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Technical Summary Report
DEVELOPMENT OF IMPROVED SEMI-ORGANIC STRUCTURAL ADHESIVES FOR ELEVATED TEMPERATURE APPLICATIONS
1 July 1964 to 29 February 1968

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FOREWORD

This report was prepared by Monsanto Research Corporation, Boston Laboratory, Everett, Massachusetts 02149, under contract NAS8-11371, "Development of Improved Semi-Organic Structural Adhesives for Elevated Temperature 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. Dr. James M. Stuckey was project manager from 1 July 1964 to 10 January 1966 and Mr. W.J. Patterson was project manager from 10 January 1966 to 29 February 1968.

For Monsanto Research Corporation, Mr. John J. O'Connell was Project Leader. Principal investigators were Dr. Stephen C. Kwan and Miss Elizabeth A. McElhill.

This report covers work done from 1 July 1964 to 29 February 1968.

ABSTRACT

An adhesive formulation consisting of a new titanium chelate polymer with silanol substituents, an arylenedisilanol reactive plasticizer, and phenylsilanetriol accelerator was developed that cures *in situ* in aluminum joints at 170°C to a resin that is infusible at 250°C. Tensile shear strengths at 250°C of joints bonded with this resin were as high as 780 psi. Several other chelate polymers, including zinc linear polymers and titanium prepolymers with alkoxy, vinyl, or isocyanate substituents, were also developed and tested in adhesive formulations in aluminum joints.

New bisbidentate ligands with flexible connecting linkages between 8-hydroxyquinoline or o-alkanoylphenol groups were prepared to improve both tractability and thermal stability of the titanium and zinc chelate polymers.

Polychelatotitanosiloxanes based on p-arylenebis(diorganosilanols) cured *in situ* in aluminum joints produced tensile shear strengths of 1300 psi at -100°C and at room temperature. The highest strength obtained at 250°C with this type polymer was 440 psi.

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I. INTRODUCTION

The primary objective of this project was the synthesis and development of semi-organic coordination polymers to provide structural adhesives usable at 600°F (315°C) and higher. Specifically, these adhesives should provide a minimum of 1000 psi shear tensile strength at 600°F (315°C) and should be curable in a practical manner at temperatures below 350°F (175°C). It was also desirable, but not essential, that these adhesives have usable strengths at cryogenic temperatures as low as -423°F (-222°C).

Our work was primarily concerned with the following two specific types of semi-organic coordination polymers:

1. Metal chelate polymers derived from 5,5'-bis-(salicyl-N-butylimino)methane and bisbidentate ligands containing 8-hydroxyquinolino groups; and

2. Polychelatotitanosiloxanes.

The specific tasks undertaken for developing these polymers as usable high temperature adhesives were as follows:

1. Develop reaction conditions for the preparation of uniformly high molecular weight linear polymers;

2. Determine the structural features of the polymers that lead to soluble, tractable resins;

3. Develop methods of crosslinking the linear polymers to cure them to infusible and mechanically strong resins; for adhesive resins for aluminum the cure must be a accomplished at 175°C or lower;

4. Characterize these polymers;

5. Determine the adhesive properties of the polymers.

During this program, many modifications of the above two basic type polymers were necessarily made to fulfill these tasks and develop usable adhesive resins. The following discussion of our work on these polymers is not chronological, but instead, presents the more pertinent and relevant aspects first. Detailed discussions of the metal chelate polymers are in Section III, A-C, and detailed discussions of the polychelatotitanosiloxanes are in Section III, H-J. Preparation of ligands, crosslinking agents, and intermediates for both these polymer systems are discussed separately in Section III, D-G, because many of these reagents were used with both polymer systems.

II. SUMMARY

A. CHELATE POLYMERS

An adhesive formulation based on a new type of titanium chelate polymer was developed that cured *in situ* in aluminum joints to a resin that was infusible at 250°C. Aluminum joints coupled with this resin had tensile shear strengths that averaged 580 psi and were as high as 780 psi at 250°C. The three-component formulation consisted of (1) a titanium chelate ladder polymer with a backbone of the ligand, 5,5'-bis(salicyl-N-butylimino)-methane, and with silanol substituents; (2) a reactive plasticizer, bis(methylphenylhydroxysilyl)biphenyl ether, which plasticizes the high melting polymer to flow at 170°C and then reacts with it during cure to render it infusible; and (3) a cure accelerator, phenylsilanetriol, that increases the degree of crosslinkage of the resin. This basic formulation requires approximately 65 hours to cure at 170°C. The cure time was shortened to under 24 hours by adding aliphatic amine catalysts, such as A-1100, to the basic formulation. Tensile shear strengths of these joints, however, were somewhat lower, apparently because of increased porosity.

Development of the above formulation involved determination of the best polymer-plasticizer ratio for good resin-aluminum substrate contact at 170°C. Those formulations that contained 20 to 25% bis(methylphenylhydroxysilyl)biphenyl ether, required about 150 hours cure time. Therefore, an extensive study of cure accelerators to increase both the rate and degree of cure was undertaken to improve the initial formulation. Several reagents, such as titanium alkoxides, alkyl phosphites, arylene diisocyanates, hexamethylcyclosiloxane, and p-phenylene-bis(phenylphosphinic acid), increased the rate of cure significantly. However, the strengths of joints coupled with resins cured with these accelerators were low because of high porosity. The most useful accelerator found was phenylsilanetriol, which accelerated the rate of cure moderately and also increased the degree of cure to yield infusible resins with low porosity. A study of a series of formulations containing varying proportions of this accelerator, the plasticizer, and the silanol-substituted titanium chelate ladder polymer resulted in the optimized formulation described above.

A major part of our effort was directed at obtaining a polymer that could be used in the formulation described above, namely, a thermally stable polymer with the ability to cure *in situ* in aluminum joints below 170°C to resins that were infusible at 250°C. Several types of chelate polymers, listed below, were developed and evaluated for this use in addition to the silanol-substituted titanium chelate polymers.

1. Zinc chelate linear polymers;
2. Titanium chelate polymers with alkoxy substituents;
3. Titanium chelate polymers with vinyl substituents;
4. Titanium chelate polymers with isocyanate substituents.

5,5'-Bis(salicyl-N-butylimino)methane was used as the bisbidentate ligand for condensation with reactive zinc or titanium reagents in initial development of all these polymers because it was known to give tractable polymers with zinc and because it was easily made. Other bisbidentate ligands, described in Section B, were then used to study the effects of polymer structure on its mechanical and adhesive properties and to improve thermal stability.

The development program with the zinc chelate polymers encompassed, first, optimization of reaction conditions to prepare high molecular weight polymer; second, determination of the structural characteristics of polymer necessary to make it soluble and tractable; thirdly, evaluation of its adhesive properties, and last, determination of methods to crosslink the polymer *in situ* at 170°C. This program resulted in preparation of a soluble linear polymer with relative viscosity of 1.6 and softening point about 220°C. The polymer gave stainless steel joints with tensile shear strengths as high as 1300 psi at room temperature. However, the polymer was not adaptable for crosslinking *in situ* to infusible resins.

The titanium polymers were developed next since titanium provided sites for crosslinking and was known to give thermally stable polymers. Alkoxy-substituted polymers cured easily at 170°C using either water or a disilanol as crosslinking agent, to resins infusible below 350°C. However, when these resins were cured *in situ* in aluminum joints, the bonds were weak because of high porosity caused by evolution of the alcohol during cure. The highest strengths obtained were 750 psi at room temperature and 250 psi at 250°C.

The titanium polymers with vinyl or isocyanate substituents were developed because these substituents crosslink and cure the polymers without production of volatile byproducts. The usefulness of the vinyl-substituted polymers was limited by low softening ranges that apparently resulted from the low molecular weight of the linear prepolymers. Attempts to increase molecular weight of these prepolymers were not successful. Attempts to substitute isocyanate groups on the basic titanium chelate polymer backbone were only partially successful, and the polymers had excessively high melting ranges, apparently caused by partial crosslinking.

B. PREPARATION OF LIGANDS, CROSSLINKING AGENTS, AND INTERMEDIATES

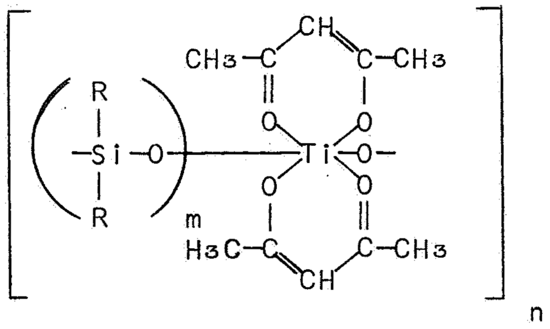
The two major portions of synthesis work involved (1) preparation of bisbidentate ligands for use as backbones of the chelate polymers and as crosslinking agents for the polychelatotitanosiloxanes; and (2) preparation of arylenebis(diorganosilanols) for use as reactive plasticizers and as intermediates in preparation of polymers. Several new bisbidentate ligands such as N,N-bis(8-hydroxy-5-quinolylmethyl)butylamine, bis[N-methyl-N-(8-hydroxy-5-quinolylmethyl)]-1,6-hexanediamine, N,N-dimethyl-N',N'-bis(8-hydroxy-5-quinolylmethyl)-1,3-propanediamine, and 1,5-bis(4-hydroxy-3-octanoylphenyl)pentane, were prepared to improve the thermal stability and the flexibility of the linear polymers. Other ligands such as the 5,5'-bis(7-alkanoyl-8-hydroxyquinolino)methanes and various Schiff bases of 5,5'-bis(salicylaldehydo)methane were also prepared to determine the effect of bulky groups in the vicinity of the metal ion in the polymer backbone on the mechanical properties of the polymer.

