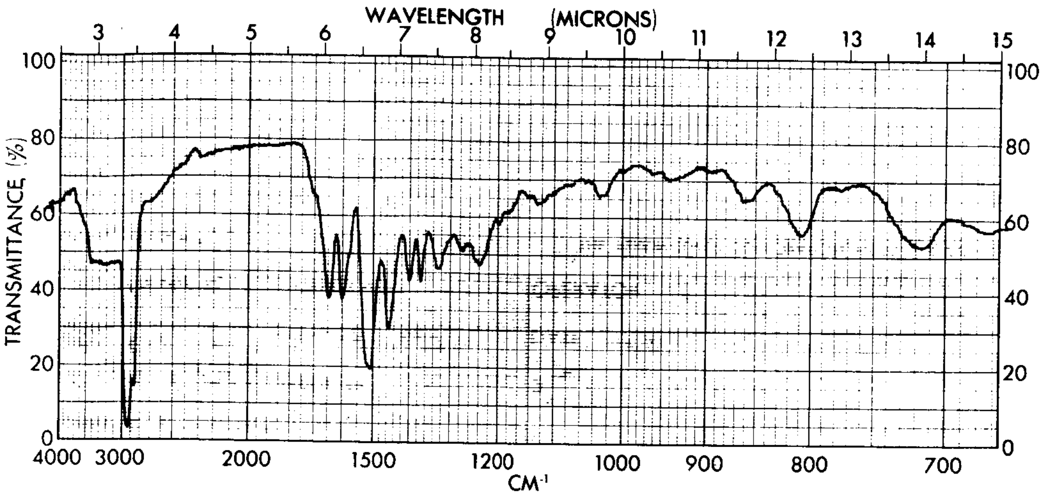


Fig. 19 - Infrared Spectrum of the Polymer from 3,3'-Dihydroxybenzidine and Isophthalyl Chloride in Dimethylacetamide-Cyclohexanone (Nujol)

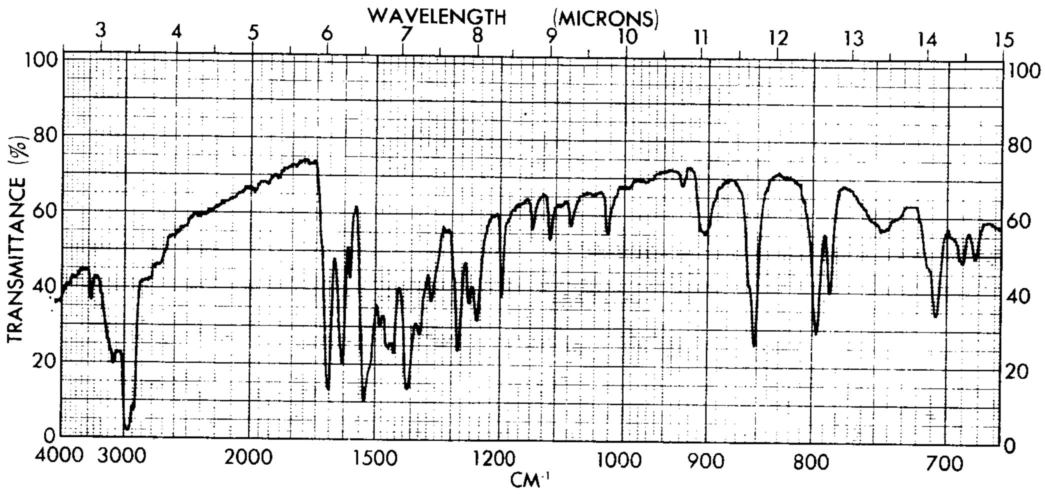


Fig. 20 - Infrared Spectrum of N,N'-Dibenzoyl-3,3'-dihydroxybenzidine (Nujol)

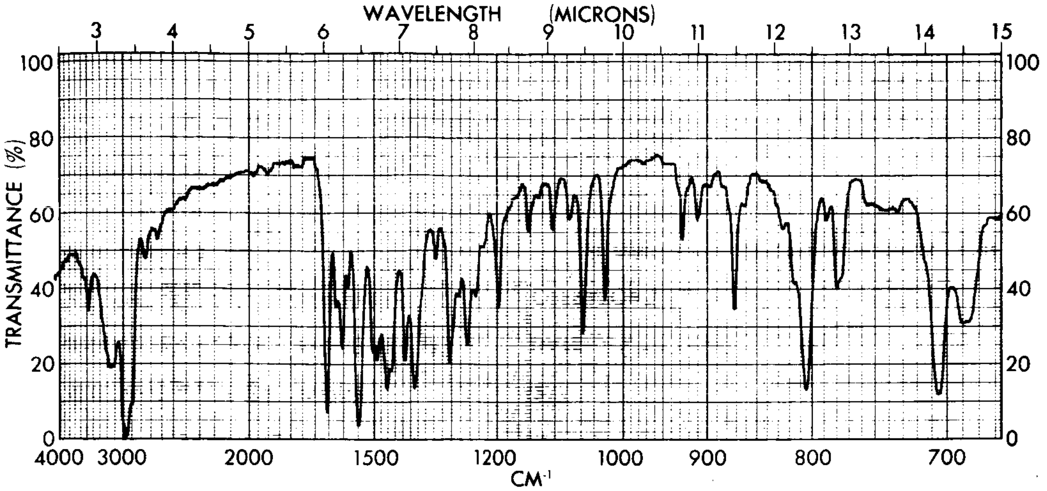


Fig. 21 - Infrared Spectrum of N,N'-Dibenzoyl-2,2'-diamino-p,p'-biphenol Heated 2 Hr. at 300° (Nujol)

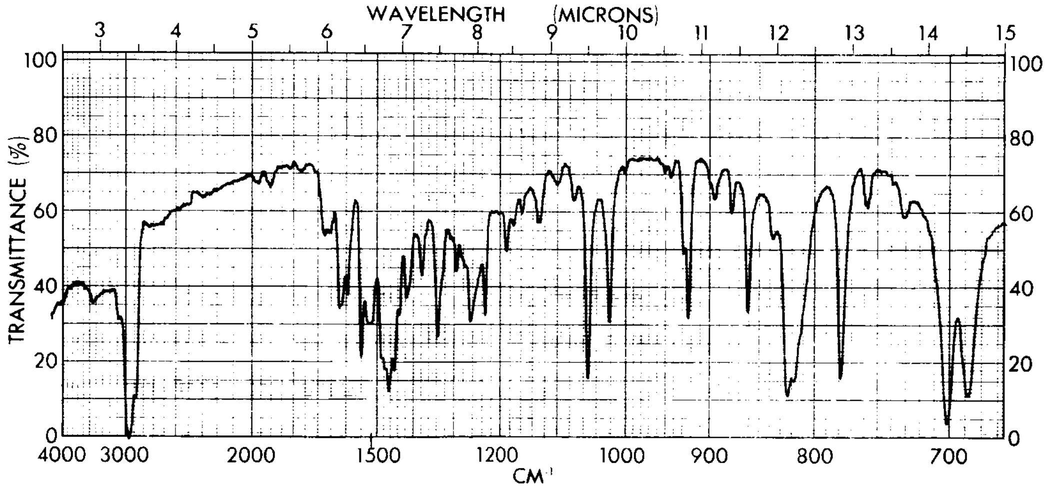
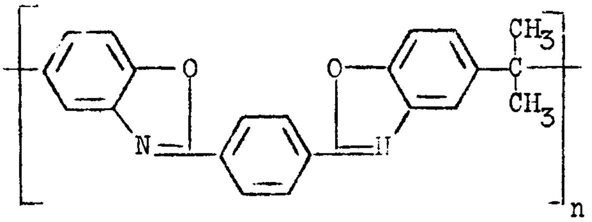


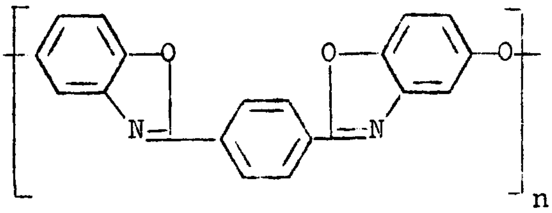
Fig. 22 - Infrared Spectrum of N,N'-Dibenzoyl-3,3'-dihydroxybenzidine Heated 2 Hr. at 300°

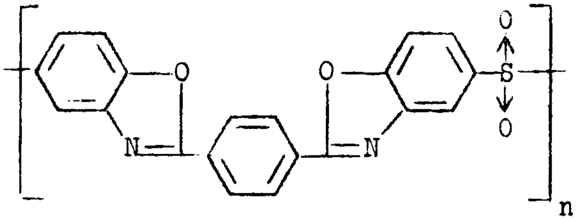
However, in a series of experiments, higher molecular weight prepolymers were not obtained when a polymerization temperature of 100° was used or when other acid acceptors, such as s-collidine or quinoline, were used at the higher temperature.

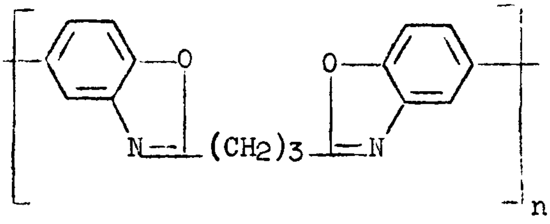
As an alternate approach to benzoxazole prepolymers, the monomers were polymerized in polyphosphoric acid at lower temperatures and for shorter time periods than had been used in preparing the cyclized polymers. At lower temperatures, unsatisfactory, low molecular weight products were obtained. Shorter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

In subsequent work, an attempt was made to improve the solubility of polymers containing the benzoxazole unit through modification of the chemical structure of the polymers. The following structures were selected for study.









When the monomers, 2,2-bis(3-amino-4-hydroxyphenyl)propane and bis(3-amino-4-hydroxyphenyl) sulfone, were polymerized with terephthalamide in polyphosphoric acid at 200°, only low molecular weight polymers were obtained. The highest inherent viscosity for any of the polymers was 0.38 when the measurement was made in sulfuric acid at a polymer concentration of 0.5 per cent. The polymer from terephthalamide and 3,3'-diamino-4,4'-dihydroxydiphenyl ether had a higher molecular weight, $\eta_{inh} = 1.92$, but like the other wholly aromatic polybenzoxazoles, was insoluble in all solvents except sulfuric acid. The heat stability of this polymer was comparable with the stability of other aromatic polybenzoxazoles. The infrared spectra of the three polymers are shown in Figs. 23, 24, and 25, and the thermogravimetric analysis of a polymer from terephthalamide and 3,3'-diamino-4,4'-dihydroxydiphenyl ether in Fig. 26.

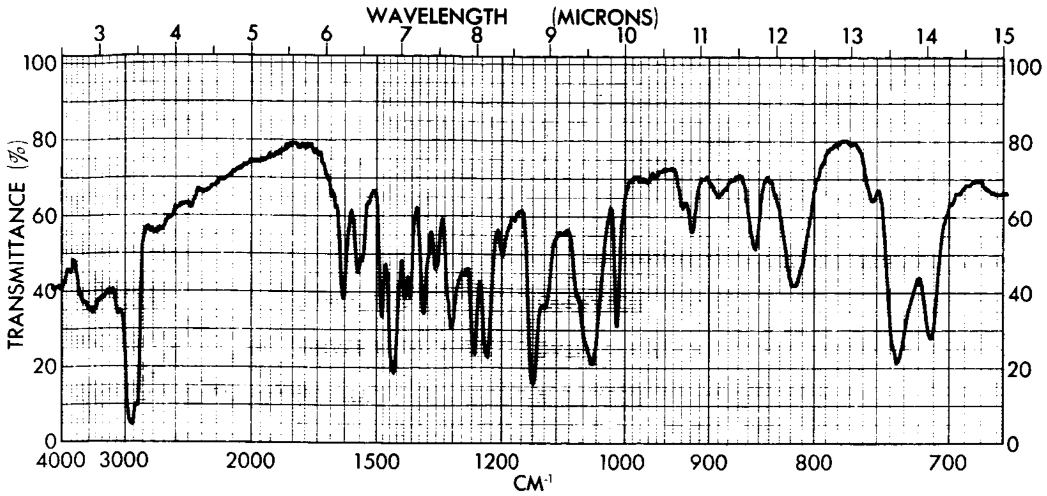


Fig. 23 - Infrared Spectrum of the Polymer From Bis(3-amino-4-hydroxyphenyl) Sulfone and Terephthalamide (Nujol)

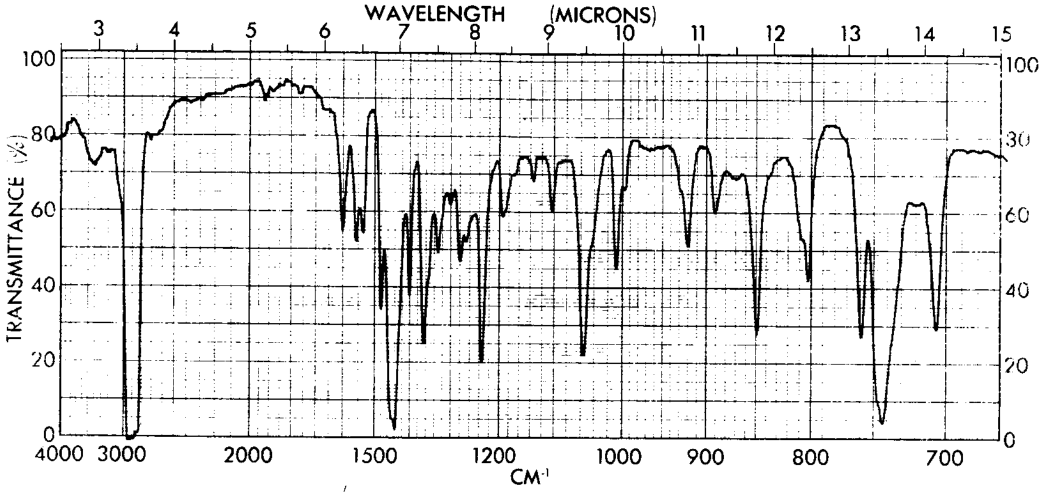


Fig. 24 - Infrared Spectrum of the Polymer From 2,2-Bis(amino-4-hydroxyphenyl)propane and Terephthalamide (Nujol)

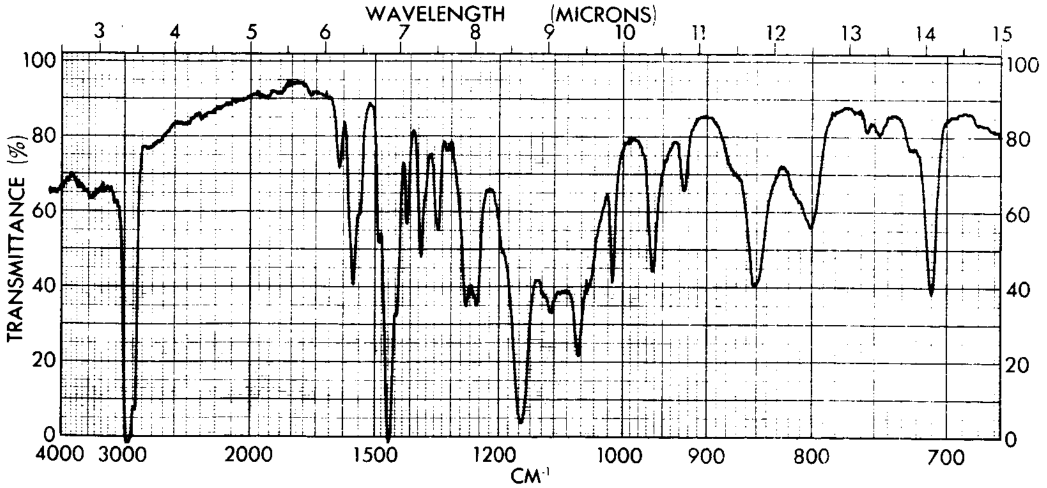


Fig. 25 - Infrared Spectrum of the Polymer From Terephthalamide and 3,3'-Diamino-4,4'-dihydroxydiphenyl Ether Dihydrochloride (Nujol)

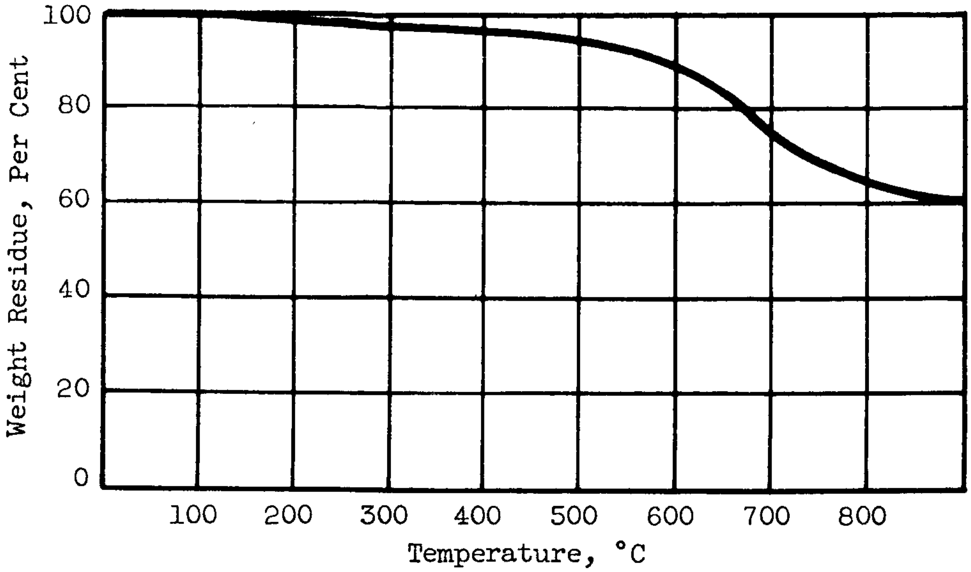


Fig. 26 - Thermogravimetric Analysis of a Polymer From Terephthalamide and 3,3'-Diamino-4,4'-dihydroxydiphenyl Ether*

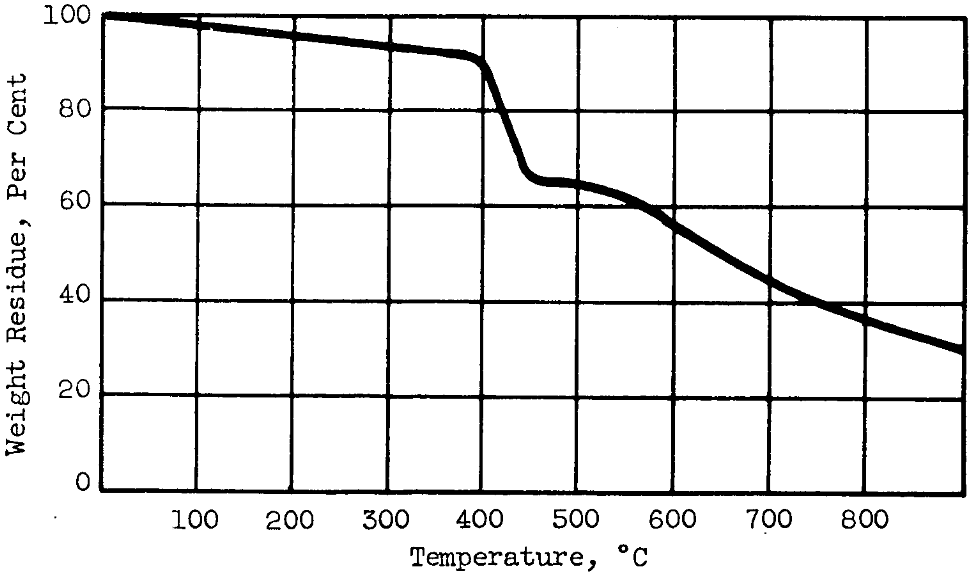


Fig. 27 - Thermogravimetric Analysis of a Polymer From Glutaric Acid and 2,2'-Diamino-p,p'-biphenol

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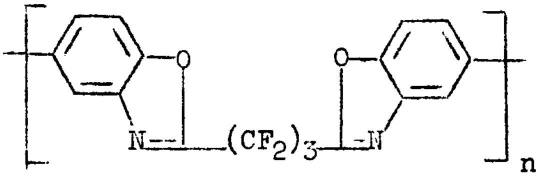
* Heating rate for all TGA = 3°/min; N_2 atmosphere.

B. Aliphatic Polybenzoxazoles

Aliphatic dicarboxylic acids and bis(aminophenols) could also be polymerized in polyphosphoric acid; for example, glutaric acid and 2,2'-diamino-p,p'-biphenol gave a polymer with an inherent viscosity of 1.23 in sulfuric acid. In spite of the aliphatic link in these polymers, they exhibited relatively good heat stabilities, showing procedural decomposition temperatures of about 400° by thermogravimetric analysis (Figs. 27, 28, and 29). The infrared spectra of the aliphatic polymers (Figs. 30 - 34) were consistent with the structures. Although the aliphatic polybenzoxazole showed improved solubilities, films cast from solutions of the polymer from 2,2'-diamino-p,p'-biphenol and glutaric acid were poorly adherent to test plates and cracked easily. Table I summarizes the solubility of these polymers in various solvents and provides a comparison with the solubilities of various aromatic polybenzoxazoles. All the aliphatic polybenzoxazoles were highly colored and produced very dark films.

In additional work, an attempt was made to incorporate the perfluoroalkylene group in the polymer as a link between benzoxazole groups. Several perfluoroglutaric acid derivatives, the phenyl ester and the amide as well as the free acid, were treated with 2,2'-diamino-p,p'-biphenol.



Under none of the conditions used could a polymer be obtained, and, frequently, unchanged monomer was the only substance recovered from the polymerization mixtures. Procedures employed included solution polymerization in polyphosphoric acid and melt polymerization of the phenyl ester and the free aminophenol.

In the first experiments, it was assumed that perfluoroglutaric acid and perfluoroglutaramide failed to polymerize with bis(aminophenols) because of the high volatility of the fluorine-containing compounds. However, in subsequent experiments, 83 per cent of the diphenyl perfluoroglutarate could be recovered when it was treated with a bis(aminophenol) in polyphosphoric acid at 150° for 16 hr.; therefore, failure of polymerization to occur was probably due to the intrinsic lack of reactivity of perfluoroglutaric acid derivatives.

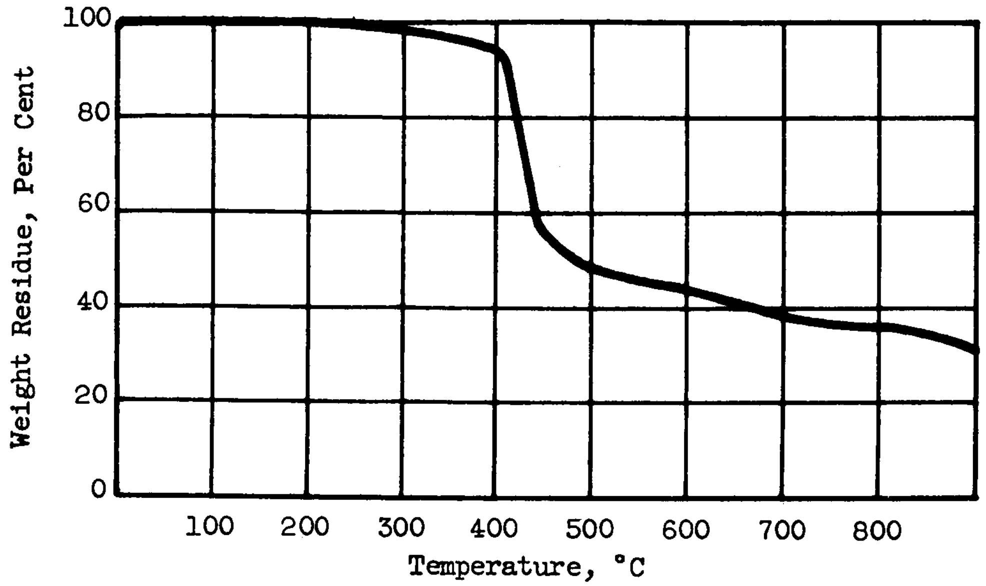


Fig. 28 - Thermogravimetric Analysis of a Polymer From Glutaric Acid and 2,2'-Dihydroxybenzidine

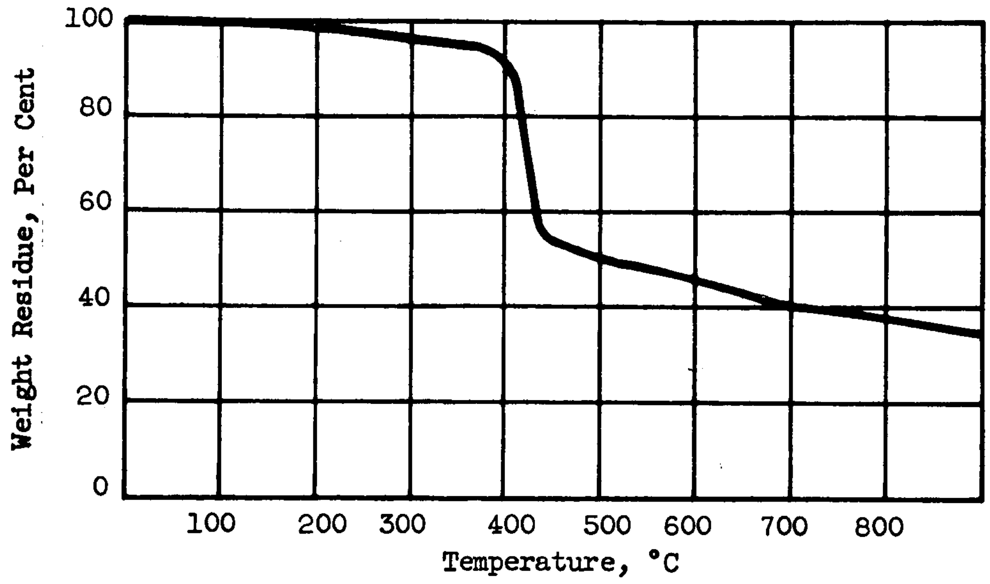


Fig. 29 - Thermogravimetric Analysis of a Polymer From 3,3'-Diamino-4,4'-dihydroxydiphenyl Ether Glutaric Acid

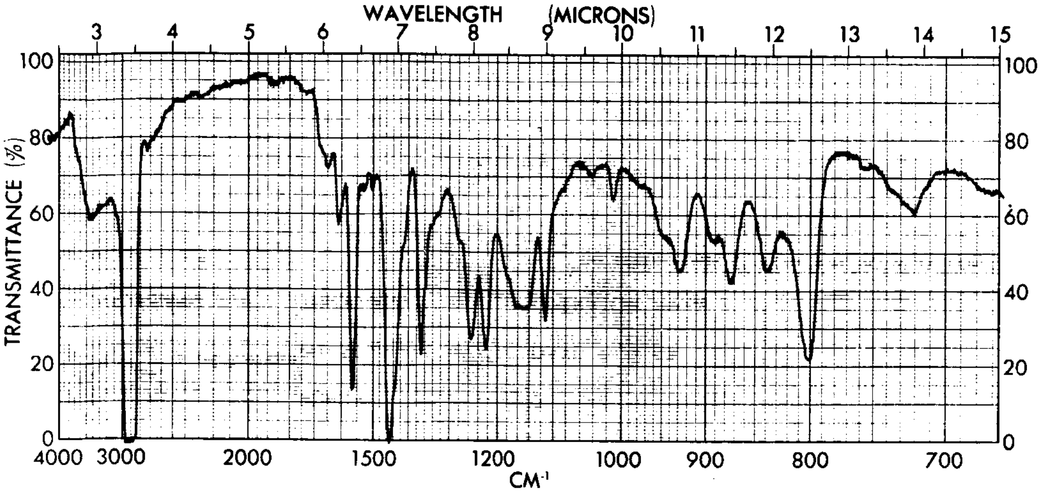


Fig. 30 - Infrared Spectrum of the Polymer From 2,2'-diamino-p,p'-biphenol and Glutaric Acid (Nujol)

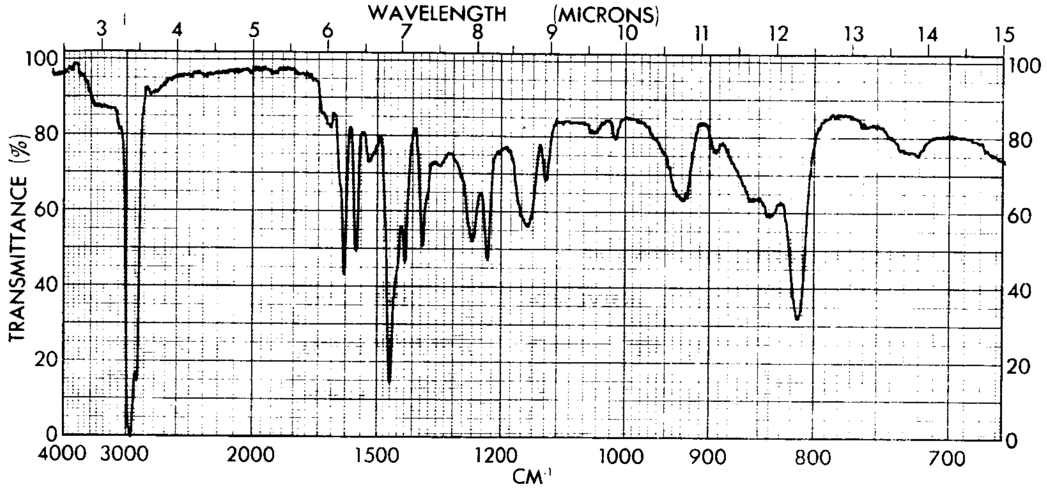


Fig. 31 - Infrared Spectrum of the Polymer From Glutaric Acid and 3,3'-Dihydroxybenzidine Dihydrochloride (Nujol)

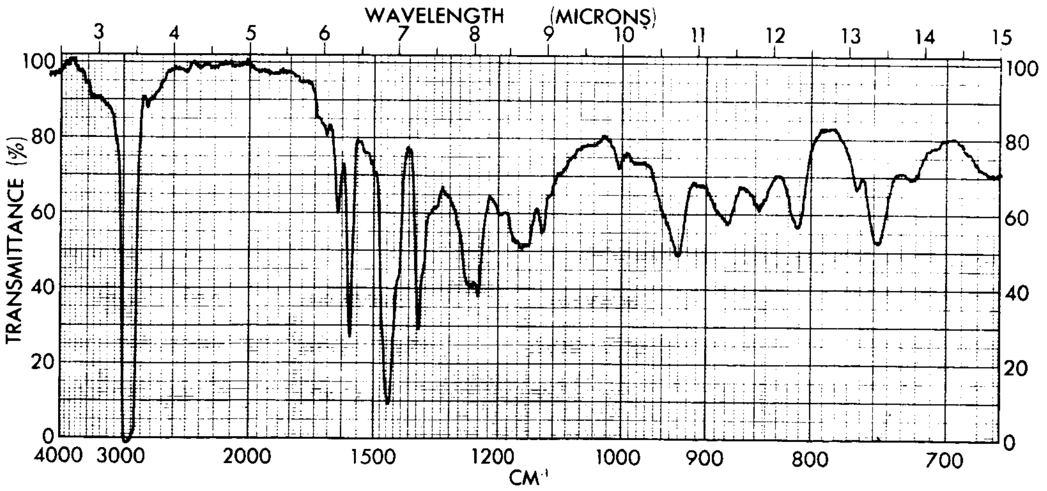


Fig. 32 - Infrared Spectrum of the Polymer From Glutaric Acid and 2,2-Bis(3-amino-4-hydroxyphenyl)propane Dihydrochloride (Nujol)

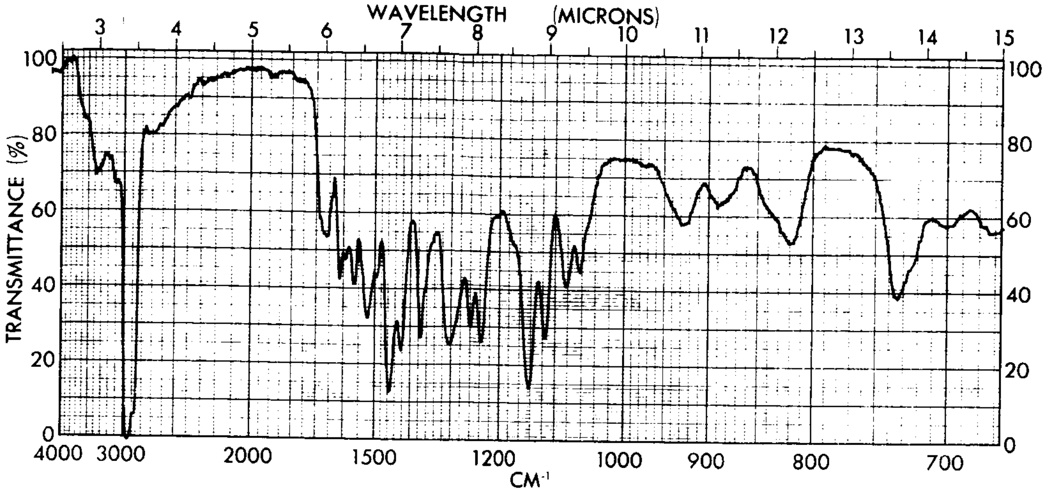


Fig. 33 - Infrared Spectrum of the Polymer From Glutaric Acid and Bis(3-amino-4-hydroxyphenyl) Sulfone Dihydrochloride (Nujol)

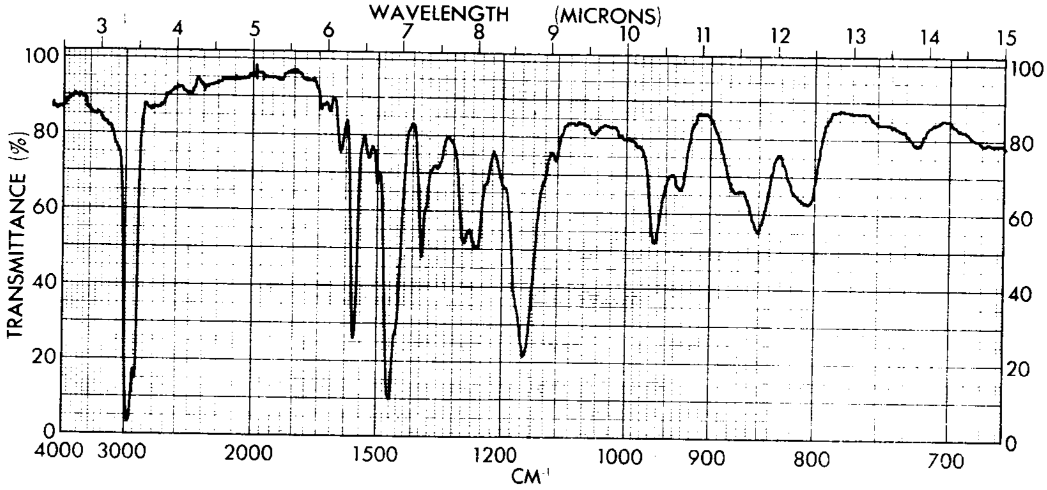


Fig. 34 - Infrared Spectrum of the Polymer From Glutaric Acid and 3,3'-Diamino-4,4'-dihydroxydiphenyl Ether Dihydrochloride (Nujol)

TABLE I

SOLUBILITY OF BENZOXAZOLE POLYMERS

(c = 0.5 per cent)

	Polymer from:						
Solvent	2,2'-Diamino-p,p'-biphenol and Terephthalamide	3,3'-Dihydroxybenzidine and Terephthalamide	3,3'-Diamino-4,4'-dihydroxydiphenyl Ether and Terephthalamide	Bis(3-amino-4-hydroxyphenyl) Sulfone and Terephthalamide	2,2'-Diamino-p,p'-biphenol and Glutaric Acid	3,3'-Dihydroxybenzidine and Glutaric Acid	3,3'-Diamino-4,4'-dihydroxydiphenyl Ether and Glutaric Acid
Sulfuric acid	A	A	A	A	A	A	A
Dimethylsulfoxide	D	D	D	D	D	D	B
Dimethylformamide	D	D	D	D	D	D	B
Dimethylacetamide	D	D	D	D	C	D	B
N-Methylpyrrolidine	D	D	D	D	B	D	B
Formic acid (90%)	D	D	D	D	A	D	A
m-Cresol	D	D	D	D	B	A	A
Toluene	D	D	D	D	D	D	D
Dichloroacetic acid	-	-	D	-	-	A	A

A = Soluble at room temperature
B = Soluble with heating.
C = Swollen.
D = Insoluble.

Although a number of high-molecular-weight polymers were obtained in the poly(benzoxazole) series, none of the polymer samples gave elemental analyses consistent with the proposed structures (Table II). Infrared spectra were in general consistent with the structures and gave little or no evidence for the presence of solvent (phosphoric acid) molecules or unclosed ring structures. All the polymers, as well as the model compounds, the C=N stretch at 1560 - 1570 cm^{-1}, the C-O-C stretch at 1250 - 1270 cm^{-1}, and benzoxazole ring deformation at 800 - 830 cm^{-1}. The analyses were seldom consistent with the presence of an inert diluent, such as water. No adequate explanation can be advanced for the disagreements.

C. Experimental

1. Synthesis of Intermediates and Monomers

a. 3,3'-Dihydroxybenzidine dihydrochloride:

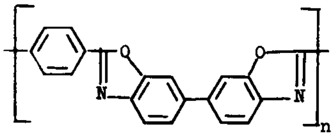
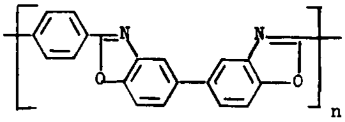
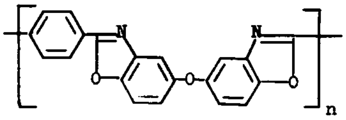
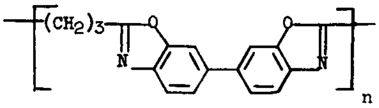
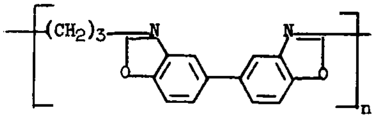
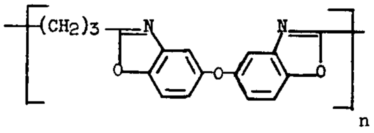
1. Via the hydriodic acid cleavage of 3,3'-dimethoxybenzidine: (Method: Reference 26) After a mixture of 24.4 g. (0.10 mole) of 3,3'-dimethoxybenzidine and 240 ml. of 57 per cent hydriodic acid was refluxed 24 hr. under an atmosphere of nitrogen, the excess hydriodic acid was removed under reduced pressure. 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. 35.

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.

2. Via the hydrobromic acid cleavage of 3,3'-dimethoxybenzidine: (Method: Reference 27) 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,

TABLE II

ELEMENTAL ANALYSES OF POLYBENZOXAZOLES

Polymer Structure	Formula	Calculated			Found		
		C	H	N	C	H	N
	$C_{20}H_{10}N_2O_2$	77.41	3.25	9.03	73.86	3.76	6.68
	$C_{20}H_{10}N_2O_2$	77.41	3.25	9.03	71.17	3.15	6.42
	$C_{20}H_{10}N_2O_3$	73.61	3.09	8.59	62.20	3.08	5.30
	$C_{17}H_{12}N_2O_2$	73.90	4.38	10.14	70.31	4.54	9.67
	$C_{17}H_{12}N_2O_2$	73.90	4.38	10.14	67.49	4.39	8.70
	$C_{17}H_{12}N_2O_3$	69.85	4.14	9.59	67.10	4.20	9.05

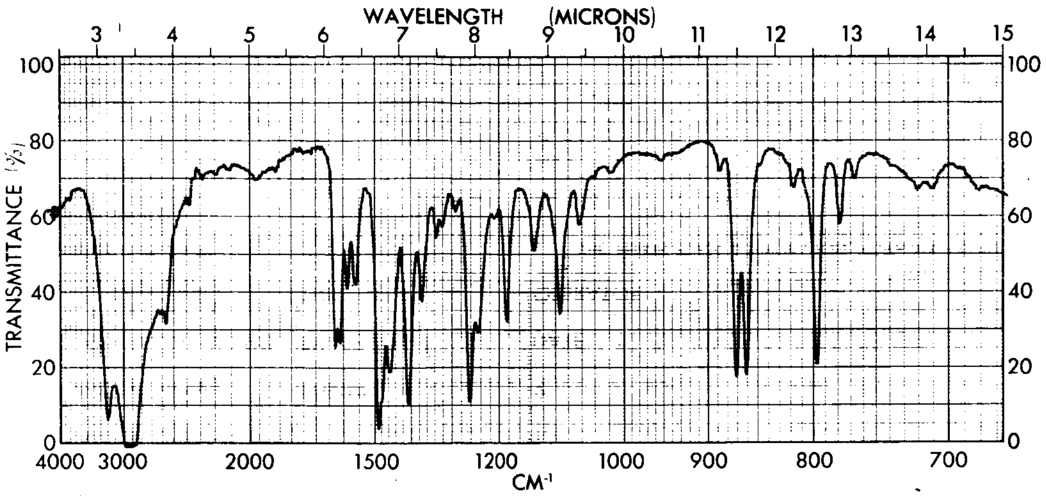


Fig. 35 - Infrared Spectrum of 3,3'-Dihydroxybenzidine Hydrochloride (Nujol)

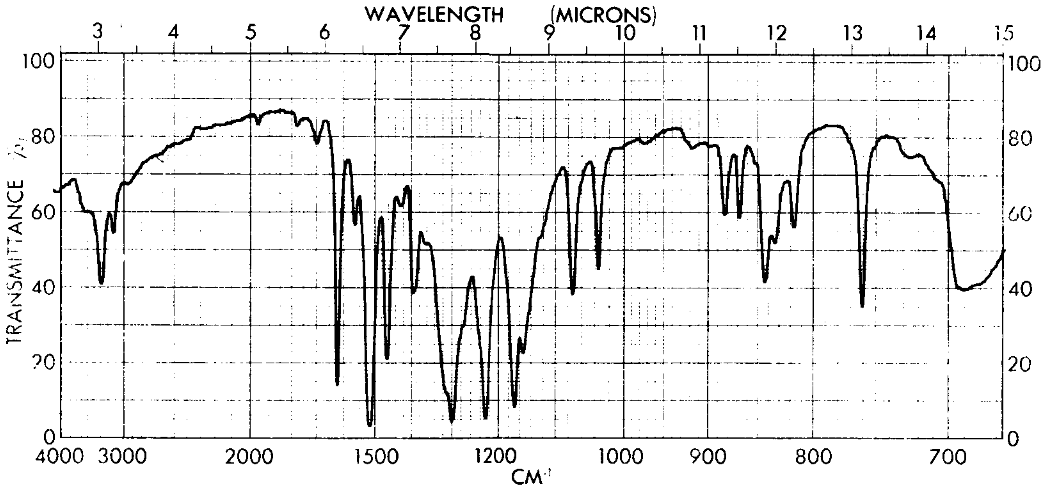


Fig. 36 - Infrared Spectrum of 2,2'-Dinitro-p,p'-biphenol (KBr)

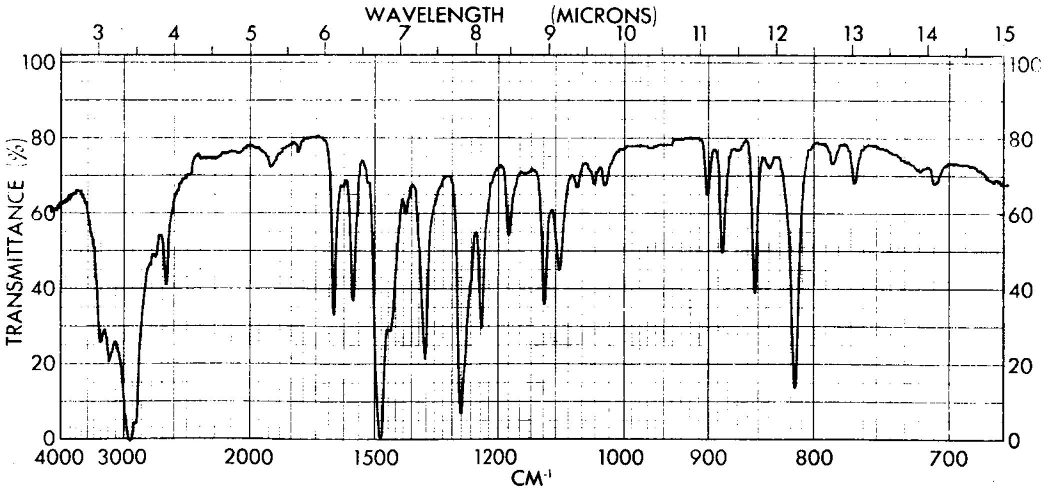


Fig. 37 - Infrared Spectrum of 2,2'-Diamino-p,p'-biphenol Hydrochloride (Nujol)

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.

b. 2,2'-Dinitro-*p*,*p*'-biphenol: (Method: Reference 27) 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 iced 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° (reported, 286°).[28] 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°. The infrared spectrum is reported in Fig. 36.

c. 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, 22.8 g. (78 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. 37.