Arylenebisdiorganosilanols (where arylene was phenylene, biphenylene, or biphenylene ether and diorgano was methylmethyl or methylphenyl or methylvinyl) were prepared by several routes. The best general procedure involved coupling of chloroalkoxydiorganosilanes to the ring via the Grignard reagent followed by hydrolysis of the alkoxy groups in ethanol solution with aqueous sodium hydroxide.

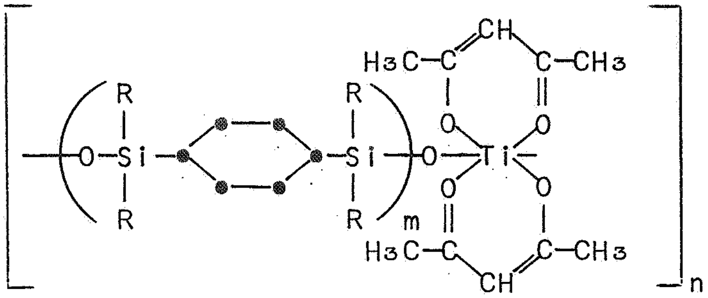
Among the other reagents and crosslinking agents that were prepared for use in this program were dialkoxybischelatotitanium compounds where the chelato moiety was acetylacetonato, 8-hydroxyquinolino, or salicylaldehydo, p-phenylenediphosphoric acid, p-phenylene-bis(phenylphosphinic acid), phenylsilanetriol, diphenylvinylsilanol, p-tolyldiphenylsilanol, heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, and bis(methylamino)methylphenylsilane.

C. POLYCHELATOTITANOSILOXANES

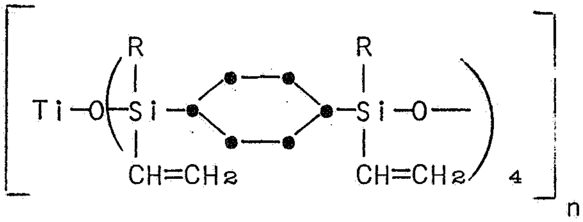
Three general types of polymers, as follows, were developed in this program.



Polydichelatotitanodiorganosiloxanes



Polydichelatotitano-p-arylene-bis(diorganosiloxanes)



Polytitanotetrakis-[p-arylene-bis(diorganosiloxanes)]

With each type of polymer, methods to prepare a prepolymer that would wet the aluminum substrates at 170°C were developed, as were methods to crosslink the prepolymers *in situ* in the aluminum joints. The original polydichelatotitanodiorganosiloxanes that were prepared by a modification of Andrianov's method were low melting elastomers. We found that crosslinking these elastomers by ligand exchange yielded resins that were soft at 250°C. Therefore, reaction conditions were altered to increase the Ti/Si ratio in the elastomers to increase the number of sites available for crosslinking. Elastomers with ratios up to 1:3.4::Ti:Si were obtained using a combination of tetramethyldisiloxane-1,3-diol and diphenylsilanediol as reagents. However, the adhesive properties of resins obtained by crosslinking these elastomers were poor and appeared to be limited by deposition of a thin layer of low molecular weight cyclic siloxane contaminant on the aluminum surface. The ligand exchange reaction did, however, successfully cure the bulk of the resin to a high melting product.

The polydichelatotitano-p-arylene-bis(diorganosiloxanes) were investigated next since the arylene groups were expected to prevent formation of cyclic products and also improve adhesive properties. These prepolymers were cured in two steps by ligand exchange with bisbidentate ligands with rigid structures. The adhesive properties of the resulting resins were excellent and joints coupled by these resins had tensile shear strengths as high as 1300 psi at -100°C and at room temperature. However, most resins were soft at 250°C, and the highest strength obtained at this temperature was about 250 psi. The strength of these resins appeared to be limited by the low molecular weight of the initial prepolymers. Analysis indicated that formation of bridged structures that terminated the polymers limited molecular weight.

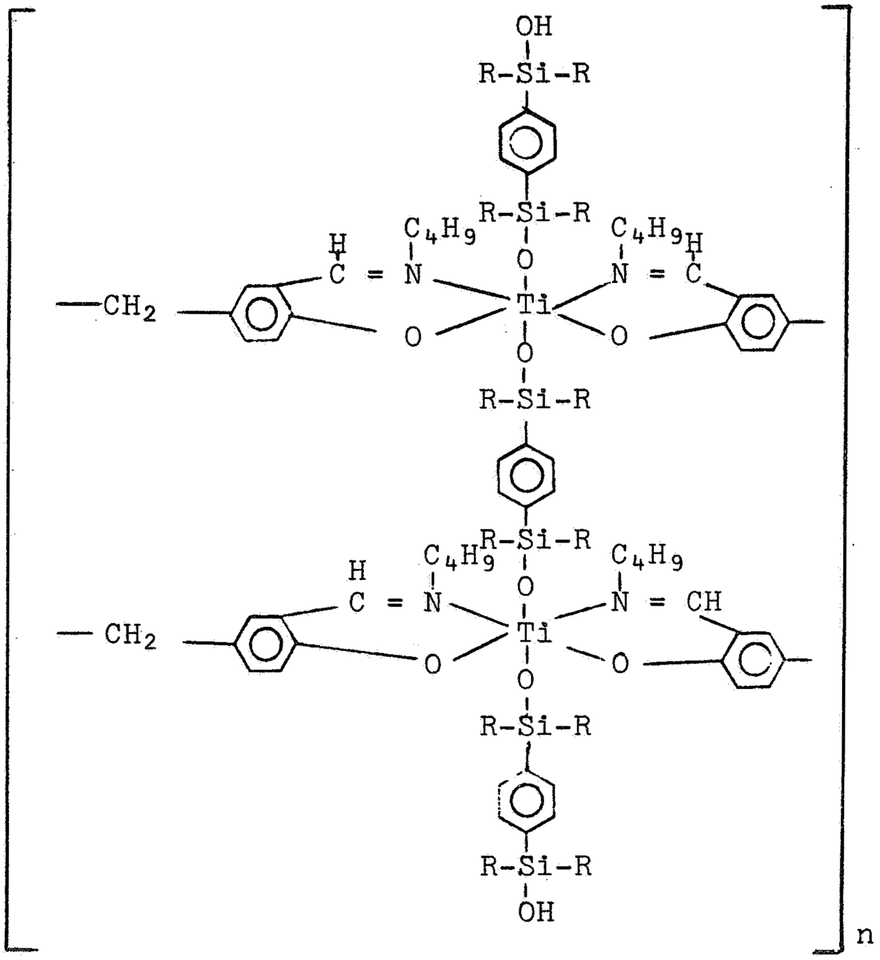
Higher molecular weight prepolymers (ca. 10,000) were obtained by substitution of all four primary valence sites on titanium by condensation with arylenesilanediols. These polymers were soluble in benzene and had high softening points. They were plasticized with arylenesilanediols and cured *in situ* by reaction of vinyl substituents on the polymer with diphenylsilane. Adhesive strengths of the best formulations averaged 440 psi at 250°C.

III. DISCUSSION OF RESULTS

A. ADHESIVE STRENGTHS OF TITANIUM CHELATE POLYMERS WITH SILANOL SUBSTITUENTS CURED *IN SITU* IN ALUMINUM JOINTS.

1. General

To be usable as an adhesive for aluminum, a polymer system must be curable *in situ* in an adhesive joint below 170°C. This special requirement makes it necessary first to develop methods to prepare a polymer in a physical form such that when it is applied to the aluminum substrate, good resin-adherend contact results at temperatures under 170°C, and second, to develop methods for the curing of these prepolymers at this relatively low temperature. From among the chelate polymers prepared in this program, the silanol-substituted titanium chelate polymers derived from 5,5'-bis(salicyl-N-butylimino)methane (structure shown below) and from the bisbidentate 8-hydroxyquinoline ligands were the most adaptable to this use. The methods used to develop



a usable formulation from these polymers to give strong resins that were infusible at 250°C after cure at 170°C are described below. Other polymer systems developed, such as the zinc chelate polymers and the vinyl- and alkoxy-substituted titanium polymers, also acted as adhesives. However, these latter polymers either were not directly adaptable for low temperature cure in adhesive joints or cured to resins with low strengths. Development work with these systems is described in part B. of this section.