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., 144.

d. 2,2-Bis(3-nitro-4-hydroxyphenyl)propane: (Method: Reference 28) Seventy milliliters of nitric acid was added slowly during 1.5 hr. to a stirred solution of 68.5 g. (0.30 mole) of Bisphenol A in 350 ml. of benzene and 230 ml. of acetic acid at 5°. After the mixture was stirred 1 hr. at 5°, the precipitate was filtered off and washed with water, ethanol, and ether. The crude material, dried in vacuum, weighed 37.5 g. (40 per cent) and melted at 130 - 131°. Recrystallization of the product from 95 per cent ethanol gave 30 g. (32 per cent) of orange 2,2-bis(3-nitro-4-hydroxyphenyl)propane, m.p. 133 - 135° (reported m.p. 135°).[28] After the filtrate was mixed with 500 ml. of water and 350 ml. of benzene, the benzene layer was separated and washed four times with water, dried over calcium sulfate, and evaporated. An additional 50.5 g. of crude product was obtained, m.p. 108 - 113°. Two recrystallizations from 95 per cent ethanol gave an additional 26.0 g. of 2,2-bis(3-nitro-4-hydroxyphenyl)propane which melted at 130 - 131°. The total yield was 59 per cent. The infrared spectrum is reported in Fig. 38.

e. 2,2-Bis(3-amino-4-hydroxyphenyl)propane dihydrochloride: (Method: Reference 28): Sodium hydrosulfite (115 g., 0.66 mole) was added during 1 hr. to a stirred solution of 31.8 g. (0.10 mole) of 2,2-bis(3-nitro-4-hydroxyphenyl)propane in 1,600 ml. of concentrated ammonium hydroxide at 30 - 35°. After 1 hr., the peach-colored precipitate was filtered off, washed with concentrated ammonium hydroxide, and dried to give 44.5 g. (172 per cent) of tan crude product, which did not melt below 400°. When a mixture of the solid in 200 ml. of water was adjusted with concentrated hydrochloric acid to pH 2, filtered, and treated with 200 ml. concentrated hydrochloric acid, 12.5 g. (38 per cent) of grey-brown 2,2-bis(3-amino-4-hydroxyphenyl)propane dihydrochloride precipitated. The compound, which was dried over potassium hydroxide, melted at 233 - 235°. Two additional precipitations with hydrochloric acid, one using charcoal to decolorize the solution, gave 6.5 g. (20 per cent) of the product, m.p. 239 - 241°. The infrared spectrum is reported in Fig. 39.

Anal. Calcd. for $C_{15}H_{18}N_2O_2 \cdot 2HCl \cdot 2H_2O$: C, 49.05; H, 6.59; N, 7.63; Neut. Equiv., 184. Found: C, 49.20; H, 6.61; N, 7.50; Neut. Equiv., 184.

f. Bis(3-nitro-4-hydroxyphenyl) sulfone: (Method: Reference 28) A mixture of 375 ml. of nitric acid and 62.6 g. (0.25 mole) of bis(4-hydroxyphenyl) sulfone was cooled and occasionally stirred in an ice bath for 1 hr. The mixture was diluted with 600 ml. of water and filtered. When the precipitate was slurried with 1 liter of hot water, filtered off, and dried, 51 g. (60 per cent) of crude nitrated sulfone, m.p. 220 - 223°, was obtained. Recrystallization from 1,100 ml. of a mixture of 95 per cent ethanol and 2-butanone gave 15 g. (18 per cent) of tan bis(3-nitro-4-hydroxyphenyl) sulfone, m.p. 233 - 234° (reported m.p., 231 - 233°,[29] 223 - 225°[28]). When the filtrate was evaporated and the residue recrystallized 95 per cent ethanol, an additional 14.0 g. of the compound, m.p. 232 - 234°, was obtained. The total yield was 34 per cent. The infrared spectrum is reported in Fig. 40.

g. Bis(3-amino-4-hydroxyphenyl) sulfone: Sodium hydrosulfite (96 g., 0.55 mole) was added during 20 min. to a stirred solution of 25.5 g. (0.075 mole) of bis(3-nitro-4-hydroxyphenyl) sulfone in 602 ml. of concentrated ammonium hydroxide at 30 - 35°. After the mixture was stirred an additional 2 hr. and filtered, the solid product was washed with water until all the soluble material had dissolved. When the filtrate and washings were evaporated to

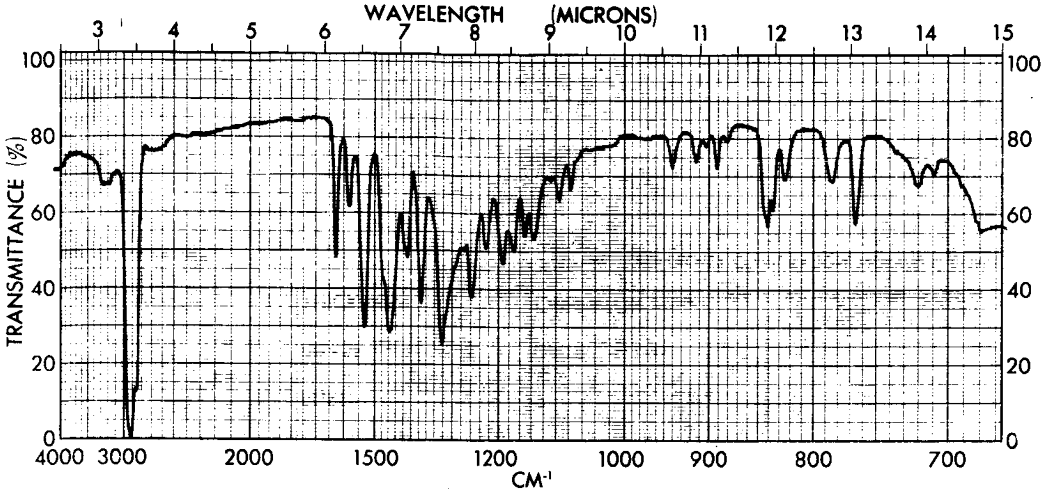


Fig. 38 - Infrared Spectrum of 2,2-Bis(3-nitro-4-hydroxyphenyl)-propane (Nujol)

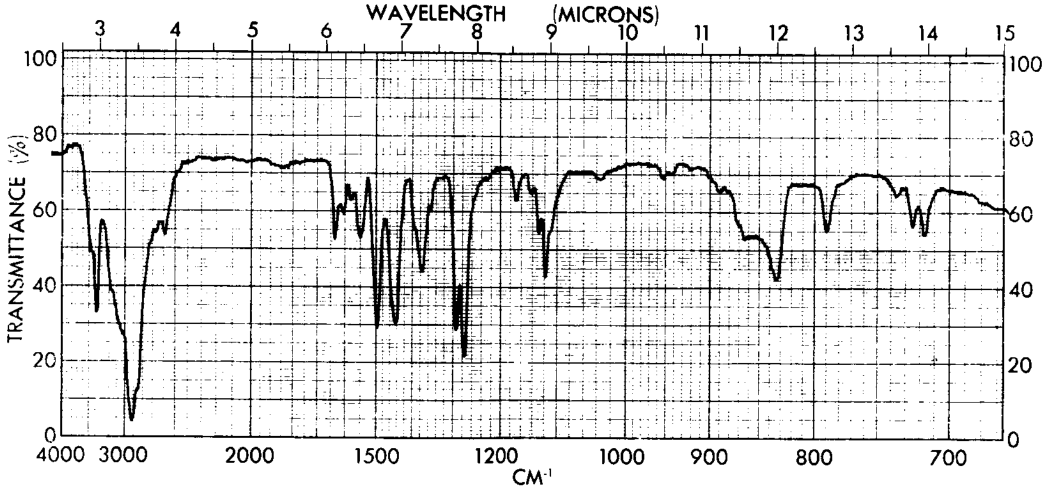


Fig. 39 - Infrared Spectrum of 2,2-Bis(3-amino-4-hydroxy-phenyl)propane Dihydrochloride Dihydrate (Nujol)

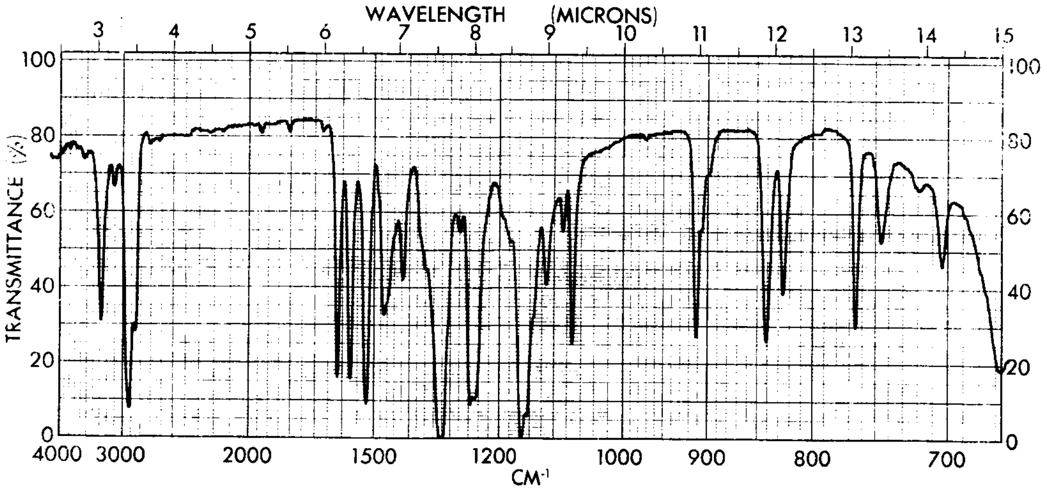


Fig. 40 - Infrared Spectrum of Bis(3-nitro-4-hydroxyphenyl) Sulfone (Nujol)

one-half their original volume and stored overnight, an opaque red gel formed, which was separated and discarded. Evaporation of the solution gave a yellow-brown solid, which was recrystallized from water to obtain 2.6 g. (12 per cent) of purple bis(3-amino-4-hydroxyphenyl) sulfone, m.p. 230 - 231° with dec. (reported m.p., 227 - 228°,[30] 233 - 235°,[31] 270 - 271°[29]). Infrared spectrum (Fig. 41) of the product and of a spectrum reported in the Sadtler files were superimposable.

A slurry of 27.2 g. (0.080 mole) of bis(3-nitro-4-hydroxyphenyl) sulfone, 13.4 g. of 95 per cent hydrazine, and 2.0 g. of Raney nickel in 260 ml. of 95 per cent ethyl alcohol and 150 ml. of water was refluxed 30 min. An additional 13.4 g. of hydrazine was added and the mixture was refluxed 1 hr. more. When the dark orange solution was filtered, the solvents removed, and the residue dried at 100° in vacuum, 28 g. of a brittle orange-brown solid was obtained. Recrystallization from water gave 4.1 g. of dark brown crystals of bis(3-amino-4-hydroxyphenyl) sulfone, m.p. 231 - 232° dec. Evaporation of the filtrate gave 8.5 g. of tan powder, m.p. 226 - 227° dec. Infrared spectra of the two crops were identical with the spectrum of authentic material. The total yield was 56 per cent.

h. 4,4'-Dihydroxy-3,3'-dinitrodiphenyl ether: (Method: Reference 31) To a stirred solution of 20.2 g. (0.10 mole) of 4,4'-oxydiphenol in 320 ml. of acetic acid and 200 ml. of benzene at 0° was added 13 ml. (0.2 mole) of concentrated nitric acid during 1 hr. The mixture was stirred 2 hr. at 0°, poured into 3 liters of cracked ice and stored overnight. When the precipitate was filtered off, washed with cold water, and dried at 80°, 20.5 g. of a yellow powder was obtained. The crude product, m.p. 148 - 152°, boiled in 850 ml. of 95 per cent ethanol and filtered, gave 7.1 g. of yellow powder, m.p. 156 - 158°. An additional 6.3 g. of brown crystals, m.p. 153 - 157°, precipitated when the filtrate was cooled. The infrared spectra of the two solids were identical. The combined fractions, recrystallized from 1,100 ml. of 95 per cent ethanol gave 8.0 g. (27 per cent) of 3,3'-dinitro-4,4'-dihydroxydiphenyl ether, m.p. 159 - 160°. The filtrates were combined and evaporated, and the solid recrystallized twice from ethanol to give an additional 1.5 g. of brown crystals, m.p. 155 - 157°. The total yield was 32 per cent. The infrared spectrum is reported in Fig. 42.

Anal. Calcd. for $C_{12}H_8N_2O_7$: C, 49.32; H, 2.76; N, 9.59. Found: C, 49.60; H, 2.79; N, 10.00.

A differential thermal analysis indicated the presence of a trace of ethanol in the analytical sample.

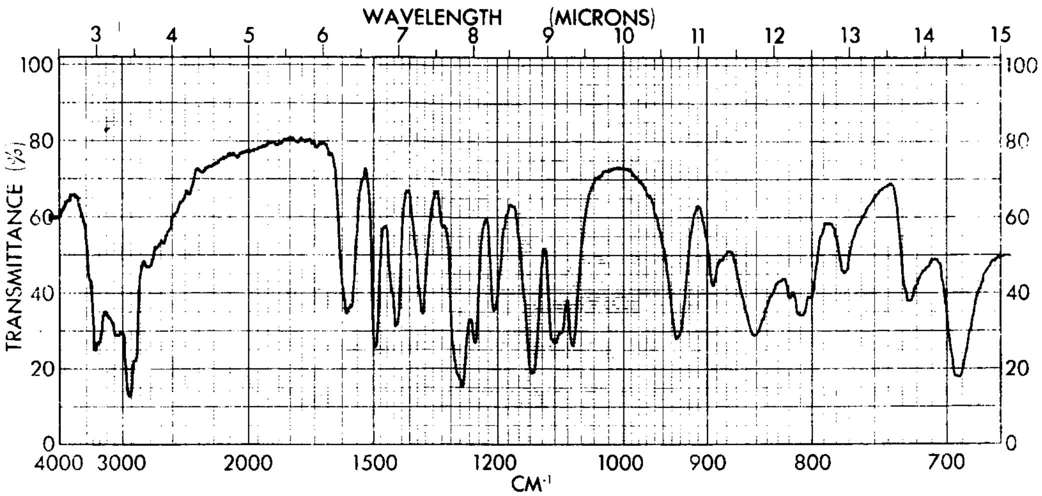


Fig. 41 - Infrared Spectrum of Bis(3-amino-4-hydroxyphenyl) Sulfone (Nujol)

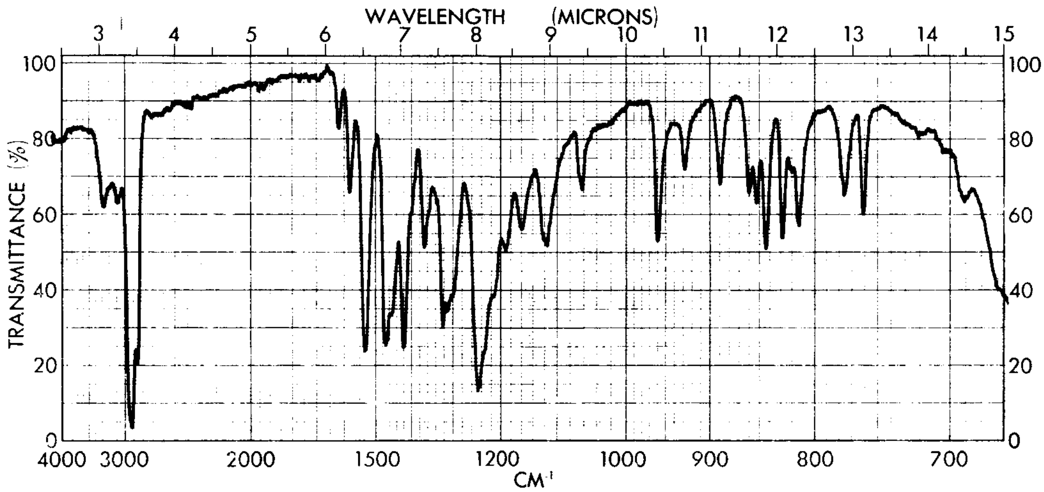


Fig. 42 - Infrared Spectrum of 4,4'-Dihydroxy-3,3'-dinitrodiphenyl Ether (Nujol)

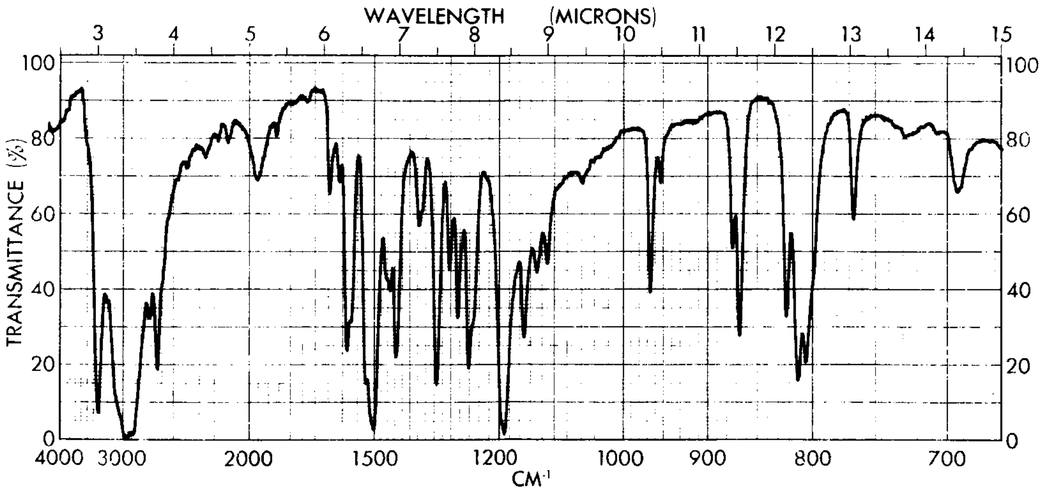


Fig. 43 - Infrared Spectrum of 3,3'-Diamino-4,4'-dihydroxydiphenyl Ether Dihydrochloride (Nujol)

i. 3,3'-Diamino-4,4'-dihydroxydiphenyl ether dihydrochloride: (Method: Reference 31) A slurry of 2.9 g. (0.010 mole) of 3,3'-dinitro-4,4'-dihydroxydiphenyl ether, 1.8 ml. of 95 per cent hydrazine, and 0.25 g. of Raney nickel in 32 ml. of 95 per cent ethyl alcohol and 20 ml. of water was refluxed for 30 min. An additional 1.8 ml. of hydrazine was added and the mixture was refluxed 30 min. The purple-black mixture was filtered, the solvents removed, and the residue dried at 100° under vacuum. To this solid was added 10 ml. of water and 15 ml. concentrated hydrochloric acid. The solid was filtered off, washed with 6 N hydrochloric acid, dissolved in 50 ml. of water and charcoal-filtered, and the solution treated with 60 ml. of concentrated hydrochloric acid. Filtration and drying over KOH gave 1.5 g. (50 per cent) of 3,3'-diamino-4,4'-dihydroxydiphenyl ether dihydrochloride, m.p. 295 - 298° dec. The infrared spectrum is consistent with the structure and is reported in Fig. 43.

Anal. Calcd. for $C_{12}H_{14}Cl_2N_2O_3$: C, 47.23; H, 4.62; N, 9.18; Neut. Equiv., 153. Found: C, 47.19; H, 4.60; N, 9.27; Neut. Equiv., 153.

j. Isophthalamide: A stirred solution of 40.6 g. (0.20 mole) of isophthalyl chloride (m.p. 43.5 - 45.0°) 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. 270 - 272° (reported, 280°).32/

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.

k. 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.

l. 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° 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°).[33]

m. 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°).[33]

n. Diphenyl perfluoroglutarate: A mixture of 36.0 g. (0.15 mole) of perfluoroglutaric acid, 28.2 g. (0.30 mole) of phenol, and 20.7 g. (0.135 mole) of phosphorus oxychloride was heated at 110° for 1.5 hr. Benzene (75 ml.) was added and the mixture was refluxed for 1.5 hr. The clear brown solution was extracted with four 60-ml. portions of water, two 50-ml. portions of 15 per cent sodium bicarbonate, and two 75-ml. portions of water and dried over calcium sulfate. The benzene solution was devolatilized and distilled under vacuum to give 5.7 g. (10 per cent) of a light yellow liquid, b.p. 137 - 140° (0.5 mm.), which crystallized on standing to an off-white solid, m.p. 41 - 42.5°. A differential thermal analysis showed a boiling point endotherm at 335° (reported m.p. 42.5 - 43°, b.p. 164 - 65.5° (5 mm.)).[34]

o. Diethyl perfluoroglutarate: (Method: Reference 35) After a solution of 19.5 g. (0.0813 mole) of perfluoroglutaric acid and 0.25 ml. of concentrated hydrochloric acid in 100 ml. of anhydrous ethanol was refluxed for 20 hr., the excess ethanol was distilled off. An additional 100 ml. of ethanol was added and slowly distilled. Distillation under reduced pressure gave 17.5 g. (73 per cent) of diethyl perfluoroglutarate, b.p. 104 - 109° (16 - 17 mm.), n_D^{20} 1.3607 (reported, b.p. 76° (3 mm.); n_D^{20} 1.3546).[35] The infrared spectrum is identical with the spectrum of the compound reported in the Sadtler file.

p. Perfluoroglutaramide: (Method: Reference 36) Ammonia was bubbled for 2 hr. into a solution of 15.0 g. (0.051 mole) of diethyl perfluoroglutarate in 120 ml. of ether. The mixture was allowed to warm to room temperature and the product was filtered off, washed with ether, and dried to give 10.0 g. (93 per cent) of perfluoroglutaramide, m.p. 210 - 211° (reported, 210°).[36]

2. Synthesis and Reactions of Model Compounds

a. 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°.

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.

b. 2,2'-Diphenyl-6,6'-bibenzoxazole: A procedure similar to the method described in section III. C. 2. a. 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°).37/

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.

c. 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 4.0 g. (94 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.

d. 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 did not change after recrystallization.

Anal. Calcd. for $C_{26}H_{20}N_{2}O_{4}$: 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.

e. *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°).[38]

f. *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 was similar to the closed ring analog, 2,2'-diphenyl-6,6'-dibenzoxazole (reported, m.p. 249 - 250°).[37]

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.

g. *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.

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 III. C. 2. f., 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.

h. 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 3350 cm^{-1} had shifted to 3450 cm^{-1}, indicating a decrease in hydrogen bonding.

3. Polymerization Reactions

a. 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.[17] The results are summarized in Table III. 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 inherent viscosity of the polymer (c = 0.5 per cent in sulfuric acid at 30°) was 0.24.

b. Polymers from bis(aminophenols) and phthalamides in polyphosphoric acid: In a typical experiment a mixture of 60.0 g. of 116 per cent polyphosphoric acid and 1.446 g. (0.00500 mole) of 3,3'-dihydroxybenzidine 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 inherent viscosity

TABLE III

POLYMERIZATION OF PHTHALYL CHLORIDES WITH BIS(AMINOPHENOLS)

	Acid Chloride	Mode of Addition	Base	Final Temp. (°C)	Yield (%)	Inherent 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	107	0.31	Olive green powder[c]
2.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Pyridine	100	94	0.21	Light green powder
3.	Isophthalyl chloride[a]	Acid Chloride to aminophenol[b]	*s*-Collidine	100	99	0.24	Green powder
4.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Quinoline	100	104	0.33	Green powder
5.	Terephthalyl chloride[d,e]	Aminophenol to acid chloride[b]	Pyridine	25	82	0.24	Yellow green powder
2,2'-Diamino-*p*,*p*'-biphenol Dihydrochloride with:							
6.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Pyridine	25	104	0.14	Tan powder
7.	Isophthalyl chloride[a]	Acid chloride to aminophenol[b]	Pyridine	100	94	0.14	Gray powder
8.	Terephthalyl chloride[d,e]	Aminophenol to acid chloride[b]	Pyridine	25	84	0.14	Yellow green powder

---

[a] Melting point 43.5 - 45° after one recrystallization from heptane.

[b] Dissolved in freshly distilled cyclohexanone and dimethylacetamide.

[c] 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 inherent viscosity of the resulting material was 0.15 (0.5 per cent in sulfuric acid).

[d] Did not form a homogeneous solution.

[e] Melting point 81 - 86°.

of a 0.5 per cent solution in sulfuric acid at 30° was 0.40. DTA and TGA data are presented in Figs. 38 and 42. The results of polymerization experiments of phthalamides with other bis(aminophenols) are summarized in Table IV.

c. 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.

d. Melt polymerization of 2,2'-diamino-p,p'-biphenol and diphenyl-terephthalate (attempted): (Method Reference 39) 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 - 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.

e. 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.

The results of a series of polymerizations are summarized in Table V.

Polymers from bis(aminophenols) and glutaric acid: In a typical experiment, a mixture of 60.0 g. of 116 per cent polyphosphoric acid and 1.446 g. (0.00500 mole) of 2,2'-diamino-p,p'-biphenol dihydrochloride was heated and stirred for 2.5 hr. at 150° under a flow of dry nitrogen. Glutaric acid (0.661 g., 0.00500 mole) was added and the mixture was heated at 200° for 1 hr. and at 150° for 2 hr. When the polymer was isolated and purified by the method described in paragraph II.C.3.b., 1.36 g. (99 per cent) of a gray polybenzoxazole, which did not melt below 400° was obtained. The inherent viscosity in sulfuric acid at 30° (0.5 per cent) was 1.23.

TABLE IV

POLYMERIZATIONS OF AROMATIC AMIDES AND BIS(AMINOPHENOLS) IN POLYPHOSPHORIC ACID

Amide	Aminophenol (as the Hydrochloride)	Temp. (°)	Time (hr.)	Inherent Viscosity (Sulfuric Acid at 30°)	Yield (%)
Terephthalamide	3,3'-Dihydroxybenzidine	200	19	0.40	101
Terephthalamide[a]	2,2'-Diamino-p,p'-biphenol	200	19	3.33	104
Terephthalamide	2,2'-Diamino-p,p'-biphenol	150	19	0.06	39
Terephthalamide	3,3'-Diamino-4,4'-dihydroxydiphenyl ether	200	19	1.92	106
Terephthalamide	2,2-Bis(3-amino-4-hydroxyphenyl)propane	200	19	0.08	91
Terephthalamide	Bis(3-amino-4-hydroxyphenyl) sulfone	200	19	0.38	76
Isophthalamide	3,3'-Dihydroxybenzidine	200	19	0.28	95

---

[a] In repetitions, the monomers were heated at 210 - 220° and the mixture gelled before the 19-hr. heating period was complete. Inherent viscosities as great as 8.00 were obtained.

TABLE V

POLYMERIZATIONS OF GLUTARIC ACIDS AND BIS(AMINOPHENOLS) IN POLYPHOSPHORIC ACID

Acid or Derivative	Aminophenol (as the Hydrochloride)	Temp. (°)	Time (hr.)	Inherent Viscosity (Sulfuric Acid at 30°)	Yield (%)
Glutaric acid	3,3'-Dihydroxybenzidine	200 150	1 2	0.70	78 -
Glutaric acid	2,2'-Diamino-*p*,*p*'-biphenol	200 150	1 2	1.23	99 -
Glutaric acid	3,3'-Diamino-4,4'-dihydroxydiphenyl ether	200 150	1 2	0.95	90 -
Glutaric acid	2,2-Bis(3-amino-4-hydroxyphenyl)propane	200 150	1 2	0.06	52 -
Glutaric acid	Bis(3-amino-4-hydroxyphenyl) sulfone	200	1	0.23	85
Perfluoroglutaric acid	2,2'-Diamino-*p*,*p*'-biphenol	150	20	-	0[a]
Perfluoroglutaramide	2,2'-Diamino-*p*,*p*'-biphenol	150	20	-	0
Diphenyl perfluoroglutarate	2,2'-Diamino-*p*,*p*'-biphenol	150	16	-	0[b]
Diphenyl perfluoroglutarate	2,2'-Diamino-p,p'-biphenol	200	20	-	0[c]

---

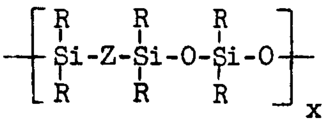
[a] Perfluoroglutaric acid sublimed from the polymerization mixture.
[b] Eighty-three per cent of the diphenyl perfluoroglutarate was recovered.
[c] Forty-three per cent of the diphenyl perfluoroglutarate was recovered.

A dark-brown poorly adherent film was obtained by applying part of a solution of 0.25 g. of the polymer in 5 ml. of dichloroacetic acid with an air brush to a 2-in. plate. The film was unevenly distributed. A solution of 0.3 g. of the polymer in 5 ml. of 90 per cent formic acid was applied to a plate with a pipette dropper and allowed to air-dry for 2 hr. The film cracked and separated from the plate. On another plate, three thin layers were applied, each one being air-dried for 20 min. before adding the next. After drying at 50° for several hours and at room temperature for one week, the film became brittle and flaked off. A third film also became brittle when air-dried at 130° for 30 min.

g. Polymer from 2,2'-diamino-*p*,*p*'-biphenol and diphenyl perfluoroglutarate (attempted melt polymerization): A mixture of 1.081 g. (0.00500 mole) of 2,2'-diamino-*p*,*p*'-biphenol (obtained by treating a solution of the dihydrochloride salt with 0.1 N sodium hydroxide till neutral, filtering off the free amine, washing with water and methanol, and drying in vacuum) and 1.963 g. (0.00500 mole) of diphenyl perfluoroglutarate was heated in an atmosphere of nitrogen at 100° for 30 min. and at 150° for 2 hr. A clear liquid slowly condensed on the flask walls. After the mixture was heated at 200° for 2 hr., the temperature was increased to 300°, and rapid refluxing occurred. The temperature of the mixture stabilized at 240°. The temperature was reduced and maintained at 150° for an additional 18 hr. At no time was there a melt; the appearance of the reactants did not change.

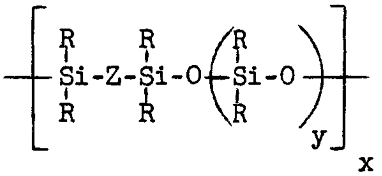
IV. SILOXANES CONTAINING ARYLENE LINKAGES

The goal of the initial polymer work on arylene-modified siloxanes was the synthesis of polymers with the following structures:



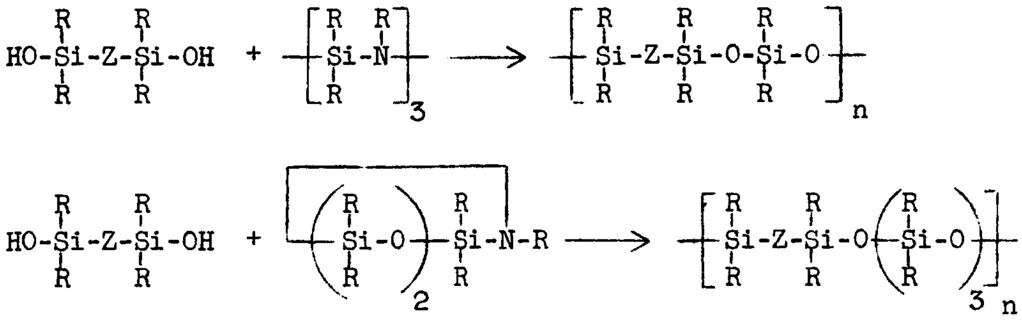
$$\left[-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-O-\overset{R}{\underset{R}{\mathrm{Si}}}-O- \right]_x$$

Subsequently, the work was extended to include polymers with longer siloxane segments between arylene groups.



$$\left[-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-O\left(-\overset{R}{\underset{R}{\mathrm{Si}}}-O- \right)_y \right]_x$$

Poly(p-phenylenetetramethyldisiloxane) ($R = CH_3$, $y = 0$), which can be obtained by the dehydration of p-phenylenebis(dimethylsilanol), has been known for a considerable time,[40] and its properties have been described in detail.[41] Methods have also been reported for the synthesis of random and block copolymers of p-phenylenebis(dimethylsilanol) and α,ω-dihydroxypoly(dimethylsiloxanes).[42] In this work, a more general method of polymer synthesis was required. Since it has been established that silylamines condense with silanols to form siloxanes under conditions in which there is no self-condensation of the silanol,[43] polymer syntheses could be effected by condensation of arylenedisilanols with diorganodiaminosilanes, cyclic diorganosilazanes, α,ω-diaminodiorganosiloxanes, or cyclic diorganosiloxazanes. For example:



$$HO-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-OH + \left[-\overset{R}{\underset{R}{\mathrm{Si}}}-\overset{R}{N}- \right]_3 \longrightarrow \left[-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-O-\overset{R}{\underset{R}{\mathrm{Si}}}-O- \right]_n$$

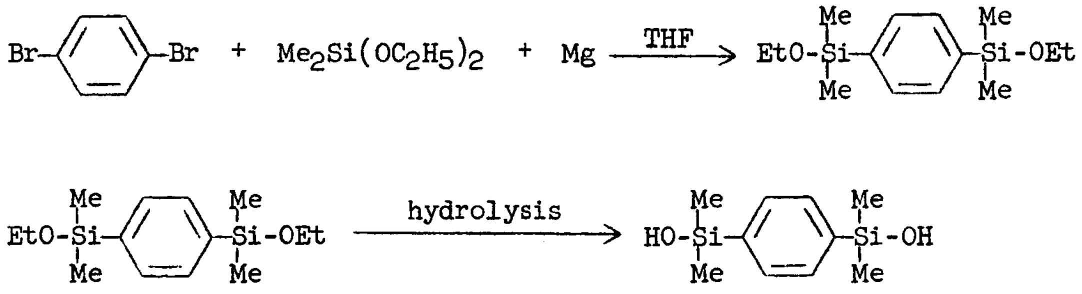
$$HO-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-OH + \boxed{\left(-\overset{R}{\underset{R}{\mathrm{Si}}}-O- \right)_2 -\overset{R}{\underset{R}{\mathrm{Si}}}-N-R} \longrightarrow \left[-\overset{R}{\underset{R}{\mathrm{Si}}}-Z-\overset{R}{\underset{R}{\mathrm{Si}}}-O\left(-\overset{R}{\underset{R}{\mathrm{Si}}}-O- \right)_3 \right]_n$$

A. Monomer Synthesis

The synthesis of the required monomers, particularly the arylenedisilanols and the cyclic siloxazanes, required the development of new or improved methods of preparation for some of the compounds.

1. Arylenedisilanols

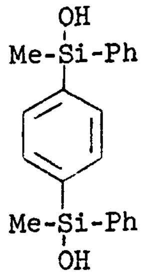
Although p-phenylenebis(dimethylsilanol) could be prepared by Sveda's[40] procedure, the compound was more conveniently prepared in higher yields by the following method:

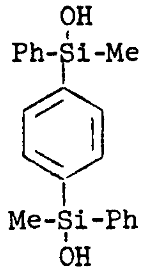


In the procedure, the arylene bromide and alkoxysilane were added concomitantly to previously activated magnesium, and the intermediate Grignard reagent was not isolated.

m-Phenylenebis(dimethylsilanol) was similarly prepared except that chlorodimethylethoxysilane was used in place of diethoxydimethylsilane in the condensation with m-dibromobenzene. Condensation of the Grignard reagent with dichlorodimethylsilane and the subsequent hydrolysis of m-phenylenebis(chlorodimethylsilane) gave lower conversions.

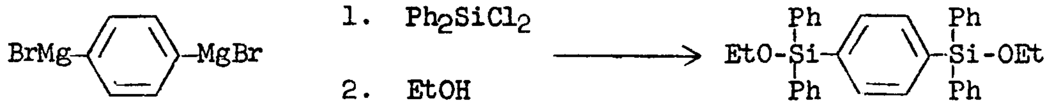
Similar *in situ* condensations of Grignard reagents were used for the preparation of p-phenylenebis(ethoxymethylphenylsilane) and m-phenylenebis(chloromethylphenylsilane), which were hydrolyzed to the corresponding silanols. p-Phenylenebis(chloromethylphenylsilane) could not be prepared by Popeleva's procedure.[44] Both hydrolyses gave mixtures of stereoisomers from which high- and low-melting compounds could be isolated. No assignment of structure for these compounds was possible from their infrared or n.m.r. spectra, which were very similar. Correct analytical data for elemental content were obtained both on isomeric mixtures and purified compounds. Possible isomeric structures for p-phenylenebis(methylphenylsilanol) can be represented as follows:





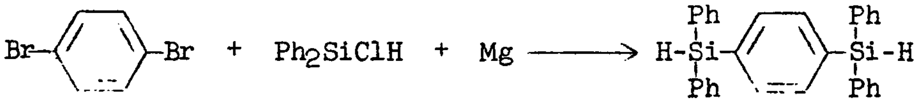
The preparation of p-phenylenebis(diphenylsilanol) offered more difficulty. The compound could not be prepared via the direct hydrolysis of the condensation product of p-dilithiobenzene and dichlorodiphenylsilane by the method described in the literature.[4] A very low yield (less than 1 per cent) of the compound was obtained by the direct hydrolysis of the condensation product of the Grignard reagent of p-dibromobenzene and dichlorodiphenylsilane.

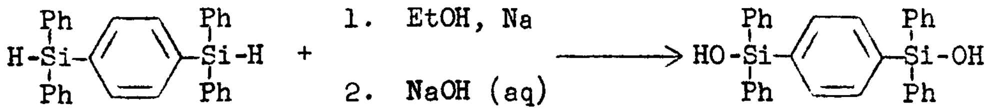
An intermediate compound, p-phenylenebis(diphenylethoxysilane), was obtained by the method described by Noltes,[45] but the yield was only 7 per cent. The low yield of the pure product can be accounted for, at least in part, by the difficulties encountered in its purification.



This intermediate, however, could be hydrolyzed to p-phenylenebis(diphenylsilanol), m.p. 224 - 6°, in an 86 per cent yield.

A similarly low yield was obtained in the in situ procedure when magnesium was treated with chlorodiphenylethoxysilane and p-dibromobenzene in tetrahydrofuran. The only really satisfactory route to p-phenylenebis(diphenylsilanol) was Beck's procedure in which p-dibromobenzene and chlorodiphenylsilane in tetrahydrofuran were added concomitantly to previously activated magnesium to produce p-phenylenebis(diphenylsilane).[46] The purified p-phenylenebisdiphenylsilane was converted to the ethoxy derivative and subsequently hydrolyzed to the diol.

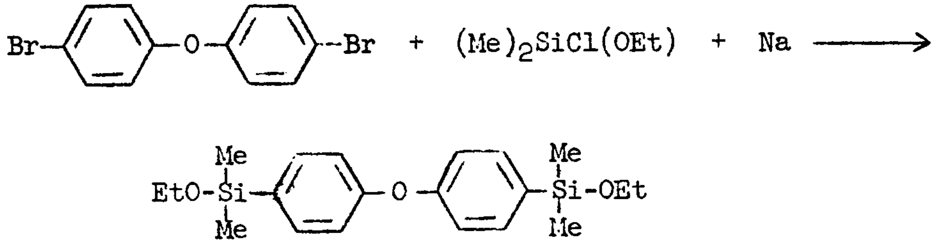


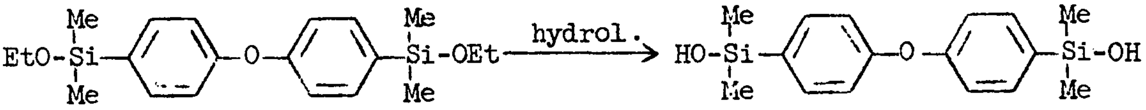


In different preparations, *p*-phenylenebis(diphenylsilanol) melted at 224 - 226° or at 216 - 217°. Both forms retained the same melting point after repeated recrystallization and both gave correct analyses for elemental content.

m-Phenylenebis(diphenylsilanol) was satisfactorily obtained by the same procedure as the *para* derivative, but the intermediate *m*-phenylenebis(diphenylsilane) could not be isolated because of its failure to crystallize and lack of sufficient heat stability for distillation.

No difficulty was encountered, however, when bis(*p*-bromophenyl) ether was condensed with chlorodimethylethoxysilane or chloroethoxymethylphenylsilane in the presence of sodium to obtain the intermediate ethoxy derivative in a manner described for related compounds in the literature.[47] The ethoxy compounds were subsequently hydrolyzed to the corresponding silanols.





Last traces of recrystallization solvents could be removed from the diol only when it was heated in a vacuum oven for a long period of time; consequently, good analyses for elements were not readily obtained from seemingly pure samples.

The α,ω-dichlorosiloxane intermediates required for the cyclosiloxazane monomers were prepared by an equilibration procedure in which dichlorodimethylsilane and diethoxydimethylsilane were heated in the presence of ferric chloride.

$$Me_2SiCl_2 + Me_2Si(OEt)_2 \xrightarrow{FeCl_3}$$

$$ClSiMe_2OSiMe_2Cl + Cl(SiMe_2O)_2SiMe_2Cl + Cl(SiMe_2O)_3SiMe_2Cl + EtCl$$

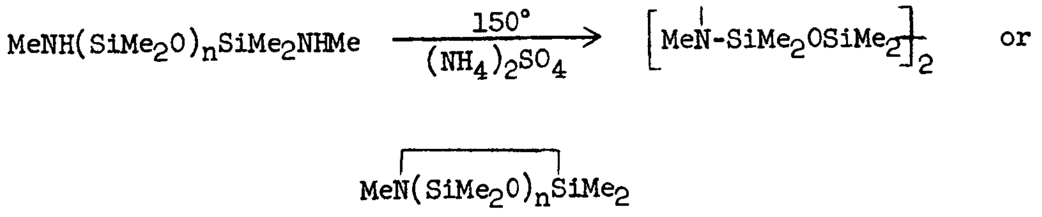
In earlier work in this laboratory, mixtures of α,ω-diaminosiloxanes and cyclosiloxazanes were obtained when methylamine was added to the α,ω-dichlorosiloxanes at 5°.[48] These results seemed in conflict with published reports that the only products of the reactions were the α,ω-diaminosiloxanes.[49] The α,ω-diaminosiloxanes could be cyclized to cyclosiloxazanes in moderate yields with heat in the presence of ammonium sulfate.

In the current work, chlorosiloxanes were added to methylamine at -10° to -20°, and the α,ω-dichlorosiloxanes were obtained in good yields with no trace of the cyclosiloxazane.

$$Cl(SiMe_2O)_nSiMe_2Cl + MeNH_2 \xrightarrow{-10^\circ \text{ to } -20^\circ} MeNH(SiMe_2O)_nSiMe_2NHMe$$

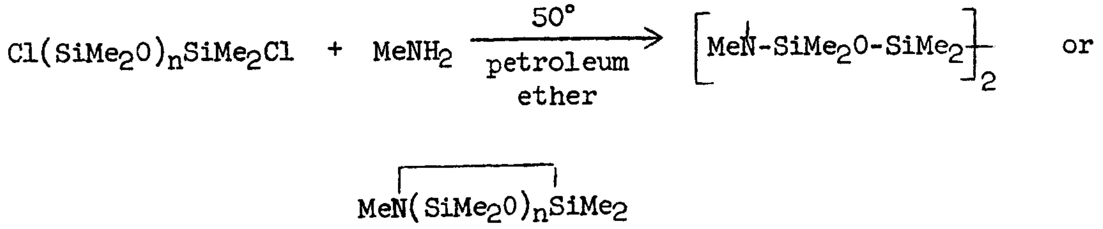
$$n = 1, 2, 3$$

Although the diaminosiloxanes could be converted to the cyclosiloxazane in the usual way, the yield did not exceed 35 per cent making the over-all conversion less than 28 per cent. But when the solution of the chlorosiloxane was heated



$$MeNH(SiMe_2O)_nSiMe_2NHMe \xrightarrow[(NH_4)_2SO_4]{150^\circ} [MeN\text{-}SiMe_2OSiMe_2]_2 \text{ or } MeN(SiMe_2O)_nSiMe_2$$

to 50° and maintained at that temperature during the methylamine addition, good yields of the cyclosiloxazanes were obtained directly, and only small quantities of the diaminosiloxanes could be isolated. A summary of these



$$Cl(SiMe_2O)_nSiMe_2Cl + MeNH_2 \xrightarrow[\text{petroleum ether}]{50^\circ} [MeN\text{-}SiMe_2O\text{-}SiMe_2]_2 \text{ or } MeN(SiMe_2O)_nSiMe_2$$

reactions is shown in Table VI. The unusual temperature effect in these reactions was verified in several repetitions of the procedure.

TABLE VI

AMINOLYSIS PRODUCTS OF α,ω-DICHLOROSILOXANES

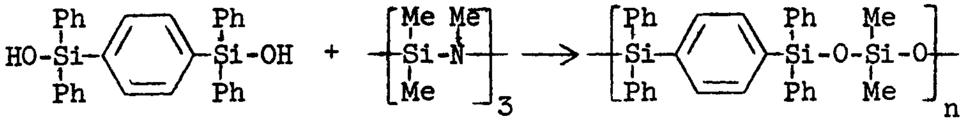
	Reaction Temperature			
	-30° Product Distribution (% yields)		+50° Product Distribution (% yields)	
α,ω-Dichlorosiloxane	Linear	Cyclic	Linear	Cyclic
1,3-Dichlorotetramethyldisiloxane	82	0	8	62
1,5-Dichlorohexamethyltrisiloxane	86	0	0	66
1,7-Dichlorooctamethyltetrasiloxane	76	0	0	61

B. Polymerization Reactions

Initially, the condensations of p-phenylenebis(dimethylsilanol) and p-phenylenebis(diphenylsilanol) were screened in a series of experiments in which the evolution of amine was monitored as a measure of the rate of the reaction when the reactants were heated 24 hr. in a toluene solution. 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 inherent 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 an inherent viscosity of 0.86 in toluene.



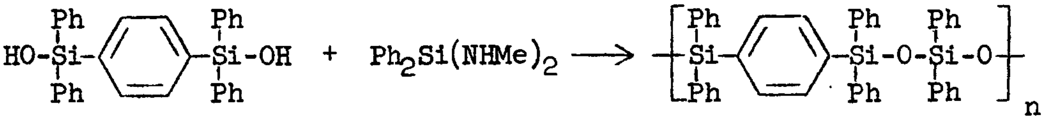
The infrared spectrum of the polymer, which is reported in Fig. 44, suggested that residual silanol, silazane, or silylamine groups were present. However, the results of the analyses for elements in this polymer agreed with the calculated values.

The procedural decomposition temperature (weight loss equals or exceeds 5 per cent per hour) of the polymer on thermogravimetric analysis (Fig. 46) was 515°. The temperature at which decomposition occurred seemed 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 - 250°; however, differential thermal analysis of the polymer (Fig. 47) did not reveal any major phase changes up to 500°.

When a sample of this polymer was heated at 300° for 1 hr., the inherent viscosity increased to 1.25, 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 inherent viscosity was about 0.36 and the infrared spectrum of this polymer, which is reported in Fig. 45, did not show residual silanol or silylamine.



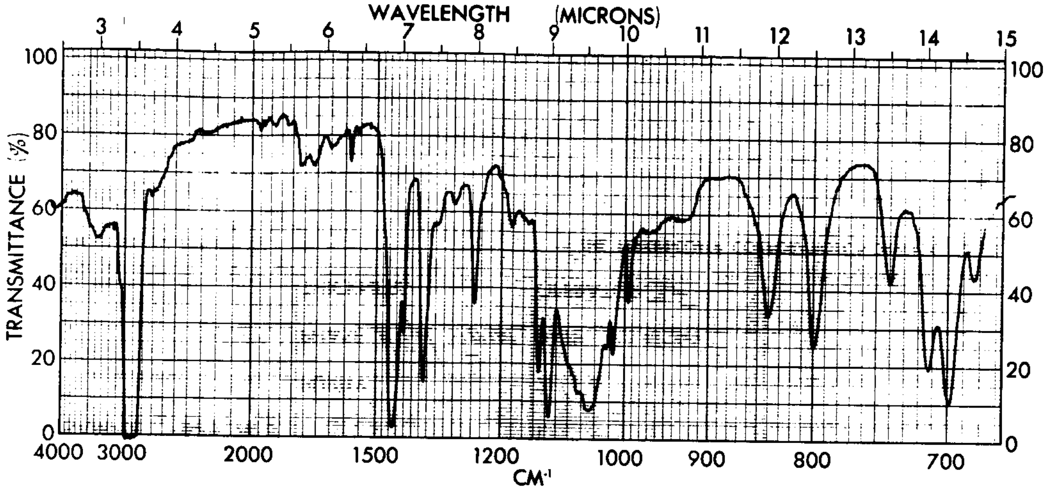


Fig. 44 - Infrared Spectrum of the Polymer From Nonamethylcyclotrisilazane and p-Phenylenebis(diphenylsilanol) (Nujol)

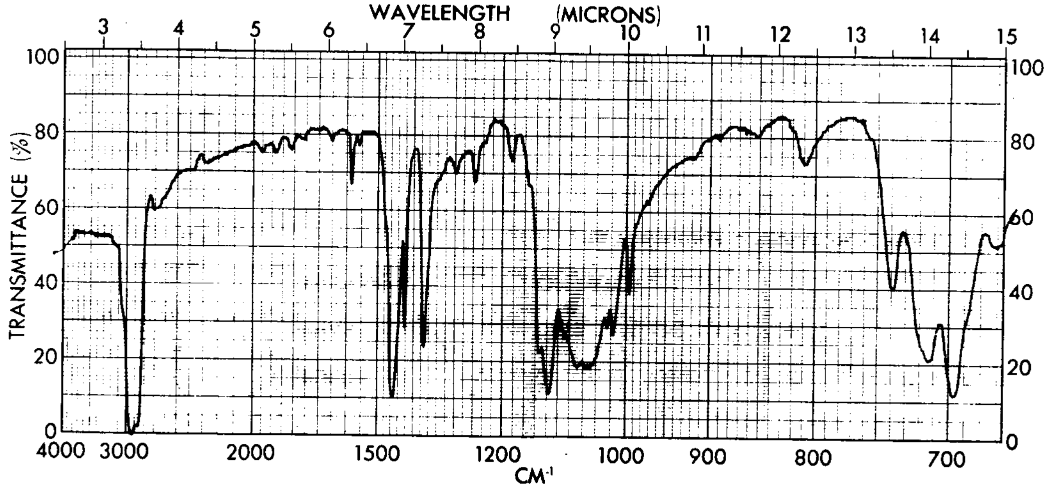


Fig. 45 - Infrared Spectrum of the polymer From Bis(methylamino)diphenylsilane and p-Phenylenebis(diphenylsilanol) (Nujol)

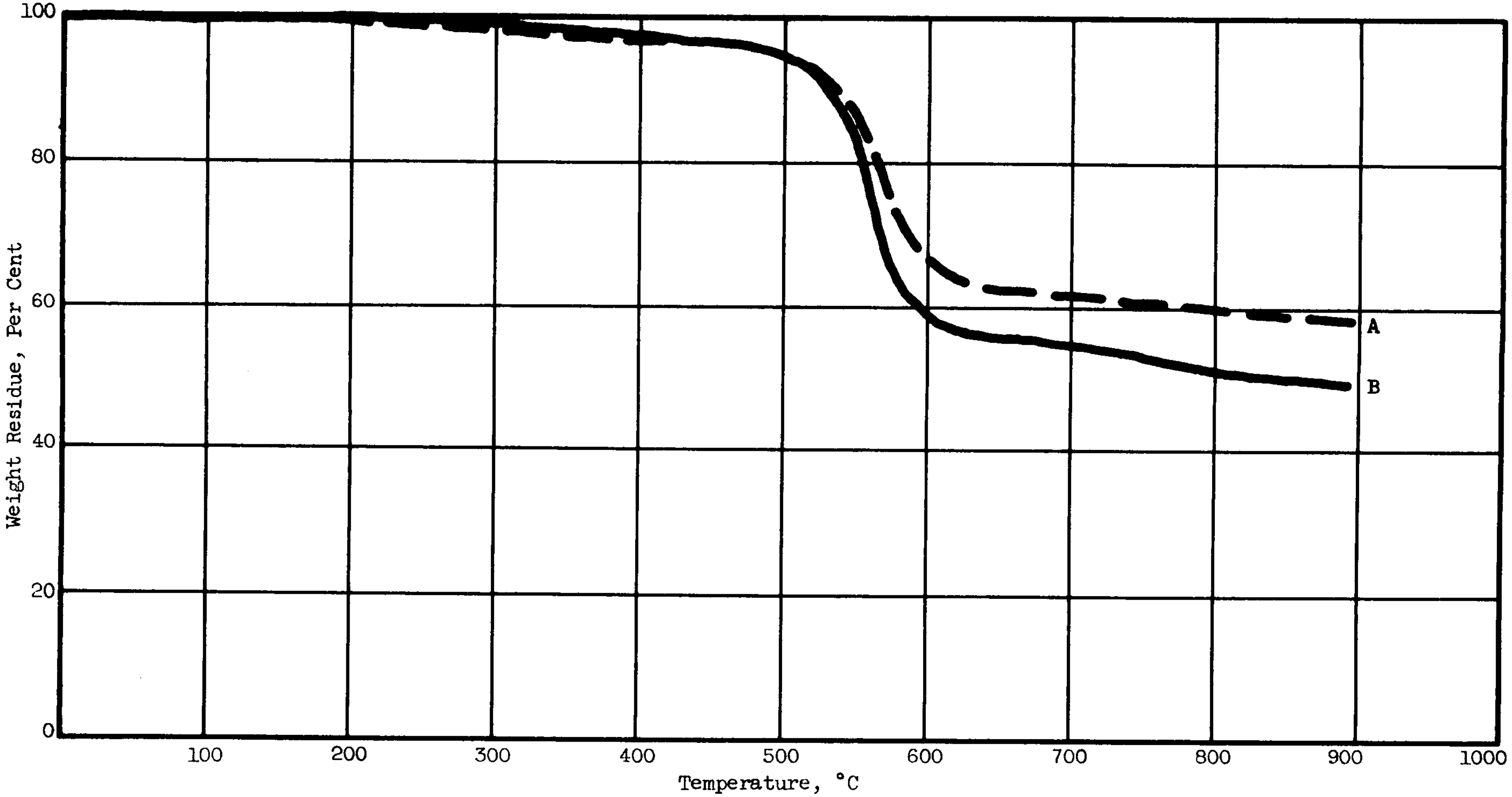


Fig. 46 - Thermogravimetric Analyses of Poly(p-phenylenesiloxanes) - Heating Rate = 3°/Min; N_2 Atmosphere

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

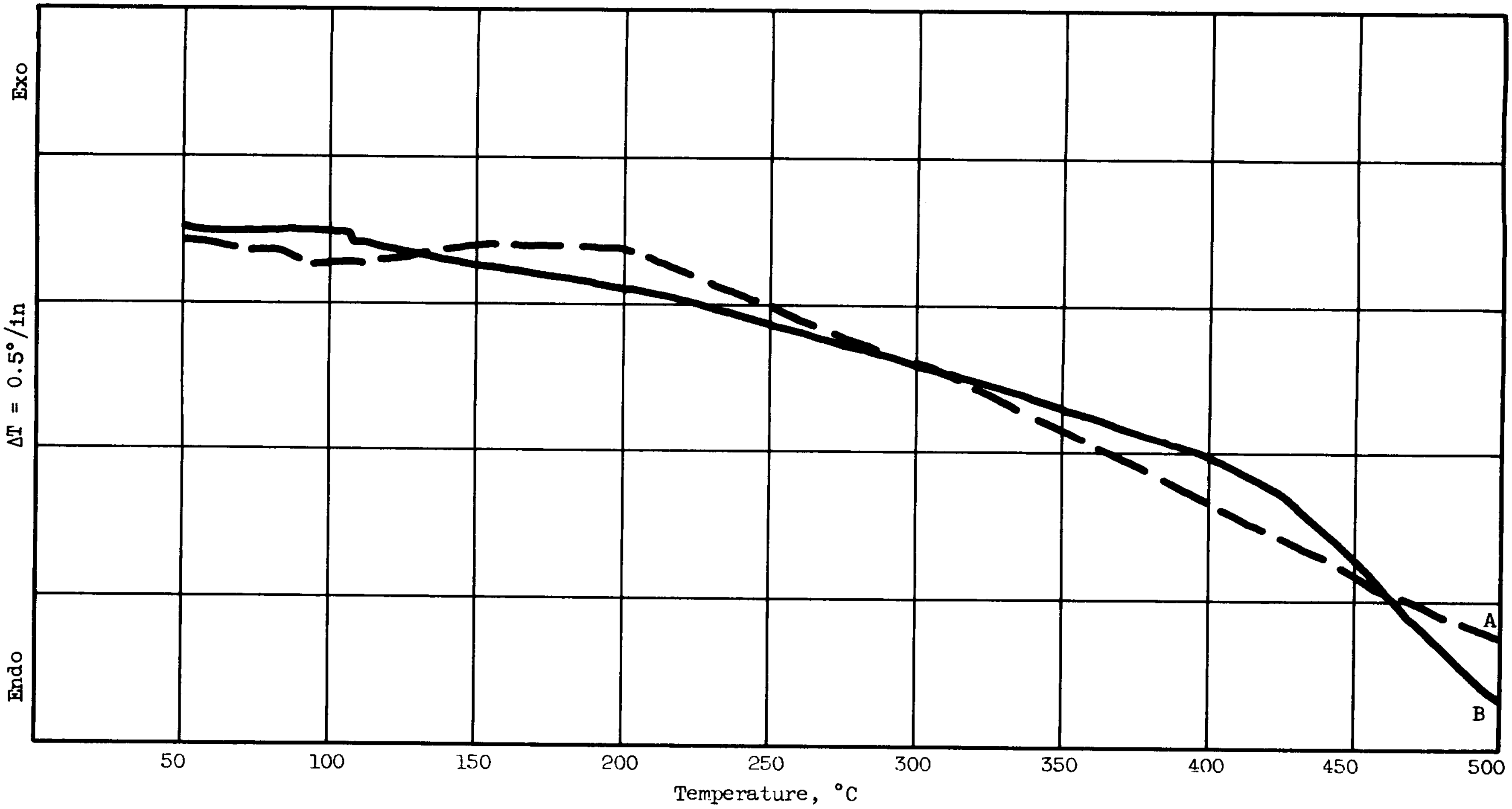
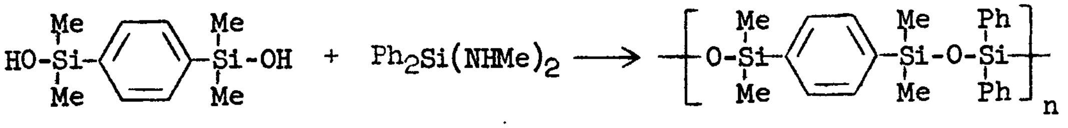


Fig. 47 - Differential Thermal Analyses of Poly(p-phenylenesiloxane) - Heating Rate = 15°/Min

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

The TGA trace of this polymer is reported in Fig. 46 and the DTA trace in Fig. 47. Both suggest good heat stability. However, the polymer was brittle and not suitable for coating applications.

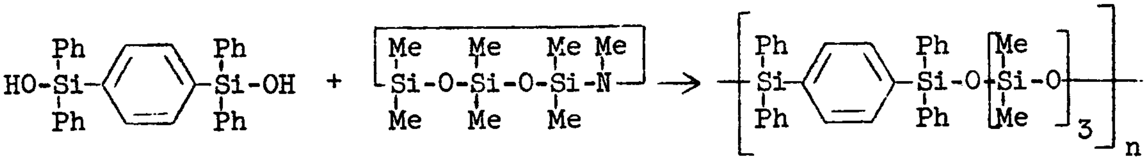
In additional experiments in which arylenedisilanols were heated with silazanes or silylamines, the polymers either were low molecular weight, tacky oils or became insoluble during the polymerizations. Even when higher molecular weights were obtained, the polymers tended to be brittle. Only one system appeared to offer any promise, the condensation product of p-phenylenebis(dimethylsilanol) and bis(methylamino)diphenylsilane.



The polymer had an inherent viscosity of 0.98, and formed a soft, elastic film.

In a series of preliminary experiments, p-phenylenebis(diphenylsilanol) was treated with various cyclosiloxazanes and diaminosiloxanes. The condensation products were either insoluble or had relatively low molecular weights; however, several of the polymers were examined in detail.

A white elastic insoluble solid was obtained from heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane and p-phenylenebis(diphenylsilanol), when the reactants were heated in xylene at 112 - 115° for 24 hr., then devolatilized at 150° under reduced pressure.



The infrared spectrum of the polymer (Fig. 48) 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. 49) and the procedure decomposition temperature on the thermogravimetric analysis was 450° (Fig. 50).

Since the polymer became insoluble only after the solvent had been removed from the polymerization mixture, a soluble polymer, prepared by heating the reactants in solvent for 5 hr., was sprayed on a metal panel and was cured at 145° to form a strong elastic film. This coated panel was used in an ultraviolet irradiation experiment described elsewhere in this report.

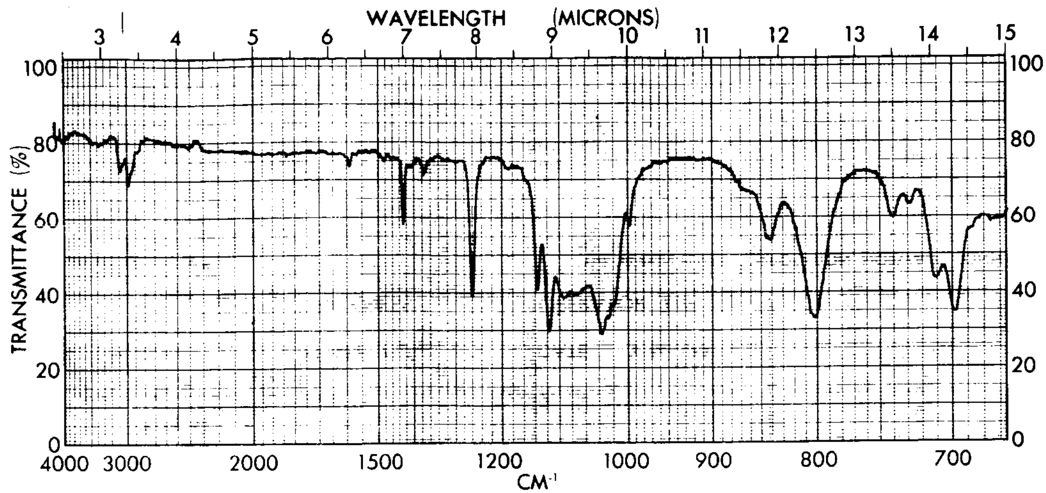


Fig. 48 - Infrared Spectrum of the Polymer From Heptamethyl-1 aza-3,5-dioxa-2,4,6-trisilacyclohexane and p-Phenylenebis(diphenylsilanol), η_{inh} 0.07 (Film)

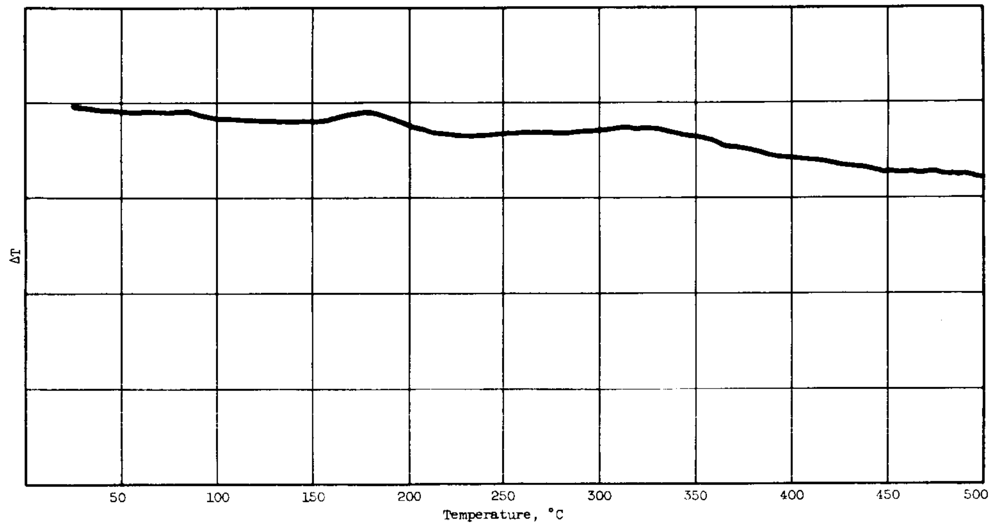


Fig. 49 - Differential Thermal Analysis of a Polymer From p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane - Heating Rate = 15°/Min

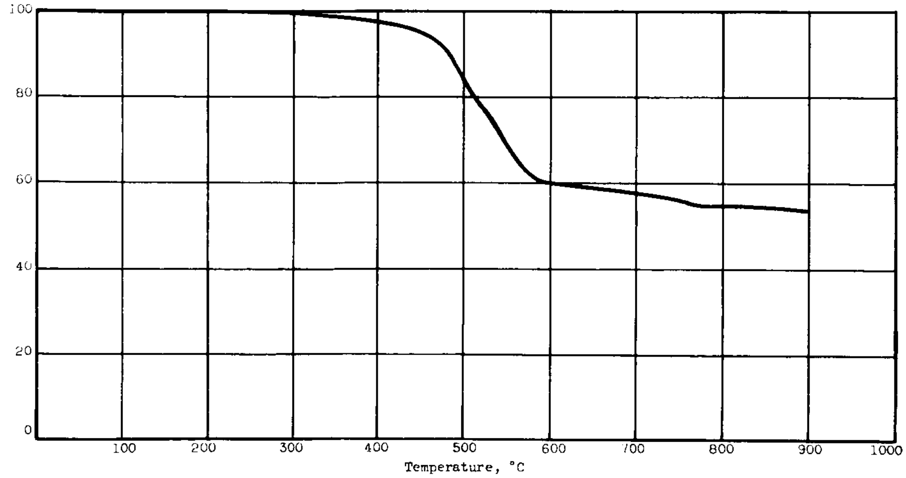
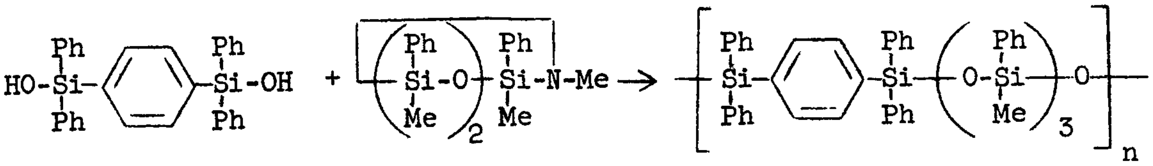


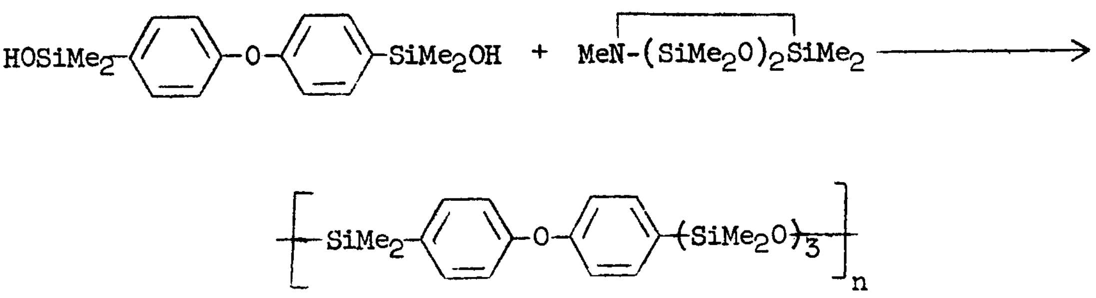
Fig. 50 - Thermogravimetric Analysis of a Polymer From p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane - Heating Rate = 3°/Min; N_2 Atmosphere

Two additional polymers were prepared for the ultraviolet stability test from p-phenylenebis(diphenylsilanol) and tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.



The inherent viscosities of these polymers were relatively low, 0.06 and 0.17, but correct analyses for elemental content were obtained. A thermogravimetric analysis showed a procedural decomposition temperature of 525° and a second knee at 775°. Solutions of the polymers could be cast on metal panels to produce somewhat brittle films. Reflectance data for these films were obtained before and after irradiation under vacuum.

Subsequently, the reactions of a variety of arylenedisilanols with heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane were screened. The highest inherent viscosities (up to 1.74) were found in the polymers prepared from bis(p-dimethylhydroxysilylphenyl) ether.



The polymer had good heat stability, showing a pdt of 495° by TGA and no phase transitions below 500° by DTA. Several other diols gave polymers with higher solution viscosities.

When polymerization parameters were investigated in a series of reactions between bis(p-dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, the most important variable appeared to be monomer purity, particularly the purity of the cyclosiloxazane. For example, in a series of 13 experiments in which 96 per cent purity (by g.l.c.) heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane was used, the highest specific viscosity obtained was 0.60. A second series of 10 experiments in which a different batch of cyclosiloxazane monomer with a purity of 99 per cent was used gave polymers with specific viscosities of 1.11 to 4.99, provided at least a slight excess of the siloxazane was present.

The small excess of siloxazane in the polymerizations appeared to be necessary because of the volatility of the cyclic compound at the polymerization temperatures. Methylamine, which was formed in the polymerization and was volatilized from the mixture carried some of the monomer with it even when appropriate condensers were used. A 5 per cent excess seemed adequate.

The most satisfactory polymerization temperature appeared to be 160°. At that temperature the polymerization could be easily controlled, and high molecular weight materials obtained within a reasonable time.

An attempt was made to follow the kinetics of the polymerizations in terms of the viscosity of samples taken at intermediate times during the polymerizations, but sampling errors proved too large to allow any meaningful results. Because of the high viscosity of the polymerization mixtures at 160°, poor mixing caused considerable differences in samples taken from different locations in the polymerization vessel.

C. Polymer Properties

Several series of polymers were prepared in order to correlate polymer properties with structures and to provide adequate characterization of the materials. Some were prepared specifically for ultraviolet-vacuum screening tests; others were prepared as larger samples for evaluation in other laboratories. Samples representing the various structures were selected for characterization.

1. Solubility

Except for several polymers that contained pendant phenyl substitution, the polymers were soluble in all proportions in toluene. The polymer prepared from bis(p-dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, was completely soluble at the 0.5 per cent concentration level in benzene, tetrahydrofuran, perchloroethylene, chloroform, acetone, carbon tetrachloride, and toluene. In some of the polymerization reactions, toluene-insoluble fractions were obtained. These materials, which could be removed by filtration of toluene solutions of the polymer, apparently formed as the result of phosphate impurities in the arylenedisilanol monomers. It is probable that some of the insolubilities observed in the preliminary polymerization reactions can be attributed also to the presence of this impurity.

2. Elemental Analyses

The excellent agreement between the calculated results of the analyses and the experimental values reported in Table VII for elemental content confirms that polymerizations proceed in the proposed manner without randomization of groups along the chain.

3. Viscosities and Molecular Weight

The inherent viscosities reported in Table VII are mean values taken from a series of random samplings from the polymers. The scatter observed in some of the samplings showed that the samples were not necessarily homogeneous with respect to molecular weight. Homogeneous samples were obtained when the polymers were dissolved in toluene and the solvent subsequently evaporated.

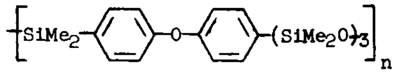
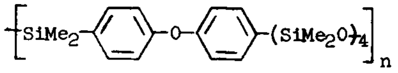
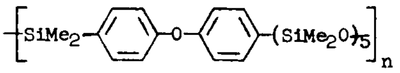
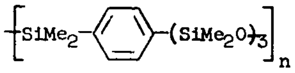
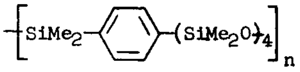
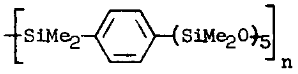
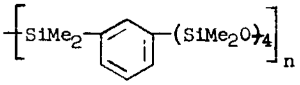
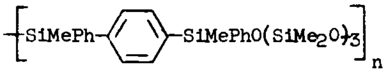
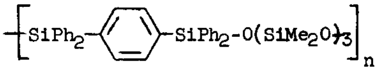
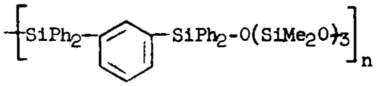
Light scattering data for polymers 2 and 5, Table VII gave weight average molecular weights of 905,000 and 820,000, respectively. Reduced viscosity-concentration curves for these two polymers are shown in Fig. 51. Intrinsic viscosities from these plots, 3.52 and 3.60 fit the molecular weight-intrinsic viscosity relationship established by Merker[41] for poly(p-phenylenetetramethyldisiloxane), $[\eta] = 1.12 \times 10^{-4} M_w^{0.75}$, reasonably well. Gel permeation chromatographic data obtained in polymer 2, Table VII, showed a number average molecular size of 4,385 angstroms and a weight molecular size of 15,967 angstroms, the distribution ratio, $\overline{A}_w/\overline{A}_n$, being 3.66 (Fig. 52).

4. Glass Transition Temperature

The polymers were rubbery gums at room temperature. Glass transition temperatures determined by differential thermal analyses (Table VII) can be directly correlated with changes in polymer structure. In the two series of polymers, one derived from p-phenylenebis(dimethylsilanol) and the other from bis(p-dimethylhydroxysilylphenyl) ether, there is a regular decrease in glass transition temperature with increase in the length of the polydimethylsiloxane chain segment. Such a correlation concurs with predictions that might be made on the basis of polymer structure. Glass transitions were the only thermal changes that were observed on differential thermal analyses between -110° and 500°C.

TABLE VII

POLYMER PROPERTIES

					Analyses Calcd/Found		
Polymer No.	Polymer Structure	η_{inh} 0.5% Solution in Toluene at 30°	T_g (°C)	Empirical Formula	C	H	Si
1		2.48	-37°	$C_{20}H_{32}O_4Si_4$	53.52 53.74	7.19 7.27	25.03 25.08
2		2.72	-52°	$C_{22}H_{38}O_5Si_5$	50.52 50.62	7.32 7.35	26.86 26.70
3		3.83	-65°	$C_{24}H_{44}O_6Si_6$	48.27 48.02	7.43 7.34	28.23 28.11
4		0.73	-62°	$C_{14}H_{28}O_3Si_4$	47.14	7.91	31.49
5		2.77	-72°	$C_{16}H_{34}O_4Si_5$	44.60 44.40	7.95 7.93	32.60 30.20
6		2.48	-80°	$C_{18}H_{40}O_5Si_6$	42.80 42.76	7.98 7.99	33.37 33.19
7		1.60	-75°	$C_{16}H_{34}O_4Si_5$	44.60 44.49	7.95 7.90	32.60 32.51
8		0.15	-	$C_{26}H_{38}O_4Si_5$	56.26 56.00	6.90 6.97	25.31 25.02
9		1.62	-42°	$C_{26}H_{38}O_4Si_5$	56.26 56.23	6.90 6.83	25.31 25.08
10		0.21	-	$C_{36}H_{42}O_4Si_5$	63.66 63.75	6.24 6.25	20.68 20.29
11		0.66	-	$C_{36}H_{42}O_4Si_5$	63.66 64.08	6.24 6.07	20.68 20.45

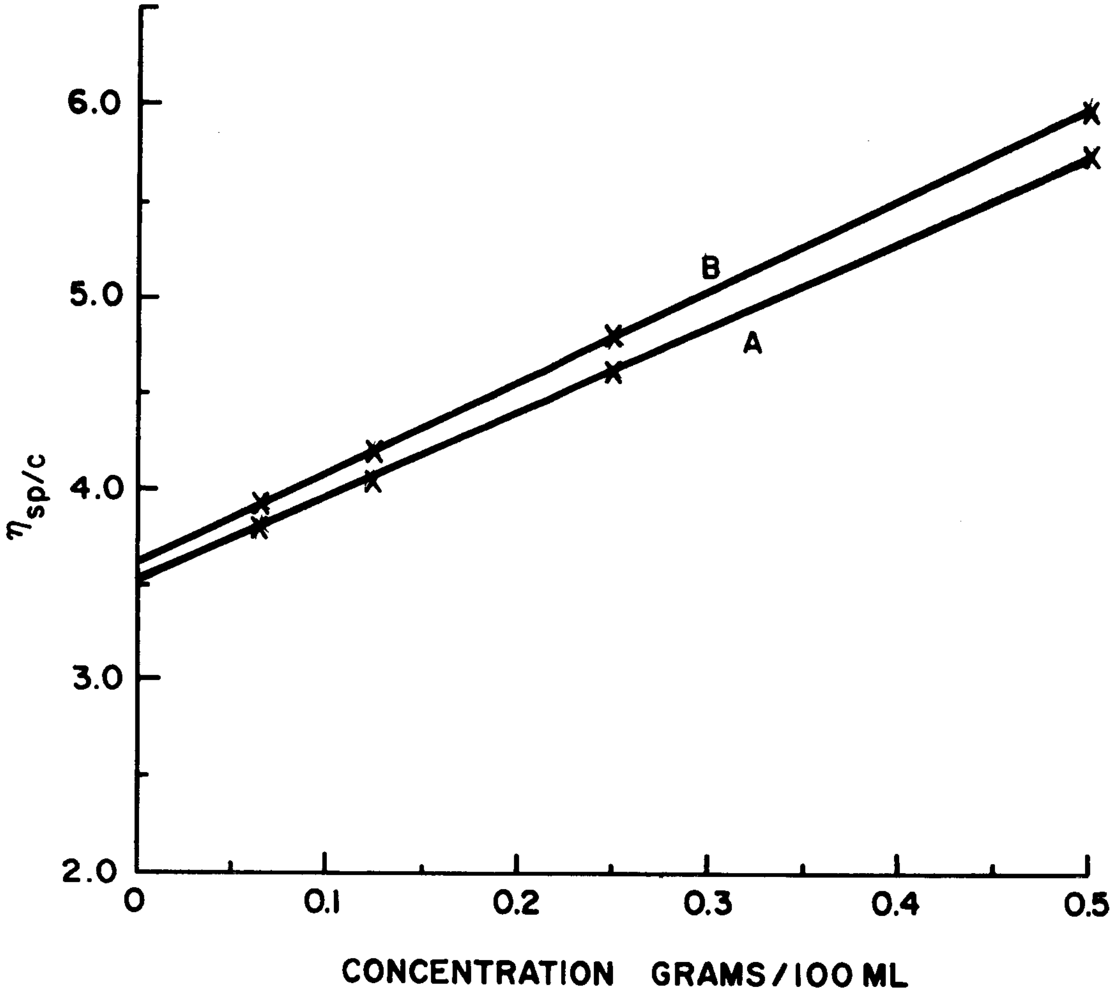


Fig. 51 - Reduced Viscosity-Concentration Curves for Polymer 2 (A) and 5 (B) Table VII

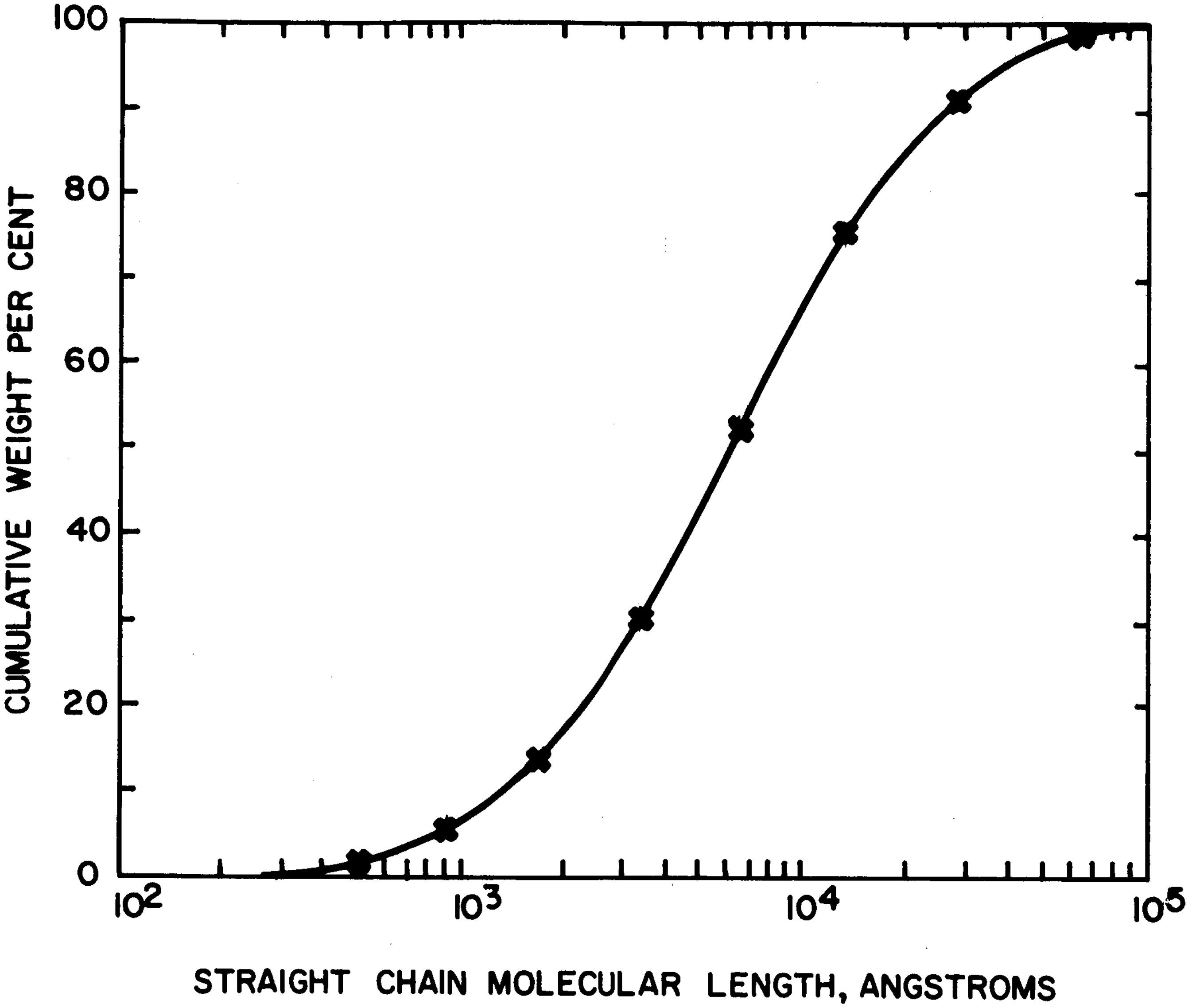


Fig. 52 - Gel Permeation Chromatography of Polymer 2, Table VII

5. Thermal Stability

Thermal stability of the polymers was screened by thermogravimetric analyses under nitrogen at a heating rate of 15°/min. The results of analyses on two series of structures are shown in Figs. 53 and 54. It is readily apparent that both the identity of the arylene group present in the chain and the number of dimethylsiloxy groups in the chain segments affect the heat stability; however, the regular decrease in heat stability with increase in the number of siloxy groups illustrated in Fig. 53 is particularly noteworthy. A typical commercial polydimethylsiloxane gum undergoes catastrophic decomposition under these conditions at 300° or below. It is apparent that chain segments containing considerable numbers of dimethylsiloxy groups can be present before the decomposition mechanism effective in the polydimethylsiloxanes (randomization and volatilization of cyclics) limits the stability of the polymer.

The result of a differential analysis of one of the polymers between room temperature and 500° is reported in Fig. 55.

6. Ultraviolet Radiation-Vacuum Stability

A series of six coated test specimens was prepared and screened under high vacuum and intense ultraviolet irradiation. The following silanediols were represented in this series: Bis(p-dimethylhydroxysilylphenyl) ether, p-phenylenebis(methylphenylsilanol), m-phenylenebis(diphenylsilanol), p-phenylenebis(diphenylsilanol); and m-phenylenebis(dimethylsilanol). The differences in the changes in reflectance between samples during irradiation were not large, and the conclusion that changes in structure of the silanol in coating compositions do not significantly affect the ultraviolet stability seems justified. The data relative to the stability of the coatings are reported elsewhere in this report.

The changes in reflectance for these experimental samples compared favorably with reflectance changes reported earlier for commercial unfilled materials, and vitrually no weight loss was observed in any of the samples.

7. Infrared Spectra

The polymers were further characterized by their infrared spectra, which are reported in Figs. 56 to 66.