2. Preliminary Tests

Silanol-substituted titanium chelate polymers used in conjunction with a reactive plasticizer were successfully cured *in situ* in aluminum joints at 170°C to resins that maintained their strength at 250°C. Tensile shear strengths as high as 1300 psi at room temperature and 790 psi at 250°C were obtained from resins of this type. The reactive plasticizer acts both as a low temperature plasticizer to insure good adhesive-adherend contact and as a crosslinking agent at 170°C. The reactive plasticizers were arylene disilanols that reacted with the prepolymer by condensation to form siloxane linkages and yielded a tough, high-melting resin.

Several parameters were studied to optimize the adhesive formulation as follows:

a. Substituents on the silanol group on the polymer;

b. Substituents on the silanol group on the reactive plasticizer;

c. Amount of reactive plasticizer;

d. Method of mixing polymer and plasticizer;

e. Amount and type of accelerator to increase cure rate;

f. Precure times in open joints;

g. Surface treatments of aluminum;

h. Primers;

i. Ligand in polymer backbone.

An initial series of tests was made with titanium chelate polymers derived from 5,5'-bis(salicyl-N-butylimino)methane varying only the first four parameters to select a basic formulation. The results of this test series are shown in Table 1.

Polymers prepared from p-phenylenebis(methylphenylsilanol) consistently gave higher strengths in tests at elevated temperatures than the dimethyl homolog, although dimethyl-substituted silanols are known to condense more readily than methylphenylsilanols. Resin formulations of the dimethyl polymer with several reactive plasticizers in amounts from 20 to 45 wt-% characteristically cured to resins that were soft at 250°C. The only exceptions were formulations containing 4,4'-bis(hydroxymethylphenylsilyl)biphenyl.

More effective and complete cure, as measured by tensile shear strength of specimens at 250°C, was obtained with methylphenyl substituents on the reactive plasticizer as well as on the polymer. The disilanols, 4,4'-bis(hydroxymethylphenylsilyl)biphenyl and 4,4'-bis(hydroxymethylphenylsilyl)biphenyl ether were more effective agents than the p-phenylene analog.

The optimum amount of reactive plasticizer is the minimum amount required to give good resin-substrate contact at 170°C. For both the biphenyl and biphenyl ether disilanols this amount was approximately 20 wt-%.

A method was developed to insure homogeneity in the prepolymer-reactive plasticizer mix, namely, freeze-drying a benzene solution of the two components to a fluffy powder. Use of this mix improved reproducibility over that obtained with mixtures prepared by grinding the two components together. In many early tests, the adhesive formulation was applied to the aluminum in benzene solution in order to obtain homogeneity. The open strips were precured at 60°C for 30 min., and then the joint was coupled and cure finished at 170°C. Results with this method were intermediate between the simple mix and freeze-dry mix methods. Its chief drawback was that it gave extremely thin (1-2 mil) joints.

3. Accelerators

Accelerators were the next parameter investigated because the prepolymer-disilanol mix [80 wt-% prepolymer plus 20 wt-% 4,4'-bis(hydroxymethylphenylsilyl)biphenyl ether (BBE)] developed in the above test series required about 150 hours cure at 170°C to give a resin that was infusible at 250°C. Since most of the agents are not plasticizers, they are used with the standard prepolymer-BBE reactive-plasticizer mix. The following three general approaches were used to improve both the rate and degree of cure at 170°C:

Table 1

TENSILE SHEAR STRENGTH OF SILANOL-CURED TITANIUM CHELATE POLYMERS ON ALUMINUM SUBSTRATES

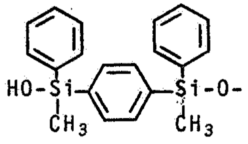
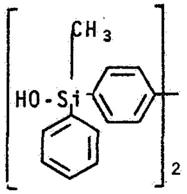
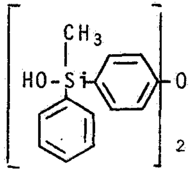
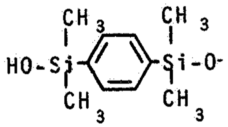
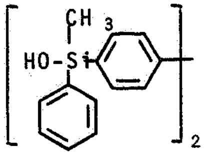
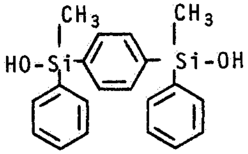
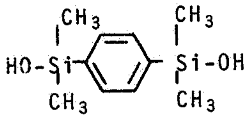
Silanol on Polymer	Reactive Silanol Plasticizer	Amt. Reactive Plasticizer Wt-% of Polymer	Method of Application*	Total Cure Time at 170 °C hr.	Tensile Shear Strength (psi) at:		
					R.T.	200°C	250°C
		25	S	60	920,930	---	530
"	"	25	S	60	1040,770	---	674,646
"	"	25	S	147	910,710	---	720,550
"	"	30	S	150	610	---	570
							280,310 (at 300°C)
"	"	45	S	60	750	---	400,450
"	"	45	S	90	920,940	---	400,350
"	"	25	M	60	290,320	---	326,324
"	"	50	M	60	490,600	---	560,424
		25	S	60	820,600	---	
"	"	"	"	250		---	700,610
"	"	20	M^1	150(+)			540 Ave. 790 High

Table 1 (Continued)

TENSILE SHEAR STRENGTH OF SILANOL-CURED TITANIUM CHELATE POLYMERS ON ALUMINUM SUBSTRATES

Silanol on Polymer	Reactive Silanol Plasticizer	Amt. Reactive Plasticizer Wt-% of Polymer	Method of Application*	Total Cure Time at 170 °C hr.	Tensile Shear Strength (psi) at: R.T.	200°C	250°C
		22	M	64	410	---	650
"	"	33	M	65	---	---	460,424
"	"	58	S	90	800,880	---	40(y)
"	"	42	S	60	754	---	290(y)
"	"	27	S	64	800	600	---
"		14	S	64	586	646,680	---
		20	M^1	230			(y)
		33	M	88	1300	124(y)	---
"	"	27	S	64	480	480	---
"	"	20	M^1	230			(y)

---

* M indicates adhesive melted on Al; M^1 indicates freeze-dry mix melted on Al
S indicates adhesive applied to Al from benzene solution

a. Use of catalysts to accelerate condensation of silanol groups on the polymer and the reactive plasticizer;

b. Use of reagents that react with silanol groups at a faster rate than the silanol condensation reaction; and

c. Use of reagents with tri- or tetrafunctional reactive groups to increase both degree and randomness of cross-linking.

The specific formulations chosen for testing were made using reagents (catalytic or reactive) that have been reported in the literature to be effective with silanols below 200°C. Approximately thirty agents were tested.

The agents fell into three classes: (1) those that were inactive; (2) those that accelerated cure rate appreciabley; and (3) those that accelerated cure principally by increasing the degree of cure. The agents that did not accelerate cure at 170°C in the aluminum joint included the catalyst, n-hexylamine 2-ethylhexanoate, and the reactants hexakis(methoxymethyl)melamine, 1,7-bis(dimethylhydroxysilyl)-m-carborane, and p-phenylene-bis-(dimethylmethoxysilane).

The second group of agents greatly accelerated cure. In most cases, reaction of these agents with the resin formulation was extremely fast even at room temperature, making it difficult to obtain good wetting of the adhesive joint before cure to infusibility. Joints made with large amounts of these accelerators also characteristically had high porosity. Agents of this type included the catalyst tetracyanoethylene and the reactants diethyl phosphite, the titanium alkoxides, P_2O_5, hexamethylcyclosiloxane, p-phenylene-bis(phenylphosphinic acid), and arylene diisocyanates. A-1100 was an effective accelerator in the formulations containing phenylsilanetriol that are described in the following section.

Several formulations were made using different amounts of each of the most promising accelerators, namely, diethylphosphite, triethylphosphite, Epon 828, tetrabutoxytitanium, bis(acetylacetonato)dibutoxytitanium, bis(acetylacetonato)diisopropoxytitanium, or bis(8-hydroxyquinolino)diisopropoxytitanium. With all these reagents, formulations that contained enough reagent to cure the resin in less than 90 hours yielded resins with high porosity and low strengths. The highest strength obtained at 250°C was about 400 psi.

A series of formulations was also made with the catalyst tetracyanoethylene, which appreciably accelerated cure rate. This compound has been described (ref. 1) as a catalyst for condensation of silanol groups that does not cause rearrangement of siloxane linkages. We found it was necessary to prepare first a complex of tetracyanoethylene with xylene (ref. 2) to deactivate its catalytic activity. This prevented premature cure of the resin during sample preparation and enabled good resin-aluminum contact to be made. In this way, the catalyst could be incorporated into the resin formulation by our standard freeze-drying procedure. The catalyst was reactivated *in situ* by heating the joint at 170°C to dissociate the complex. Complexes of tetracyanoethylene with diethyl ether, tetrahydrofuran, and pyridine were also tested for this use, but the ether complexes did not give sufficient stabilization during sample preparation, whereas the pyridine complex did not dissociate at 170°C.