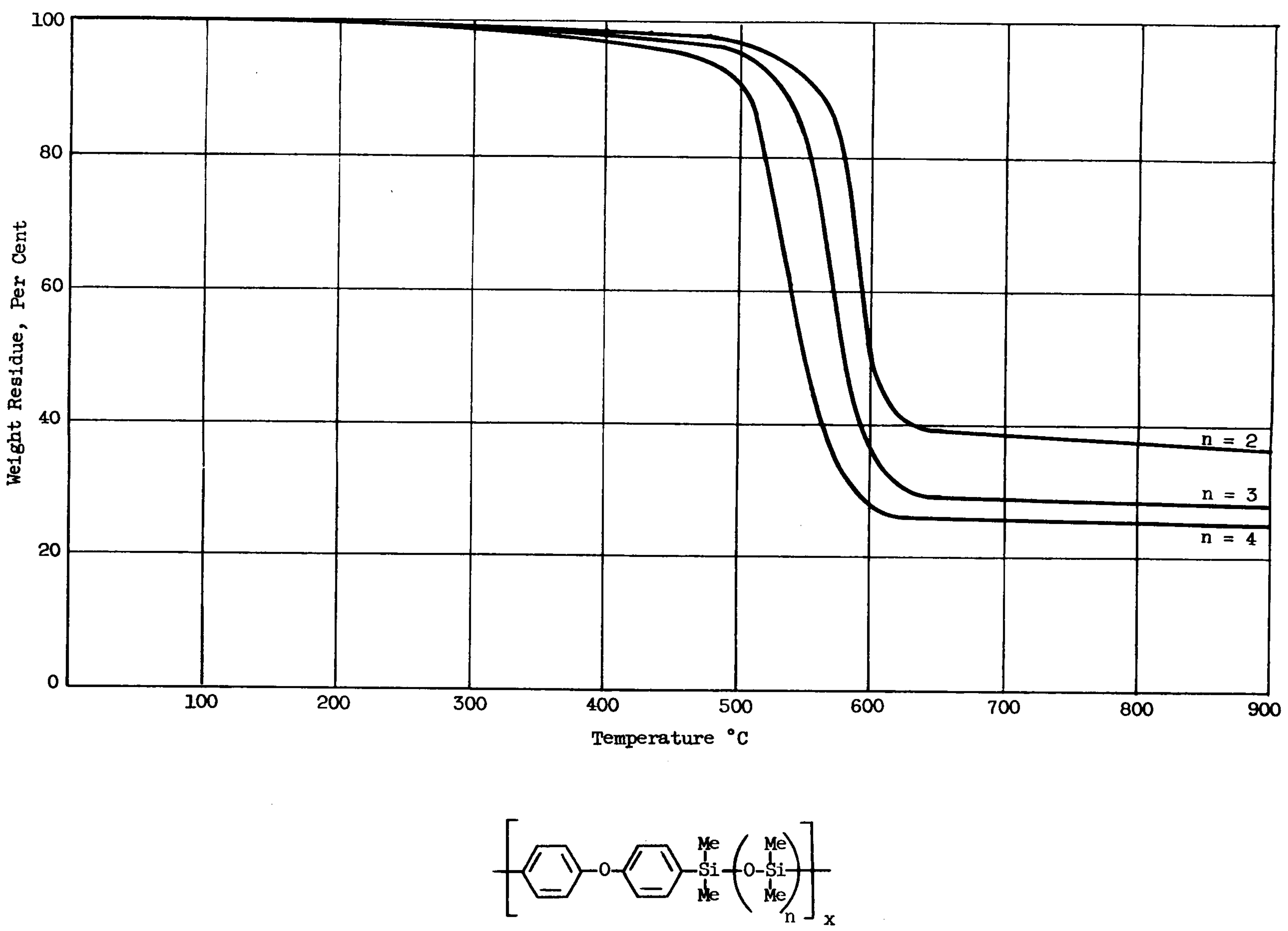
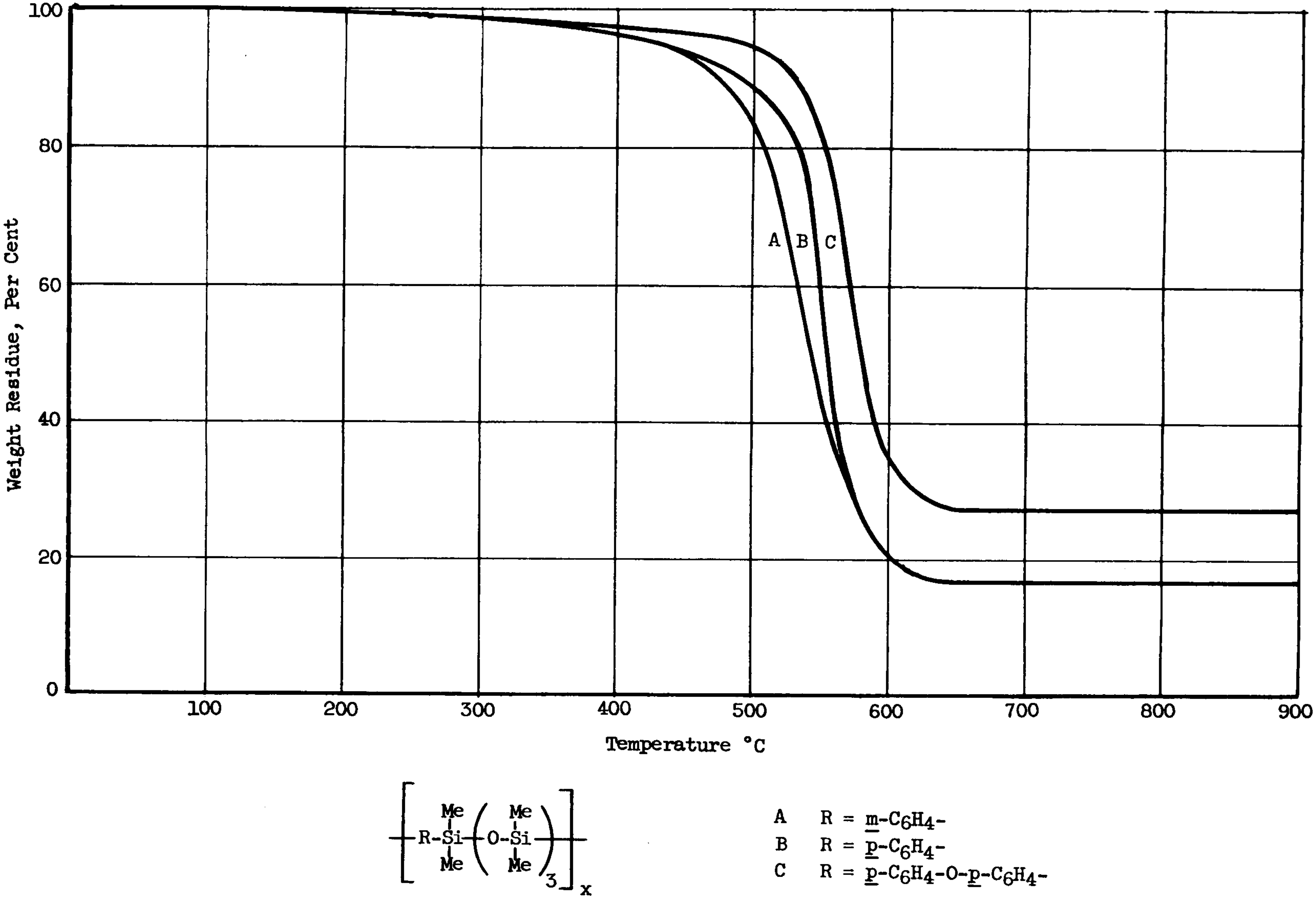


Fig. 53 - Thermogravimetric Analysis of Poly(arylenesiloxanes)
(Heating Rate = 3°/Min; N_2 Atm.)



A R = $\underline{m}$-C_6H_4-
B R = $\underline{p}$-C_6H_4-
C R = $\underline{p}$-C_6H_4-O-$\underline{p}$-C_6H_4-

Fig. 54 - Thermogravimetric Analysis of Poly(arylenesiloxanes)
(Heating Rate = 3°/Min; N_2 Atm.)

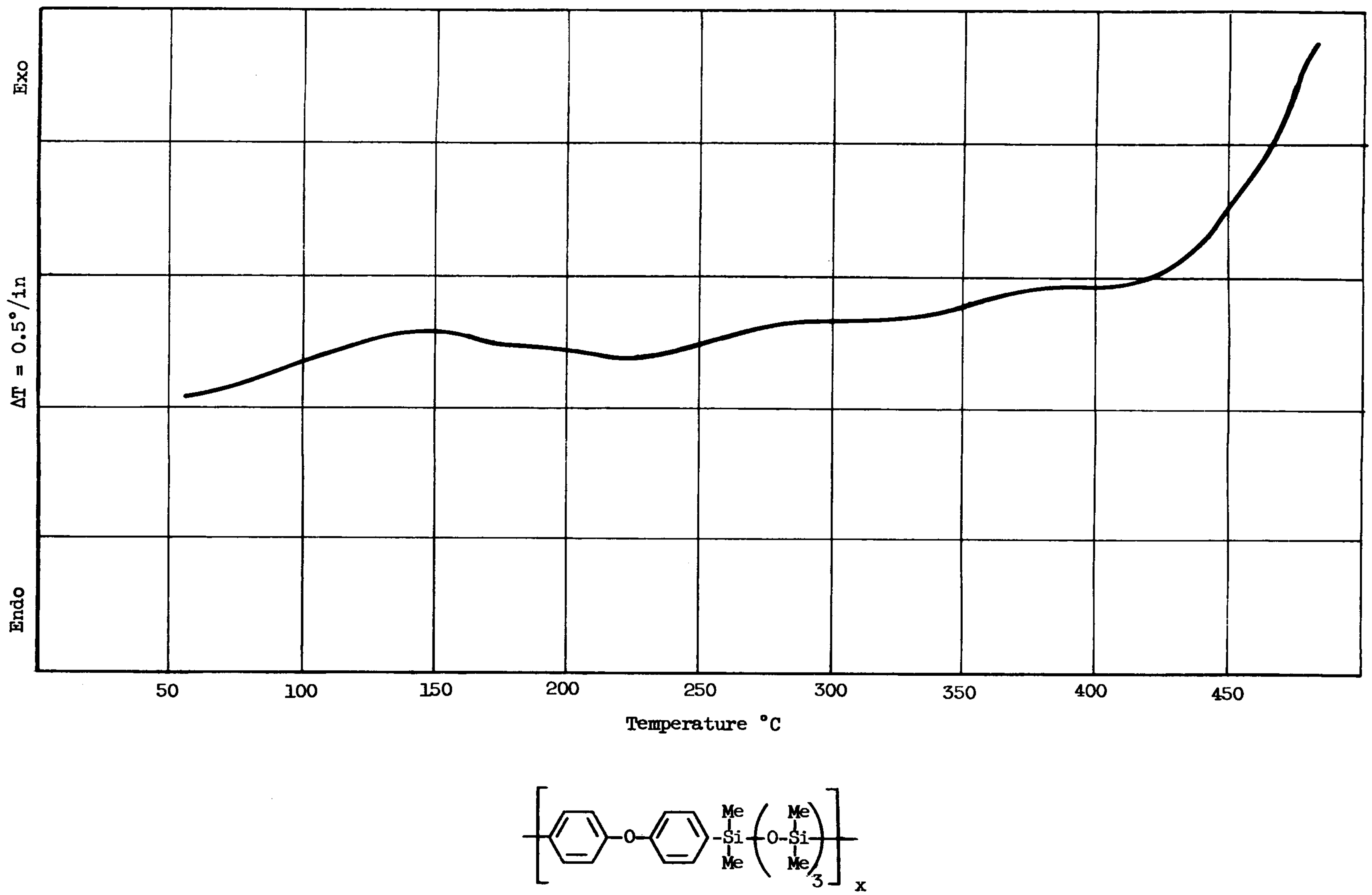


Fig. 55 - Differential Thermal Analysis of a Poly(arylenesiloxane)
(Heating Rate = 15°/Min; N_2 Atm.)

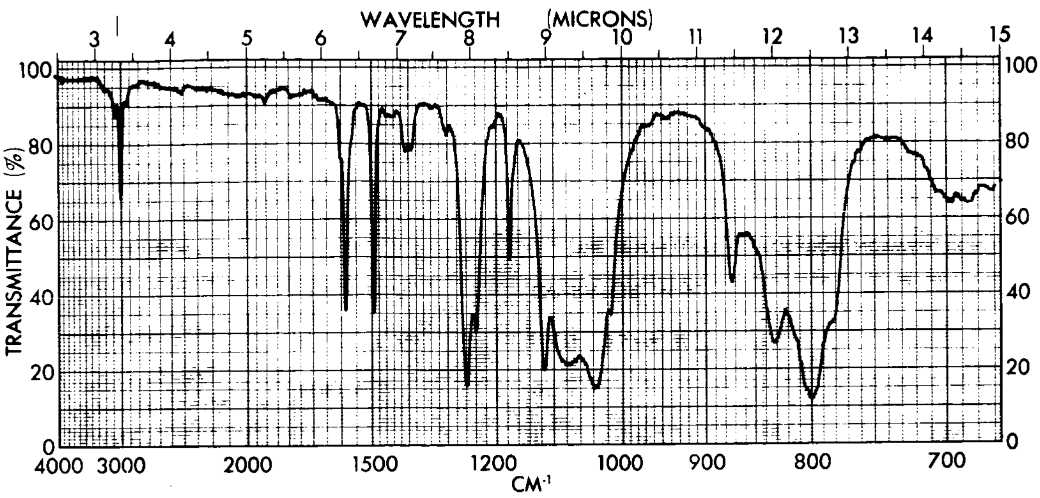


Fig. 56 - Infrared Spectrum of a Polymer From Bis(p-dimethylhydroxysilylphenyl) Ether and Decamethyl-1,5-diaza-3,7-dioxa-2,-4,6,8,-tetrasilacyclooctane (Film) - See Table VII, Polymer 1

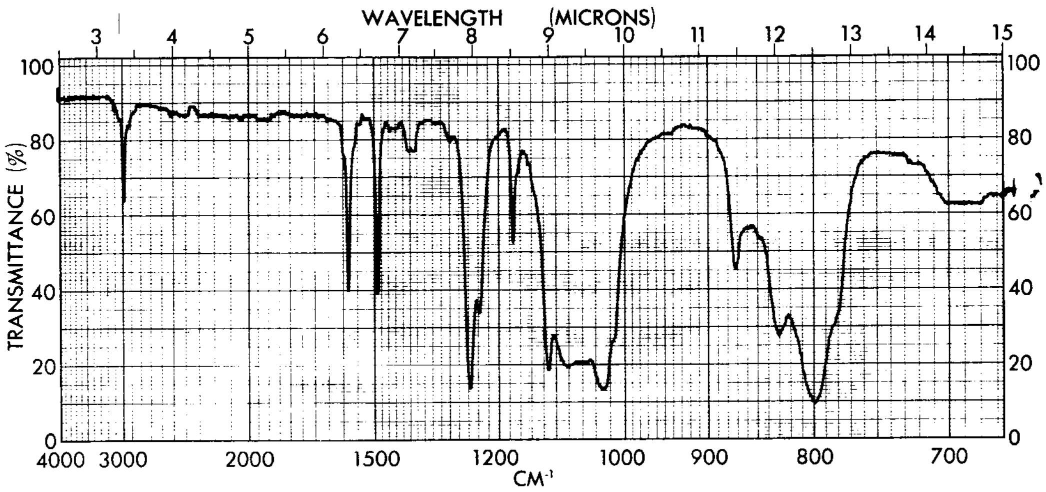


Fig. 57 - Infrared Spectrum of a Polymer From Bis(p-dimethylhydroxysilylphenyl) Ether and Heptamethyl-1-aza-3,5-dioxa-2,-4,6,-trisilacyclohexane (Film) - See Table VII, Polymer 2

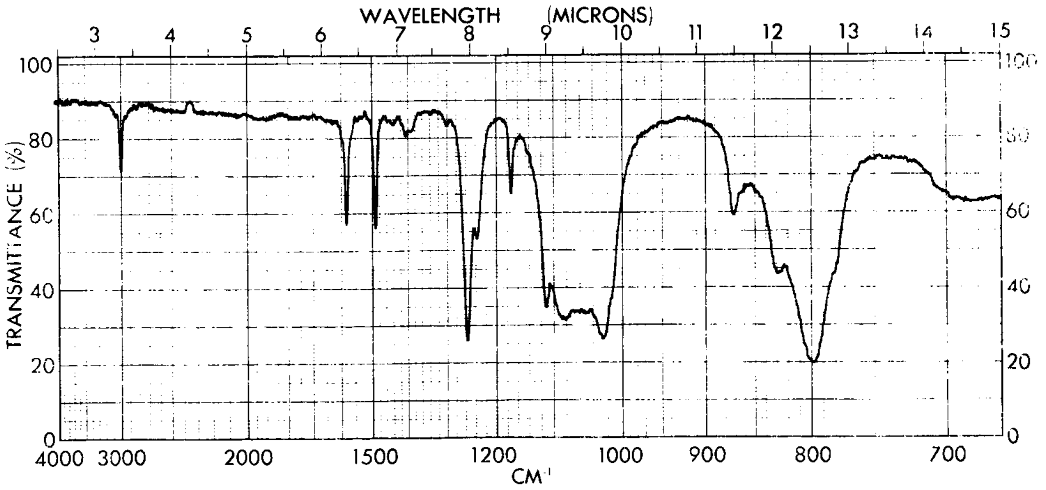


Fig. 58 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and Nonamethyl-1-aza-3,5,-7-trioxa-2,4,6,8-tetrasilacyclooctane (Film)
See Table VII, Polymer 3

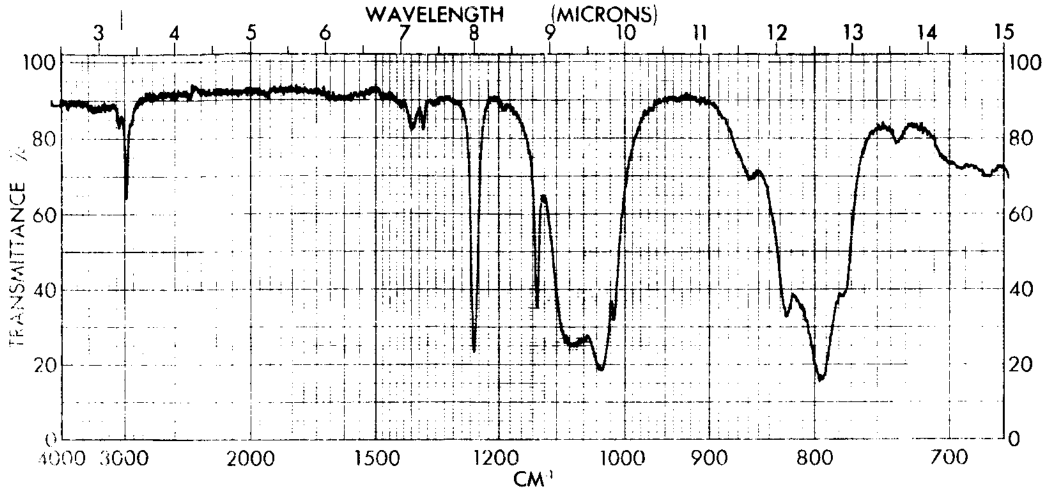


Fig. 59 - Infrared Spectrum of a Polymer From p-Phenylenebis-(dimethylsilanol) and Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (Film) - See Table VII, Polymer 4

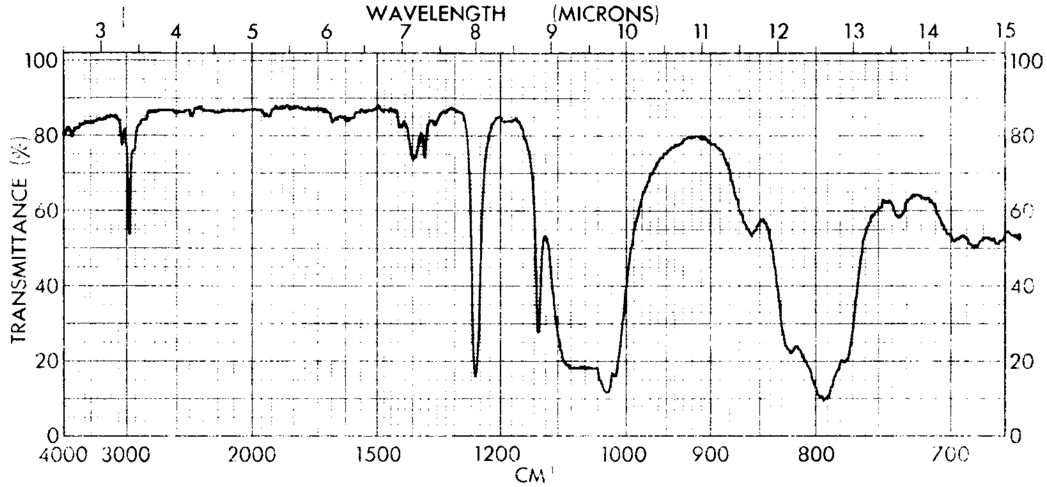


Fig. 60 - Infrared Spectrum of a Polymer From p-Phenylenebis-(dimethylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-tri-silacyclohexane (Film) - See Table VII, Polymer 5

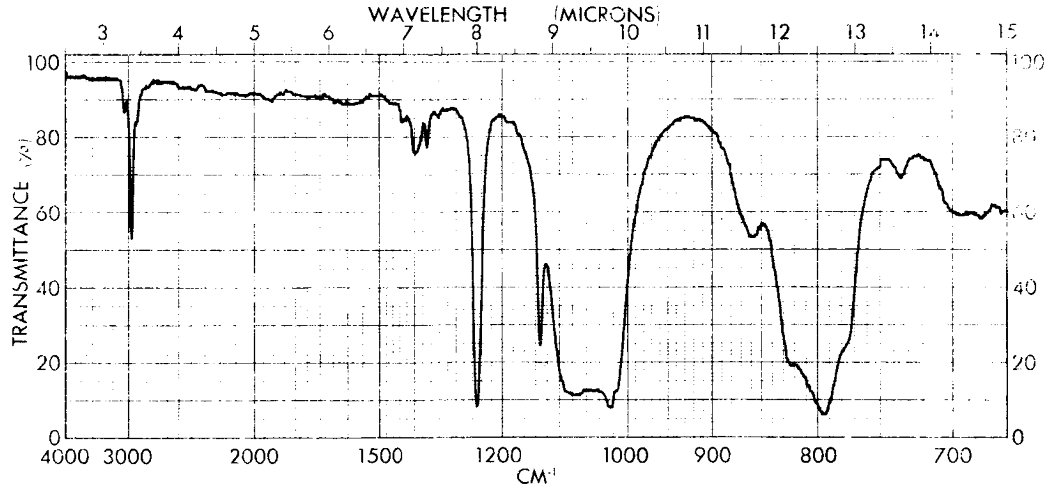


Fig. 61 - Infrared Spectrum of a Polymer From p-Phenylenebis-(dimethylsilanol) and Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane (Film) - See Table VII, Polymer 5

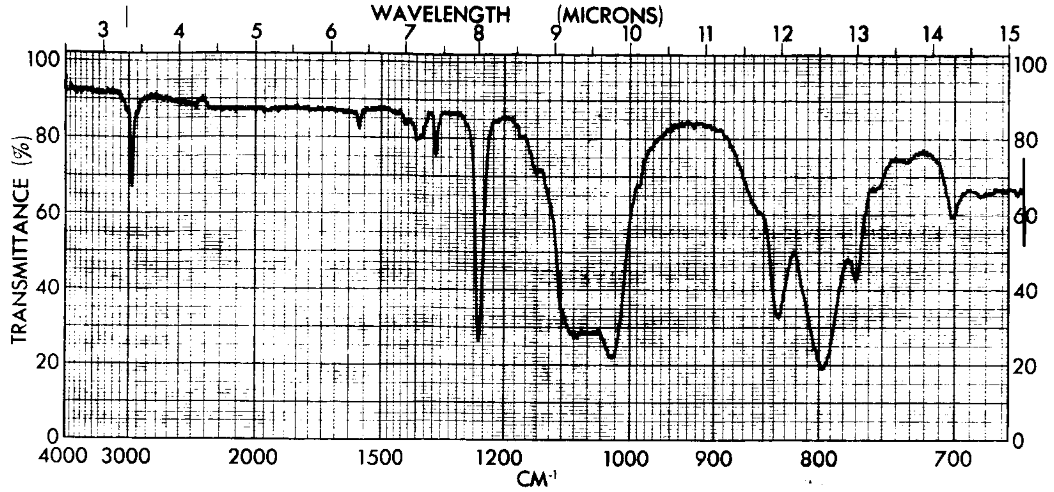


Fig. 62 - Infrared Spectrum of a Polymer From m-Phenylenebis-(dimethylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (Film) - See Table VII, Polymer 7

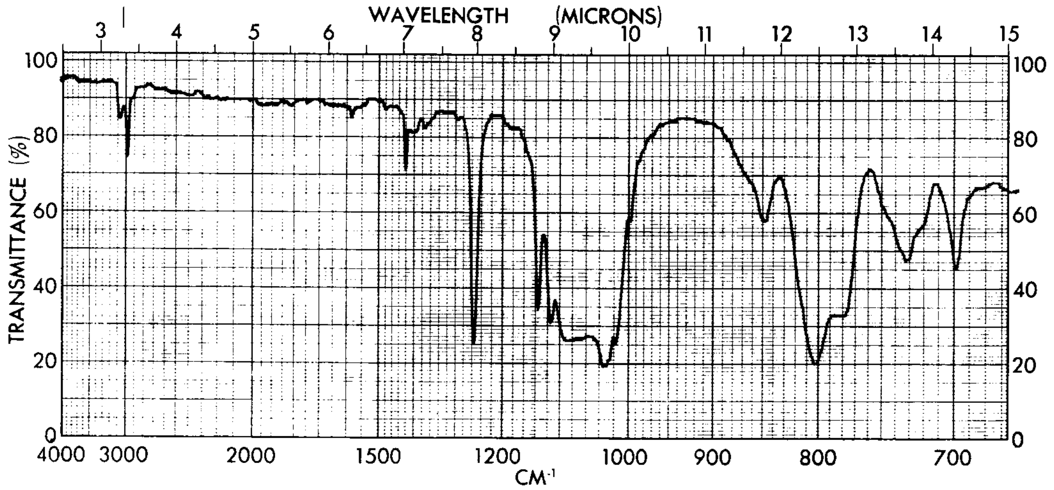


Fig. 63 - Infrared Spectrum of a Polymer From p-Phenylenebis-(methylphenylsilanol) and Heptamethyl-1-aza-3,5-dioza-2,-4,6-trisilacyclohexane (Film) - See Table VII, Polymer 8

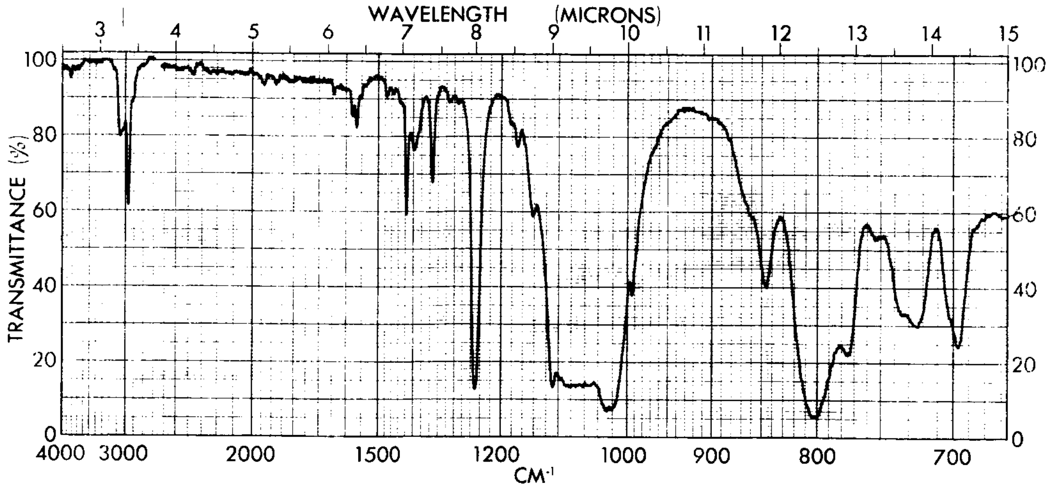


Fig. 64 - Infrared Spectrum of a Polymer From m-Phenylenebis-(methylphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,-4,6-trisilacyclohexane (Film) - See Table VII, Polymer 9

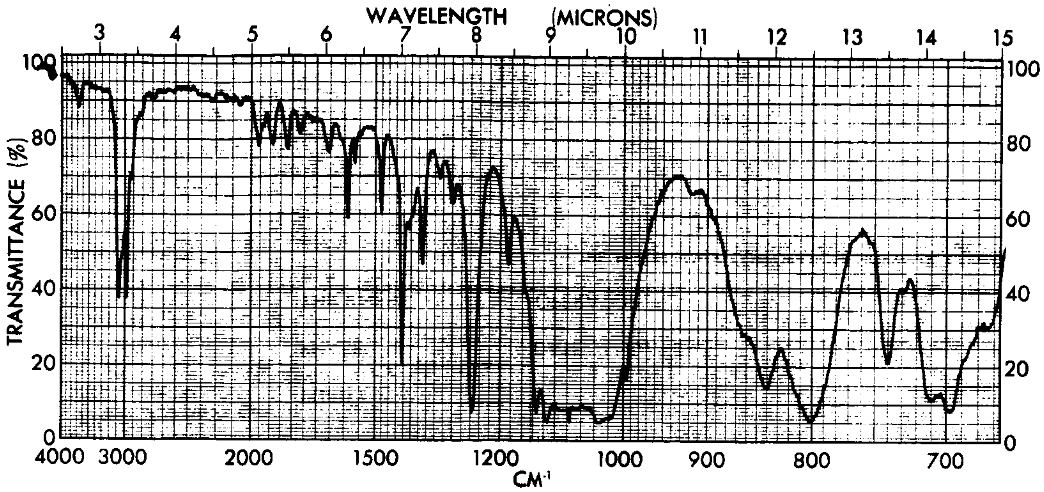


Fig. 65 - Infrared Spectrum of the Polymer From p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (Film) - See Table VII, Polymer 10

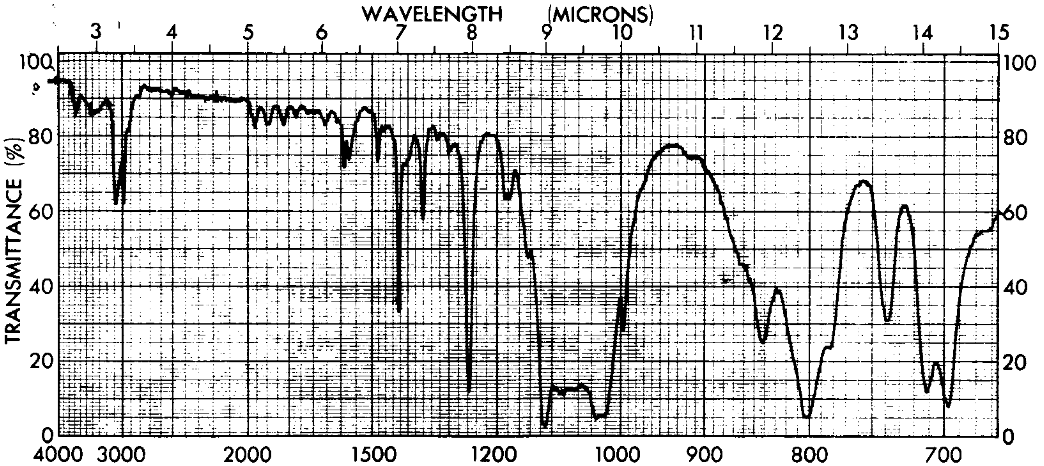


Fig. 66 - Infrared Spectrum of the Polymer From m-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (Film) - See Table VII, Polymer 11

D. Experimental

1. Synthesis of Arylenedisilanol Monomers and Intermediates

a. Intermediate silanes: Chlorodiphenylethoxysilane was prepared by adding a mixture of 25.3 g. (0.55 mole) of anhydrous ethanol and 43.5 g. (0.55 mole) of pyridine 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. When the combined filtrate and washings were fractionally distilled through a 30-cm. vacuum-jacketed column, 116 g. (81 per cent) of chlorodiphenylethoxysilane, b.p. 116 - 119° (0.7 mm.), was obtained.

Anal. Calcd. for $C_{14}H_{15}ClOSi$: C, 63.98; H, 5.75; Cl, 13.49. Found: C, 63.91; H, 5.80; Cl, 13.70.

Other intermediates, which were prepared by established methods, are reported in Table VIII.

b. p-Phenylenebis(chlorodimethylsilane): (Method: Reference 56) 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°).[56]

c. p-Phenylenebis(dimethylsilanol): (Method: Reference 56) 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 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. 134 - 136° (reported, 135°)[56] was obtained. Repetitions of the procedure afforded the same product in yields of 44 to 57 per cent.

d. p-Phenylenebis(ethoxydimethylsilane): To 32.1 g. (1.32 g. atom) of magnesium covered with 50 ml. of tetrahydrofuran was added slowly 141.6 g. (0.60 mole) of p-dibromobenzene in 440 ml. of tetrahydrofuran.

TABLE VIII

PREPARATION OF SILICON-CONTAINING INTERMEDIATES

Compound	Method of Preparation	Yield	Boiling Point	
			Found	Reported
Chlorodimethylethoxysilane	Addition of ethanol to dichlorodimethylsilane	38-76%	93-95°	94-95[a]
Chloroethoxymethylphenylsilane	Addition of ethanol to dichloromethylphenylsilane	85-89%	105-107° (23 mm.)	101° (20 mm.)[b]
Chlorodiphenylsilane	Addition of phenylmagnesium bromide in ether to trichlorosilane in ether	38-64%	115-122° (2 mm.)	140-145° (7 mm.)[c]
Dichlorophenylsilane	Addition of phenylmagnesium bromide in ether to trichlorosilane in ether	36-46%	103° (52 mm.)	65° (10 mm.)[d]
Chloromethylphenylsilane	Addition of methylmagnesium bromide in ether to dichlorophenylsilane in ether	33%	114-115° (103 mm.)	113° (100 mm.)[e]
Bis(methylamino)methylphenylsilane	Addition of excess methylamine to dichloromethylphenylsilane in petroleum ether	48%	95-96° (7 mm.)	95-96° (6 mm.)[f]
Bis(methylamino)diphenylsilane	Addition of excess methylamine to dichlorodiphenylsilane	82%	105-108° (0.1 mm.)	108-112° (0.1 mm.)[g]
1,3-Diallylpentamethyldisilazane	Addition of allylchlorodimethylsilane to excess methylamine in petroleum ether at -70°	36%	62-64° (98 mm.)	64° (98 mm.)[h]
Allyldimethyl(methylamino)silane		22%	131-132° (45 mm.)	128-130° (45 mm.)[h]

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[a] Ref. 50.
[b] Ref. 51.
[c] Ref. 52.
[d] Ref. 53.
[e] Ref. 53.
[f] Ref. 54.
[g] Ref. 54.
[h] Ref. 55.

After the addition was complete, the mixture was stirred and heated 1 hr., cooled, and treated with 177.7 g. (1.20 moles) of diethoxydimethylsilane. The mixture was refluxed 20 hr., cooled, filtered, the solvent was distilled out, and the residue was refiltered. Flash distillation at 2.8 - 3.0 mm. gave 86.9 g. of a crude mixture that was redistilled on a spinning band column. p-Phenylenebis(dimethylethoxysilane), b.p. 128 - 130° (2.8 - 3.0 mm.), n_D^{20} 1.4788 - 1.4780 (reported b.p. 127 - 128° (3.5 mm.), n_D^{25} 1.4752[57/]) was obtained in 62.2 g. (38 per cent) yield. In a repetition of the experiment, the yield was 43 per cent. The n.m.r. spectrum of this compound is reported in Table IX.

e. p-Phenylenebis(dimethylsilanol): A solution of 9.1 g. (0.227 mole of sodium hydroxide in 8 ml. of water and 53 ml. of methanol was mixed with a solution of 23.2 g. (0.0815 mole) of redistilled p-phenylenebis(dimethylethoxysilane, b.p. 119 - 120° (3.6 mm.), n_D^{20} 1.4782, in 20 ml. of anhydrous ethanol. After 5 min., a solution of 9.1 g. (0.227 mole) of sodium hydroxide in 60 ml. of water was added with swirling. An hour later, the mixture was slowly poured into an ice-cold solution of 78 g. of potassium dihydrogen phosphate in 570 ml. of water. After 2 hr., the crystalline precipitate was filtered off, washed well with water, and dried in vacuum at 70° to give 18.0 g. (97 per cent) of crude product. Recrystallization from 400 ml. of toluene gave 10.0 g. of p-phenylenebis(dimethylsilanol), m.p. 136 - 137°. The filtrate was evaporated to give an additional 1 g. of product, m.p. 135.5 - 136.5°. The total yield was 60 per cent. The infrared spectrum of this compound is reported in Fig. 66 and the n.m.r. spectrum in Table IX.

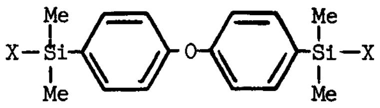
f. m-Phenylenebis(chlorodimethylsilane): A solution of 47.2 g. (0.2 mole) of m-dibromobenzene in 130 ml. of ether was added in 2 hr. to a mixture of 77.4 g. (0.6 mole) of dichlorodimethylsilane, 14.6 g. (0.6 g. atoms) of magnesium turnings, and 70 ml. of ether. The mixture was refluxed an additional 5 hr., filtered, and the filtrate was devolatilized. Distillation gave 19.5 g. (35 per cent) m-phenylenebis(chlorodimethylsilane) boiling at 89 - 95° (0.4 mm.). The product was used directly in the synthesis of m-phenylenebis-(dimethylsilanol).

g. m-Phenylenebis(dimethylsilanol): By a procedure similar to paragraph IV.D.1.c., m-phenylenebis(chlorodimethylsilane) was converted to m-phenylenebis(dimethylsilanol) in a 38 per cent yield, m.p. 78 - 79° (from toluene) (reported, 82 - 83°).[46/] The infrared spectrum of the compound is reported in Fig. 67.

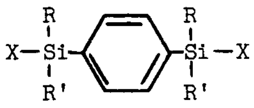
Anal. Calcd. for $C_{10}H_{18}O_2Si_2$: C, 53.04; H, 8.01; Si, 24.81. Found: C, 53.11; H, 7.89; Si, 24.70.

TABLE IX

PROTON CHEMICAL SHIFTS OF ARYLENEDISILANES



(A)



(B)

Structure	X	R	R'	τ (C_6H_4Si)	τ (C_6H_4O)	τ (SiOH)	τ (CH_2-C-)	τ (CH_3-C-)	τ (CH_3Si)	τ (SiH)
A[a]	OH			2.31 doublet J = 7 cps	2.92 doublet J = 6 cps	4.09			9.67	
A[b]	OEt			2.76 doublet J = 8 cps	3.30 doublet J = 7 cps		6.62 quadruplet J = 7 cps	9.14 triplet J = 7 cps	9.94	
B(*p*-)[a]	OH	Me	Me	2.34		4.12			9.67	
B(*p*-)[c]	OEt	Me	Me	2.39			6.32 quadruplet J = 7 cps	8.85 triplet J = 7 cps	9.66	
B(*p*-)[a]	OH	Ph	Me	2.80-3.24 complex multiplet		3.58			9.60	
B(*m*-)[a]	OH	Ph	Me	2.19-2.58 complex multiplet		3.42			9.35	
B(*p*-)[a]	OH	Ph	Ph	2.40-2.83 complex multiplet		2.99				
B(*m*-)[a]	OH	Ph	Ph	2.20-2.57 complex multiplet		2.68				
B(*p*-)[c]	H	Ph	Ph	2.32-2.73 complex multiplet						4.52

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[a] In dimethylsulfoxide. [b] Neat liquid. [c] In carbon tetrachloride.

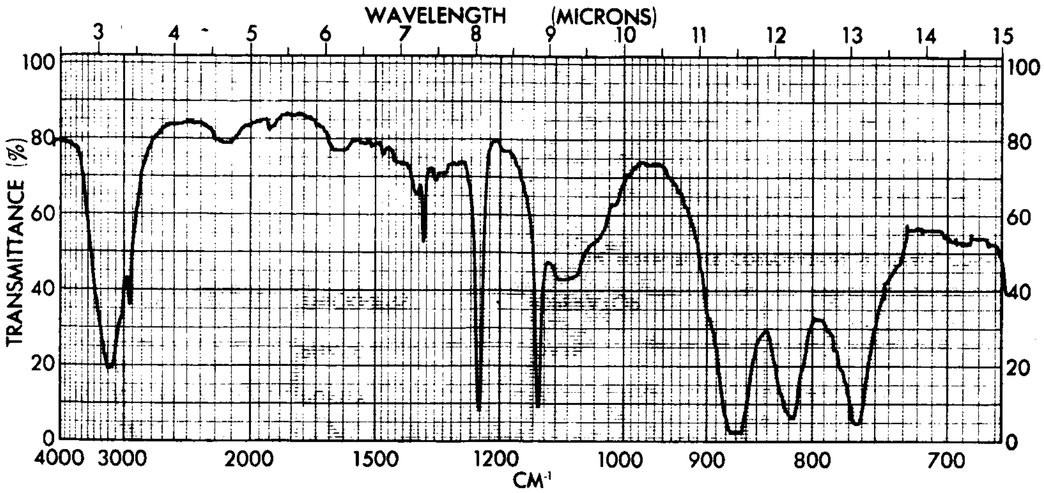


Fig. 67 - Infrared Spectrum of p-Phenylenebis(dimethylsilanol) (KBr)

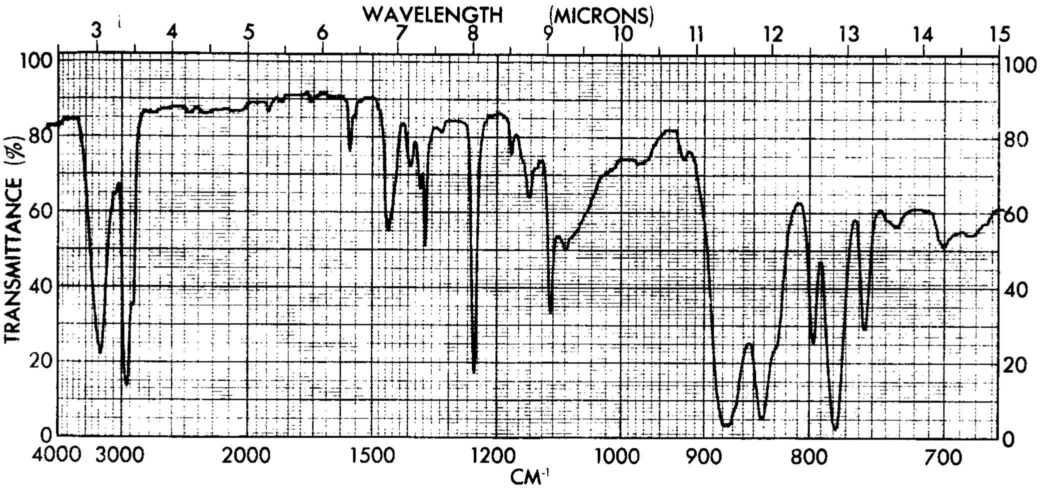


Fig. 68 - Infrared Spectrum of m-Phenylenebis(dimethylsilanol) (Nujol)

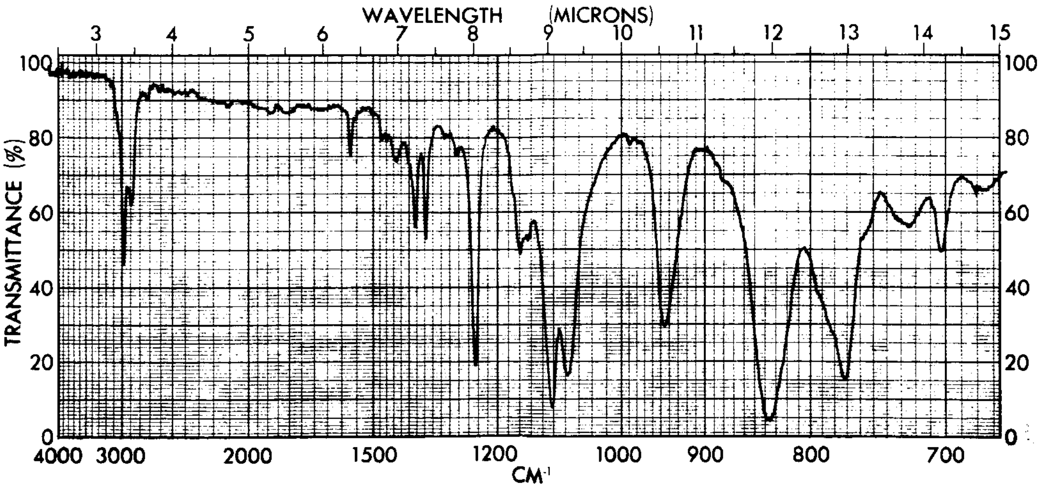


Fig. 69 - Infrared Spectrum of m-Phenylenebis(dimethylethoxysilane) (Smear)

h. m-Phenylenebis(dimethylethoxysilane): To 10.8 g. (0.44 g. atom) of magnesium turnings activated with 50 ml. of tetrahydrofuran, 15 g. of chlorodimethylethoxysilane, 47.2 g. of m-dibromobenzene, and a crystal of iodine, was added a mixture of 45.9 g. (0.44 mole, total) of chlorodimethylethoxysilane, 44.8 g. (0.20 mole, total) of m-dibromobenzene, and 100 ml. of tetrahydrofuran. After the addition was complete, the mixture was stirred and refluxed for 5 hr., then filtered and stripped of solvent. Fractional distillation of the residue gave 3.4 g. of unidentified material boiling at 70 - 89° (0.5 mm.), n_D^{20} 1.4730, and 22.4 g. (40 per cent) of m-phenylenebis(dimethylethoxysilane) boiling at 93 - 95° (0.47 mm.), n_D^{20} 1.4757. The infrared spectrum is reported in Fig. 68.

Anal. Calcd. for $C_{14}H_{26}O_2Si_2$: C, 59.51; H, 9.28; Si, 19.88. Found: C, 59.27; H, 9.08; Si, 19.55.

i. m-Phenylenebis(dimethylsilanol): A solution of 21.4 g. (0.076 mole) of m-phenylenebis(dimethylethoxysilane) was hydrolyzed by the procedure described in paragraph IV.D.1.e. to give 9.7 g. (56 per cent) of the diol melting at 79 - 81° (reported 82 - 83°).46/

j. p-Phenylenebis(ethoxymethylphenylsilane): To 10.9 g. (0.45 g. atom) of magnesium turnings in 40 ml. of tetrahydrofuran was added 47.2 g. (0.2 mole) of p-dibromobenzene, 90.0 g. (0.45 mole) of chloroethoxymethylphenylsilane, and 100 ml. of tetrahydrofuran over a 1.5-hr. period. The mixture was refluxed and stirred for 3 hr., cooled, treated with 100 ml. of petroleum ether (b.p. 60 - 90°) to precipitate the salts, and filtered. Distillation of the filtrate gave 43.0 g. (53 per cent) of p-phenylenebis(ethoxymethylphenylsilane) boiling at 187 - 188° (0.055 mm.). The infrared spectrum is reported in Fig. 70.

Anal. Calcd. for $C_{24}H_{30}O_2Si_2$: C, 70.88; H, 7.44. Found: C, 70.81; H, 7.43.

k. 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. sodium hydroxide (0.030 mole) in 8 ml. of water was added. An hour later, the mixture was poured into an ice-cold solution of 10.3 g. of potassium dihydrogen phosphate in 75 ml. of 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. The infrared spectrum is reported in Fig. 71.

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.

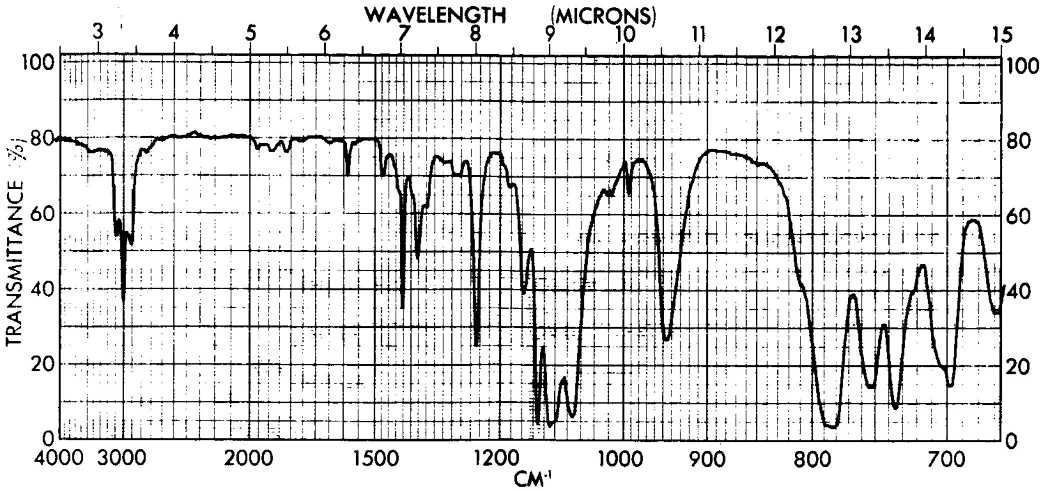


Fig. 70 - Infrared Spectrum of p-Phenylenebis(methylphenylethoxysilane) (Smear)

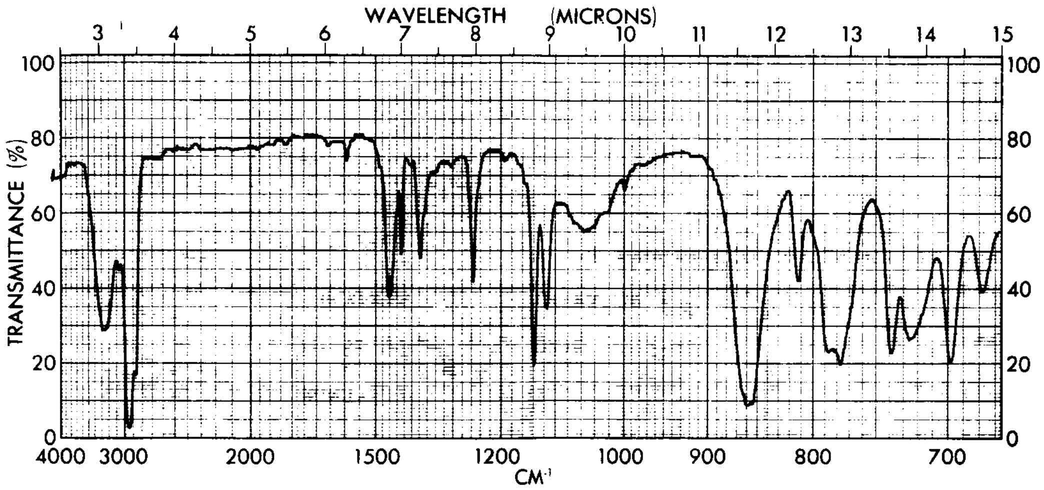


Fig. 71 - Infrared Spectrum of p-Phenylenebis(methylphenylsilanol), m.p. 127 - 140° (Nujol)

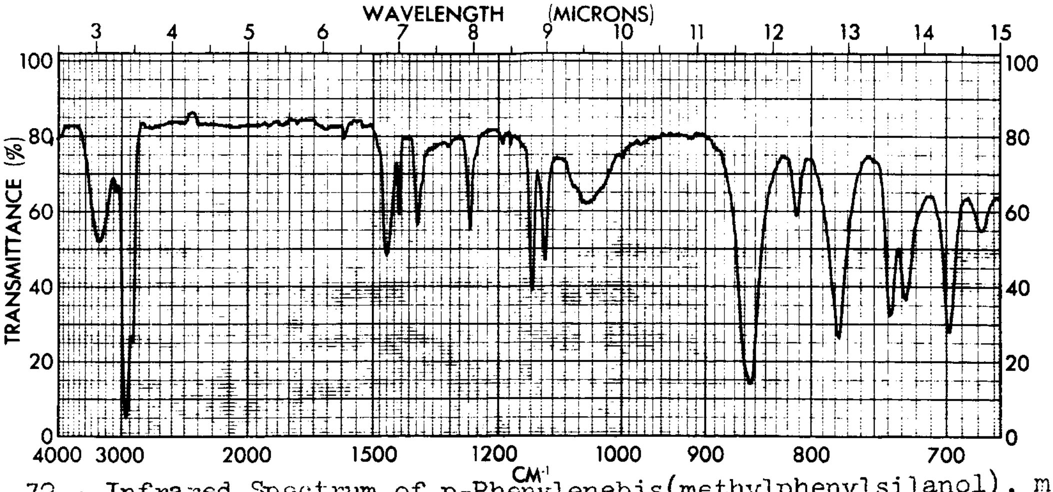


Fig. 72 - Infrared Spectrum of p-Phenylenebis(methylphenylsilanol), m.p. 156 - 158° (Nujol)

In a second experiment, 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°. The infrared spectrum is reported in Fig. 72.

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 an isomeric mixture, m.p. 127 - 141° was recovered. The only difference between the n.m.r. spectra of the isomeric mixture and the pure isomer (Table IX) was the sharpness of the SiOH absorption peak.

When the experiment was repeated, 4.2 g. of an isomer melting at 128 - 129° was separated as well as 24.2 g. of a mixture melting at 125 - 128° and 1.3 g. of the high melting isomer, 151 - 155°. The infrared spectrum of the low melting isomer is reported in Fig. 73.

l. *m-Phenylenebis(chloromethylphenylsilane)*: To 14.6 g. (0.60 g. atom) of magnesium turnings under 70 ml. of ether was added a solution of 47.2 g. (0.20 mole) of *m*-dibromobenzene and 114.6 g. (0.6 mole) of dichloromethylphenylsilane in 130 ml. of ether in 1.5 hr. The mixture was stirred and refluxed for 19 hr., cooled, treated with 100 ml. of petroleum ether (b.p. 60 - 90°), and filtered. Fractional distillation gave 20.7 g. of material boiling at 180 - 197° (0.1 mm.). Redistillation afforded 16.0 g. (21 per cent) of *m*-phenylenebis(chloromethylphenylsilane), b.p. 179 - 85° (0.07 mm.).

Anal. Calcd. for $C_{20}H_{20}Cl_2Si_2$: C, 62.00; H, 5.20; Si, 14.50. Found: C, 61.97; H, 5.17; Si, 14.33.

m. *m-Phenylenebis(methylphenylsilanol)*: A solution of 15.6 g. (0.0381 mole) of *m*-phenylenebis(chloromethylphenylsilane) in 175 ml. of ether was added over a 25-min. period to 3.0 g. (0.076 mole) of sodium hydroxide in 100 ml. of water which was stirred rapidly at 0 - 5°. The ether layer was separated quickly and dried over anhydrous sodium sulfate. After the ether was evaporated and the viscous liquid residue was crystallized from toluene, 3.2 g. (23 per cent) of an isomer of *m*-phenylenebis(methylphenylsilanol), m.p. 139 - 140°, was isolated. The infrared spectrum is reported in Fig. 74.

Anal. Calcd. for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.33; Si, 16.02. Found: C, 68.47; H, 6.23; Si, 15.96.

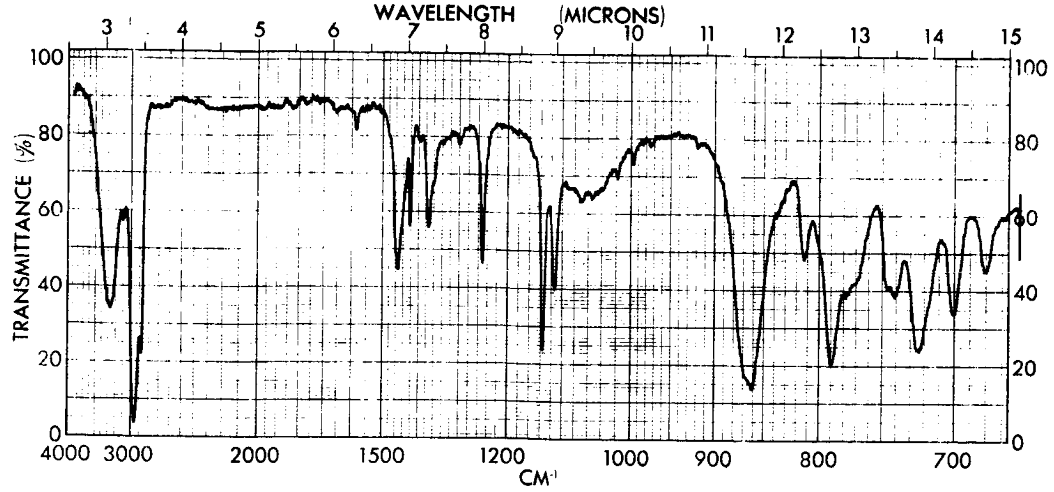


Fig. 73 - Infrared Spectrum of p-Phenylenebis(methylphenylsilanol), m.p. 128 - 129° (Nujol)

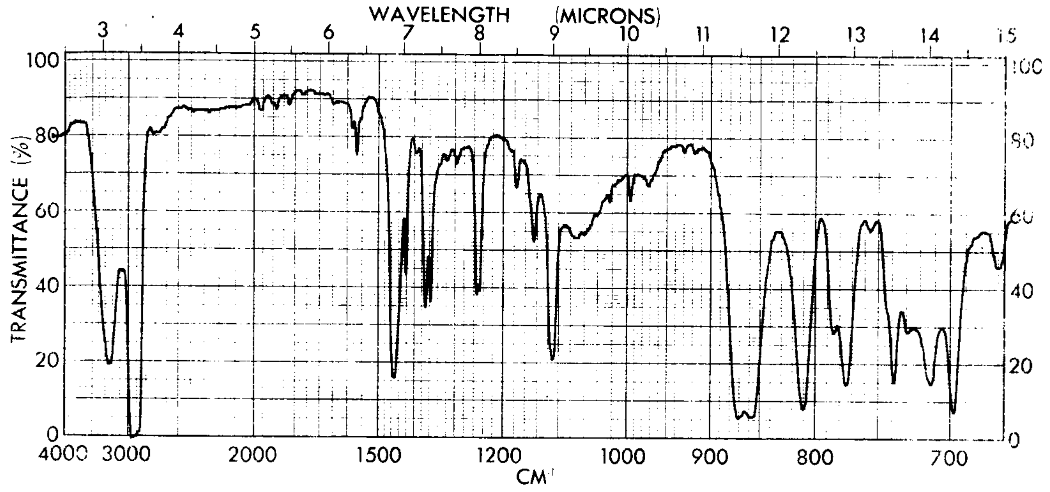


Fig. 74 - Infrared Spectrum of m-Phenylenebis(methylphenylsilanol), m.p. 139 - 140° (Nujol)

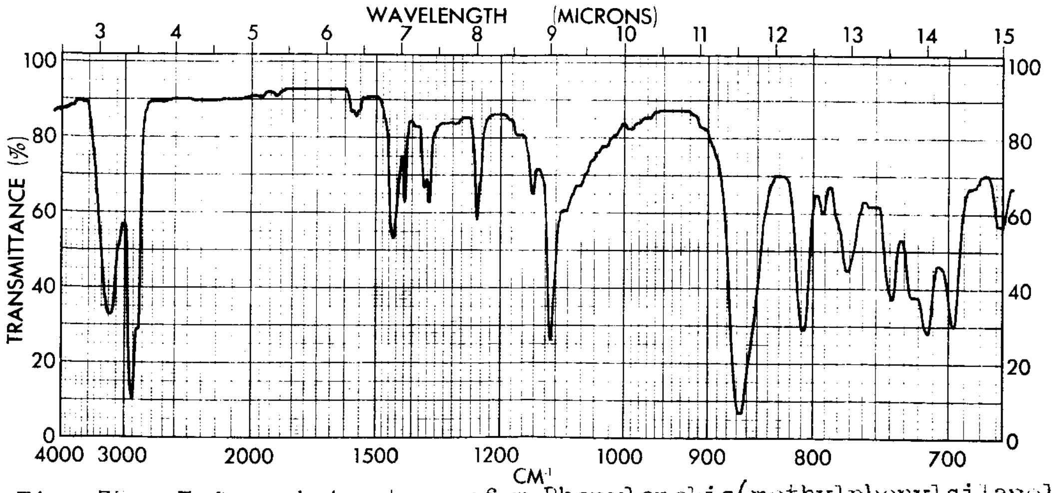


Fig. 75 - Infrared Spectrum of m-Phenylenebis(methylphenylsilanol), m.p. 101 - 102° (Nujol)

A second isomer was isolated upon evaporation of the toluene solution. Recrystallization from cyclohexane gave 3.1 g. (20 per cent) of isomer B, m.p. 101 - 102°. The infrared spectrum is reported in Fig. 75 and the n.m.r. spectrum in Table IX. The n.m.r. spectra of the two isomers were identical.

Anal. Calcd. for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.33; Si, 16.02. Found: C, 68.72; H, 6.26; Si, 15.93.

n. p-Phenylenebis(diphenylethoxysilane): (Method: Reference 45) 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°).45/ The infrared spectrum (Fig. 76) is consistent with the structure.

o. p-Phenylenebis(diphenylsilanol) (via the hydrolysis of p-phenylenebis(diphenylethoxysilane)): 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°. Hydrolysis of several combined samples of p-phenylenebis(diphenylethoxysilane), 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°).4/

Anal. Calcd. for $C_{30}H_{26}O_2Si_2$: C, 75.90; H, 5.52; Si, 11.84. Found: C, 76.19; H, 5.76; Si, 11.77.

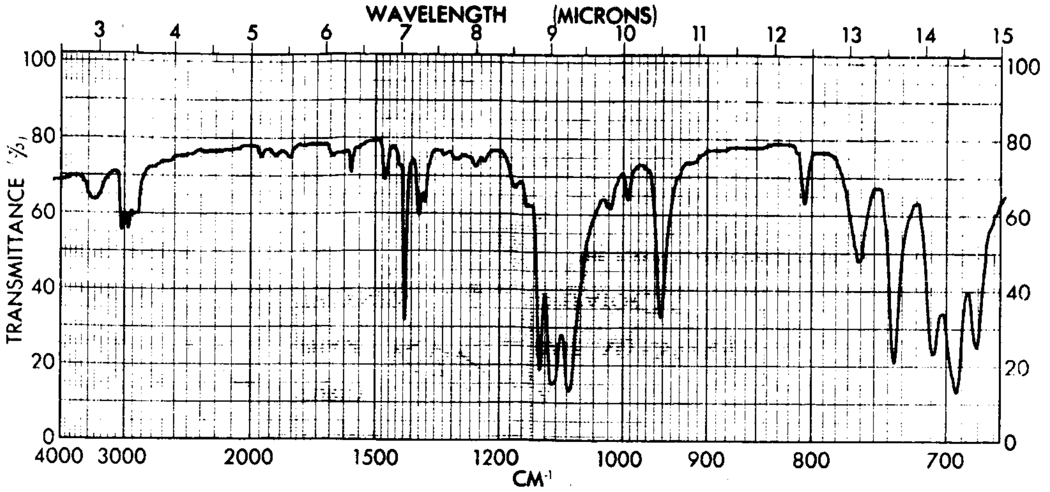


Fig. 76 - Infrared Spectrum of p-Phenylenebis(diphenylethoxysilane) (KBr)

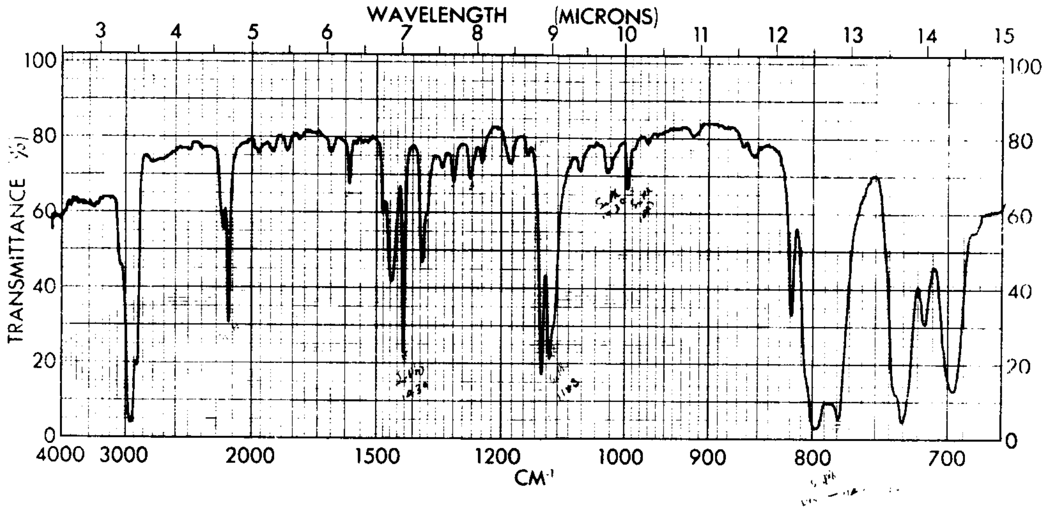


Fig. 77 - Infrared Spectrum of p-Phenylenebis(diphenylsilane) (Nujol)

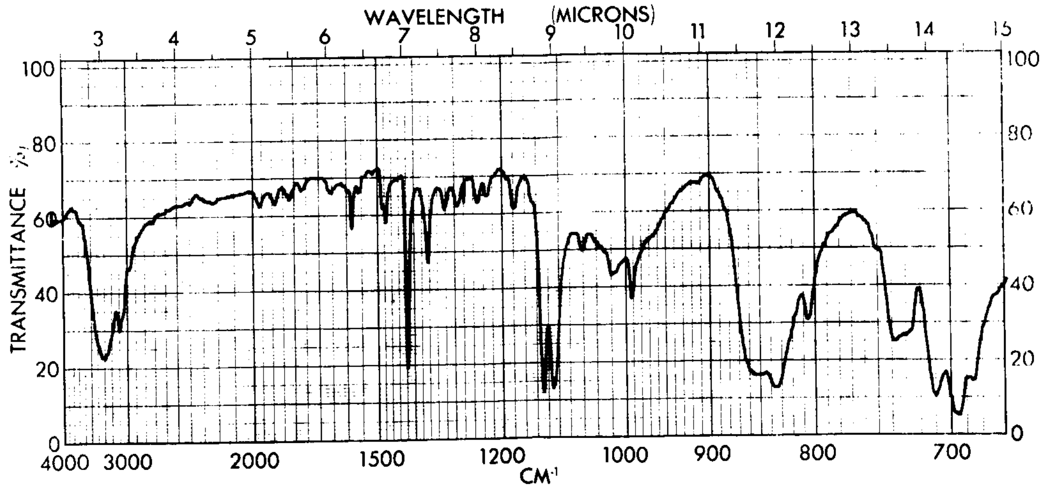


Fig. 78 - Infrared Spectrum of p-Phenylenebis(diphenylsilanol), m.p. 224 - 226° (KBr)

p. *p*-Phenylenebis(diphenylsilane): (Method: Reference 6) A mixture of 8.4 g. (0.346 g. atom) 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 107 - 108°).[46] The infrared spectrum of this compound is reported in Fig. 77 and the n.m.r. spectrum in Table IX.

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.

q. *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 under vacuum 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°).[4] The infrared spectrum of the compound was consistent with its structure (Fig. 78).

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 and the n.m.r. spectra of the two compounds were superimposable. The n.m.r. spectra are reported in Table IX.

r. m-Phenylenebis(diphenylsilanol): A solution of 30.7 g. (0.13 mole) of m-dibromobenzene and 56.8 g. (0.26 mole) of chlorodiphenylsilane in 100 ml. of tetrahydrofuran was added in 1.5 hr. to 6.3 g. (0.26 g. atom) of magnesium turnings in 30 ml. of tetrahydrofuran. After the mixture was refluxed an additional 2 hr., cooled, and poured over cracked ice, the hydrolyzed product was extracted with 250 ml. of petroleum ether (b.p. 60 - 90°) and dried over sodium sulfate. Evaporation of the solvent gave 36.4 g. (63 per cent) of liquid residue that would not distill at 225° or crystallize from petroleum ether (b.p. 60 - 90°) or ethanol.

The crude residue (35 g., 0.0792 mole) in 100 ml. of anhydrous ethanol was mixed with 40 ml. of anhydrous ethanol containing a small piece of sodium and refluxed until hydrogen evolution had ceased (1 hr.). The cooled mixture was poured into a stirred solution of 23.2 g. (0.58 mole) of sodium hydroxide, 140 ml. of methanol, and 20 ml. of water. After a solution of 23.2 g. (0.58 mole) of sodium hydroxide in 160 ml. of water was added, the mixture was stirred occasionally for 0.5 hr. then poured into an ice-cold solution of 200 g. of potassium dihydrogen phosphate. When the crude white product was removed by filtration, two recrystallizations from toluene gave 10.2 g. (27 per cent) of m-phenylenebis(diphenylsilanol), which melted at 111 - 113°. The infrared spectrum of the compound is reported in Fig. 79 and the n.m.r. spectrum in Table IX.

Anal. Calcd. for $C_{30}H_{26}O_2Si_2$: C, 75.90; H, 5.52; Si, 11.84. Found: C, 76.88; H, 5.78; Si, 11.31.

s. Bis(p-dimethylethoxysilylphenyl) ether: A mixture of 43.0 g. (0.131 mole) of bis(p-bromophenyl) ether, 39.0 g. (0.282 mole) of chlorodimethylethoxysilane, and 13.0 g. (0.564 g. atom) of 1 mm. diameter sodium wire in 500 ml. of ether was stirred at reflux for 24 hr. The mixture was filtered, and the filtrate was stripped of solvent. The residue was distilled on a spinning-band column to obtain the following fractions: A, b.p. to 130° (0.1 mm.); B, b.p. 130 - 140° (0.1 mm.), 15.9 g., n_D^{20} 1.5217; C, b.p. 141 - 142° (0.1 mm.); 11.5 g., n_D^{20} 1.5213. The combined weight of fractions B and C was 27.4 g. (56 per cent). In repetition of the procedure, the yields were 42 - 58 per cent.

Anal. Calcd. for $C_{20}H_{30}O_3Si_2$; C, 64.12; H, 8.07; Si, 15.00. Found, (fraction B): C, 64.27; H, 8.04; Si, 15.16. Found, (fraction C): C, 63.92; H, 8.10; Si, 15.03.

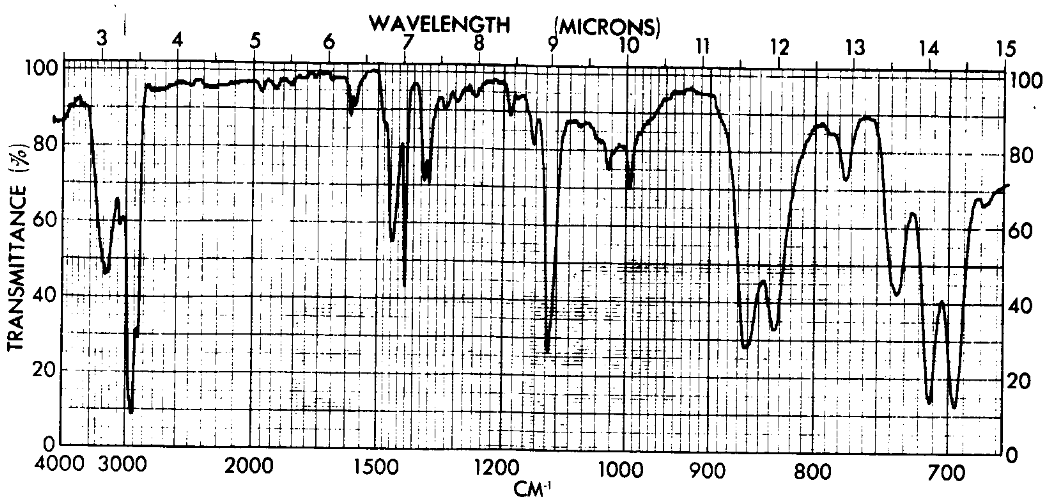


Fig. 79 - Infrared Spectrum of m-Phenylenebis(diphenylsilanol) (Nujol)

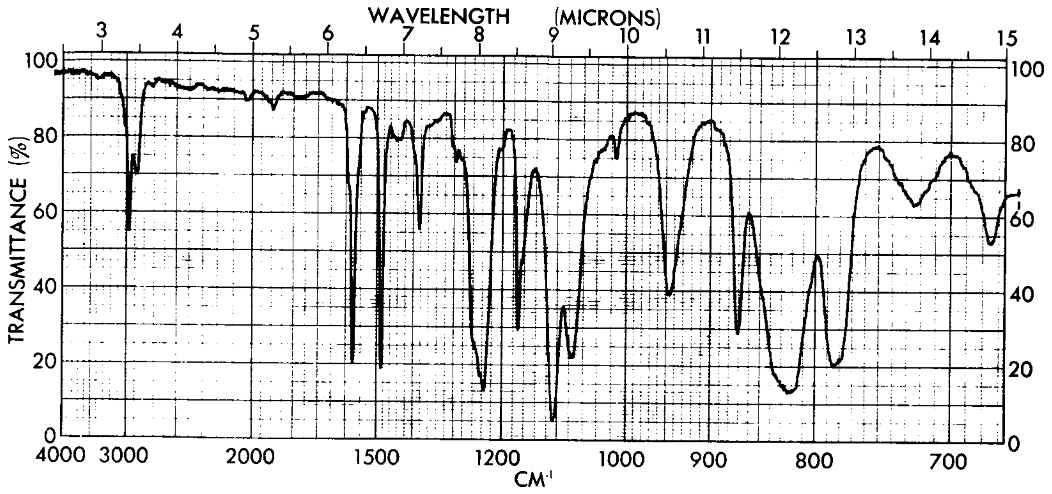


Fig. 80 - Infrared Spectrum of Bis(p-dimethylethoxysilylphenyl) Ether (Smear)

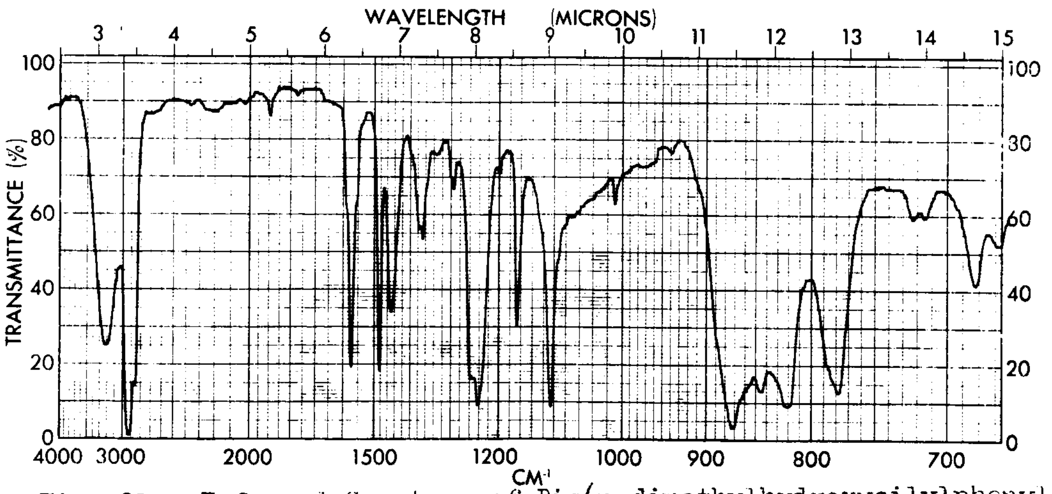


Fig. 81 - Infrared Spectrum of Bis(p-dimethylhydroxysilylphenyl) Ether (Smear)

By an alternate method, a quantity of a solution of 55.4 g. (0.4 mole) of chlorodimethylethoxysilane in 120 ml. of tetrahydrofuran was added to 9.7 g. (0.4 g. atom) of magnesium turnings (flame-dried in the flask) sufficient to cover the magnesium. About 5 ml. of a solution of 49.2 g. (0.15 mole) of bis(p-bromophenyl) ether in 100 ml. of tetrahydrofuran and a crystal of iodine were added to initiate the reaction. The remaining silane solution was added rapidly while the reaction mixture was maintained at a gentle reflux, then the bis(p-bromophenyl) ether was added dropwise without stirring at a rate which maintained a gentle reflux. After the addition was completed (1.5 hr.), the mixture was heated at reflux and stirred for 5 hr., filtered, and stripped of solvent. Fractional distillation of the residue on a spinning-band column gave 20.1 g. (36 per cent) of bis(p-dimethylethoxysilylphenyl) ether boiling at 140 - 145° (0.086 - 0.11 mm.), n_D^{20} 1.5215. There was 13.8 g. of residue. The infrared spectrum of the compound is reported in Fig. 80 and the n.m.r. spectrum in Table IX.

t. Bis(p-dimethylhydroxysilylphenyl) ether: A solution of 58.0 g. (0.155 mole) of bis(p-dimethylethoxysilylphenyl) ether in 140 ml. of anhydrous ethanol was added slowly with stirring to a solution of 24.0 g. (0.60 mole) of sodium hydroxide in 100 ml. of methanol and 15 ml. of water. A solution of 24.0 g. (0.60 mole) of sodium hydroxide in 105 ml. of water was added in 10 min., and the mixture was stored for 1 hr. The mixture was added dropwise during 0.5 hr. to a stirred solution of 175 g. (1.28 moles) of potassium diacid phosphate in 2.5 liters of water and about 1.5 kg. of ice. The gummy precipitate crystallized in about 1.5 hr., was collected by filtration, and was dried under vacuum at 60°. The yield of crude bis(p-dimethylhydroxysilylphenyl) ether was 49.0 g. (99 per cent). The infrared spectrum of the compound is reported in Fig. 81 and the n.m.r. spectrum in Table IX. Five grams of the crude material was separated, washed well with water and dried for 4 hr. at 75° (0.05 mm.). The compound melted at 102 - 104° and showed a single melting exotherm on DTA at 105°.

Anal. Calcd. for $C_{16}H_{22}O_3Si_2$: C, 60.33; H, 6.96; Si, 17.64. Found: C, 60.09; H, 6.88; Si, 17.50.

The remainder of the crude material (44 g.) was dissolved in 130 ml. of ether, and the ether solution was filtered, dried over sodium sulfate and 600 ml. of petroleum ether (b.p. 60 - 90°) was added to precipitate the diol. The diol was collected by filtration (m.p. 101 - 104°) and recrystallized from a mixture of 530 ml. of petroleum ether (b.p. 60 - 90°) and 65 ml. of acetone and dried at 75° (0.05 mm.) for 4 hr. to give 37 g. of bis(p-dimethylhydroxysilylphenyl) ether, m.p. 103 - 104°. The compound showed two DTA endotherms, one at 96° and the other at 102°. The filtrate was evaporated to one-half volume to give 4.7 g. of additional product, m.p. 103 - 104° (reported, 96°;[46/] 85 - 91°[58/]). The total yield was 89 per cent.

Anal. Found: C, 60.48; H, 7.18; Si, 17.49.

In repetitions of the experiment, yields from 62 to 88 per cent were obtained. Poor analytical results were obtained on samples, unless they were very carefully dried to remove traces of recrystallization solvents before analysis. Difficulties in removing traces of solvent from bis(p-dimethylhydroxysilylphenyl) ether are evident from the following experiments. A sample, recrystallized from benzene and dried at 76° for 4 hr. at 0.1 mm., still showed a benzene peak in its n.m.r. spectrum. Another sample recrystallized from acetone-petroleum ether showed an acetone peak in its n.m.r. spectrum after being dried at 55° for 4 hr. at 0.1 mm.

u. Bis(p-ethoxymethylphenylsilylphenyl) ether: A mixture of 32.8 g. (0.10 mole) of bis(p-bromophenyl) ether, 44.1 g. (0.22 mole) of chloroethoxymethylphenylsilane, 10.0 g. (0.44 g. atom) of sodium, and 500 ml. of ethyl ether was refluxed with rapid stirring for 41 hr. The mixture was filtered to give 32.4 g. (100 per cent of theory) of salts. Distillation of the filtrate gave 20.3 g. (41 per cent) of bis(p-ethoxymethylphenylsilylphenyl) ether boiling at 226 - 243° (0.04 mm.), n_D^{20} 1.5783. The infrared spectrum is reported in Fig. 82.

Anal. Calcd. for $C_{30}H_{34}O_3Si_2$: C, 72.24; H, 6.87; Si, 11.26. Found: C, 72.01; H, 6.71; Si, 11.11.

v. Bis(p-hydroxymethylphenylsilylphenyl) ether: A solution of 20.0 g. (0.04 mole) of bis(p-ethoxymethylphenylsilylphenyl) ether in 100 ml. of anhydrous ethanol was hydrolyzed in the manner described in IV.D.1.t. The white solid collected by filtration was dissolved in ether, dried over anhydrous sodium sulfate, and evaporated to obtain 16.4 g. of a tacky gum that would not recrystallize from toluene, benzene, or a mixture of benzene-petroleum ether (b.p. 60 - 90°). The gum was dissolved in 200 ml. of petroleum ether (b.p. 60 - 90°) and 100 ml. of benzene. A second liquid layer formed on cooling, and after 21 days it began to crystallize to a white, amorphous solid. The material was dried in a vacuum desiccator overnight at 0.05 mm. to give 9.0 g. (50.8 per cent) of the bis(p-hydroxymethylphenylsilylphenyl) ether melting at 48 - 55°. The infrared spectrum is reported in Fig. 83.

Anal. Calcd. for $C_{26}H_{26}O_3Si_2$: C, 70.54; H, 5.92; Si, 12.69. Found: C, 70.73; H, 6.09; Si, 12.51.

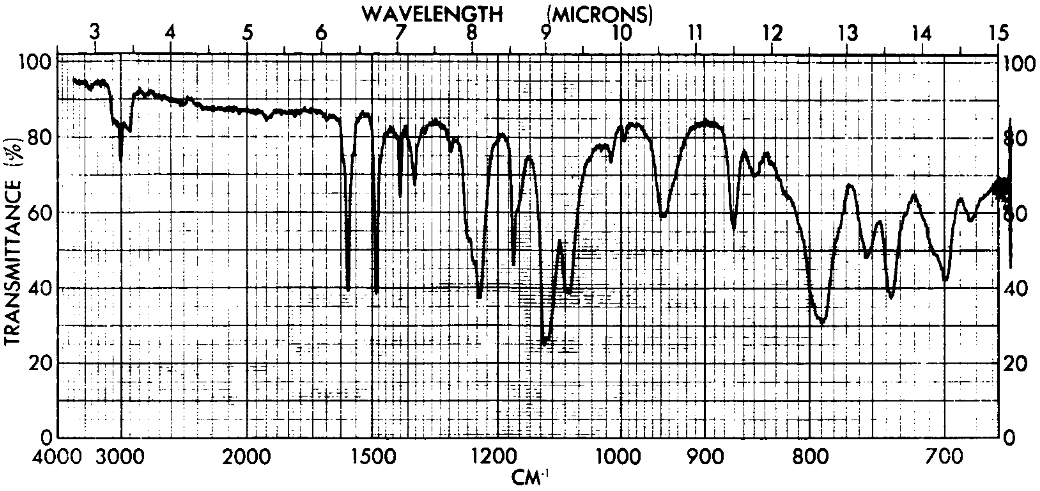


Fig. 82 - Infrared Spectrum of Bis(p-ethoxymethylphenylsilylphenyl) Ether (Smear)

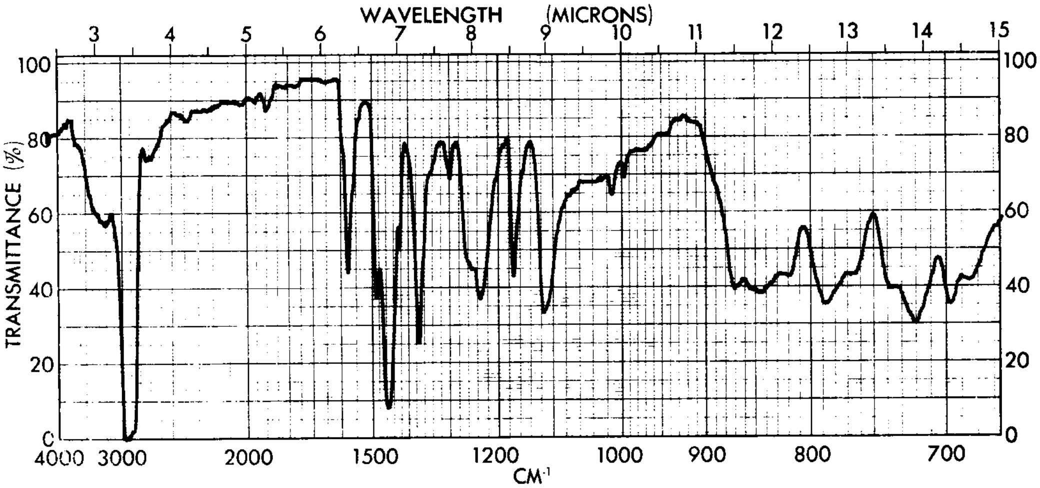


Fig. 83 - Infrared Spectrum of Bis(p-methylphenylhydroxysilylphenyl) Ether (Nujol)

2. Synthesis of Cyclosiloxazane Monomers and Intermediates

a. 1,3-Dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane and 1,7-dichlorooctamethyltetrasiloxane: (Method: Reference 59) A solution of 32.1 g. (1.75 moles) of water in 32 ml. of dioxane was added in 1 hr. to a solution of 387 g. (3.0 moles) of dichlorodimethylsilane in 350 ml. of ether. Distillation gave the following fractions: 43.0 g. (7 per cent) of 1,3-dichlorotetramethyldisiloxane boiling at 136 - 139°; 50.2 g. (18 per cent) of 1,5-dichlorohexamethyltrisiloxane boiling at 170 - 180°; and 20.9 g. (10 per cent) of 1,7-dichlorooctamethyltetrasiloxane boiling at 102 - 115° (19 mm.).

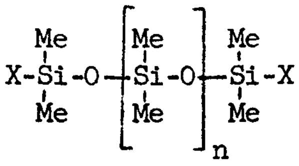
The following procedure was usually used for preparing α,ω-dichlorosiloxanes: After a mixture of 248 g. (2 moles) of diethoxydimethylsilane, 1,132 g. (8 moles) of dichlorodimethylsilane and 1.5 g. of ferric chloride were heated at 85° for 7 hr., ethyl chloride was no longer evolved. Upon distillation, 514 g. of dichlorodimethylsilane was recovered and 547 g. of oligomers boiling between 25 - 140° (40 mm.) was obtained. Fractional distillation of the oligomers gave the following compounds: 1,3-dichlorotetramethyldisiloxane, 287 g., b.p. 57 - 58° (40 mm.) (reported, 41° (20 mm.));59/ 1,5-dichlorohexamethyltrisiloxane, 138 g., b.p. 94 - 96° (40 mm.) (reported, 79° (20 mm.));59/ and 1,7-dichlorooctamethyltetrasiloxane, 23.6 g., b.p. 127 - 128° (41 mm.) (reported, 111° (20 mm.)).59/ The n.m.r. spectra of the compounds are reported in Table X.

In a modification of the latter procedure, 104 g. (0.8 mole) of dichlorodimethylsilane was treated with 18.4 g. (0.4 mole) of dry ethanol over a period of 1 hr., the mixture was refluxed to expel hydrochloric acid, cooled to 25°, and transferred to a flask containing about 0.1 weight per cent ferric chloride. After the mixture was heated at 82° for 4.5 hr., fractional distillation gave 12.5 g. of 1,3-dichlorodisiloxane, 14.4 g. of 1,5-dichlorotrisiloxane, 7.5 g. of 1,7-dichlorotetrasiloxane, and 14.2 g. of a residue.

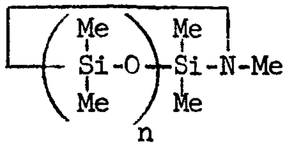
b. 1,3-Bis(methylamino)tetramethyldisiloxane: To 300 ml. of methylamine in 1,500 ml. of petroleum ether (b.p. 30 - 60°) at -30° was added 284 g. (1.40 moles) of 1,3-dichlorotetramethyldisiloxane during 1 hr., with the temperature of the mixture maintained at -10 to -20°. After the addition was complete, the mixture was allowed to warm to room temperature, refluxed for 2 hr., filtered, and the solvents removed. The residue was devolatilized at 120° and fractionally distilled through a 30-cm., vacuum-jacketed column packed with Berl saddles to obtain 220.4 g. (82 per cent) of 1,3-bis(methylamino)tetramethyldisiloxane, b.p. 65 - 68° (20 mm.), n_D^{20} 1.4138 (reported, b.p. 63 - 65° (20 mm.), n_D^{27} 1.4085).48/ The infrared spectrum of the compound is reported in Fig. 84 and the n.m.r. spectrum in Table X.