These complexes in concentrations of 0.5 to 3% effected cure of most formulations with plasticizer contents as high as 30% to resins that were infusible at 250°C after cure times of 90 hours at 170°C. The highest tensile shear strengths, obtained with formulations containing 15 and 20% silanediol plasticizer, were 440 to 505 psi at 250°C. However, the degree of cure of these catalyzed resins was not reproducible. The poor reproducibility appeared to be caused by the fact that the cured resins had softening points very close to 250°C, the test temperature. The resins are hard at 200°C.

A series of these formulations was also cured at 80°C, but cure rate at this temperature was found to be excessively low.

Initial tests for catalytic activity were also made with other Π-acids, such as chloranil and tetracyanoquinodimethane. Both compounds exhibited catalytic activity, but neither appeared to offer any advantage over tetracyanoethylene.

4. Optimized Formulation with Phenylsilanetriol

The third type of accelerator tested, phenylsilanetriol, was used primarily to increase the degree of cure, but also was found to increase cure rate. Formulations with plasticizer contents of from 15 to 30 weight percent and mole ratios of SiOH in phenylsilanetriol to SiOH in the adhesive formulation from 0.50 to over 4.0 were tested. As expected, the cure time at 170°C required to produce a resin infusible at 250°C increased with an increase in plasticizer content and a decrease in phenylsilanetriol content. However, formulations with a ratio above 4 of SiOH in the triol to SiOH in the formulation gave marked decreases in adhesive strength in the joints.

The formulation that gave the highest strengths consisted of 71 parts by weight of titanium chelate polymer plasticized with 4,4'-bis(methylphenylhydroxysilyl)biphenyl ether and 29 parts by weight phenylsilanetriol. This formulation cured at 170°C in less than 90 hours to resins with tensile shear strengths averaging 580 psi and reaching 780 psi at 250°C. Details of the procedure for applying this formulation to aluminum and curing the joints are given in the Experimental Section. This method resulted from a study of the effect of variations in the amount of sample, in precure times in open joints and in surface treatments of aluminum on adhesive strength of the cured resin. In this study, we found that precure times of less than 2 to 3 minutes caused high porosity in the joints, and precure times longer than 4 minutes hindered coupling of the joints because of increase in softening point of the resin. The results of tests for tensile shear strength of this resin formulation on aluminum prepared by various surface treatments are summarized in Table 2.

The following variations from the standard dichromate etch-distilled water rinse treatment were tested:

a. Chromic acid etch of Vincent (ref. 3);

b. Standard etch treatment with aqueous rinse at 60°C (ref. 4). Wegman and coworkers found large variations in adhesive strengths on aluminum specimens depending on whether the aluminum was rinsed in deionized water, tap water, or water containing acidic or basic additives. Sodium bicarbonate and ferric chloride additives were tested.

c. Standard etch, followed by priming with primers such as A-1100.

The highest strengths (Table 2) were obtained with joints treated by the standard etch procedure, or by the standard etch procedure followed by priming with A-1100 or γ-glycidoxypropyltrimethoxysilane.

Joint strengths (Table 2) of aluminum pairs etched with dichromate and coupled with samples of the large batch of formulation prepared for the Propulsion and Vehicle Engineering Laboratory, Materials Division, of the George C. Marshall Space Flight Center were also measured and found to be equivalent to joints coupled with formulations prepared on much smaller scales.

Several test samples of titanium alloy supplied by the Flight Center were also coupled with this formulation and tested. Joint strengths of titanium samples etched with acid averaged 290 psi at 250°C. Similar joints using titanium treated with chlorine trifluoride, using a procedure developed in our laboratories (ref. 5) to improve adhesion of conventional resins to titanium, had strengths of 340 psi.

Table 2

EFFECT OF VARIATIONS OF ALUMINUM SURFACE TREATMENT ON ADHESIVE STRENGTH OF TITANIUM CHELATE POLYMER FORMULATION AFTER CURE AT 170°C

Surface Treatment	Number of Specimens	Tensile Shear Strength at 250°C, psi	
		Ave.	High
Standard dichromate etch with distilled water wash	14 4	580 625*	785 640*
Standard etch and wash with A-1100 primer	10	475	626
Standard etch and wash with γ-glycidoxypropyltrimethoxysilane primer	6	500	636
Vincent chromic acid etch	3	312	454
Standard etch with cold tap water rinse	4	310	414
Standard etch with 60°C tap water rinse	4	370	624
Standard etch with 0.075% aqueous $NaHCO_3$ rinse	4	308	348
Standard etch with 0.3% aqueous $NaHCO_3$ rinse	10	380	590
Standard etch with 3% aqueous $NaHCO_3$ rinse	12	455	680
Same as above with A-1100 primer	7	390	450
Standard etch with 0.05% aqueous $FeCl_3$ rinse	3	321**	466

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* Sample of formulation prepared for Flight Center

** High ratio cohesive to adhesive failure

We also found that aliphatic amine additives markedly accelerated cure of this basic formulation and at the same time made it more difficult to obtain good wetting of the aluminum by the adhesive during joint fabrication. The additive α-aminopropyltrimethoxysilane (A-1100) was used in amounts from 10 to 0.2 weight percent. The joints made with the larger amounts generally had strengths under 200 psi at 250°C due both to poor substrate-resin contact and to high porosity. High strengths were obtained with formulations containing smaller amounts of A-1100. For example, formulations with 0.3 weight percent A-1100 gave joints with strengths about 400 psi at 250°C, although joint strength still appeared to be limited by some porosity and incomplete substrate-resin contact. The results indicate that there is a maximum cure rate that can be tolerated to avoid loss in joint strength from high porosity.

Tetracyanoethylene was also added to formulations containing phenylsilanetriol to increase the degree of cure. However, cure rate of these formulations was lowered rather than accelerated. It is possible that the catalyst caused the triol to condense with itself preferentially, leaving the resin with a lower degree of crosslinking.

5. Polymers Derived from the 8-Hydroxyquinoline Bisbidentate Ligands

Similar formulations containing titanium chelate polymers derived from the 8-hydroxyquinoline bisbidentate ligands, bis[N-methyl-N(8-hydroxy-5-quinolylmethyl)]-1,6-hexanediamine [BHQH] and N,N-bis(8-hydroxy-5-quinolylmethyl)-butylamine [BHQB] as well as zinc-titanium chelate polymers derived from 5,5'-bis(salicyl-N-butylimino)methane were also evaluated. A combination of 4,4'-bis(methylphenylhydroxysilyl)biphenyl ether [BBE] and phenylsilanetriol was used as reactive plasticizer. They cured to resins that were infusible at 250°C after curing less than 95 hours at 170°C. The aliphatic amine catalysts lowered the cure time at 170°C to under 24 hours.

The highest strengths with these formulations were obtained from resins containing polymers derived from BHQH. Joints with the highest strength were in the range of 550 to 780 psi at 250°C and broke principally by adhesive failure.

The formulation of BHQH that gave a cured resin with the highest strength (average 550 psi and high of 710 psi) contained 30 weight percent BBE to obtain good flow at 170°C during joint fabrication plus sufficient phenylsilanetriol to give a mole ratio of 4.5 SiOH in the triol to SiOH in the plasticized polymer mix. Formulations with lower ratios of triol gave weaker joints.

B. DEVELOPMENT OF TITANIUM CHELATE POLYMERS

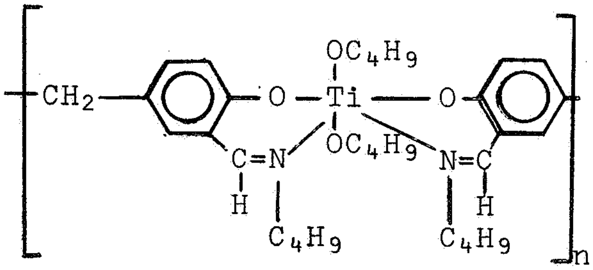
Having found that zinc chelate polymers (described in Section C, following) did not lend themselves to low temperature curing, we concentrated on developing a series of titanium chelate polymers. Polymers of this type were of interest for two reasons:

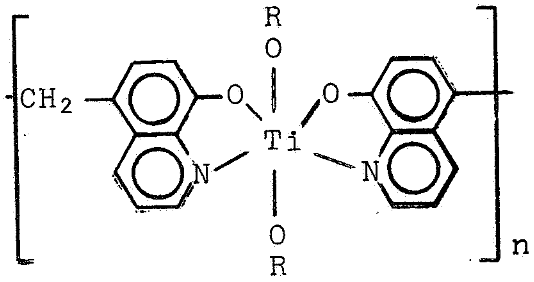
1. Titanium forms thermally stable polymers; and
2. Each titanium atom in the polymer chain is a potential site for crosslinking.

This latter property is especially useful in adhesives that must be cured at relatively low temperatures.