TABLE X

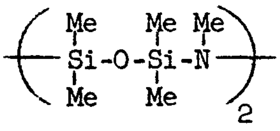
PROTON CHEMICAL SHIFTS OF SILOXANE DERIVATIVES



(A)



(B)



(C)

Structure	X	n	τ (-OMe$_2$SiCl)	τ (-OMe$_2$SiN-)	τ (-Me$_2$SiO)	τ (NHMe)
A	Cl	0	9.53			
A	Cl	1	9.57		9.83	
A	Cl	2	9.58		9.87	
A	NHMe	0		9.98		7.51 doublet J = 6.5 cps
A	NHMe	1		9.98	9.98	7.51 doublet J = 6.5 cps
A	NHMe	3		9.92	9.94	7.48 doublet J = 6.5 cps
B		2		9.92	9.93	7.63
B		3		9.86	9.94	7.50
C				9.88		7.58

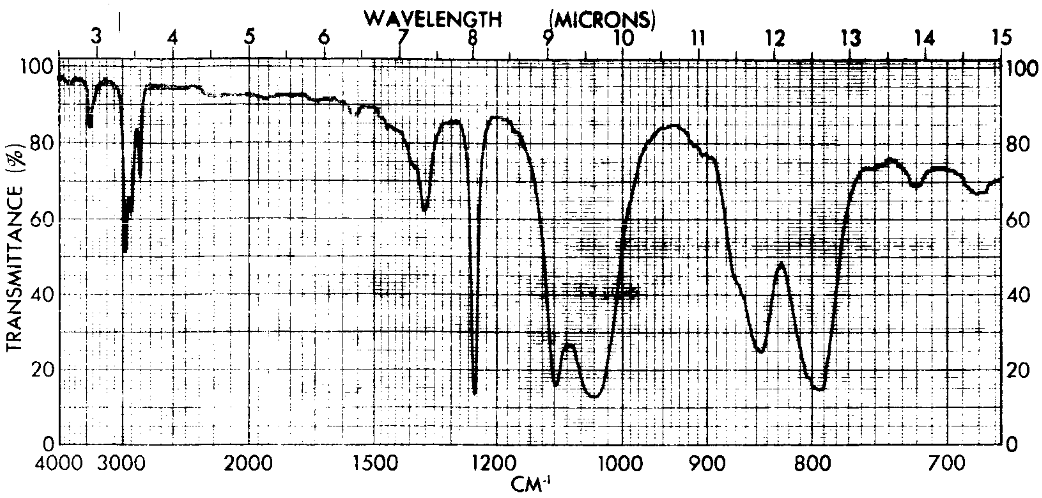


Fig. 84 - Infrared Spectrum of 1,3-Bis(methylamino)tetramethyldisiloxane (Smear)

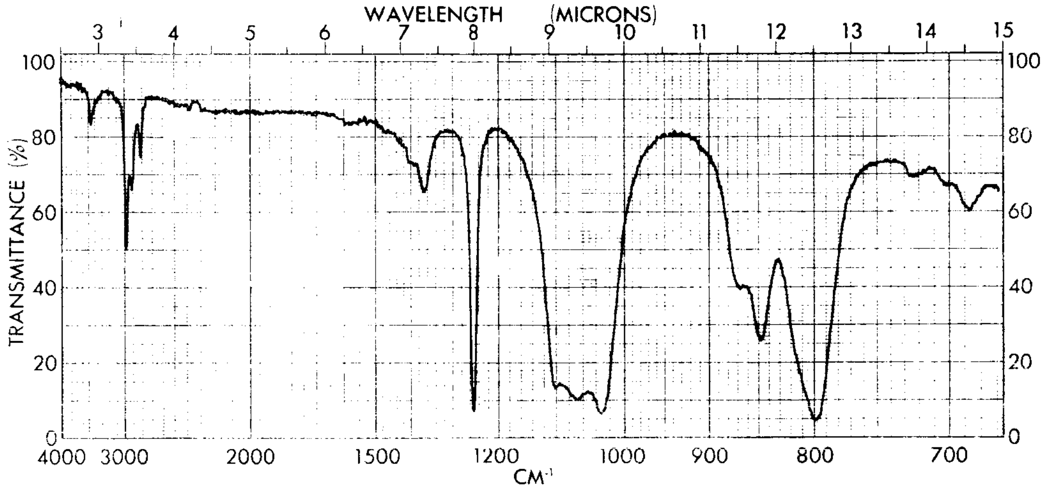


Fig. 85 - Infrared Spectrum of 1,5-Bis(methylamino)hexamethyltrisiloxane (Smear)

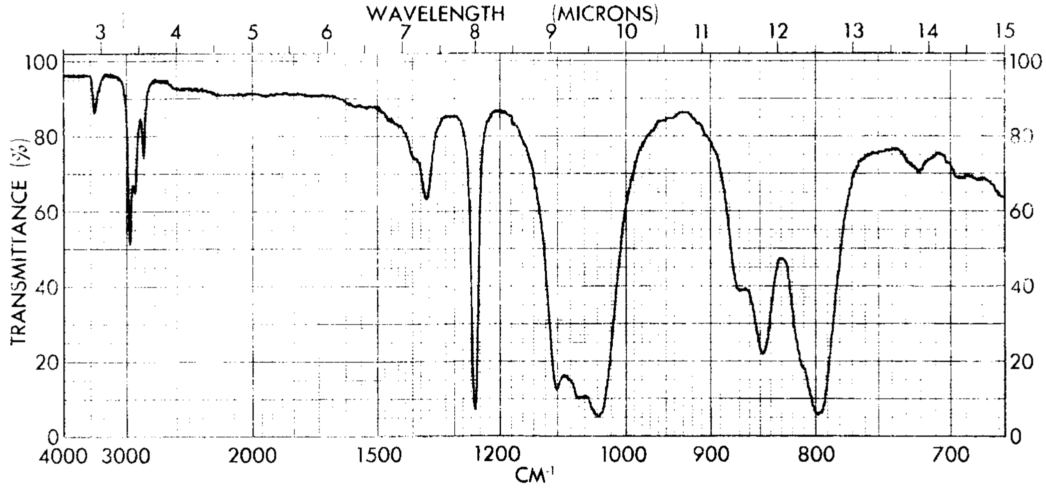


Fig. 86 - Infrared Spectrum of 1,7-Bis(methylamino)-octamethyltetrasiloxane (Smear)

c. 1,5-Bis(methylamino)hexamethyltrisiloxane: A solution of 100 ml. of methylamine in 500 ml. of petroleum ether (b.p. 30 - 60°) at -30° was treated with 138 g. (0.50 mole) of 1,5-dichlorohexamethyltrisiloxane during 1 hr., while the temperature of the mixture was maintained at -10 to -20°. The mixture was allowed to warm to room temperature, heated at reflux for 2 hr., filtered, and the solvents removed. When the residue was devolatilized and fractionally distilled through a 30-cm., vacuum-jacketed column packed with Berl saddles, 113.8 g. (86 per cent) of 1,5-bis(methylamino)hexamethyltrisiloxane was obtained, b.p. 92 - 94° (15 - 18 mm.), n_D^{20} 1.4102 (reported, b.p. 97 - 98° (20 mm.), n_D^{20} 1.4070).[48] The infrared spectrum of the compound is reported in Fig. 85 and the n.m.r. spectrum in Table X.

d. 1,7-Bis(methylamino)octamethyltetrasiloxane: After 40.5 g. (0.115 mole) of 1,7-dichlorooctamethyltetrasilazane was added to 25 ml. of methylamine in 100 ml. of petroleum ether (b.p. 30 - 60°), which was maintained at -10 to -20° during the addition, the mixture was warmed to room temperature, refluxed 2 hr., filtered, and the solvents were removed. Fractional distillation gave 29.7 g. (76 per cent) of 1,7-bis(methylamino)octamethyltetrasiloxane, b.p. 114 - 115° (9 mm.), n_D^{20} 1.4100. The infrared spectrum of the compound is reported in Fig. 86 and the n.m.r. spectrum in Table X.

Anal. Calcd. for $C_{10}H_{32}N_2O_3Si_4$: C, 35.24; H, 9.46; N, 8.22; Si, 32.97. Found: C, 35.06; H, 9.20; N, 7.98; Si, 32.74.

e. Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane: When a mixture of 220 g. (1.15 moles) of 1,3-bis(methylamino)tetramethyldisiloxane and 2.2 g. of ammonium sulfate was heated at 176° for 24 hr. and subsequently fractionally distilled, 116 g. (66 per cent of crude decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, b.p. 93 - 96° (5 mm.) (reported, 82 - 85° (0.2 mm.))[48] was obtained. Lower boiling fractions (37 g.) contained some 1,3-bis(methylamino)tetramethyldisiloxane. Redistillation on a spinning band column gave 60.0 g. (34 per cent) of the pure compound, b.p. 87 - 88° (5 mm.), m.p. 27 - 28°, n_D^{30} 1.4321.

Into a solution of 194 g. (0.96 mole) of 1,3-dichlorotetramethyldisiloxane in 600 ml. of petroleum ether, which was heated to 50°, was distilled 200 ml. of methylamine while the temperature of the mixture was maintained at 50°. After the addition was complete, the mixture was cooled, filtered, and the salts were washed with petroleum ether. Evaporation of the solvent and distillation through a spinning-band column gave 12.5 g. (8 per cent) of 1,3-bis(methylamino)tetramethyldisiloxane, b.p. 42 - 43° (5 mm.) and 91.4 g. (62 per cent) of decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, b.p. 86 - 87° (5 mm.), n_D^{30} 1.4318, m.p. 29 - 30°. The compound showed a g.l.c. purity of about 100 per cent. The infrared spectrum of the compound is reported in Fig. 87 and the n.m.r. spectrum in Table X.

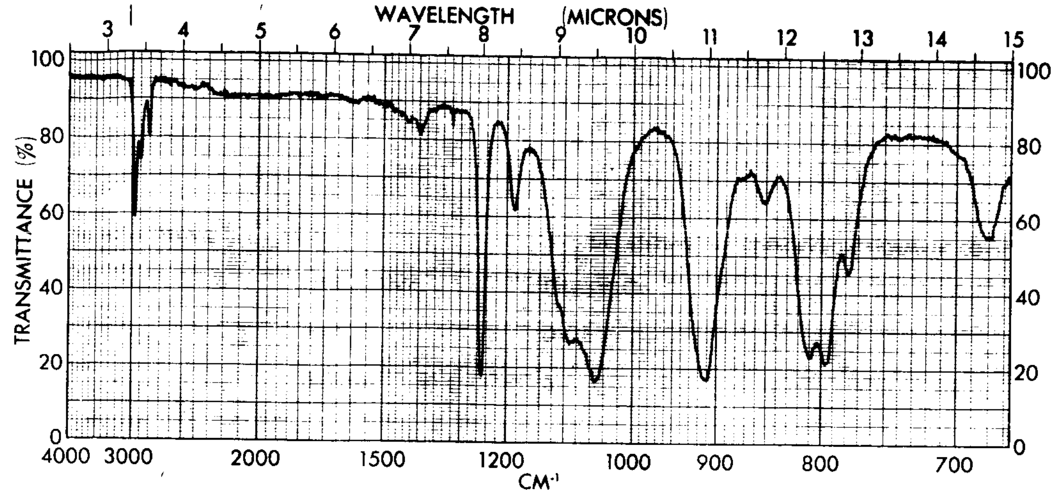


Fig. 87 - Infrared Spectrum of Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (Smear)

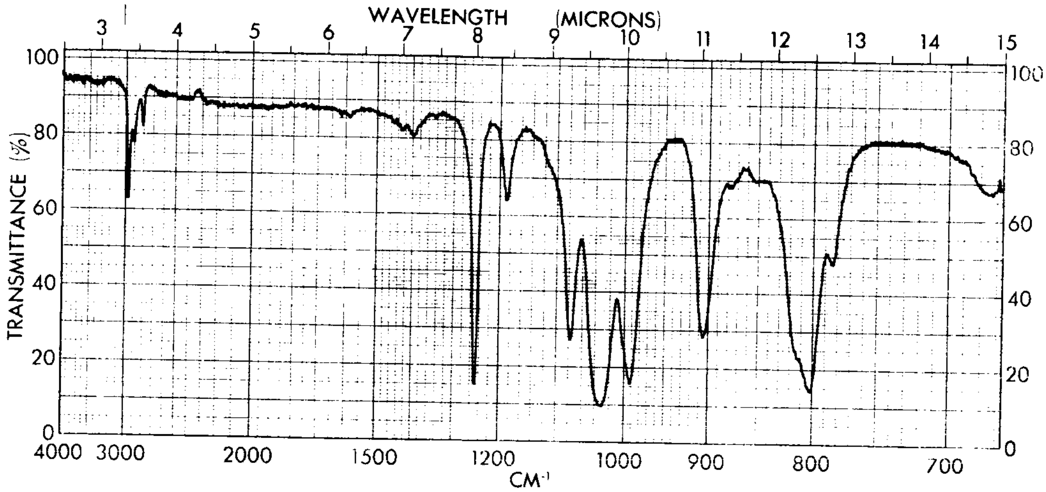


Fig. 88 - Infrared Spectrum of Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (Smear)

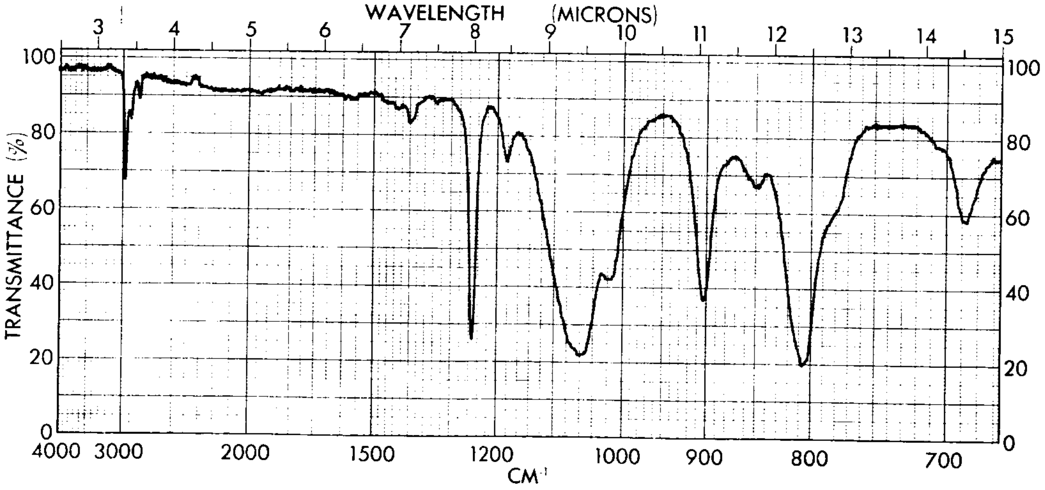


Fig. 89 - Infrared Spectrum of Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane (Smear)

f. Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: A mixture of 114 g. (0.427 mole) of 1,5-bis(methylamino)hexamethyltrisiloxane and 1.1 g. of ammonium sulfate was heated at 150° under nitrogen for 16 hr. The solution was fractionally distilled through a 30-cm., vacuum-jacketed column packed with Berl saddles to give 52.8 g. (47 per cent) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, b.p. 62 - 66° (20 - 23 mm.). Redistillation through a spinning-band column gave 41.7 g. (32 per cent) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, b.p., 60 - 61° (16 - 18 mm.), n_D^{20} 1.4103 (reported, b.p. 65 - 70° (20 mm.), n_D^{27} 1.4059).[48] The g.l.c. purity of the compound was 98.7 per cent. The infrared spectrum of the compound is reported in Fig. 88 and the n.m.r. spectrum in Table X.

When excess methylamine was added to a solution of 50.2 g. (0.181 mole) of 1,5-dichlorohexamethyltrisiloxane in 500 ml. of petroleum ether (b.p. 60 - 90°) in 1 hr., and the mixture was not cooled, the maximum temperature of the reaction mixture was 51°. Filtration and distillation gave 20.0 g. (47 per cent) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane boiling at 65 - 72° (21 mm.), n_D^{25} 1.4057 (reported b.p., 65 - 70° (20 mm.), n_D^{27} 1.4059)[15] and 7.4 g. (15 per cent) of 1,5-bis(methylamino)hexamethyltrisiloxane boiling at 85 - 100° (21 mm.). There was 10.7 g. of higher boiling residue.

In another experiment, 100 ml. of methylamine was condensed and subsequently distilled into a mixture of 108 g. (0.39 mole) of 1,5-dichlorohexamethyltrisiloxane and 500 ml. petroleum ether, b.p. 60 - 90°, which was heated to 50° prior to the addition. The temperature did not rise above 56° during the addition. After the addition was complete, the mixture was cooled, filtered, and the solids were washed with petroleum ether. Distillation of the solvents and fractional distillation of the residue through a spinning-band column gave 56.7 g. (66 per cent) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, b.p. 60 - 61° (17 mm.), n_D^{20} 1.4100. The g.l.c. purity was 98.4 per cent.

g. Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane: Fifty milliliters of methylamine was condensed and subsequently distilled into a flask containing 40.2 g. (0.11 mole) of 1,7-dichlorooctamethyltetrasiloxane in 200 ml. petroleum ether, b.p. 60 - 90°, which was heated to 50° . The reaction was exothermic and external cooling was applied to the reaction vessel, maintaining the temperature at 57 - 60°C. The mixture was cooled, filtered and the solids washed with petroleum ether. The solvent was removed from the mixture through an unpacked column, and the residue, fractionated through a column packed with Berl saddles, gave 20.7 g. (61 per cent) of nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane, b.p. 84 - 85° (8 mm.), n_D^{20} 1.4202. The g.l.c. purity of the compound was 98.6 per cent. The infrared spectrum of the compound is reported in Fig. 89 and the n.m.r. spectrum in Table X.

Anal. Calcd. for $C_9H_{27}NO_2Si_4$: C, 34.90; H, 8.79; N, 4.52; Si, 36.28. Found: C, 35.19; H, 8.54; N, 4.80; Si, 36.15.

3. Polymerization of Phenylenedisilanols and Cyclotrisilazanes or Silylamines

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 inherent viscosity of a 0.5 per cent solution of the polymer in toluene was 0.86 at 30°.

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 inherent viscosity increased to 1.25.

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, and an inherent viscosity (c = 0.5 per cent in toluene at 30°) of 0.36.

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 XI.

The results of a second series of polymerizations are reported in Table XII. Unless stated otherwise, all polymers in this series were devolatilized with heat for 1 hr. at 150° (0.1 mm.). In a typical preparation, a mixture of 1.13 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 an inherent viscosity of 0.98 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.

TABLE XI

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

Reactants		Per Cent Amine Evolved After					Polymer Yield (%)	Softening Point (°C)	Inherent Viscosity (Toluene 30°) (c = 0.5%)
Silanol	Silazane or Silylamine	0.5 Hr.	1 Hr.	2 Hr.	4 Hr.	24 Hr.			
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Nonamethylcyclotrisilazane (0.00166 mole)	8.0	20.0	43.5	66.3	91.0	93	Sinters 225-35°	0.78
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Hexaphenyl-1,3,5-trimethylcyclotrisilazane (0.00166 mole)	0.0	0.0	1.3	1.3	3.6	-	-	-
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-Triphenylhexamethylcyclotrisilazane (0.00166 mole)	0.6	0.6	0.6	-	1.9	-	-	0.04
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Diphenylbis(methylamino)-silane (0.00500 mole)	75.0	80.2	83.0	87.0	91.0	93	Some shrinkage at 200°	0.33
p-Phenylenebis-(diphenylsilanol) (0.00500 mole)	Phenylmethylbis(methylamino)silane (0.00500 mole)	88.2	93.1	96.7	96.7	98.7	95	-	0.08

TABLE XII

POLYMERS FROM p-PHENYLENEDISILANOLS AND SILAZANES OR SILYLAMINES

	Silanol	Silazane or Silylamine	Procedure (solvent) (°C/hr)	Amine Evolved (%)	Polymer Yield (%)	Inherent Viscosity (toluene, 30°) (c = 0.5%)	Polymer Description
1.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	Toluene 110°/24 hr 160°/19 hr	36.2	107	0.02	Light colored, elastic gum
2.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	No Solvent 160-195°/4 hr 200° (0.1 mm)/1 hr	77.3	102	0.98	Clear, slightly tacky elastic solid
3.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Dimethyldianilinosilane (0.005 mole)	No Solvent 165°/0.5 hr 200° (0.1 mm)/5 hr	-	91	0.57	Violet colored, soft tacky gum
4.	p-Phenylenebis(dimethylsilanol) (0.005 mole)	Dimethyldianilinosilane (0.005 mole)	No Solvent 200°/1 hr 200-220° (0.1 mm)/2.5 hr	-	87	0.54	Violet colored, tacky gum
5.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	Diphenylbis(methylamino)silane (0.005 mole)	No Solvent 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)	No Solvent 180°/2 hr 210° (0.1 mm)/4.5 hr	-	87	Insoluble	Dark colored, brittle solid
7.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	Nonamethylcyclotrisilazane (0.00166 mole)	Toluene 112-120°/24 hr	70	96	Insoluble	White, hard solid
8.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	Dimethyldianilinosilane (0.00285 mole)	No Solvent 180°/1 hr 200° (0.1 mm)/4 hr	-	96	Insoluble	Dark colored, elastic solid

4. Polymerization of p-Phenylenedisilanols With Cyclosiloxazanes or Diaminosiloxanes: Preliminary Experiments

a. Miscellaneous polymerizations: In a typical experiment, 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 an inherent viscosity of 0.52 in a 0.5 per cent solution in toluene at 30°. A film prepared from a toluene solution was hard and brittle.

Data relating to similar experiments are reported in Table XIII. Unless stated otherwise, all polymers were devolatilized with heat for 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.

Similar monomer compositions remained soluble throughout the polymerization in solvent, and one of these solutions containing a low molecular weight polymer was cast as a film for vacuum-ultraviolet evaluation.

b. Polymerization of p-phenylenebis(diphenylsilanol) with siloxaazanes and aminosiloxanes:

(1) 1,5-Bis(methylamino)hexamethyltrisiloxane: A mixture of 4.74 g. (0.01 mole) of p-phenylenebis(diphenylsilanol) and 2.66 g. (0.01 mole) of 1,5-bis(methylamino)hexamethyltrisiloxane was refluxed in 20 ml. of xylene for 18 hr. at 132 - 145°. The polymer became insoluble. Solvent was removed at 95° (0.1 mm.) for 2 hr. The polymer, a clear, elastic solid, was insoluble in tetrahydrofuran, dimethyl sulfoxide, and dimethyl formamide. A differential thermal analysis showed no transition temperatures to 470°, the temperature at which decomposition began.

(2) Tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: A mixture of 2.37 g. (0.005 mole) of p-phenylenebis(diphenylsilanol) and 2.11 g. (0.005 mole) of the siloxazane was refluxed in 20 ml. of

TABLE XIII

POLYMERS FROM p-PHENYLENEDISILANOLS AND SILOXAZANES

	Silanol	Siloxazane	Procedure (solvent) (°C/hr)	Amine Evolved (%)	Polymer Yield (%)	Inherent Viscosity (toluene, 30°) (c = 0.5%)	Polymer Description	Film Description
1.	p-Phenylenebis(diphenylsilanol) (0.005 mole)	$(SiMePhOSiMePhNMe)_2$ (0.0025 mole)	Toluene 112-125°/30 hr	53	93	0.15	Light colored, brittle solid	Hard, brittle
2.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$(SiMePhOSiMePhNMe)_2$ (0.0015 mole)	Xylene 150-175°/3 hr	-	97	0.52	Light colored, brittle	Hard, brittle
3.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMePhOSiMePhNMe)_2$ (0.001425 mole)	Xylene 150°/6 hr	63	103	0.24 Some insoluble	Light colored, elastic solid	Soft, slightly tacky
4.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMe_2OSiMe_2NMe)_2$ (0.001425 mole)	Xylene 144-150°/8 hr	69	100	0.14	Light colored, tacky gum	Tacky gum
5.	p-Phenylenebis(methylphenylsilanol) (0.00285 mole)	$(SiMe_2OSiMe_2NMe)_2$ (0.001425 mole)	Xylene 135°/17 hr	86	100	0.17	Light colored, tacky gum	Tacky gum
6.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	$\overline{SiMe_2OSiMe_2OSiMe_2N}Me$ (0.003 mole)	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)	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)	Xylene 130-5°/5.5 hr	-	-	0.14	White, elastic gum	Cured in air oven at 145°/48 hr to a strong, elastic film
9.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	1,3-Dianilinotetramethyldisiloxane (0.003 mole)	No Solvent 170°/1 hr 200°(0.1 mm)/4 hr	-	93	Insoluble	Dark colored, slightly elastic solid	-
10.	p-Phenylenebis(diphenylsilanol) (0.003 mole)	1,3-Dianilinotetramethyldisiloxane (0.003 mole)	Toluene 125°/6 hr	-	-	0.21	Brown, hard solid	Tough, flexible

xylene at 135° for 7.5 hr. A small amount of the polymer solution was placed in an air oven at 145° for 15 hr. to give a clear, elastic film. One-half of the polymer solution was used to coat a plate for an ultraviolet-vacuum study, and the solvent was stripped off of the remaining material to give a white, slightly brittle polymer that softened near 80°. The inherent viscosity (0.5 per cent concentration in toluene at 30°) was 0.04. When the polymer was heated at 150° (0.1 mm.) for 1 hr., the inherent viscosity increased to 0.06.

In a similar experiment, the monomers were heated in 10 ml. of xylene for 20 hr. at 135 - 137°. The methylamine that collected in an acid trap was 83.4 per cent of the calculated quantity. A small amount of solution gave a clear, hard, but slightly brittle film. One-half of the polymer solution was used to coat a plate for an ultraviolet-vacuum study, and the remaining material was stripped of solvent to give a white, slightly elastic solid with an inherent viscosity (0.5 per cent concentration in toluene at 30°) of 0.17.

Anal. Calcd. for $C_{51}H_{48}O_4Si_5$: C, 70.78; H, 5.59; Si, 16.23. Found: C, 70.93; H, 5.73; Si, 16.07.

(3) A 1:1 mixture of tetramethyl-2,4-6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane and the corresponding heptamethyl derivative: A mixture of 2.37 g. (0.005 mole) of p-phenylenebis(diphenylsilanol), 1.055 g. (0.0025 mole) of tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, and 0.587 g. (0.0025 mole) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane in 10 ml. of xylene was heated at 130 - 138° for 48 hr. The amount of methylamine collected in an acid trap was 85.2 per cent of the expected quantity. A small amount of the polymer cured at 145° for 15 hr. to a clear, elastic, flexible film. The solvent was removed from part of the solution to give a white elastic solid with an inherent viscosity in toluene at 30° of 0.08.

c. Polymerization of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane with various silanols: The results of a series of polymerizations are reported in Table XIV. Two polymerization procedures were used. In one procedure, the monomers were refluxed in xylene (138°) for 24 hr. unless stated otherwise and devolatilized at 150° (0.1 mm.) for 1 hr. The second procedure was a bulk polymerization in which the sample was heated initially at 155° for 1 hr. and finally at 200° or higher.

Films of several of the polymers were prepared by dissolving the polymer in a minimum amount of solvent, pouring the solution into an aluminum dish, evaporating off the solvent, and heating the polymer in a 145° oven for 24 hr. or more. These results are also shown in Table XIV.

TABLE XIV

POLYMERS FROM DISILANOLS AND HEPTAMETHYL-1-AZA-3,5-DIOXA-2,4,6-TRISILACYCLOHEXANE

Disilanol	Procedure (Solvent) (°C/hr)	Inherent Viscosity (c = 0.5%, 30°)	Polymer Description	Film Description
m-Phenylenebis(dimethylsilanol) (0.005 mole)	Xylene (138°/24 hr)	0.05	Liquid	Viscous liquid
m-Phenylenebis(methylphenylsilanol) (0.005 mole)	Xylene (138°/24 hr)	0.31	Tacky, elastic gum	Tacky gum
m-Phenylenebis(diphenylsilanol) (0.005 mole)	Xylene (138°/24 hr)	Insoluble	An elastic solid	-
Bis(p-dimethylhydroxysilylphenyl) ether (0.005 mole)	Xylene (138°/24 hr)	0.06	A viscous liquid	Viscous liquid
p-Phenylenebis(dimethylsilanol) (0.001 mole)	Xylene (138°/48 hr)	-	Left in solution	Viscous liquid after 72 hr.
Bis(p-dimethylhydroxysilylphenyl) ether (0.005 mole)	No Solvent (195°/0.5 hr)	0.95	Clear, elastic gum	Clear, slightly tacky
Bis(p-dimethylhydroxysilylphenyl) ether (0.0025 mole)[a]	No Solvent (190°/2 hr)	1.19	An elastic gum	-
Bis(p-dimethylhydroxysilylphenyl) ether (0.005 mole)[a]	No Solvent (185°/1 hr)	1.74	Clear, elastic solid	-
Bis(p-methylphenylhydroxysilylphenyl) ether (0.005 mole)[a]	No Solvent (200-210°/3 hr)	0.08	Viscous liquid	-
m-Phenylenebis(diphenylsilanol) (0.005 mole)[a]	No Solvent (155°/45 min)	0.66	Elastic solid	-
p-Phenylenebis(diphenylsilanol) (0.005 mole)[a]	No Solvent (215°/30 min)	Insoluble	Cloudy, elastic solid	-
m-Phenylenebis(dimethylsilanol) (0.005 mole)[a]	No Solvent (185°/4 hr)	0.14	Viscous liquid	-
m-Phenylenebis(methylphenylsilanol) (0.005 mole)[a]	No Solvent (190°/4 hr)	0.43	A tacky gum	-
p-Phenylenebis(dimethylsilanol) (0.005 mole)[a]	No Solvent (185°/5 hr)	0.17	A viscous liquid	-

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[a] A 10 per cent excess of the cyclosiloxazane was used.

[b] The polymer was also heated at 200° (0.05 mm.).

A polymer prepared from bis(dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane with an inherent viscosity of 1.74 was investigated in detail. The melting point was above 235° (Fisher-Johns melting point apparatus). A differential thermal analysis to 500° showed no decomposition, and the polymer was still clear and elastic at the conclusion of the run experiment. Thermogravimetric analysis to 900° showed a procedural decomposition temperature of 495°, and a weight residue of 24.3 per cent at 900°.

Anal. Calcd. for $C_{22}H_{38}O_5Si_5$: C, 50.52; H, 7.32; Si, 26.86. Found: C, 47.79; H, 7.12; Si, 20.75.

d. Polymers from bis(p-dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: The polymerization of bis(dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane was studied by bulk polymerization. The reactions were carried out in a 25 x 150 mm. reaction tube with a Wood's metal bath providing the desired temperature.

The monomers were analytically weighed into the polymerization vessel and immersed into the heating bath for the specified time. The inherent viscosity (0.5 per cent concentration in toluene at 30°) was determined on polymer samples at various time intervals. It was noted during the first few runs that some cyclosiloxazane was being swept from the system by evolving methylamine, consequently a reflux condenser was added for the remaining runs to minimize the loss of monomer. The data and the results are reported in Table XV.

The diol used throughout these runs was recrystallized from a mixture of petroleum ether (b.p. 60 - 90°) and acetone, dried at 75° (0.1 mm.) for 4 hr., and had a m.p. of 103 - 104°. The cyclosiloxazane used in experiments 1 through 3 boiled at 65° (21 mm.), n_D^{20} 1.4100, g.l.c. purity, 96.3 per cent; the cyclosiloxazane used in experiments 4 through 6 boiled at 59 - 61° (16 - 18 mm.), n_D^{20} 1.4103; g.l.c. purity 98.7 per cent; the cyclosiloxazane used on experiments 7 and 8 boiled at 59 - 60° (16 mm.), n_D^{20} 1.4100, g.l.c. purity, 98.4 per cent.

e. Preparation of polymers for ultraviolet-stability film studies:

(1) Polymer from bis(p-dimethylhydroxysilylphenyl)ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: A mixture of 1.59 g. (0.0050 mole) of the diol and 1.29 g. (0.0055 mole) of the siloxazane was heated at 155° for 1 hr. and subsequently at 185° for 1 hr. The polymer, which was a clear elastic gum, had an inherent viscosity of 1.63 (c = 0.5 per cent, in toluene at 30°).

TABLE XV

MELT POLYMERIZATION OF BIS(p-DIMETHYLHYDROXYSILYLPHENYL) ETHER AND HEPTAMETHYL-1-AZA-3,5-DIOXA-2,4,6-TRISILACYCLOHEXANE

Run No.	Moles of Diol	Moles of Cyclosiloxazane	Polymerization Temp. (°C-hr.)	Inherent Viscosity (0.5% solution in Toluene at 30°) at Time (hr.)							Polymer Description
				1	2	4	5	6	7	8	
1	0.0100	0.0100	180° - 7 hr.	0.18	0.18	0.19	-	-	0.21	-	A clear Viscous liquid
2	0.0100	0.0100	180° - 8 hr.	-	0.28	0.34	-	0.41	-	0.36	Viscous liquid
3	0.0100	0.0110 (10% excess)	180° - 8 hr.	0.22	1.06	1.59	-	-	-	1.73	A rubbery solid
4	0.0100	0.0105 (5% excess)	180° - 8 hr.	0.47	0.67	1.30	-	-	-	2.11	Rubbery solid
5	0.0100	0.0105 (5% excess)	160° - 8 hr.	0.27	0.46	0.74	-	-	-	2.31	Rubbery solid
6	0.0100	0.0105 (5% excess)	160° - 8 hr.	0.25	0.50	-	1.65	-	-	1.91	Rubbery solid
7	0.0100	0.0105 (5% excess)	160° - 8 hr.	0.22	0.43	0.76	-	-	-	1.49	Rubbery gum
8	0.0200	0.0210 (5% excess)	160° - 8 hr.	-	-	-	1.45	-	-	3.58	Rubbery solid

Anal. Calcd. for $C_{22}H_{38}O_5Si_5$: C, 50.52; H, 7.32; Si, 26.86. Found: C, 47.79; H, 7.12; Si, 20.75.

(2) Polymer from bis(p-dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: When a mixture of 1.75 g. (0.0055 mole) of the diol, 1.18 g. (0.00525 mole) of the siloxazane, and 0.055 g. (0.00025 mole) of 1,3-bis(methylamino)-1,3-divinyltrimethyldisilazane was heated from 120° to 190° over a period of 45 min., a clear gum, which was not completely soluble in toluene, was obtained. Thermogravimetric analysis of the polymer is reported in Fig. 90.

Anal. Calcd. for $C_{22}H_{38}O_5Si_5$: C, 50.52; H, 7.32; Si, 26.86. Found: C, 50.28; H, 7.10; Si, 27.05.

(3) Polymer from p-phenylenebis(methylphenylsilanol) and hexamethylcyclotrisiloxane: The polymer obtained by heating 1.75 g. (0.0050 mole) of the diol and 1.11 g. (0.0050 mole) of the cyclotrisiloxane in the presence of about 0.00005 g. of potassium hydroxide at 180° for 4 hr. was a clear tacky gum with an inherent viscosity of 0.33 (c = 0.5 per cent, in toluene at 30°). Thermogravimetric analysis of the polymer is reported in Fig. 91.

Anal. Calcd. for $C_{26}H_{38}O_4Si_5$: C, 56.26; H, 6.90; Si, 25.31. Found: C, 57.97; H, 6.58; Si, 23.53.

(4) Polymer from m-Phenylenebis(diphenylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: A mixture of 2.37 g. (0.0050 mole) of the diol and 1.29 g. (0.0055 mole) of the siloxazane was heated at 155° for 45 min. The polymer, which was an elastic solid, had an inherent viscosity of 0.66 (c = 0.5 per cent, in toluene at 30°). Thermogravimetric analysis of the polymer is reported in Fig. 92.

Anal. Calcd. for $C_{36}H_{42}O_4Si_5$: C, 63.66; H, 6.24; Si, 20.68. Found: C, 64.08; H, 6.07; Si, 20.45.

(5) Polymer from p-Phenylenebis(diphenylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: When a mixture of 2.37 g. (0.0050 mole) of the diol, 1.29 g. (0.0055 mole) of the siloxazane, and 10 ml. of toluene were heated at 107° for 7 hr. and the resulting polymer solution was devolatilized at 150° (0.1 mm.) for 1 hr., an elastic solid with an inherent viscosity of 0.21 (c = 0.5 per cent, in toluene at 30°) was obtained. Thermogravimetric analysis of the polymer is shown in Fig. 93.

Anal. Calcd. for $C_{36}H_{42}O_4Si_5$: C, 63.66; H, 6.24; Si, 20.68. Found: C, 63.75; H, 6.25; Si, 20.29.

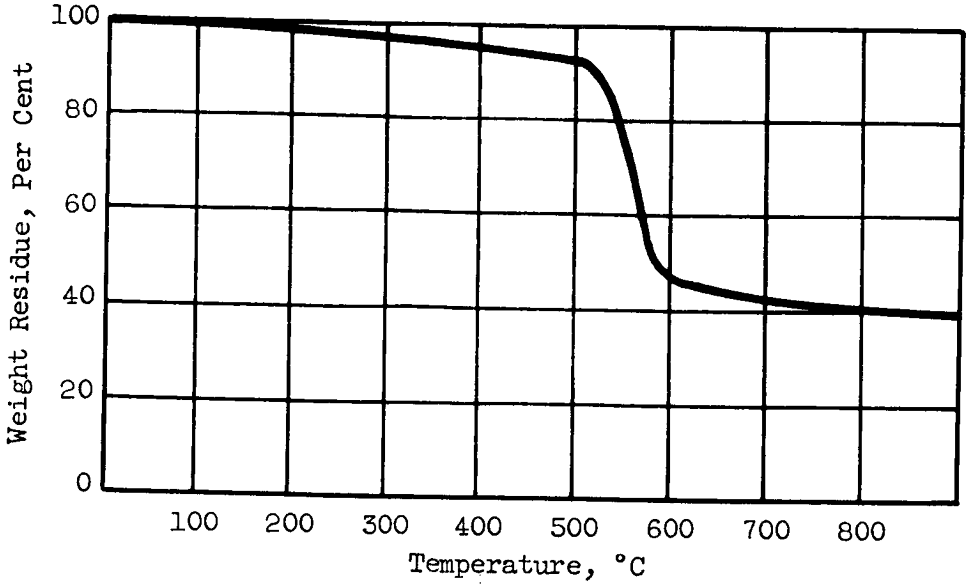


Fig. 90 - Thermogravimetric Analysis of a Polymer From Bis(p-dimethylhydroxysilylphenyl) Ether and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

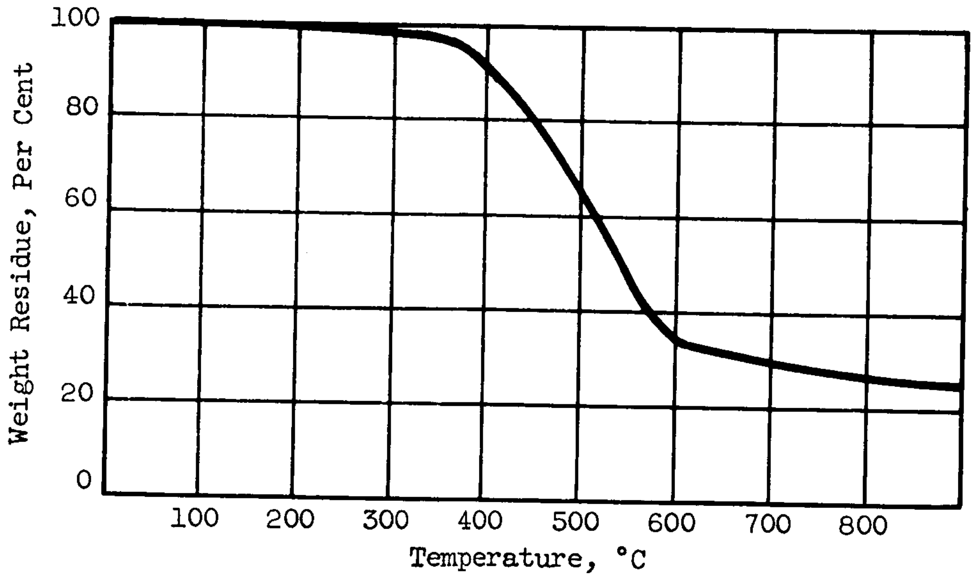


Fig. 91 - Thermogravimetric Analysis of a Polymer From p-Phenylenebis(methylphenylsilanol) and Hexamethylcyclotrisiloxane

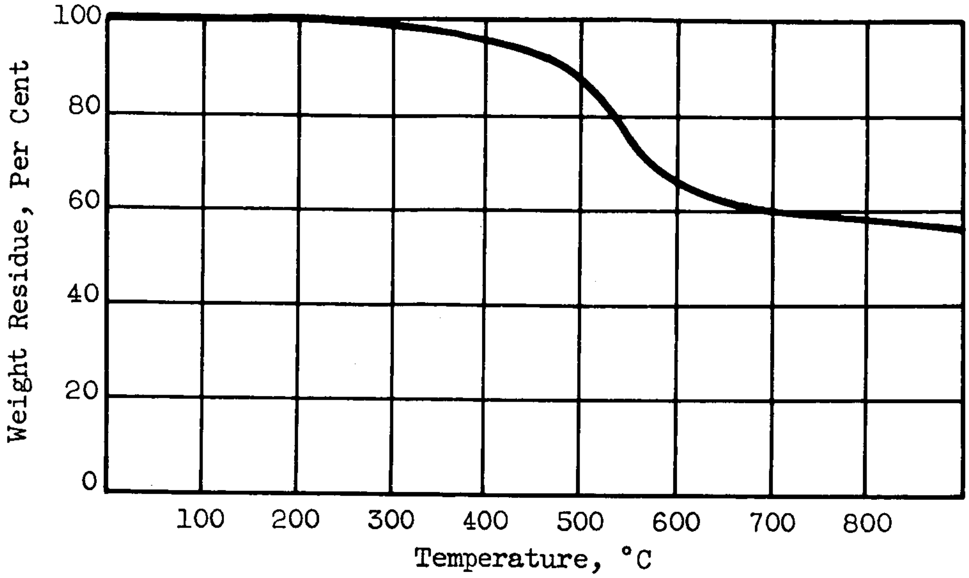


Fig. 92 - Thermogravimetric Analysis of a Polymer From m-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

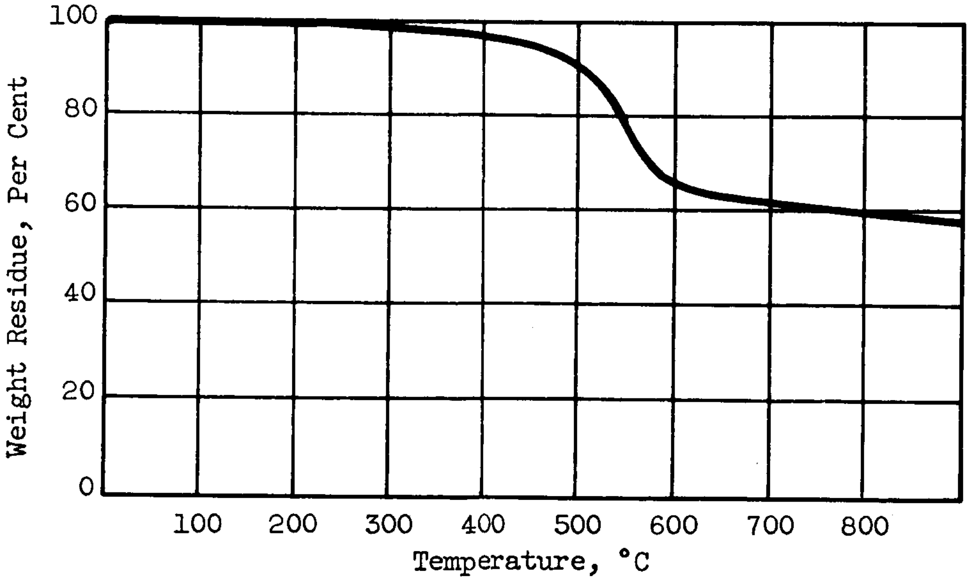


Fig. 93 - Thermogravimetric Analysis of a Polymer From p-Phenylenebis(diphenylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

6. Polymer from m-Phenylenebis(dimethylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane: The polymer obtained by heating 1.24 g. (0.0055 mole) of the diol, 1.18 g. (0.0053 mole) of the siloxazane, and 0.055 g. (0.00025 mole) of 1,3-bis(methylamino)-1,3-divinyltrimethyldisilazane from 120° to 160° over a period of 30 min. was a tacky gum that was not completely soluble in toluene. Thermogravimetric analysis of the polymer is reported in Fig. 94.