1. Titanium Polymers with Alkoxy Sites

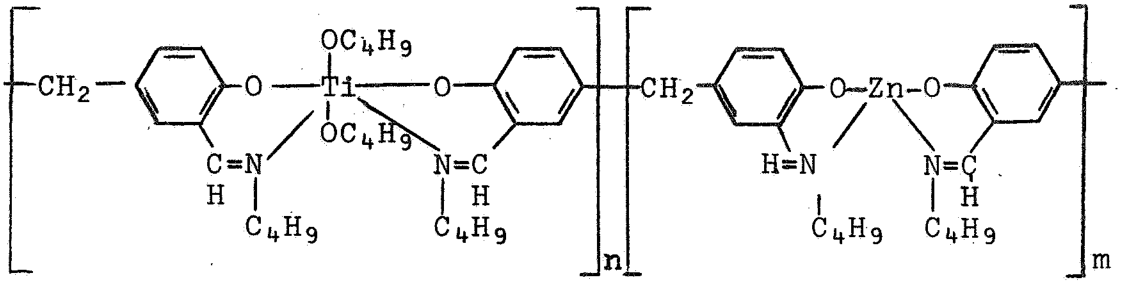
Linear titanium chelate polymers were prepared by condensing tetraalkoxytitanium with either 5,5'-bis(salicyl-N-butylimino)-methane or 5,5'-bis(8-hydroxyquinolino)methane. The structures of these polymers are shown below.





These polymers can be prepared in anhydrous pyridine, quinoline, benzene, or the alkylbenzenes by adding the tetra-alkoxytitanium compound to the ligand dissolved in the solvent and removing solvent and product alcohol by distillation. The polymers are completely soluble in these solvents under anhydrous conditions. The linear polymer from tetraisopropoxytitanium and 5,5'-bis(8-hydroxyquinolino)methane melts above 230°C while that from 5,5'-bis(salicyl-N-butylimino)methane melts in the range from 90 to 110°C.

Mixed polymers of titanium and zinc were similarly prepared in pyridine or quinoline.



In these condensations, zinc was incorporated into the polymer first, by reaction of ligand with diethylzinc using the same procedures developed for the zinc chelate polymers (Section C). Then titanium was introduced via its tetraalkoxide. The properties of several of these polymers are compared in Table 3 below:

Table 3

PROPERTIES OF ZINC-TITANIUM CHELATE POLYMERS FROM 5,5'-BIS(SALICYL-N-BUTYLIMINO)METHANE

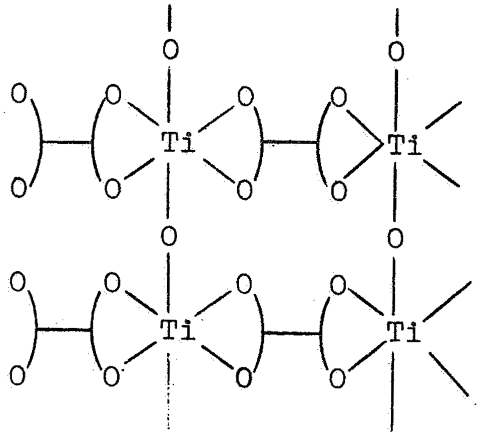
Ratio Zn/Ti	Appearance	Softening Point, °C
0/1	Dark amber	90-110
1/1	Amer	110-130
3/1	Light amber	140-170
9/1	Yellow	170-185

These polymers can be isolated and cured directly on aluminum by either of the following two methods:

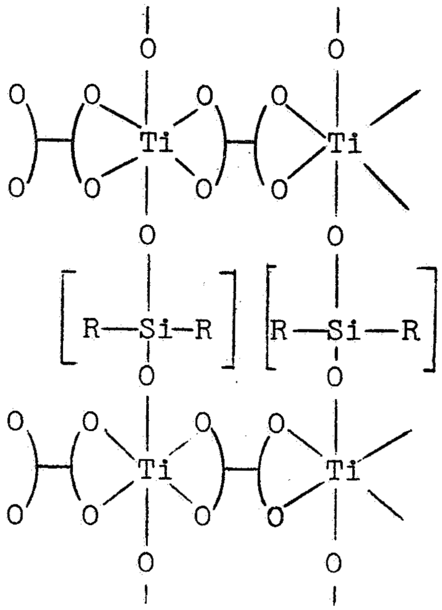
a. Reaction of the titanium alkoxide groups with water to form the dihydroxymetal species followed by dehydration to form Ti-O-Ti crosslinking sites; and

b. By reacting the titanium alkoxide groups with a silanediol such as α,ω-methylphenylsiloxanediol or p-phenylene-bis(dimethylsilanol) to yield a titanium siloxane crosslinking unit.

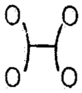
The proposed structure of these crosslinked resins is given below.



(Water Hydrolysis Cross-linking)



(Siloxane Crosslinking)

where  is a bis-bidentate ligand.

Resins that were infusible below 350°C were obtained by both of these methods using a cure temperature of 170°C. However, in initial attempts to cure these resins *in situ* in the aluminum joints, incomplete cure was obtained. These initial tests disclosed two factors that were limiting the strength of the adhesive joint. First, inflexible crosslinking groups limited the strength of the resin itself. This effect was most noticeable in resins cured by water. Second, butanol trapped inside the joints caused nonhomogeneous cure and produced a highly porous joint.

Systematic development work to improve the adhesive properties of these resins cured in the aluminum joint was therefore undertaken (1) to develop fabrication and cure techniques that lead to uniform resin-adherend contact and cure, and (2) to improve the mechanical properties of the cured resin by obtaining the lowest amount of crosslinking with the most efficient crosslinking agent.

As a result of the program, which included study of different crosslinking agents and the use of reinforcements and softening agents, uniform cure at 170°C to resins infusible at 250°C was obtained. However, joint strength was still limited by high resin porosity and the highest joint strengths obtained in the series were 750 psi at room temperature and 245 psi at 250°C. The general conclusion reached at the end of this test series was that it was virtually impossible to obtain completely cured resins of this type without excessive porosity in the aluminum joint because of the large amount of high boiling butanol evolved in cure. Therefore, new methods of cure were devised that do not evolve high boiling products, as follows:

a. Crosslinking through condensation of silanol substituents on polymer backbone;

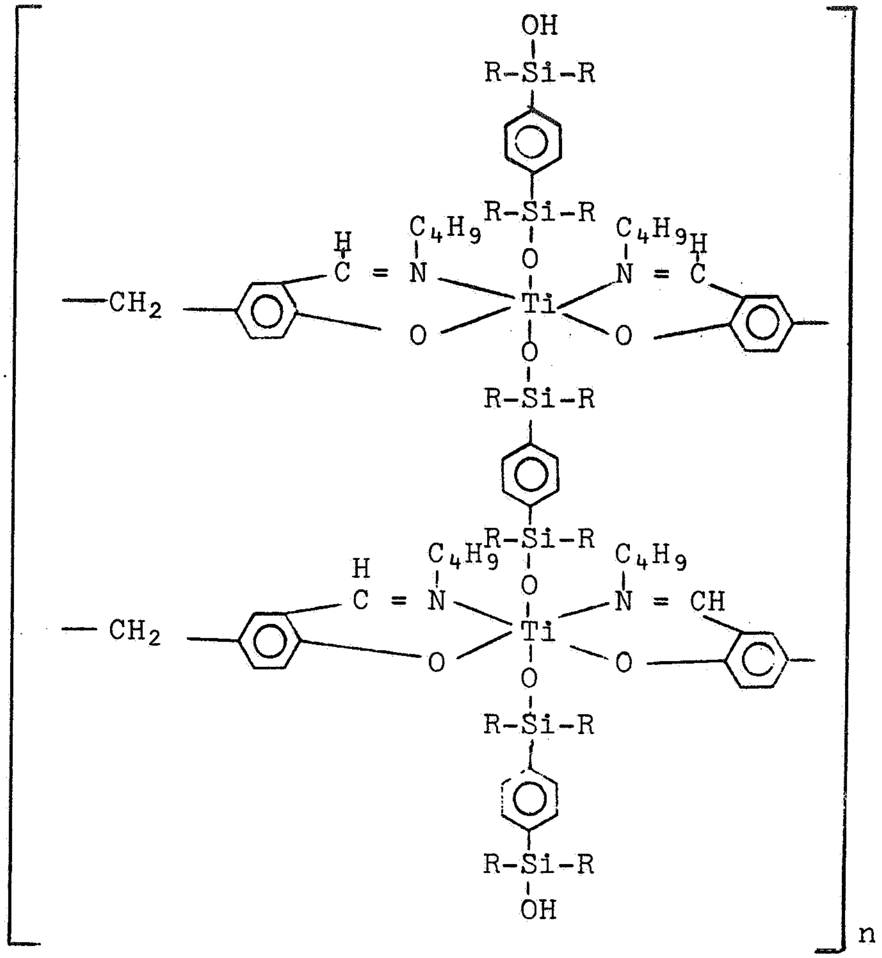
b. Crosslinking through addition of silanes to vinyl substituents;

c. Crosslinking through trimerization of isocyanate substituents.