Anal. Calcd. for $C_{16}H_{34}O_4Si_5$: C, 44.60; H, 7.95; Si, 32.60. Found: C, 44.39; H, 7.78; Si, 32.90.

f. Polymers from arylenedisilanols and cyclosiloxazanes: A bulk polymerization procedure similar to the one described in paragraph IV.D.4.d. was used in the experiments reported in Table XVI. The following were the melting points of the silanediol monomers: Bis(dimethylhydroxysilylphenyl) ether, 103 - 104°; m-phenylenebis(dimethylsilanol), 79 - 80°; p-phenylenebis-(methylphenylsilanol) (mixture of isomers), 126 - 136°; m-phenylenebis(methylphenylsilanol), 138.5 - 139.5°; and p-phenylenebis(dimethylsilanol), 135.5 - 136.5°. Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, b.p. 95° (5 mm.), n_D^{30} 1.4324, m.p. 27 - 28°, g.l.c. purity, 100 per cent was used; nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane, b.p. 84 - 85° (8 mm.), n_D^{20} 1.4202, g.l.c. purity, 98.6 per cent, was used; and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, b.p. 59 - 60° (16 mm.), n_D^{20} 1.4100, g.l.c. purity 98.4 per cent was used.

g. Large-scale preparation of polymers: The following is an example of a typical experiment: To 33.4 g. (0.105 mole) of bis(p-dimethylhydroxysilylphenyl) ether in a 250-ml., two-necked flask was added 24.7 g. (0.110 mole) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane. The mixture was heated at 160° for 7.5 hr. The following inherent viscosities were observed at the specified time intervals (0.5 per cent solution in toluene at 30°); 2 hr., 0.35; 3 hr., 0.45; 4.5 hr., 0.73; 5.5 hr., 0.92; 6.5 hr., 0.97; and 7.5 hr., 1.05. After the polymer was heated at 54° under vacuum for 4.5 hr., the average inherent viscosity of several randomly selected samples was 1.12. The yield was 52 g. (95 per cent). The results of similar preparations are reported in Table XVII.

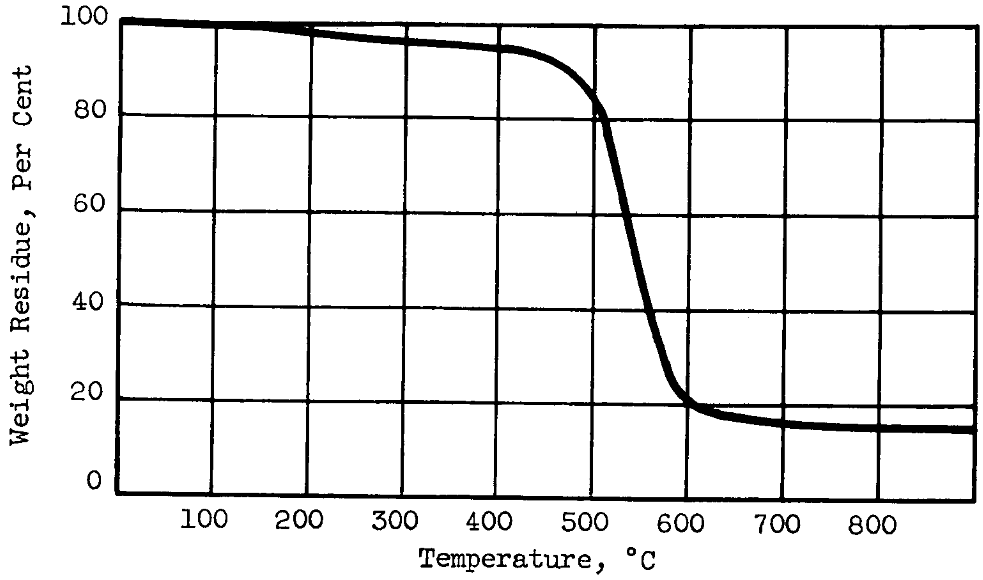


Fig. 94 - Thermogravimetric Analysis of a Polymer From m-Phenylenebis(dimethylsilanol) and Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

TABLE XVI

POLYMERIZATION OF SILANEDIOLS AND CYCLOSILOXAZANES

Run No.	Diol	Cyclosiloxazane	Polymerization Temp.(°C-hr.)	Inherent Viscosity (0.5% Solution in Toluene at 30°) at Time (hr.) 1	2	5	8	Polymer Description
1	Bis(p-dimethylhydroxysilylphenyl) ether (0.0100 mole)	Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane[a] (0.0051 mole, 2% excess)	160 - 8 hr.	0.36	0.61	2.45	2.48	Rubbery solid
2	Bis(p-dimethylhydroxysilylphenyl) ether (0.011 mole)	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (0.0105 mole, 5% excess)	180 - 8 hr.	0.47	0.67	1.30	2.11	Rubbery solid
3	Bis(p-dimethylhydroxysilylphenyl) ether (0.0100 mole)	Nonamethyl-1-aza-3,5,7,-trioxa-2,4,6,8-tetrasilacyclooctane (0.0105 mole, 5% excess)	160 - 8 hr.	0.09	1.34	2.42	3.09	Rubbery solid
4	m-Phenylenebis(dimethylsilanol) (0.0100 mole)	Heptamethyl-1-aza-3,5,-dioxa-2,4,6-trisilacyclohexane (0.0105 mole, 5% excess)	160 - 8 hr.	0.18	0.34	0.74	1.31	A gum
5	p-Phenylenebis(methylphenylsilanol) (isomer mixture) (0.0100 mole)	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (0.0105 mole, 5% excess)	160 - 8 hr.	0.10	0.12	0.14	0.16	Liquid
6	m-Phenylenebis(methylphenylsilanol) (0.0100 mole)	Heptamethyl-1-aza-3,4-dioxa-2,4,6-trisilacyclohexane (0.0105 mole, 5% excess)	160 - 8 hr.	1.61	1.29	1.68	1.61	A gum
7	p-Phenylenebis(dimethylsilanol) (0.0100 mole)	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (0.0105 mole, 5% excess)	160 - 8 hr.	0.30	0.82	2.66	2.39	A gum
8	p-Phenylenebis(dimethylsilanol) (0.0100 mole)	Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (0.00525 mole, 5% excess)	160 - 8 hr.	0.47	1.49	2.29	1.84	A gum
9	p-Phenylenebis(dimethylsilanol) (0.0100 mole)	Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane (0.0105 mole, 5% excess)	160 - 8 hr.	0.49	1.59	2.46	2.61	A gum

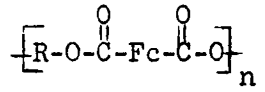
TABLE XVII

LARGE SCALE POLYMER PREPARATIONS

Run No.	Diol	Siloxazane	Comments	Inherent Viscosity (c = 0.5% in toluene at 30°)	Yield
1	Bis(*p*-dimethylhydroxysilylphenyl) ether (0.1 mole)	Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane (0.105 mole)	--	3.37	56.8 g. 95 %
2	*p*-Phenylenebis(dimethylsilanol) (0.12 mole)	Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane (0.126 mole)	--	2.21	57.9 g. 97 %
3	*p*-Phenylenebis(dimethylsilanol) (0.15 mole)	Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (0.084 mole)	--	1.19	50.9 g. 93 %
4	Bis(*p*-dimethylhydroxysilylphenyl) ether	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	Samples recovered from five preparations	2.66	60.1 g.
5	Bis(*p*-dimethylhydroxysilylphenyl) ether	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	Samples recovered from two preparations	3.30	11.9 g.

V. FERROCENE POLYESTERS

A part of the initial goals of the research was the synthesis of ferrocene polyesters.

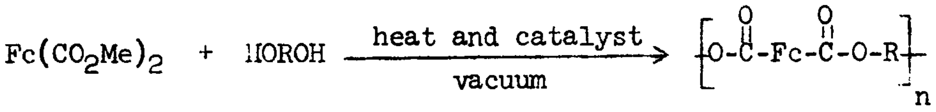


$$\left[R-O-\overset{O}{\overset{\|}{C}}-Fc-\overset{O}{\overset{\|}{C}}-O \right]_n$$

Fc = ferrocene

A. Discussion

Two approaches to the polymerization of ferrocene-containing monomers by transesterification 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.



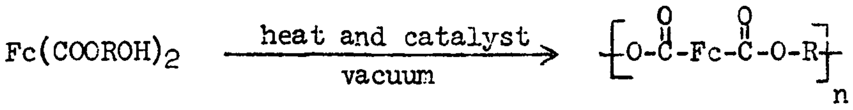
$$Fc(CO_2Me)_2 + HOROH \xrightarrow[\text{vacuum}]{\text{heat and catalyst}} \left[O-\overset{O}{\overset{\|}{C}}-Fc-\overset{O}{\overset{\|}{C}}-O-R \right]_n$$

The required monomer, 1,1'-dimethyl ferrocenedicarboxylate, was most satisfactorily prepared *via* the hypochlorite oxidation of 1,1'-diacetylferrocene[60,61] 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[62] 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. Temperatures of 150° were employed and catalysts 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 carefully 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.

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



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

The acid chloride, which was prepared according to the method described by Knoblock[61] 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.

$$\mathrm{Fc(COCl)_2} + \mathrm{HOCH_2CMe_2CH_2OH} \longrightarrow \mathrm{Fc(COOCH_2CMe_2CH_2OH)_2}$$

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. 95) and the spectrum of the residue (Fig. 96).

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.

B. Experimental

1. Dimethyl 1,1'-ferrocenedicarboxylate (from the lithium intermediate): (Method: Reference 62)

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.

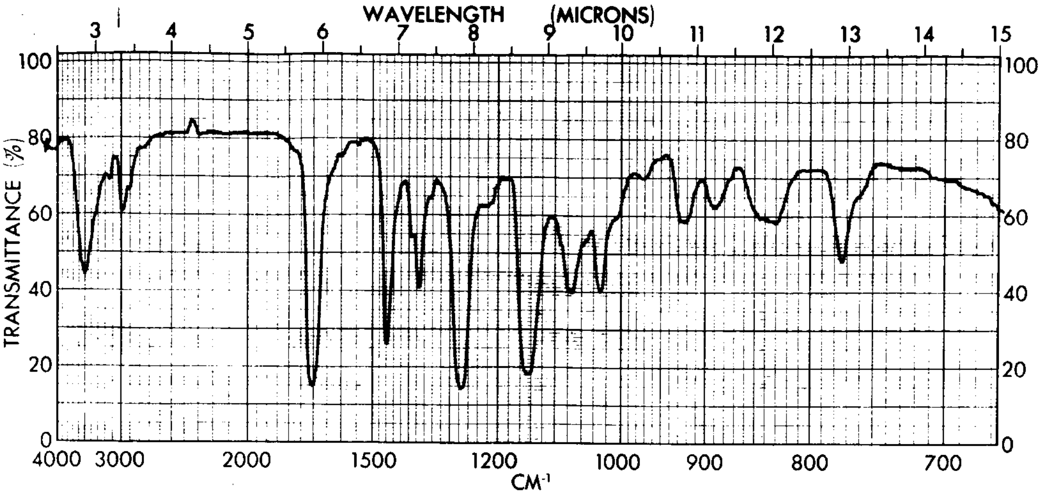


Fig. 95 - Infrared Spectrum of 1,1'-Bis(2-hydroxyethoxycarbonyl)ferrocene (Smear)

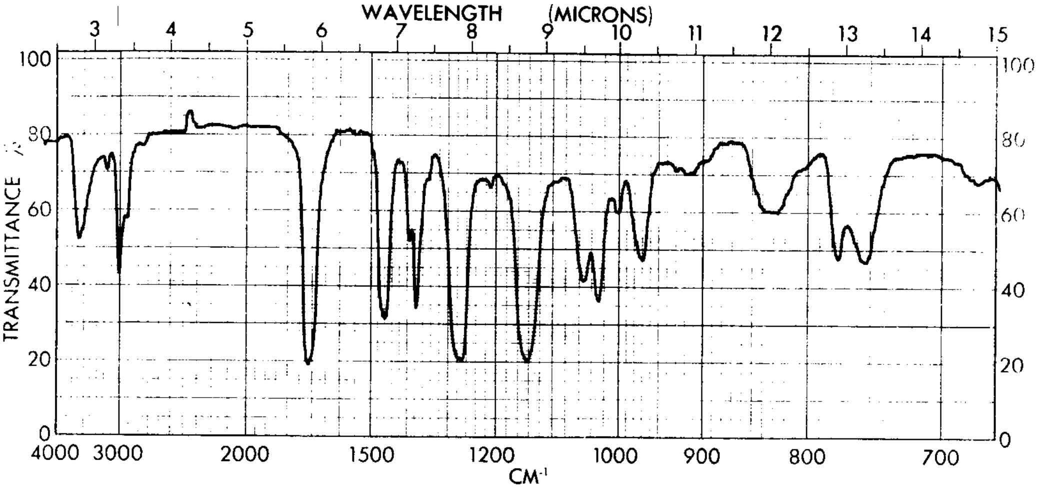


Fig. 96 - Infrared Spectrum of 1,1'-Bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene (Smear)

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 on 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°),[63] and 9.9 g. (16.4 per cent) of dimethyl 1,1'-ferrocenedicarboxylate, m.p. 110 - 115° (reported, 114 - 115°).[64] 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 60) 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. When the methylene chloride solution was washed with water to remove hydrogen chloride, dried with sodium sulfate, and distilled under vacuum, the residue afforded, after recrystallization, 21.2 g. (45 per cent) of 1,1'-diacetylferrocene, m.p. 125 - 128° (from cyclohexane), (reported, 127.0 - 127.5°).[60]

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 61) A mixture of 21.2 g. (0.079 mole) of 1,1'-diacetylferrocene and 500 ml. of commercial 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).

c. Dimethyl 1,1'-ferrocenedicarboxylate: 1,1'-Ferrocenedicarboxylic acid was esterified by the procedure described in paragraph V. B. 1. b. 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°).[64]

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. The 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. 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°).

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 mmole) 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°).

4. 1,1'-Bis(3-hydroxy-2,2,4,4-tetramethyl-1-cyclobutoxycarbonyl)ferrocene (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.

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°).

5. 1,1'-Ferrocenedicarbonyl Chloride (Method: Reference 61)

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°).[61]

6. 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. 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°.

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

7. 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 of crude 1,1'-bis(3-hydroxy-2,2-dimethyl-1-propoxycarbonyl)ferrocene, which was identified by its infrared spectrum.

8. Bis(2-hydroxyethyl)terephthalate (Method: Reference 51)

A mixture of 50 g. (0.258 mole) 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°).65/

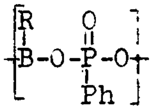
9. Poly(ethylene Terephthalate)

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.

10. 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.

VI. BORON CHELATE POLYMERS

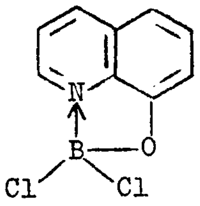
In considering candidate monomers for polymers containing the structural unit,  $\left[-\overset{\displaystyle R}{\overset{|}{B}}-O-\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-\right]$, chelated boron compounds were selected because they offered improved oxidative, 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.

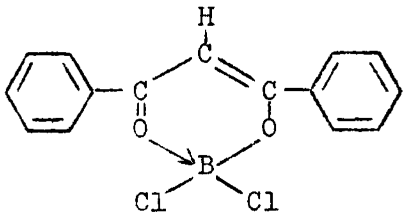
A. Discussion

Although chelate derivatives of boron were first reported by Dilthey in 1906,[66] little is known of their chemistry. Very recently, a method for preparing a difunctional monomer, dichloro(8-oxyquinoline)boron, was reported in the literature.[67] 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:

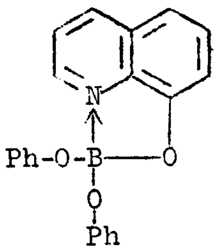


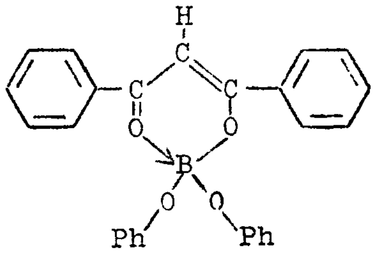


Although these compounds were difunctional monomers, condensation reactions with phenylphosphonic acid to produce a polymer would split out hydrogen chloride as a small molecule. The polymerization reaction would be considerably more useful if a less reactive compound were formed. Therefore, an attempt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

B. Experimental

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. 97) of the compound showed -OH absorption at 3400 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.

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) of the dibenzoylmethane was recovered.

5. Dichloro(8-oxyquinoline)boron (Method: Reference 67)

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°),67/ was obtained. The infrared spectrum is shown in Fig. 98.

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. 99.

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.

7. Triphenyl Borate (Method: Reference 68)

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 triphenyl borate which boiled at 158 - 159° (0.1 mm.) (reported, 157 - 158° (0.05 mm.)).68/

8. Diphenoxy(8-oxyquinoline)boron

By the procedure described in paragraph VI. B. 9., 2.56 g. (8.83 mmoles) of triphenyl borate 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

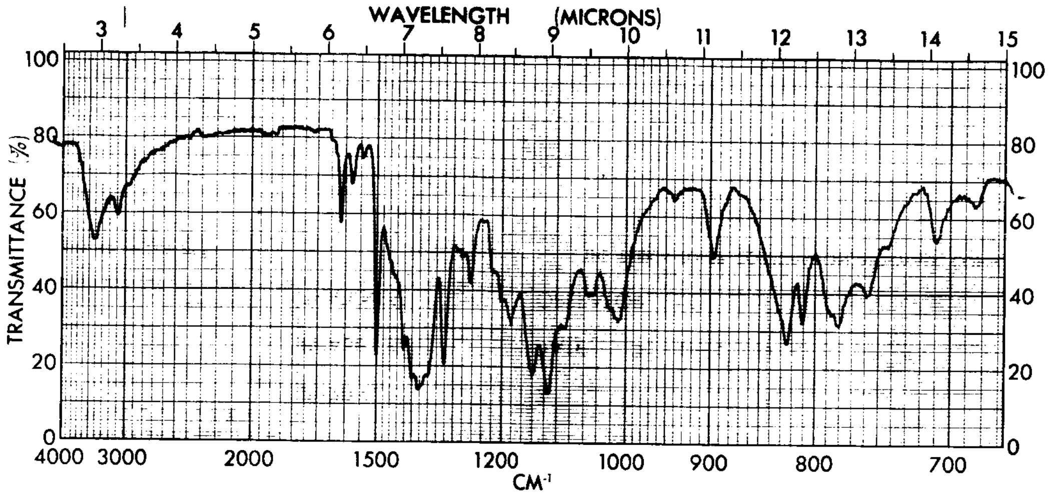


Fig. 97 - Infrared Spectrum of the Product from 8-Hydroxyquinoline and Isopropylborate (KBr)

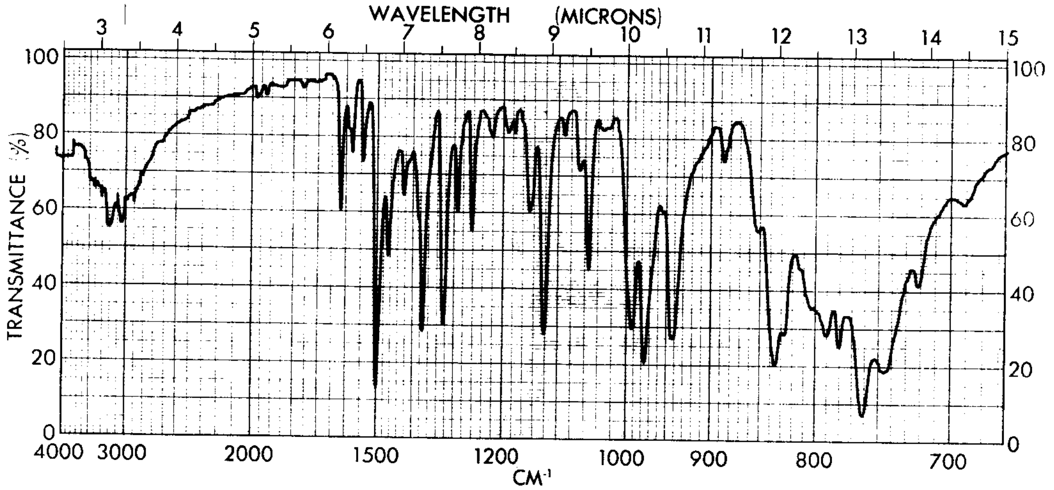


Fig. 98 - Infrared Spectrum of Dichloro(8-oxyquinoline)boron (KBr)

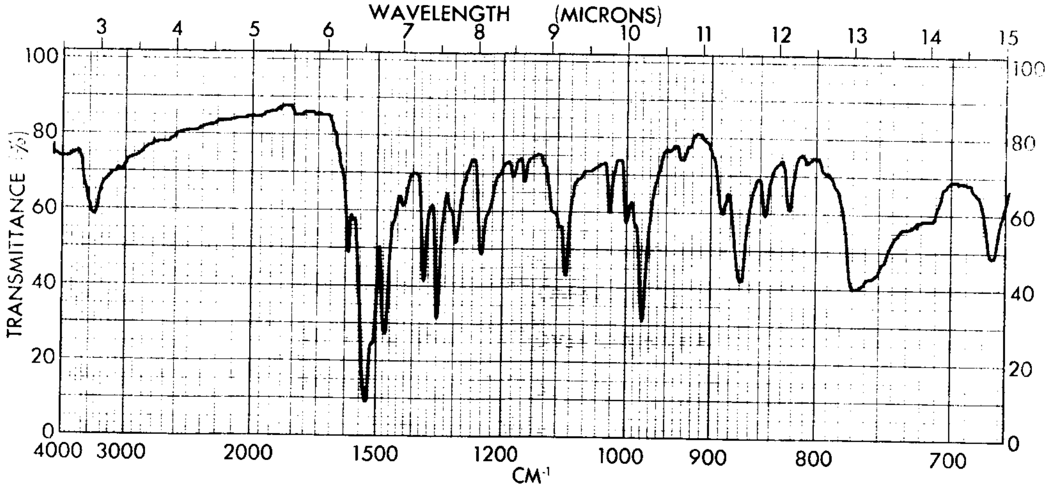


Fig. 99 - Infrared Spectrum of Dichloro(1-oxy-1-propene-1,3-diphenyl-3-one)boron (KBr)

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. 100.

Anal. 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.

9. Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (from Triphenyl Borate and Dibenzoylmethane)

Methylene chloride was distilled from phosphorus pentoxide into a flask containing 6.1 g. (0.021 mole) of triphenyl borate 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. 101.

Anal. 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.

10. 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)

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 1400 cm^{-1} and a medium intensity band at 950 cm^{-1}.

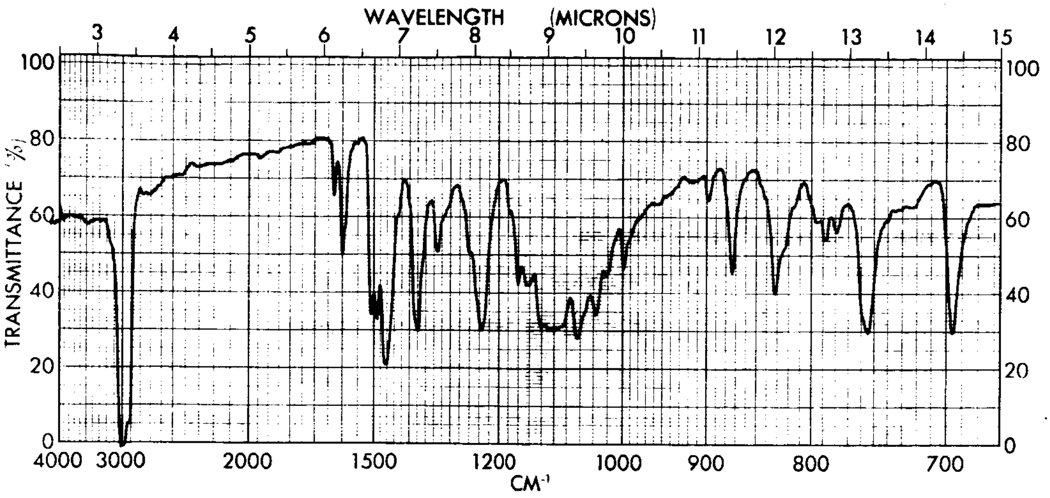


Fig. 100 - Infrared Spectrum of Diphenoxy(8-oxyquinoline)-boron (Nujol)

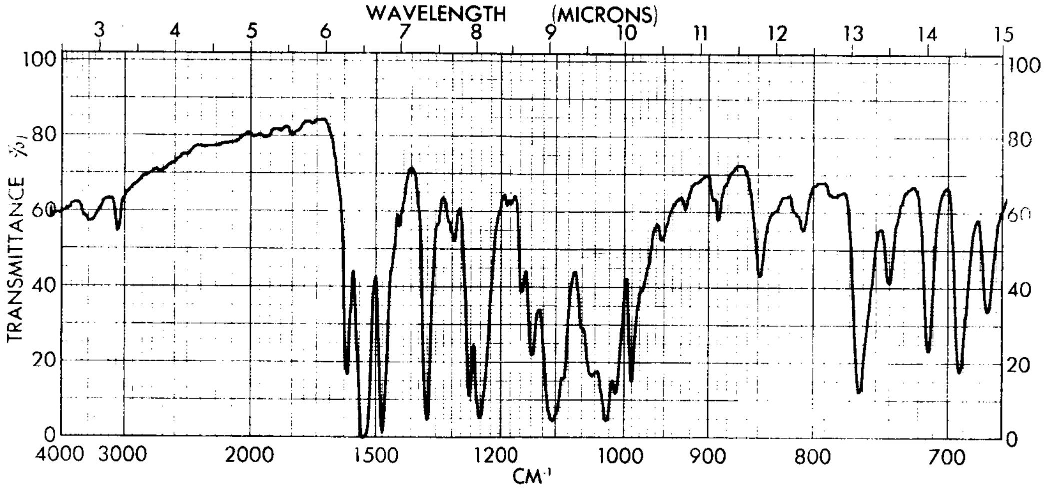


Fig. 101 - Infrared Spectrum of Diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron (KBr)

11. Phenylphosphonic Acid (Method: Reference 69)

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°),69/ was dried in a vacuum desiccator over Drierite for 24 hr. The yield was 33 g. (81 per cent).

12. 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.

13. Diphenylphosphonic Acid (Method: Reference 70)

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 183 - 186° after recrystallization from a petroleum ether-benzene mixture (reported, m.p. 190 - 192°).70/

14. Bis(diphenylphosphinico)(1-oxy-1-propene-1,3-diphenyl-3-one)boron (Attempted)

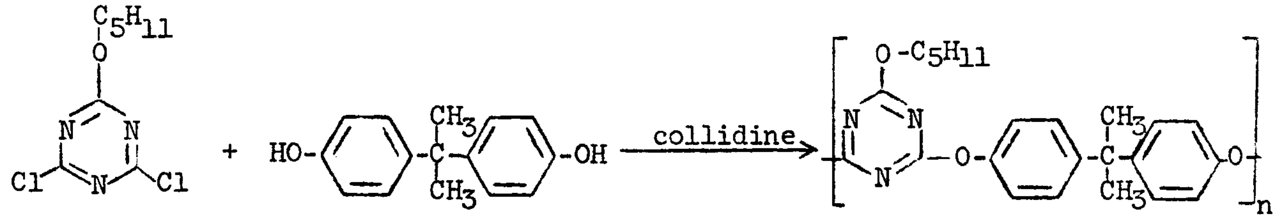
A solution of 1.0 g. (2.94 mmoles) of diphenoxy(1-oxy-1-propene-1,3-diphenyl-3-one)boron, 1.22 g. (5.88 mmoles) of diphenylphosphinic acid, and 30 ml. of chlorobenzene was refluxed in an atmosphere of nitrogen for 22 hr. When the solvent was distilled to 90° (0.1 mm.), no phenol could be detected in 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 2650 cm^{-1} and spurious peaks of low intensity at 1060 cm^{-1} and in the 700 - 800 cm^{-1} region.

15. 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.

VII. POLY(s-TRIAZINYL ETHERS)

Previous work in this laboratory has demonstrated that high molecular weight poly(s-triazinyl ethers) can be prepared by the condensation of alkoxydichloro-s-triazines with difunctional phenols in the presence of s-collidine.



These polymers were soluble in nonpolar solvents and could be solvent-cast into transparent, flexible films. However, difficulties were encountered in reproducing the polymerization reaction. The current work on this polymer system has been concerned chiefly with defining the variables that might be responsible for the irreproducibility.

A. Discussion

Less soluble, lower molecular weight polymers were obtained in most of the experiments. The degree of purity of the chloroform was investigated in several experiments and found to have little effect. Reactant concentration also did not seem to be important. An attempt at static interfacial polymerization in a manner recently reported to be successful with this system[71] failed to give a continuous film.

Since the s-triazine monomer and the Bisphenol A were known to be pure and of consistent quality, the possibility of variation in the nature of the s-collidine was considered. Since amines are known to be oxidatively sensitive, a sample of s-collidine was shaken in an open flask overnight and subsequently used in a polymerization reaction. An increase in molecular weight of the polymer was observed. The infrared spectrum of the polymer (Fig. 102) was consistent with the structure, and elemental analyses agreed well with the calculated values. A film could be applied with a chloroform solution of this polymer, but the film cracked and separated from the plate. It was apparent that higher-molecular-weight polymers were required.

Since none of the changes in procedure were effective in increasing the molecular weight of the polymer sufficiently for coating applications, the

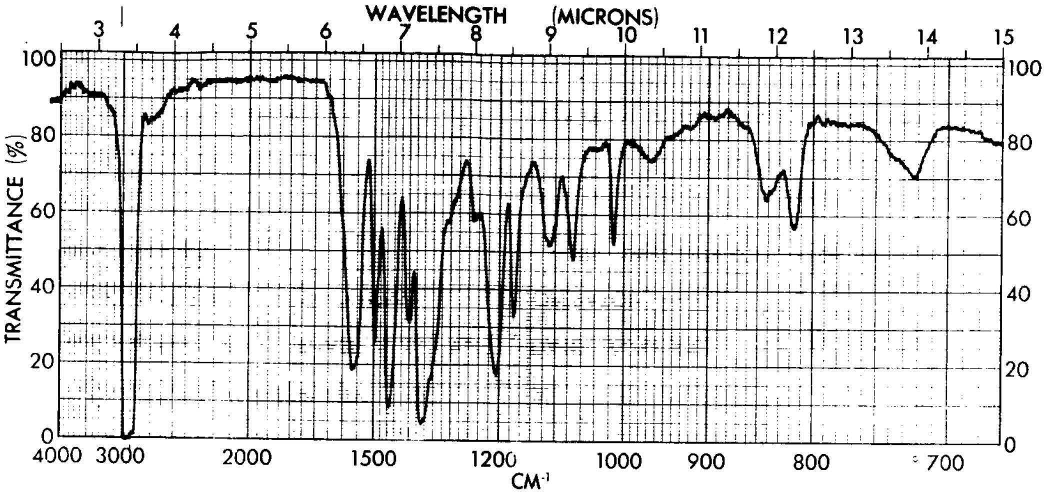


Fig. 102 - Infrared Spectrum of the Polymer From Bisphenol A 2,4-Dichloro-6-pentoxy-s-triazine

purity of the s-triazine monomer was reconsidered. Different fractions of carefully fractionated monomers were polymerized, but again no significant effects were observed.

Because work on other polymer systems appeared more promising, work on this system was discontinued.

B. Experimental

1. 2,4-Dichloro-6-pentoxy-s-triazine

Solutions of 61.7 g. (0.70 mole) of n-amyl alcohol in 80 ml. of ether and 84.6 g. (0.70 mole) of sym-collidine in 100 ml. of ether were added consecutively during 45 min. to a stirred solution of 129 g. (0.70 mole) of cyanuric chloride in 1,500 ml. of ether. The mixture was refluxed 2 hr., cooled, and the collidine hydrochloride was filtered off (99.6 g., 91 per cent). The filtrate was evaporated under reduced pressure, filtered to remove additional salts, and distilled through a 30 cm. vacuum-jacketed column packed with Berl saddles to give 126 g. (76 per cent) of 2,4-dichloro-6-pentoxy-s-triazine, b.p. 114 - 116° (2.0 mm.) (reported, 95 - 103° (0.5 mm.)).[72]

When a preparation of 2,4-dichloro-6-pentyloxy-s-triazine was redistilled on a spinning band column, the following fractions were collected: A, n_D^{20} 1.5062; B, n_D^{20} 1.5059; C, n_D^{20} 1.5059; and D, n_D^{20} 1.5058.

2. 2,4-Dichloro-6-(1,1,7-tri-H-Perfluoroheptyloxy)-s-triazine

Redistillation of 2,4-dichloro-6-(1,1,7-tri-H-perfluoroheptyloxy)-s-triazine on a spinning band column gave the following fractions: A, n_D^{20} 1.4139; B, n_D^{20} 1.4140; C, n_D^{20} 1.4140; and D, n_D^{20} 1.4142.

3. Polymers from 2,4-dichloro-6-pentoxy-s-triazine and Bisphenol A

To a suspension of 5.707 g. (0.0250 mole) of Bisphenol A in 50 ml. of water were added solutions of 5.903 g. (0.0250 mole) of 2,4-dichloro-6-pentoxy-s-triazine in 25 ml. of a chloroform, which had been treated with sulfuric acid and redistilled, and 6.665 g. (0.0550 mole) of freshly distilled s-collidine in 25 ml. of chloroform. After the mixture was stirred 10 min. in a Waring Blendor, the organic phase was separated, washed with 20 ml. of water, evaporated on a steam bath, and devolatilized at 80° in a vacuum oven. The polymer was broken up and washed with 2 per cent hydrochloric acid and water in the blender and redried. There was obtained 8.6 g. (87 per cent) of an olive powder, m.p. 288 - 295°, η_{inh} (0.5 per cent in sulfuric acid at 30°) = 0.10.

The results of similar experiments are described in Table XVIII. In experiments Nos. 1 and 4 unpurified reagent grade chloroform was used; in experiment No. 2, spectral grade chloroform was used. Experiment No. 3 was a repetition of the original experiment. Sodium hydroxide was substituted for s-collidine in experiment No. 5 and the s-collidine used in experiment 6 was air oxidized for 15 hr. in experiment 6.

TABLE XVIII

POLYMERIZATION OF 2,4-DICHLORO-6-PENTOXY-s-TRIAZINE WITH BISPHENOL A: I

Experiment No.	Organic Phase (ml. $CHCl_3$)	Aqueous Phase (ml.)	Yield (%)	M.P. (°C)	η_{inh} ($CHCl_3$ at 30°)
1	100	50	-	210 - 340	0.08[a]
2	100	50	92	88 - 91	-
3	50	50	97	205 - 215	0.28
4	50	50	102	152 - 170	0.18
5	50	50	110	132 - 142	0.12
6	50	50	80	165 - 350	0.46

---

a/ In sulfuric acid.

The polymer from experiment 6 could be cast from chloroform solution as a flexible film. The infrared spectrum of the polymer did not differ significantly from the spectrum of the lower molecular weight polymers obtained from freshly distilled s-collidine. DTA showed a decomposition exotherm commencing at about 260°.

Anal. Calcd. for $C_{23}H_{25}N_3O_3$: C, 70.57; H, 6.44; N, 10.73. Found C, 69.81; H, 6.32; N, 10.59.

The results in Table XIX were obtained in a second series of experiments.

TABLE XIX

POLYMERIZATION OF 2,4-DICHLORO-6-PENTOXY-s-TRIAZINE WITH BISPHENOL A: II

s-Triazine Fraction No.	Moles of Triazine	Moles of Cyanuric Chloride	Yield (%)	M.P. (°C)	η_{inh} ($CHCl_3$ at 30°)
B	0.025	-	102	180 - 275	0.70
C	0.025	-	95	180 - 270	0.66
D	0.025	-	87	185 - 270	0.36
C	0.025	-	103	150 - 160	0.28
C	0.02475	0.000167	102	150 - 160	0.35
C	0.0245	0.000333	101	308 - 335	a/

---

a/ The polymer was insoluble in chloroform.

4. Polymers from 2,4-Dichloro-6-(1,1,7-tri-H-perfluoroheptyloxy)-s-triazine and Bisphenol A

To a suspension of 5.7075 g. (0.025 mole) of Bisphenol A in 50 ml. of water were added 12.0025 g. (0.025 mole) of 2,4-dichloro-6-(1,1,7-tri-H-perfluoroheptyloxy)-s-triazine in 25 ml. of chloroform and 6.666 g. of redistilled s-collidine in 25 ml. of chloroform. After the mixture had been stirred 10 min. in a Waring Blendor, the organic layer was separated, washed with 20 ml. water, evaporated on a water bath, and devolatilized at 80° in a vacuum oven. The polymer was broken up and washed with 2 per cent hydrochloric acid and water in the Waring Blendor, filtered, and redried in the vacuum oven at 80°. The results of a series of similar experiments are reported in Table XX.

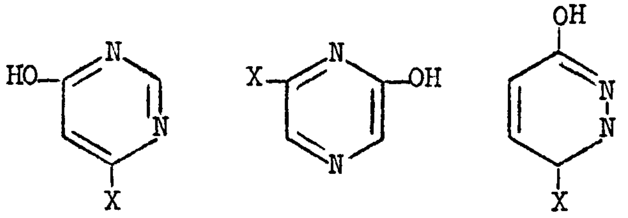
TABLE XX

POLYMERIZATION OF 2,4-DICHLORO-6-(1,1,7-TRI-H-PERFLUOROHEPTYLOXY)-s-TRIAZINE WITH BISPHENOL A

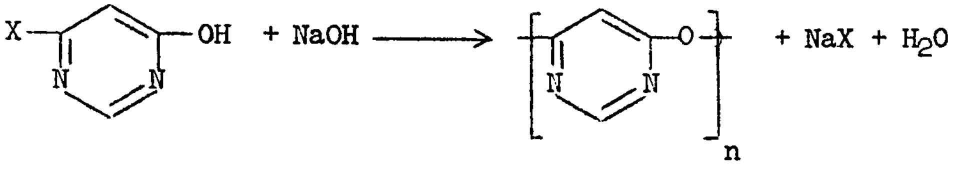
s-Triazine Fraction No.	Yield (%)	η_{inh} ($CHCl_3$ at 30°)
A	95	0.60
B	96	0.57
C	86	0.51
D	91	0.49

VIII. POLY(HETEROCYCLIC) ETHER

On the basis of an analogy with known methods of polymerizing p-bromophenols,[73] an attempt was made to prepare and polymerize the corresponding halogenated derivatives of hydroxypyrimidines, pyrazines, and pyridazines.

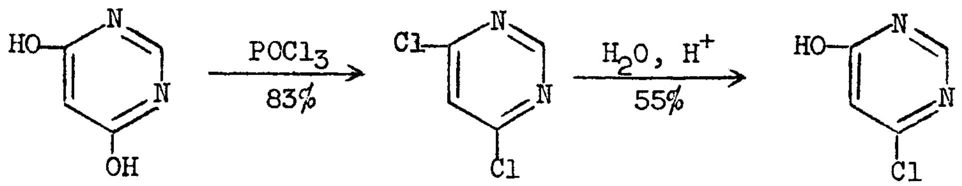


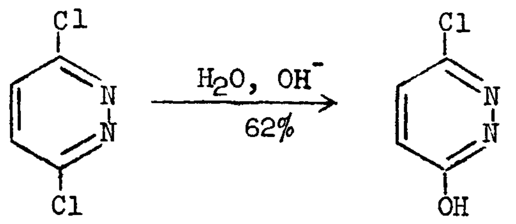
For example, a suitable pyrimidine derivative should be polymerized in the following manner:



A. Discussion

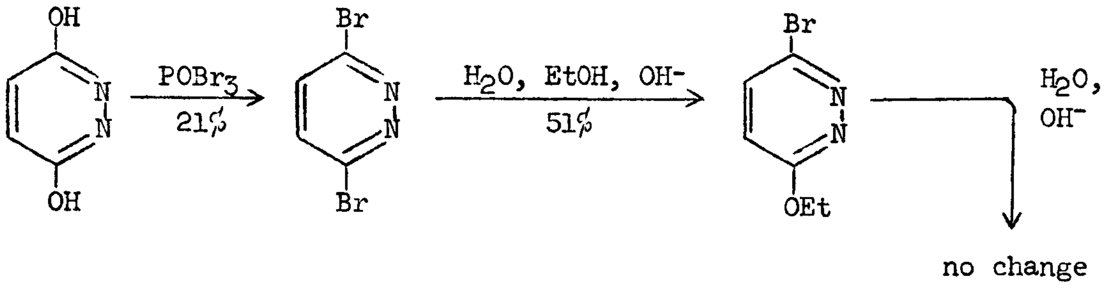
Chloropyrimidines and chloropyridazines were readily prepared according to the following established procedures:





Polymerization of the chlorine-containing monomers could not be effected when they were heated in a variety of solvents, including dimethylsulfoxide, diphenyl ether, dimethylformamide, and xylene in the presence of potassium hydroxide or in liquid tertiary amine bases. Attempts to prepare sodium salts which could be homopolymerized also failed. A low molecular weight polymer soluble in dimethylacetamide was obtained when either the chloropyridazine or the chloropyrimidine was heated with potassium hydroxide in nitrobenzene in the presence of copper. The polymer was a dark brown solid not melting below 400°.

The lack of reactivity of chlorine-containing derivatives prompted an attempt to prepare the corresponding bromine-containing monomers. However, hydrolysis of 3,6-dibromopyridazine in the presence of ethanol, which was used to provide homogeneity, gave an ethoxy derivative. Some effort was also completed on the synthesis of 2-hydroxy-6-bromopyridazine, but the work was discontinued because of the apparent lack of promise of the polymer system.



B. Experimental

1. 4,6-Dichloropyrimidine (Method: Reference 73)

A mixture of 23.4 g. (0.18 mole) of 4,6-dihydroxypyrimidine, 330 ml. of freshly distilled phosphorus oxychloride, and 12.2 ml. of freshly distilled N,N-dimethylaniline was refluxed 3 hr. The excess phosphorus oxychloride was removed under reduced pressure on a steam bath, and the syrupy residue was slowly poured over ice with stirring. The cold mixture was extracted with three 200-ml. portions of ether, and the combined ether extracts were washed with 100 ml. of 10 per cent sodium carbonate, dried over sodium sulfate, and filtered with charcoal. The filtrate was evaporated to give 22.0 g. (82 per cent) of yellow needles of 4,6-dichloropyrimidine, m.p. 66 - 68° (reported m.p. 68°).74/

2. 4-Chloro-6-hydroxypyrimidine (Method: Reference 75)

A mixture of 19.4 g. (0.13 mole) of 4,6-dichloropyrimidine and 270 ml. of 3N hydrochloric acid was heated and stirred at 100° for 1 hr. The clear, warm solution was adjusted to pH 9 with concentrated ammonia and filtered with charcoal. The filtrate was acidified to pH 2 - 3 with concentrated hydrochloric acid and cooled at 5° overnight. Filtration and drying in vacuum over KOH gave 5.4 g. of light yellow crystals of 4-chloro-6-hydroxy pyrimidine, m.p. 194 - 197°. The filtrate was evaporated to two-thirds volume and cooled to give an additional 0.8 g., m.p. 194 - 196° (reported, m.p. 192 - 193°).75/ The total yield was 37 per cent.