The methods used to prepare titanium chelate polymers with silanol, vinyl, or isocyanate substituents are described in the following sections.

2. Silanol-Substituted Titanium Polymers Derived from 5,5'-Bis(salicyl-N-butylimino)methane

These prepolymers have the advantage of being stable to hydrolysis since all the Ti-O-R groups are replaced by the more stable Ti-O-Si linkages. These prepolymers are prepared by reacting the alkoxy-substituted linear prepolymer with disilanols or mixtures of mono- and disilanols. Two methods have been used to prepare these polymers. In the first method , a benzene solution of the linear, alkoxy-substituted prepolymer was added slowly to a large excess of disilanol in benzene. In the second method, a stoichiometric amount (Ti-to-Si atom ratio of 1:4) of disilanol was added all at once to the linear alkoxy-substituted prepolymer. The products isolated by the two methods are almost identical. The crude product isolated in both cases softened below 120°C. It contained unreacted disilanol and a small amount of low molecular weight polymer, both of which were soluble in ether. Approximately 25% of the disilanol was recovered unreacted in the runs with 4-to-1 silicon-to-titanium ratios. The product that remained after trituration with ether had a softening range of 250-280°C. One such polymer derived from the methylphenyl-substituted silanol when dissolved in benzene had an intrinsic viscosity of 1.29. Infrared and NMR analyses of this polymer suggest that this polymer had at least some ladder structure in it similar to that shown below.



These prepolymers have been prepared using the disilanols, p-phenylene-bis(dimethylsilanol) and p-phenylene-bis(methylphenylsilanol) and with mixtures of p-phenylene-bis(dimethylsilanol) with either triethylsilanol or dimethyl-p-tolylsilanol. The methylphenyl disilanol was preferred for two reasons. First, it is more resistant to self-condensation. This property was essential in the formation of our prepolymer to avoid extensive premature crosslinking at low temperatures. The methylphenyl silanol group also appeared to give a tougher final polymer. Higher values for adhesive strength were obtained with this polymer system. Based on these results, we chose the polymer prepared using p-phenylene-bis(methylphenylsilanol) reagent in stoichiometric amounts (Ti:Si of 1:4) as the standard polymer for use in development of an adhesive resin.

Successive batches of polymer when prepared with the 1:4 Ti:Si charge at an initial concentration of titanium compound of 0.02 mole/liter had a softening range of 250 to 280°C and intrinsic viscosities in benzene from 1.1 to 1.3. Batches of polymer prepared at a concentration of 0.04 mole/liter had lower molecular weights (0.6-0.8 intrinsic viscosity). How the variation in dilution affects molecular weight is not clear. It is possible that the isopropanol byproduct is more effectively removed by the larger volume of benzene in the dilute runs.

Large batches of polymer were also made by the same procedure. For example, the procedure used to prepare batch 88554 with intrinsic viscosity of 1.29 that is described in the experimental section was repeated with 0.291 mole of tetraisopropoxytitanium in a 12-liter reaction flask. The product polymer had an intrinsic viscosity of 1.13 and weighed 230 g after four ether washes.

These polymers apparently crosslinked very slowly at room temperature, since solubility in benzene decreased after they had stood for one week. However, the polymers can be stored at -10°C without change in properties for at least six weeks.

A limited amount of work was done on determining the feasibility of using blocking groups at some of the crosslinking sites to limit the extent of crosslinking. However, the usefulness of this method to control the mechanical properties of the cured polymer depends on the stability of the blocking groups. We found that under our reaction conditions, a silanol of higher acidity will displace a siloxy substituent on the chain. For example, p-phenylene-bis(dimethylsilanol) partially displaced triethylsiloxy substituents.

3. Silanol-Substituted Titanium Chelate Polymer Derived From 5,5'-Bis(salicyl-N-γ-dimethylaminopropylimino)methane

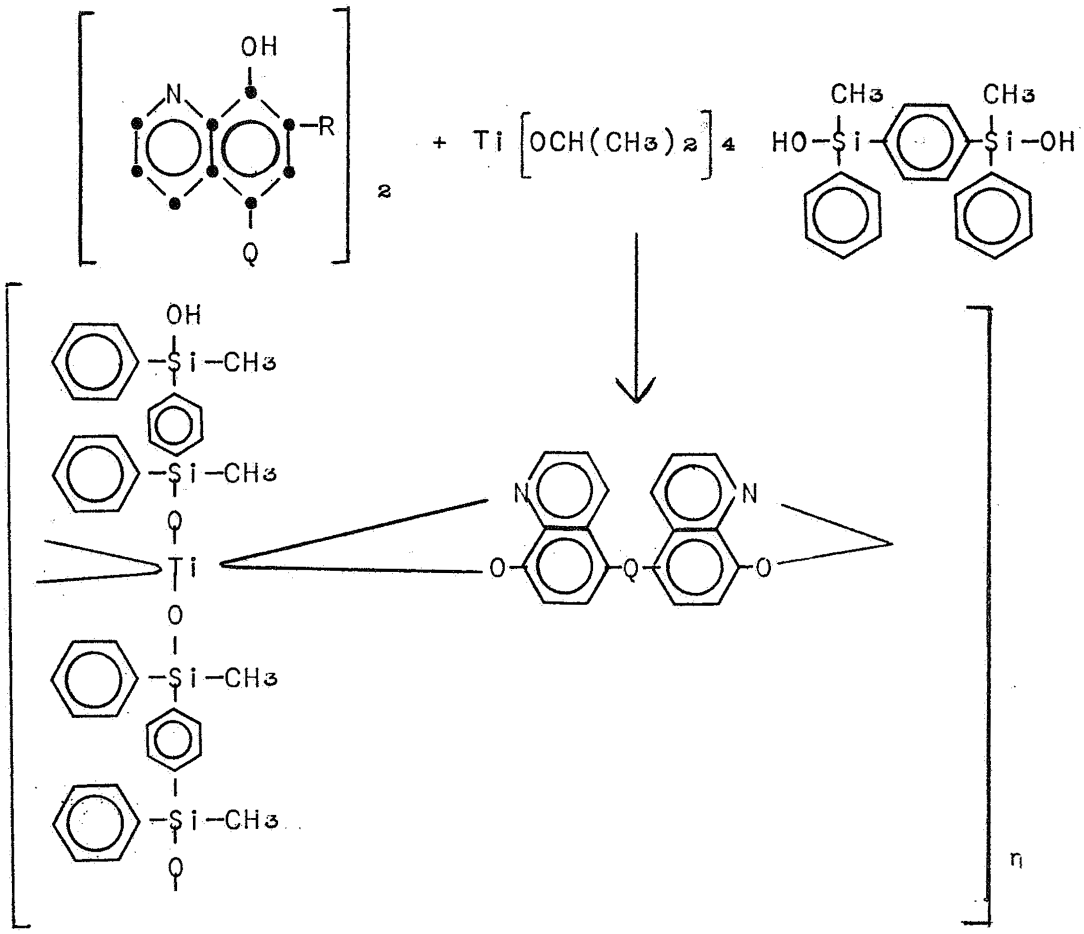
A modified titanium chelate prepolymer containing a dimethylamino substituent on the imine nitrogen, which should enhance the adhesive characteristics of the polymers, was prepared. The ligand used to prepare this polymer, 5,5'-bis(salicyl-N-γ-dimethylaminopropylimino)methane, was synthesized by the same method used to prepare the corresponding n-butyl-substituted ligand. Details of the preparations are in the experimental section.

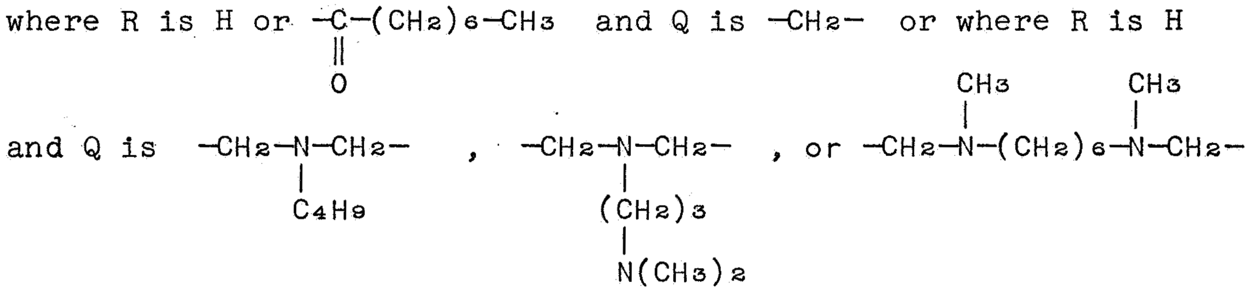
These polymers have lower softening ranges (150-180°C lower than polymers prepared from the n-butyl-substituted ligand) and can be fabricated in the aluminum joints below 170°C without addition of reactive plasticizer.

Adhesive tests after *in situ* cure in aluminum joints were made on the polymer alone and in formulations with 4,4'-bis-(hydroxymethylphenylsilyl)biphenyl ether. Tensile shear strengths of this polymer at room temperature were 1100 to 1380 psi, indicating that the substituent improved the adhesive properties of the resin. Adhesive strengths at 250°C, however, were low (250-350 psi) due to softening of the polymer.

4. Silanol-Substituted Titanium Polymers Derived From 8-Hydroxyquinoline Bisbidentate Ligands

Ligands containing the very stable 8-hydroxyquinoline group were used to prepare titanium chelate polymers with improved thermal stability. Ligands that have different degrees of flexibility as a result of the type of connecting linkage between the two 8-hydroxyquinoline groups in the ligand were used.




where R is H or $-\underset{\underset{O}{\|}}{C}-(CH_2)_6-CH_3$ and Q is $-CH_2-$ or where R is H and Q is $-CH_2-\underset{\underset{C_4H_9}{|}}{N}-CH_2-$, $-CH_2-\underset{\underset{\underset{N(CH_3)_2}{|}}{\underset{(CH_2)_3}{|}}}{N}-CH_2-$, or $-CH_2-\overset{\overset{CH_3}{|}}{N}-(CH_2)_6-\overset{\overset{CH_3}{|}}{N}-CH_2-$

Initially these polymers were prepared by the same procedure used to prepare the titanium chelate polymers derived from 5,5'-bis(salicyl-N-butylimino)methane (Section B.2 above). However, these polymers generally had lower solubility in benzene and, in some cases, precipitated from solution during preparation. Several variations in reactive procedure were made to increase polymer solubility and molecular weight. The individual variations made are described in detail in the experimental section.

Products prepared from 5,5'-bis(8-hydroxyquinolyl)methane (Q = $-CH_2-$) had the lowest solubility. These products precipitated during preparation when made in either benzene or pyridine. An attempt to increase solubility by adding the silanediol, p-phenylene-bis(methylphenylsilanol), to the reaction mixture as soon as the titanium compound had been added was not successful.

Products derived from the two ligands bis[N-methyl-N(8-hydroxy-5-quinolylmethyl)]-1,6-hexanediamine (Q = $-CH_2-\overset{\overset{CH_3}{|}}{N}-(CH_2)_6-\overset{\overset{CH_3}{|}}{N}-CH_2-$) and 5,5'-bis(7-octanoyl-8-hydroxyquinolino)methane (Q is $-CH_2-$ and R is $-\overset{\overset{O}{\|}}{C}-(CH_2)_6-CH_3$) had the highest solubilities. They remained soluble during preparation. Fractions of the products, however, did not redissolve in benzene or pyridine after removal of soluble, low molecular weight fractions.

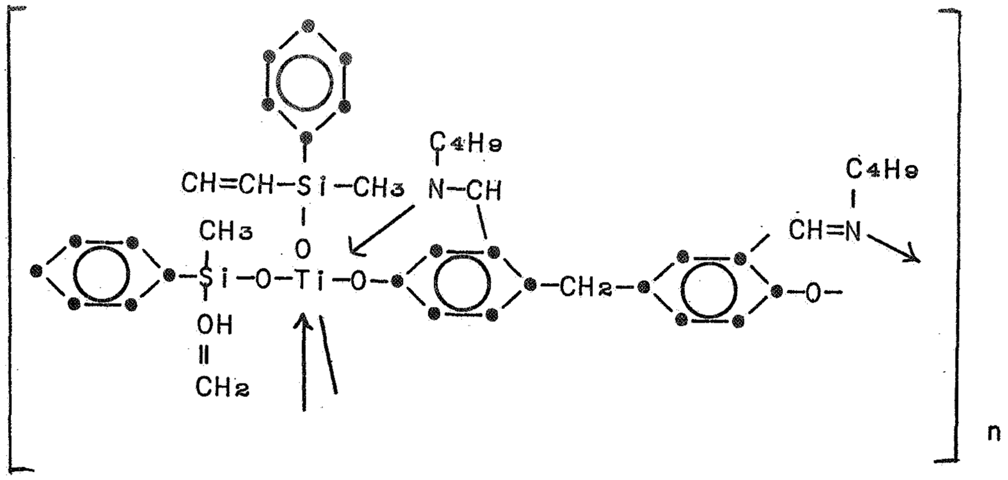
Every ligand gave products with a range of solubility characteristics and, presumably, range of molecular weight. The values of the high molecular weight fractions could not be measured because of insolubility.

All the products, both soluble and insoluble, were plasticized by arylenesilanediols to give adhesive formulations that flowed below 170°C.

5. Titanium Chelate Polymers with Vinyl Substituents

a. Preparation

These polymers were first prepared by the same general method used to prepare the silanol-substituted polymers, except that diphenylvinylsilanol was substituted in the second stage in place of the disilanol. The products of these preparations which are described in detail in the experimental section had



low molecular weights. Therefore, modified procedures, designed to increase the molecular weight of the prepolymer before substitution of the siloxy substituents, were run as follows:

(1) Condensation in toluene, together with an increase in the amount of solvent removed, to increase efficiency of removal of isopropanol byproducts;

(2) Condensation with tetrakis(dimethylamino)-titanium in place of tetraisopropoxytitanium;

(3) Reverse addition of ligand to titanium reagent with one-half of the ligand added before and one-half after addition of the silanol;

(4) Condensation in high concentration of ligand in benzene solution.

The products isolated from modifications (1) and (2) were completely soluble and had molecular weights under 2000. Their NMR spectra showed a 2-to-1 mole ratio of the siloxy substituent to the ligand and showed no SiOH or OC_4H_9 groups.

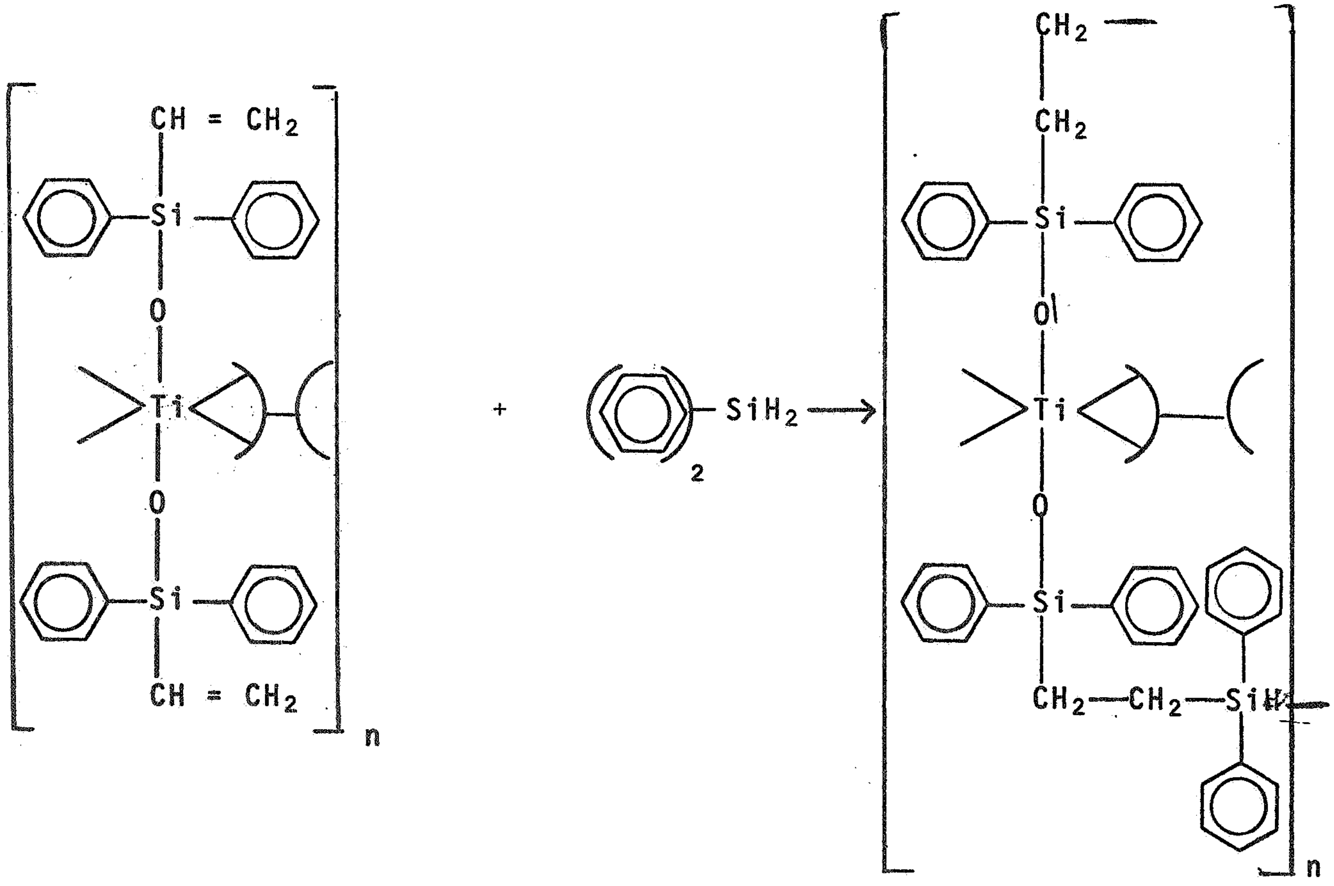
The products isolated from modifications (3) and (4) apparently had a range of molecular weights, since they could be separated by solubility into ether-soluble, ether-insoluble/benzene-soluble, and benzene-insoluble fractions. The molecular weight of the ether-insoluble/benzene-soluble fraction of modification (4) was 2900. The benzene-insoluble fraction of this modification, which was expected to have the highest molecular weight, was 15% of the total product.