3. 4,6-Dibromopyrimidine (Attempted)

A mixture of 23.4 g. (0.18 mole) of 4,6-dihydroxypyrimidine, 375 g. of liquid phosphorus oxybromide, and 12 ml. of dimethylaniline was heated at 150° for 3 hr., during which time a heavy precipitate appeared. The excess phosphorus oxybromide was removed under reduced pressure and the solid residue added slowly to ice. The cold mixture was extracted with three 200-ml. portions of ether and the combined ether extracts were washed with 100 ml. of 10 per cent sodium carbonate, dried over sodium sulfate, and filtered with charcoal. The filtrate was evaporated to give 2.3 g. of a gummy solid, which was insoluble in hot petroleum ether. The infrared spectrum was not consistent with the structure of 4,6-dibromopyrimidine.

4. Sodium Salt of 4-Chloro-6-hydroxypyrimidine (Attempted)

A solution of 1.30 g. (0.010 mole) of 4-chloro-6-hydroxypyrimidine in 30 ml. of anhydrous methanol was added to a solution of 0.54 g. (0.010 mole) of sodium methoxide in 20 ml. of methanol, and the solution was allowed to stand 60 hr. The solution was filtered, evaporated to dryness, and the solid dried at 0.1 mm. to give 1.7 g. (112 per cent) of solid, which darkened at 230° and decomposed at 241 - 242°.

Anal. Calcd. for $C_4H_2ClN_2ONa$: C, 31.49; H, 1.32; N, 18.36. Found: C, 30.73; H, 2.15; N, 16.46.

5. Polymerization of 4-Chloro-6-Hydroxypyrimidine

When a mixture of 1.305 g. (0.010 mole) of 4-chloro-6-hydroxypyrimidine, 0.660 g. (0.010 mole) of 85 per cent potassium hydroxide, and 0.010 g.

of copper powder in 25 ml. of nitrobenzene was refluxed and stirred under nitrogen for 18 hr. and poured into water, a black precipitate formed in the organic layer. Filtration, washing with methanol, and drying gave 0.36 g. (38 per cent) of red-brown powder, which did not melt below 400°. The inherent viscosity (c = 0.5, 30° in dimethylacetamide) was 0.10.

When the experiment was repeated using dimethylformamide, no polymer was formed.

6. 6-Chloro-3-hydroxypyridazine (Method: Reference 76)

3,6-Dichloropyridazine (20.1 g., 0.135 mole) was added in portions during 15 min. to stirred 3N sodium hydroxide (200 ml.) at 95°. The brown solution was refluxed 30 min., adjusted to pH 3 with concentrated hydrochloric acid, and cooled to 5°. The precipitate was filtered off and dried in air to give 17.0 g. of crude solid, m.p. 134 - 136°. Recrystallization from 125 ml. of 10 per cent hydrochloric acid and drying in vacuum over KOH gave 11.0 g. (62 per cent) of opaque, off-white crystals of 6-chloro-3-hydroxypyridazine, m.p. 138 - 140° (reported, 144 - 145°76/).

7. 3,6-Dibromopyridazine (Method: Reference 77)

A mixture of 9.0 g. (0.08 mole) of maleic hydrazide and 130 ml. of melted phosphorus oxybromide was heated and stirred at 150° for 2 hr. Some solid sublimed, and the reaction mixture became stiff. The excess phosphorus oxybromide was removed under reduced pressure and the residue was slowly added to ice with stirring. The cold mixture was adjusted to pH 8 - 9 with concentrated ammonia and 10.7 g. of black precipitate was filtered off, m.p. 109 - 115°. Recrystallization from methanol gave 4.1 g. (21 per cent) of 3,6-dibromopyridazine, m.p. 115 - 116° (reported m.p. 115 - 116°77/).

8. 3-Bromo-6-hydroxypyridazine (Attempted)

A mixture of 4.0 g. (0.0176 mole) of 3,6-dibromopyridazine and 3.2 g. (0.08 mole) of sodium hydroxide in 20 ml. of water and 16 ml. of 95 per cent ethanol was heated and stirred at 95° for 1 hr. When the mixture was acidified with concentrated hydrochloric acid and cooled in ice water, 1.82 g. (51 per cent) of white platelets of 3-bromo-6-ethoxypyridazine was obtained, m.p. 77 - 78°. The infrared and n.m.r. spectra were consistent with the product being 3-bromo-6-ethoxypyridazine. Recrystallization of a portion of the product from petroleum ether (b.p. 60 - 90°) raised the m.p. to 79 - 80°.

Anal. Calcd. for $C_6H_7BrON_2$: C, 35.49; H, 3.48; N, 13.80. Found: C, 35.92, 36.04; H, 3.93, 3.91; N, 13.89, 13.92.

9. 3-Bromo-6-hydroxypyridazine (Attempted)

A mixture of 1.15 g. (0.0057 mole) of 3-bromo-6-ethoxypyridazine and 1.6 g. (0.040 mole) of sodium hydroxide in 15 ml. of water was heated and stirred at 100° for 3 hr. The mixture remained as two phases. After being cooled, the aqueous layer was decanted, and the solid, m.p. 78 - 80°, was identified as recovered 3-bromo-6-hydroxypyridazine. The solid was washed with water, dried, and heated at reflux for 1.5 hr. with 3 ml. of boron tribromide and 25 ml. of benzene. After the mixture was stored overnight, 20 ml. of water was added dropwise during 10 min. and a crude solid was filtered off, m.p. 142 - 148°. Recrystallization from 50 per cent ethanol-water gave 0.07 g. of a white solid, m.p. 169 - 172°. The solid was identified by infrared analysis as being mostly boric acid.

10. Sodium Salt of 3-Chloro-6-hydroxypyridazine (Attempted)

A solution of 0.54 g. (0.010 mole) of sodium methoxide in 10 ml. of anhydrous methanol was added to a solution of 1.30 g. (0.010 mole) of 3-chloro-6-hydroxypyridazine in 15 ml. of methanol and the resultant solution allowed to stand 60 hr. The solvent was removed and the solid dried at 0.1 mm. for 2 hr. to give 1.55 g. (102 per cent) of white powder, which darkened at 230° and decomposed at 248 - 255° with a black residue. When the crude product was recrystallized from 150 ml. of 99 per cent ethanol, 0.62 g. of white solid was obtained, which charred at 320°, but did not melt below 400°. It was soluble in water, burned with a white smoke, gave a negative silver nitrate test for chloride ion, and exhibited an inconclusive Beilstein test. Infrared spectra of the crude and recrystallized solids were not identical.

Anal. Calcd. for $C_4H_2ClN_2ONa$: C, 31.49; H, 1.32; N, 18.36. Found: C, 31.27; H, 1.75; N, 16.76.

When the experiment was repeated with 2.61 g. (0.020 mole) of 3-chloro-6-hydroxypyridazine and 1.08 g. (0.020 mole) of sodium methoxide, 3.2 g. (106 per cent) of crude solid was obtained, which darkened at 230° and decomposed at 242 - 243° with a black residue.

Anal. Calcd. for $C_4H_2ClN_2ONa$: C, 31.49; H, 1.32; N, 18.36. Found: C, 34.67; H, 1.62; N, 16.19.

11. Polymerization of 3-Chloro-6-hydroxypyridazine

A mixture of 1.305 g. (0.0100 mole) of 3-chloro-6-hydroxypyridazine and 0.660 g. (0.0100 mole) of 85 per cent potassium hydroxide in 50 ml. of xylene was stirred and refluxed under nitrogen for 18 hr. The mixture, which contained a heavy white precipitate was poured into 100 ml. of water. When the organic layer was separated, washed with 10 ml. of water, and evaporated to dryness, 0.2 g. of a waxy solid was obtained.

In a similar experiment, in which dimethylformamide was used as the solvent, a brown precipitate formed. The mixture was poured into 100 ml. of water, which dissolved the precipitate and gave a clear solution. The solvents were removed and the black solid residue was boiled with 100 ml. of toluene for 24 hr. Filtration and removal of solvents gave 0.6 g. of a gummy solid, which was soluble in water. An infrared spectrum of the solid was very similar to the spectrum of the starting material.

A mixture of 1.305 g. (0.010 mole) of 3-chloro-6-hydroxypyridazine and 0.660 g. (0.010 mole) of 85 per cent potassium hydroxide in 25 ml. of diphenyl ether was stirred and refluxed under nitrogen for 18 hr. The grey mixture was poured into 400 ml. of water, and the clear organic layer was poured into 300 ml. of methanol. There was no precipitate.

When a solution of 1.004 g. (0.0080 mole) of 3-chloro-6-hydroxypyridazine in 20 ml. of pyridine was refluxed for 18 hr. and poured into 400 ml. of water, there was no precipitate. About 0.6 g. (57 per cent) of starting material was recovered, m.p. 140 - 142°.

When the experiment was repeated with 20 ml. of triethylamine as solvent, about 0.7 g. (67 per cent) of starting material was recovered.

Approximately 10 mg. of potassium hydroxide was added to a solution of 1.305 g. (0.01 mole) of 3-chloro-6-hydroxypyridazine in 50 ml. of dimethyl sulfoxide and the mixture was refluxed for 18 hr. The dimethyl sulfoxide decomposed, and there was no precipitate when the solution was poured into 500 ml. of water.

Repetition of the experiment with 50 ml. of xylene as the solvent gave 0.80 g. (62 per cent) of starting material, m.p. 138 - 139°.

When a mixture of 1.305 g. (0.010 mole) of 3-chloro-6-hydroxypyridazine, 0.660 g. (0.010 mole) of 85 per cent potassium hydroxide, and 0.010 g. of copper powder in 25 ml. of nitrobenzene was refluxed and stirred under nitrogen for 18 hr. and poured into 400 ml. of water, a black precipitate formed in the organic layer. Filtration, washing with methanol, and drying at 90° at 0.1 mm. gave 0.62 g. (66 per cent) of brown solid, which did not melt below 400°. The solid gave a negative Beilstein test for halogen and burned slowly with no residue. The specific viscosity in dimethyl acetamide was 0.08 (c = 0.5).

12. Hydroxypyrazine (Method: Reference 78)

Sodium nitrite (19 g., 0.030 mole) was added in portions during 30 min. to 150 ml. of concentrated sulfuric acid, which was stirred at -5 - 0°. When the mixture was allowed to warm to room temperature, then heated to 65°, a clear solution formed. It was cooled to 0° and a cold solution of 23.8 g. (0.25 mole) of aminopyrazine in 100 ml. of sulfuric acid was added dropwise with stirring during 30 min. at 0 - 5°. The cold diazonium solution was then added dropwise to ice with stirring until the evolution of nitrogen ceased. The solution, still containing ice, was neutralized to pH 7 with a solution of 40 per cent sodium hydroxide at a temperature below 25°. The brown solution was stored overnight at 5°, and the heavy precipitate of sodium sulfate was filtered off and washed with cold water. The combined filtrate and washings were evaporated to a thick slurry and then air dried. The solid was extracted in a Soxhlet extractor for two days with 2 liters of acetone. Repeated evaporation of the acetone extract gave: A, 2.4 g., which charred above 230°; B, 1.7 g., m.p. 180 - 182°, and C, 8 g., m.p. 148 - 152°. Crops B and C were combined and recrystallized from 100 ml. of 95 per cent ethanol containing charcoal to give 4.2 g. (18 per cent) of white crystals of hydroxypyrazine, m.p. 184 - 186° (reported, m.p. 187 - 188°).[78]

A mixture of 0.95 g. (0.010 mole) of aminopyrazine and 15 ml. of 20 per cent sodium hydroxide was heated in a 20 ml. stainless steel Parr bomb at 170° for 20 hr.[79] After the bomb was cooled, the contents were rinsed out with an equal volume of water, and the clear solution was neutralized with concentrated hydrochloric acid. When the solution was evaporated to dryness and the solid extracted with 500 ml. of benzene for two days in a Soxhlet extractor, 0.61 g. (64 per cent) of hydroxypyrazine was obtained, m.p. 185 - 187°.

IX. ULTRAVIOLET-VACUUM FILM STUDIES

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

A. Apparatus

Specimen total reflectance and diffuse reflectance curves from 0.24 - 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. 103, 104, and 105, 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.

B. Irradiation - Preliminary Experiments

Ceramic-coated metal plates (supplied by NASA) were coated by a Paasch VL airbrush with materials shown in Table XXI. The experimental coatings were cured in an air oven at 145° for 48 hr. The plates were irradiated for 48 hr., at a pressure of 2×10^{-5} - 9.2×10^{-6} mm. Hg. Weight losses of the films during irradiation are shown in Table XXI.

Fig. 103 - Solar Simulator System

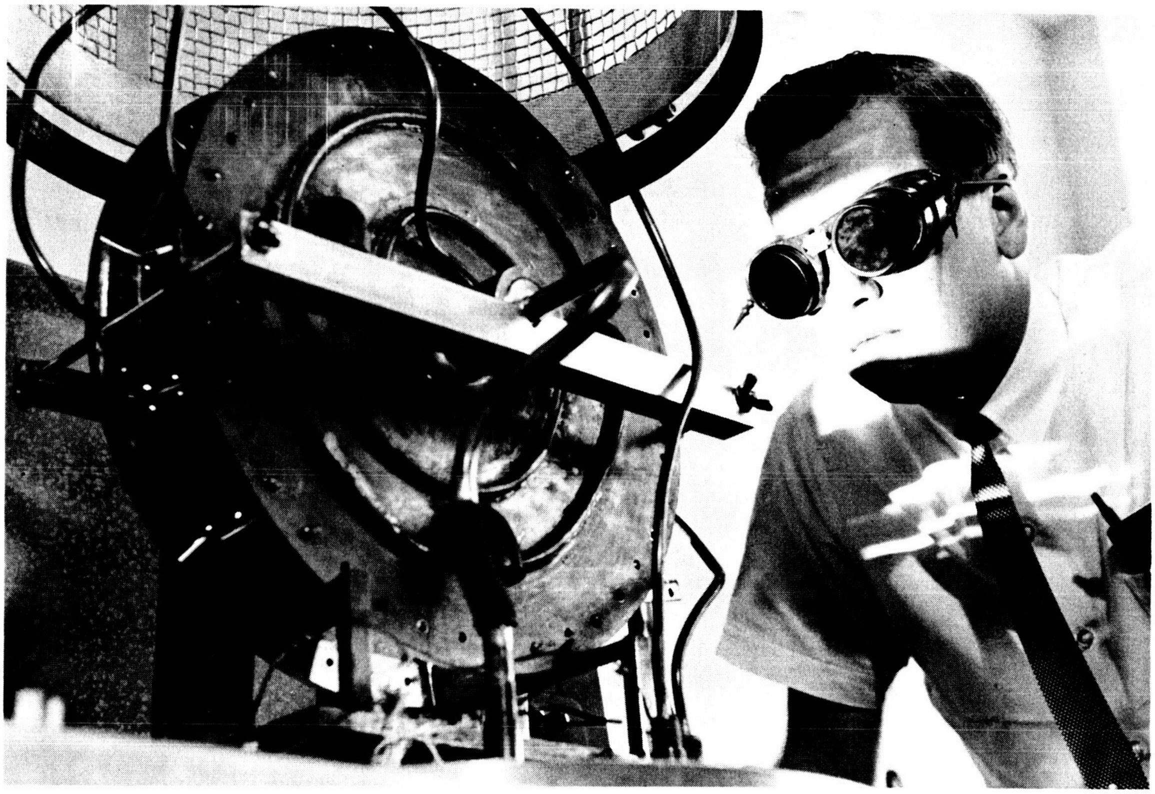


Fig. 104 - Lamp During Operation

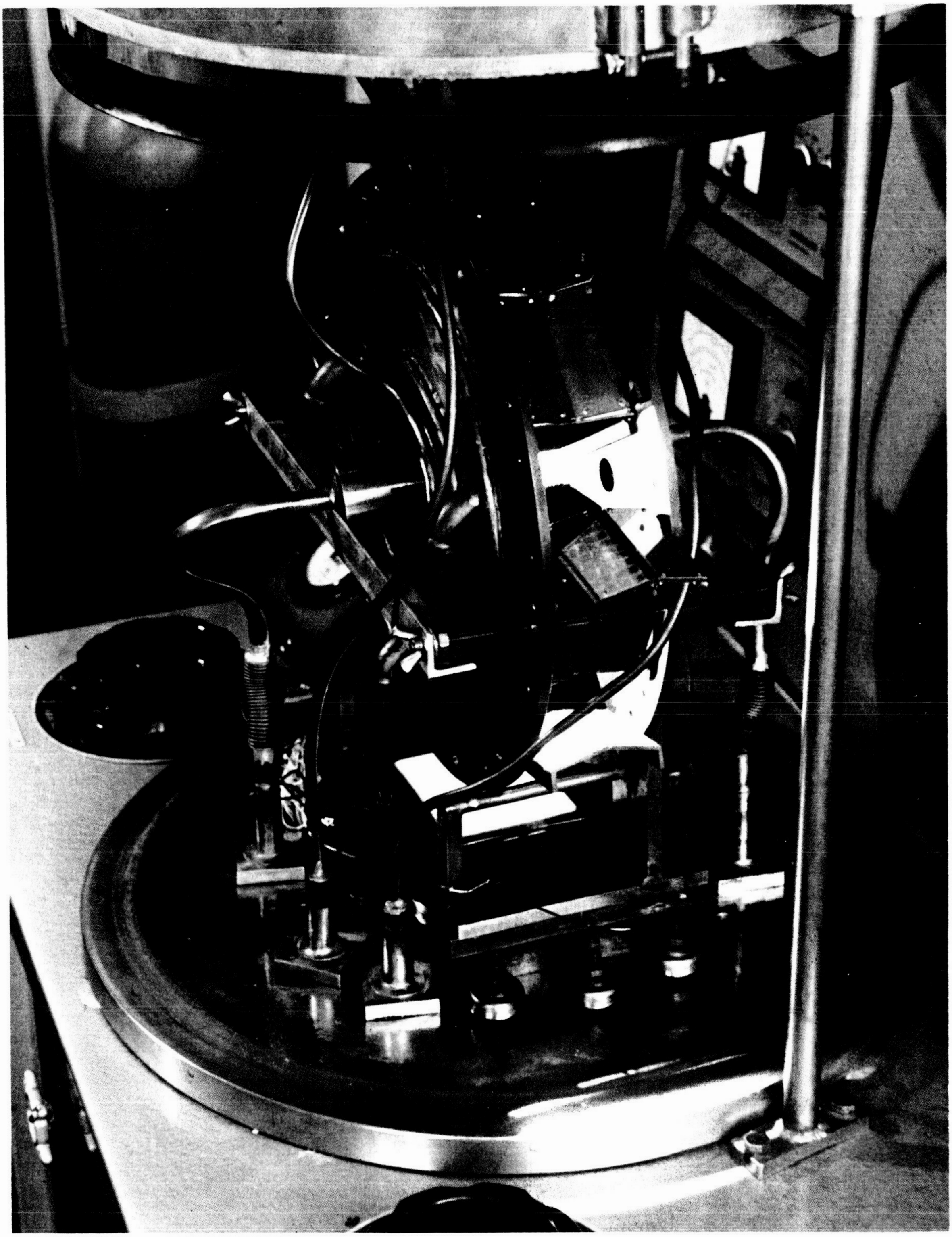


Fig. 105 - Irradiation Chamber

TABLE XXI

ULTRAVIOLET IRRADIATION TEST SPECIMENS

Plate	Coating	Thickness (mils)	Initial Wt. (g.)	Final Wt. (g.)	Wt. Loss (%)
Group I					
1	LTV-602	1.7	0.1064	0.1010	5.4
2	LTV-602	1.9	0.1212	0.1117	8.5
3	Experimental Polymer A[a]	2.0	0.1262	0.1262	0.0
4	S-13	6.7	0.6836	0.6776	0.89
5	S-13	6.2	0.6334	0.6275	0.94
Group II					
1	DC-808	5.9	0.3664	0.3657	0.192
2	Experimental Polymer B[a]	5.4	0.2722	0.2718	0.110
3	LTV-602	4.7	0.2589	0.2504	3.28
4	Experimental Polymer C[b]	4.1	0.1874	0.1833	2.19
5	Experimental Polymer D[b]	8.5	0.5412	0.5380	0.592

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

b/ A polymer prepared from p-phenylenebis(diphenylsilanol) and tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

In Group I plates were initially clear and shiny, but after irradiation Group I plates 1, 2, and 3 were light brown in color. No change in appearance was observed in plates 4 and 5. Plate 3 was the only one that did not lose weight during exposure. Failure of the cooling water supply during the experiments allowed the Group II samples to overheat; consequently, several of the experimental coatings flowed. After irradiation Group II plate 3 was slightly yellow and shiny, plate 1 was yellow and shiny, and plates 2, 4, and 5 were yellow, dull, and very wrinkled. The total per cent reflectance of the plates in both groups in the 400 - 700 mμ region is shown in Table XXII.

TABLE XXII

ULTRAVIOLET RADIATION (400-700 mμ)

Group I

Wavelength (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

Group II

Wavelength (mμ)	Total Reflectance (%)									
	Plate 1		Plate 2		Plate 3		Plate 4		Plate 5	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
400	64.0	13.0	78.0	7.0	75.5	43.0	77.5	8.0	61.5	7.0
425	78.0	20.0	87.5	12.0	86.0	58.0	87.5	12.0	74.0	10.0
450	80.0	29.0	90.5	18.0	89.0	63.0	90.5	18.0	77.5	15.0
475	84.0	40.0	92.5	26.0	90.5	68.0	92.5	27.0	81.0	22.0
500	87.5	51.0	93.5	35.0	91.5	74.0	94.5	35.0	85.0	31.0
550	91.5	70.0	95.0	55.0	94.5	83.0	96.5	55.0	88.5	50.0
600	95.5	85.0	99.0	75.0	96.5	89.0	99.0	74.0	94.0	69.0
650	98.0	91.0	100.0	85.0	98.0	94.0	100.0	87.0	97.0	83.0
700	98.0	94.0	100.0	91.0	98.0	94.0	100.0	90.0	98.0	88.0

C. Irradiation Experiments On Unpigmented Experimental Polymers

The preparation and properties of the polymers used in these irradiation experiments are reported in paragraphs IV.D.4.e. The coatings of experimental panels 2, 3, 4, 5, and 6 were applied with an airbrush using toluene solutions. Polymer 1 was too viscous even in a dilute solution for an airbrush application; so it was poured onto plate 1, leaving a rough film. Coatings 1 and 5 were cured by heating at 150° for 72 hr., then 48 hr. in a 200° forced-air oven. Coating 3 was cured after heating at 150° for 24 hr. and 72 hr. in a 200° forced-air oven. Coating 4 cured at 150° for 48 hr. Coatings 2 and 6 containing about 1 per cent *t*-butyl peroxybenzoate were cured at 135° for 65 hr.

Initially, coatings 2, 3, 5, and 6 were clear and smooth, coating 1 was clear and rough, coating 4 was slightly yellow, and all were elastic. After irradiation all plates were yellow to light-brown in color; plates 1, 2, and 4 were elastic and less colored; and plates 3, 4, and 6 were harder and darker. The weight loss of the plates after irradiation is shown in Table XXIII. The total per cent reflectance of the plates before and after irradiation in the 400 - 700 mμ region is shown in Table XXIV.

TABLE XXIII

WEIGHT LOSS OF IRRADIATED FILMS

Plate	Thickness (mils)	Initial Weight (g.)	Final Weight (g.)	Weight Loss (%)
1[a]	6.1	0.3997	0.3994	0.08
2[a]	6.0	0.3243	0.3242	0.03
3[b]	2.1	0.1237	0.1237	0.00
4[c]	4.7	0.3119	0.3118	0.02
5[d]	7.9	0.4675	0.4675	0.00
6[e]	3.7	0.1849	0.1849	0.00

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a/ Polymer from bis(*p*-dimethylsilyl)phenyl ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

b/ Polymer from hexamethylcyclotrisiloxane and *p*-phenylenebis(methylphenylsilanol).

c/ Polymer from *m*-phenylenebis(diphenylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

d/ Polymer from *p*-phenylenebis(diphenylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

e/ Polymer from *m*-phenylenebis(dimethylsilanol) and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane.

TABLE XXIV

ULTRAVIOLET-VACUUM IRRADIATION (400 - 700 mμ)

Wavelength (mμ)	Total Reflectance (%)											
	Plate 1		Plate 2		Plate 3		Plate 4		Plate 5		Plate 6	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
400	72.0	20.0	46.5	18.0	56.5	14.0	70.0	13.0	74.5	13.5	62.0	7.0
425	84.5	28.5	62.0	26.0	77.0	20.0	83.0	20.0	86.0	19.0	75.5	11.0
450	87.0	35.5	69.0	32.5	81.5	26.5	86.0	26.5	89.0	26.0	80.0	17.0
475	89.5	42.5	75.0	40.0	85.0	33.0	88.5	36.0	91.0	35.0	84.0	24.0
500	91.5	49.0	80.5	47.0	87.5	41.0	91.0	43.0	92.5	44.0	87.5	52.5
550	93.0	60.5	87.5	59.0	91.5	56.0	93.5	60.0	94.0	60.0	91.5	49.5
600	95.5	70.0	93.0	69.5	94.0	68.0	96.0	73.5	96.0	73.5	95.5	64.5
650	95.0	75.5	94.0	75.0	94.0	74.5	96.0	80.5	96.0	80.0	95.5	72.0
700	93.5	76.0	93.5	76.5	93.5	76.0	95.0	81.5	95.0	81.5	94.5	75.5

D. Preparation of Coated Specimens for Irradiation Studies at NASA-Huntsville Laboratories

1. Coating Studies

a. Milling procedure: Zinc oxide (New Jersey Zinc SP-500) was milled into polymer solution by the following procedure: A 4-dram glass vial half-filled with steel shot was charged with 0.5 g. of RTV-602 (formerly LTV-602 potting compound), 1.2 g. of zinc oxide (SP-500), and 5 ml. of toluene. The vial was capped and placed horizontally on a slow variable speed stirrer. The mill, operating at 90 - 120 rpm, gave good pigment dispersion after 1.5 - 5 hr. of grinding time; however, if the grinding was continued for 11 hr. or more, yellowing of the zinc oxide occurred. Grinding time was generally 1.5 - 2 hr.

In another milling procedure, a 100-ml. stainless steel cylinder was similarly charged and placed on a mechanical paint shaker. After 5 min., the mixture became grey (iron contamination) and the zinc oxide was not completely dispersed.

Experimental poly(arylenesiloxanes), with specific viscosities from 1.38 to 2.45, were successfully milled by the glass-vial procedure. It was necessary to adjust the viscosity of the polymer solution by toluene dilution for higher molecular weight polymers. Generally a 5 per cent concentration (0.5 g. of polymer in 10 ml. of toluene) was adequate for good pigment dispersion.

b. Spraying procedure: The application of S-13 paint (New Jersey Zinc SP-500 zinc oxide-240, General Electric RTV-602 silicone-100, and toluene-170 in parts by weight) to panels was accomplished by spraying with a Paaschs VL airbrush at 30 psig nitrogen pressure. Smooth, white coatings were obtained.

Pigmented experimental poly(arylenesiloxanes) were also successfully sprayed on panels; however, the much higher viscosity of the polymer solutions required additional dilutions in order to obtain a smooth coating. Polymers with an inherent viscosity of 1.39 to 2.5 could be sprayed at about a 5 per cent concentration in toluene with a pigment (zinc oxide) to polymer ratio of 120:100 parts by weight. Higher ratios of pigment to polymer (240:100) gave a crazed coating. Polymers with inherent viscosities higher than 2.5 became difficult to spray at a 5 per cent concentration in toluene. A 2.5 per cent solution of polymer (inherent viscosity 3.10) emerged from the spray gun in a stream rather than a spray, and smooth coatings could not be obtained.

c. Curing studies: Cured coatings of unpigmented poly(arylenesiloxanes) were obtained by adding 1 per cent stannous octoate to the polymer solution prior to spraying. A heating cycle of 1 hr. at 100 - 130° gave smooth, clean, tack-free, rubbery coatings.

Pigmented coatings were cured by adding 1 per cent stannous octoate and 2 per cent tert-butylperoxybenzoate prior to spraying. The plates were heated at 135° for 1 hr. to obtain white, rubbery, tack-free coatings. A cure could not be obtained with 1 per cent stannous octoate alone, or with 1 or 2 per cent of the peroxide alone, or with 1 per cent each of stannous octoate and the peroxide.

In an attempt to crosslink a coating by air oxidation, an experimental poly(arylenesiloxane), inherent viscosity 1.48, was applied to a panel and placed in a 200° oven with a slow air flow for 72 hr. The coating was not cured.

In a study of the use of peroxides, panels coated with poly(arylenesiloxanes) and containing 1 - 2 per cent tert-butylperoxybenzoate, di-tert-butylperoxide or benzoyl peroxide were heated at 135° for 2 hr. Only the panel containing benzoyl peroxide was partially cured. A panel containing di-tert-butylperoxide was partially cured after heating at 170° for 2 hr.

When driers were examined, only coated panels containing 1 per cent stannous octoate were cured after heating at 100 - 130° for 1 hr. Lead naphthoate and dibutyltin dilaurate were ineffective under similar conditions.

2. Coated Test Specimens

At the request of NASA, the following plates were coated and forwarded to the George C. Marshall Space Flight Center, Huntsville, Alabama:

1. Ten 2 x 2-in. ceramic-coated plates coated with the poly(arylenesiloxane) prepared from bis(p-dimethylhydroxysilylphenyl) ether and heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane only.

2. Ten 2 x 2-in. ceramic-coated plates coated with the poly(arylenesiloxane) pigmented with zinc oxide.

3. Ten aluminum disks, 15/16 in. in diameter, coated with the polymer only (from 6061-T6 aluminum, 1/16 in. thick).

4. Ten aluminum disks, 15/16 in. in diameter, coated with zinc oxide filled polymer.

For coating the ceramic-coated plates with polymer only, the following procedure was used: A stock solution containing 5 per cent polymer was prepared by dissolving the five polymer samples (10.0 g.) with a mean inherent viscosity of 1.63 in 200 ml. of toluene. All plates and disks were washed with Alconox solution prior to spraying. A 10-ml. aliquot (0.5 g. of polymer) of the stock solution was further diluted with 15 ml. of toluene and 5 ml. of xylene. (The polymer solution was too viscous to spray without the excess solvent.) One per cent stannous octoate was added and mixed in the polymer solution. A plate was sprayed with an airbrush and cured at 100° for 1 hr. The weight of the coating was obtained by weighing the plates before and after filming. The thickness of the coating was determined similarly with a Starrett No. 1010 dial indicator gage. The data for 10 plates are shown in Table XXV.

TABLE XXV

UNPIGMENTED COATED PLATES

Plate No.	Weight of Film and Plate (g.)	Weight of Film (g.)	Thickness of Plate and Film (mils)	Thickness of Film (mils)
1	17.0791	0.2049	43.2	3.5
2	16.8636	0.2202	41.9	3.4
3	16.7609	0.2506	42.3	3.8
4	17.1895	0.1845	43.4	2.8
5	17.1315	0.2132	42.5	2.9
6	17.0350	0.2075	42.1	3.1
7	17.4159	0.2085	44.1	3.4
8	16.7707	0.1925	40.9	3.2
9	17.4106	0.1911	42.2	2.8
10	16.7725	0.2112	41.3	3.3

The coatings of the ceramic-coated plates with zinc oxide-filled polymer were prepared as follows: Five grams of a poly(arylenesiloxane), inherent viscosity 1.08, was dissolved in 100 ml. of toluene. A 10-ml. aliquot (0.5 g. of polymer) was milled with 0.6 g. of SP-500 zinc oxide for 1 hr. The mix was filtered through a wire screen, and the mill was washed with about 3 ml. of toluene. The washings, 1 per cent stannous octoate, and 2 per cent *t*-butylperoxybenzoate were added to the mixture. The plates were sprayed with an airbrush and cured at 135° for 1 hr. The data for 10 plates are shown in Table XXVI.

TABLE XXVI

PIGMENTED COATED PLATES

Plate No.	Weight of Film and Plate (g.)	Weight of Film (g.)	Thickness of Plate and Film (mils)	Thickness of Film (mils)
11	17.1135	0.3322	41.4	3.1
12	17.0114	0.3436	40.9	3.0
13	17.0295	0.3562	42.2	3.1
14	17.4280	0.4117	43.2	3.9
15	16.7167	0.3955	40.5	3.9
16	16.9574	0.4137	42.2	3.7
17	16.9915	0.3574	41.2	3.4
18	16.6620	0.3566	39.9	3.3
19	17.0538	0.3126	42.9	3.2
20	16.9686	0.3694	41.9	3.2

Twenty disks of 6061-T6 aluminum, 1/16 in. thick and 15/16 in. diameter were coated similarly: 10 disks with 1.0 g. of unpigmented polymer in 50 ml. of toluene and 10 disks with 1.0 of polymer, 1.2 g. of zinc oxide, and 20 ml. of toluene. The data for 10 unpigmented disks are shown in Table XXVII, and the data for 10 pigmented disks are shown in Table XXVIII.

TABLE XXVII

UNPIGMENTED COATED DISKS

Disk No.	Weight of Film and Disk (g.)	Weight of Film (g.)	Thickness of Film and Disk (mils)	Thickness of Film (mils)
1	1.9952	0.0421	70.5	5.4
2	2.0003	0.0338	69.7	4.2
3	2.0175	0.0356	69.4	3.8
4	1.9956	0.0366	69.2	4.1
5	2.0026	0.0335	70.4	5.1
6	1.9908	0.0298	69.1	3.8
7	1.9844	0.0266	68.2	3.2
8	1.9902	0.0271	68.2	2.1
9	1.9694	0.0281	67.4	2.8
10	1.9881	0.0295	68.5	3.0

TABLE XXVIII

PIGMENTED COATED DISKS

Disk No.	Weight of Film and Disk (g.)	Weight of Film (g.)	Thickness of Film and Disk (mils)	Thickness of Film (mils)
11	2.0056	0.0486	68.5	3.4
12	2.0325	0.0492	68.4	2.9
13	1.9997	0.0563	67.6	2.8
14	2.0375	0.0468	68.3	2.9
15	2.0278	0.0585	68.7	3.4
16	2.0381	0.0528	68.6	3.3
17	2.0081	0.0539	68.7	3.7
18	2.0236	0.0560	68.7	3.4
19	2.0102	0.0541	68.0	3.1
20	2.0115	0.0591	69.2	4.3

Two ceramic-coated plates were filmed with LTV-602 as a control. The plates were washed with Alconox solution and primed with General Electric's proprietary SS-4044 prior to spraying. The unpigmented coating was sprayed with a solution of 1.0 g. of LTV-602 and 5 ml. of toluene. The pigmented coating was sprayed with a mixture of 1.2 g. SP-500 zinc oxide, 0.5 g. LTV-602, and 5 ml. of toluene (grinding time 1.5 hr.). Both coatings were catalyzed with SRC-05 at about a 0.4 per cent concentration just prior to application. The data for the two plates are shown in Table XXIX.

TABLE XXIX

LTV-602 COATED PLATES

Plate No.	Weight of Film and Plate (g.)	Weight of Film (g.)	Thickness of Film and Plate (mils)	Thickness of Film (mils)
21 Pigmented	16.9891	0.3485	41.3	3.0
22 Unpigmented	16.9691	0.2886	43.2	4.3

REFERENCES

1. Breed, L. W., and W. J. Haggerty, Jr., WADC-TR-57-143, Part V (1960).
2. Towers, R. S., T. M. Thomas, C. W. Newing, and P. F. Rodesiler, Summary Report No. 2, Contract No. NAS8-1532, May 1963.
3. Breed, L. W., and W. J. Haggerty, Jr., J. Org. Chem., 27, 257 (1962).
4. Geipal, L. E., R. S. Towers, F. C. Davis, and P. F. Rodesiler, Final Summary Report, Contract No. NAS8-1532, June 1964.
5. Zeitler, V. A., and C. A. Brown, J. Am. Chem. Soc., 79, 4616 (1957).
6. Anderson, R. P., and M. M. Sprung, WADC-TR-59-61, June 1959.
7. Joyner, R. D., and M. E. Kinney, Inorg. Chem., 1, 717 (1962).
8. Frank, R. L., A. Baldoni, and T. R. Patterson, Jr., AFOSR-TR-58-18 (1958).
9. Eglin, S. B., A. Landis, and J. Rust, Fourth Quarterly Report, Contract No. DA-04-495-ORD-3079, July 1, 1961.
10. Thomas, I. M., F. C. Davis, and R. S. Towers, Summary Report No. 1, Contract No. NAS8-1532, May 1962.
11. Bradley, D. C., and I. Thomas, J. Chem. Soc., 3857 (1960).
12. Elvidge, J. A., and R. P. Linstead, J. Chem. Soc., 5000 (1952).
13. Lawton, E. A., and D. D. McRitchie, WADC-TR-57-642, November 1957.
14. Barrett, P. A., C. E. Dent, and R. P. Linstead, J. Chem. Soc., 1719 (1963).
15. Brinker, K. C., D. C. Cameron, and I. M. Robinson, U. S. Patent 2,904,537, September 15, 1959.
16. Kubota, T., and R. Nakanishi, J. Polymer Sci. (B) 2, 655 (1964).
17. Moyer, W. W., Jr., C. Cole, and T. Anyos, J. Polymer Sci. (A) 3, 2107 (1965); French Patent 1,365,114, June 26, 1964.

18. Imai, Y., I. Taoka, K. Uno, and Y. Iwakura, Makromolekulare Chemie, 83, 167 (1965).

19. Imai, Y., K. Uno, and Y. Iwakura, Makromolekulare Chemie, 83, 179 (1965).

20. Korshak, V. V., G. M. Tseitlin, and A. I. Pavlov, Dokl. Akad. Nauk SSSR 163, 116 (1965); C. A., 63:13427.

21. E. I. du Pont de Nemours & Co., Netherland Patent Application 6,414,610, June 17, 1965; C. A., 64:879: French Patent 1,399,076, May 14, 1965; C. A. 64:3775: Belgian Patent 649,333, December 16, 1964; C. A. 64:9915.

22. Stacy, R. D., N. P. Loire and H. H. Levine, American Chemical Society Polymer Preprints, 7,161 (1966).

23. Lilyquist, R., and J. R. Holsten, ASTD-TDR 62-485 (II) (1963).

24. Hergenrother, P. M., W. Wrasidlo, and H. H. Levine, Am. Chem. Soc. Polymer Preprints, 5, 153 (1964).

25. Iwakura, Y., K. Uno, and Y. Imai, J. Polymer Sci. (A) 2, 2605 (1964).

26. Burkhardt, G. N., and H. Wood, J. Chem. Soc., 151 (1929).

27. McCloskey, A. L., and others, ASD-TDR-62-251, p. 37, March 1962.

28. Marvel, C., L. Audrieth, and J. Bailar, WADC-TR 58-51, Part II, May 1959.

29. Okon, K., and T. Urbanski, Roczniki Chem. 27, 348 (1953); C.A., 49:918 (1955).

30. Machek, G., Monatsh. Chem. 80, 9 (1949).

31. Korpics, C. J., W. T. Smith, Jr. and J. R. Meadow, Trans. Kentucky Acad. Sci. 22, 60 (1961).

32. Aschan, O., Annalen der Chemie, 387, 36 (1912).

33. Schreder, J., Chem. Ber., 7, 707 (1874).

34. Rozantsev, G. G., G. I. Braz and A. Yakubovich, Zh. Obshch. Khim. 34, 2974 (1964).

35. McBee, E., P. Wiseman, and G. Bachman, Ind. Eng. Chem., 39, 415 (1947).

36. Henne, A. L., and W. F. Zimmer, J. Am. Chem. Soc., 73, 1103 (1951).

37. Cassela Farbwerke Mainkur Akt.-Ges., German Patent 850,008 (1952).

38. Starke, P., J. pr. chemie, [2], 59, 215 (1899).

39. Borg-Warner Corporation, French Patent 1,365,114, June 26, 1964.

40. Sveda, M., U. S. Patent 2,562,000 (1951).

41. Merker, R. L., and M. J. Scott, J. Polymer Sci. (A) 2, 15 (1964).

42. Merker, R. L., M. J. Scott, and G. G. Haberland, J. Polymer Sci., (A) 2, 31 (1964).

43. Pike, R. M., J. Polymer Sci., 50, 151 (1961).

44. Popeleva, G. S., V. Savishkina, K. Andrianov, and S. Golubtsov, Zh. Obshch. Khim., 32, 557 (1962).

45. Noltes, J. G., and G. J. M. Van Der Kerk, Rec. Trav. Chim., 81, 576 (1962).

46. Beck, H. N., and R. G. Chaffee, J. of Chem. and Eng. Data, 4, 602 (1963).

47. Breed, L. W., J. Org. Chem., 25, 1198 (1960).

48. Elliott, R. L., and L. W. Breed, Inorg. Chem., 4, 1455 (1965).

49. Krueger, C. R., and E. G. Rochow, Inorg. Chem., 2, 1295 (1963).

50. Shorr, L. N., J. Am. Chem. Soc., 76, 1390 (1954).

51. Chappelow, C., Jr., R. Elliott, and J. Goodwin, Jr., J. Chem. and Eng. Data, 8, 82 (1963).

52. Emeleus, H., and S. R. Robinson, J. Chem. Soc., 1592 (1947).

53. Dow Chemical Company, British Patent 622,970, May 10, 1949.

54. Breed, L. W., and R. L. Elliott, Inorg. Chem., 3, 1622 (1964).

55. Elliott, R. L., and L. W. Breed, J. Chem. Eng. Data, in press (1966).

56. Sorenson, W., and T. Campbell, Preparative Methods of Polymer Chemistry, Interscience, New York (1961).

57. Breed, L. W., W. J. Haggerty, Jr., and F. Baiocchi, J. Org. Chem., 25, 1633 (1960).

58. Omietonski, G. M., U. S. Patent 3,187,029, June 1, 1965.

59. Patnode, W. I., and D. F. Wilcock, J. Am. Chem. Soc., 68, 358 (1946).

60. Vogel, M., M. Rausch, and H. Rosenberg, J. Org. Chem., 22, 1016 (1957).

61. Knoblock, F. W., and W. H. Rauscher, J. Polymer Sci., 54, 651 (1961).

62. Schaaf, R. L., J. Org. Chem., 27, 107 (1962).

63. Benkeser, R. A., D. Goggin, and G. Schroll, J. Am. Chem. Soc., 76, 4025 (1954).

64. Woodward, R. B., M. Rosenblum, and M. C. Whiting, J. Am. Chem. Soc., 74, 3458 (1952).

65. Wolff, I. A., British Patent No. 623,669 (1949); C.A., 44, 2028 (1950).

66. Dilthey, W., F. Edwardoff, and F. J. Schumacher, Ann., 344, 300 (1906).

67. Saha, H. K., J. Inorg. Nucl. Chem., 26, 1617 (1964).

68. Colclough, T., W. Gerrard, and M. F. Lappert, J. Chem. Soc., 907 (1955).

69. Burger, A., and N. Dawson, J. Org. Chem., 16, 1250 (1951).

70. Kosolapoff, G. M., J. Am. Chem. Soc., 64, 2982 (1942).

71. Picklesimer, L. G., and T. F. Saunders, J. Polymer Sci. (A) 3, 2673 (1965).

72. Koopman, H., Rec. Trav. Chim., 78, 967 (1959).

73. Brown, G. P., and A. Goldman, ASD-TDR 62-372 (1962).

74. Kenner, G. W., B. Lythgoe, A. R. Todd, and A. Topham, J. Chem. Soc., 574 (1943).

75. Brown, D. J., and J. S. Harper, J. Chem. Soc., 1298 (1961).

76. Du Breuil, S., J. Org. Chem., 26, 3382 (1961).

77. Steck, E. A., R. P. Brundage, and L. T. Fletcher, J. Am. Chem. Soc., 76, 3225 (1954).

78. Erickson, A. E., and P. E. Spoerri, J. Am. Chem. Soc., 68, 400 (1946).

79. Weijlard, J., M. Tishler, and A. E. Erickson, J. Am. Chem. Soc., 67, 802 (1945).