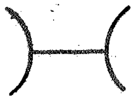
A similar condensation polymer was prepared, using the standard method, with the ligand 5,5'-bis(salicylaldehydo)methane. This polymer precipitated from solution during the initial condensation reaction and was probably highly crosslinked.

A titanium chelate polymer with mixed vinyl and silanol substituents was also prepared, using 5,5'-bis(salicyl-N-butylimino)methane as the ligand and diphenylvinylsilanol and phenylenebis(methylphenylsilanol) as reagents to substitute the side groups. The polymer was insoluble in benzene after purification and therefore its molecular weight could not be measured. However, it had a much higher softening range (170-280°C) than the low molecular weight vinyl polymers. The polymer plasticized normally with 4,4'-bis(methylphenylhydroxysilyl)biphenyl ether to give adhesive formulations that flowed well at 170°C.

b. Adhesive Properties

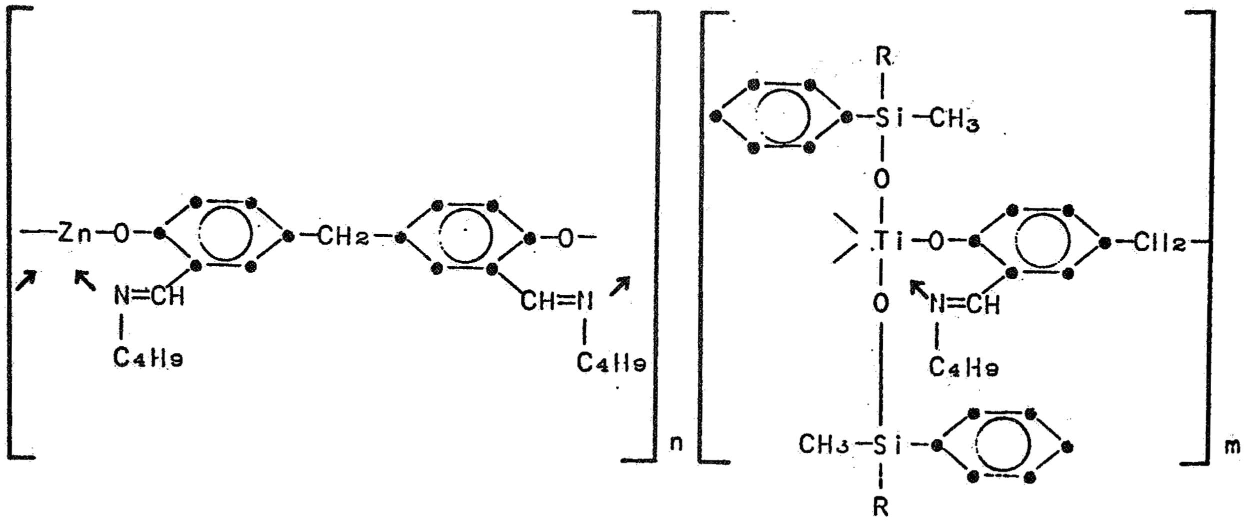
The vinyl-substituted polymers were of special interest because they cure by addition reactions that evolve no volatile byproducts to cause porosity in the adhesive joints. The general methods developed to crosslink vinyl substituted polymers by coupling with diphenylsilane as shown below are described fully in the experimental section. Silane-type prepolymers derived from 5,5'-bis(salicyl-N-butylimino)methane cured at 170°C to resins that were soft at 250°C. Resins that were hard at 250°C were obtained by adding phenylsilanetriol to these formulations. Joints coupled by these resins had strengths up to 270 psi at 250°C.



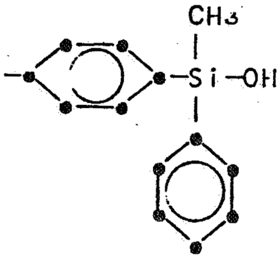
where  is a bisbidentate ligand.

6. Preparation of Titanium-Zinc Chelate Polymer

Mixed titanium-zinc chelate polymers were also prepared to obtain both vinyl- and silanol-substituted polymers with higher molecular weight. These polymers are prepared by first making a low molecular weight prepolymer by condensation of 5,5'-bis-(salicyl-N-butylimino)methane in pyridine solution with 0.6 to 0.95 mole fraction of diethylzinc, then completing the condensation of linear polymer by reaction with tetraisopropoxytitanium (0.4 to 0.05 mole ratio respectively), and finally substituting the unreacted isopropoxy sites by reaction with silanol. Details of the method used to prepare these polymers are described in the experimental section.



where R is $CH_2{=}CH-$ or



These polymers were insoluble in benzene and the polymer with a Zn-to-Ti ratio of 19 to 1 was also insoluble in pyridine. All the polymers flowed well at 170°C when plasticized by silanediols.

7. Titanium Chelate Polymers with Isocyanate Substituents

Another method evaluated to crosslink the titanium chelate polymers involved *in situ* trimerization of isocyanate substituents on the polymer backbone to isocyanurate rings. This method has four advantages:

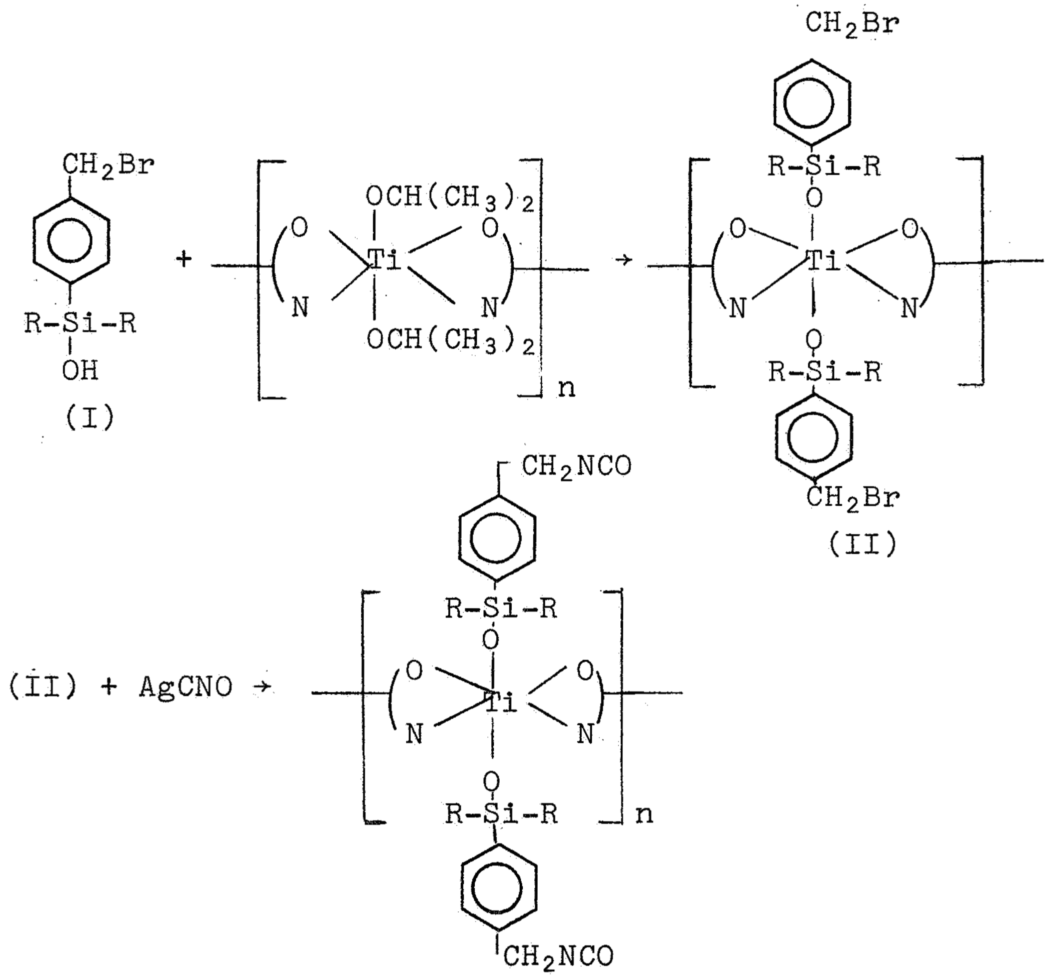
a. The isocyanurate ring has high thermal stability;

b. Cure is effected at moderate temperature (below 170°C);

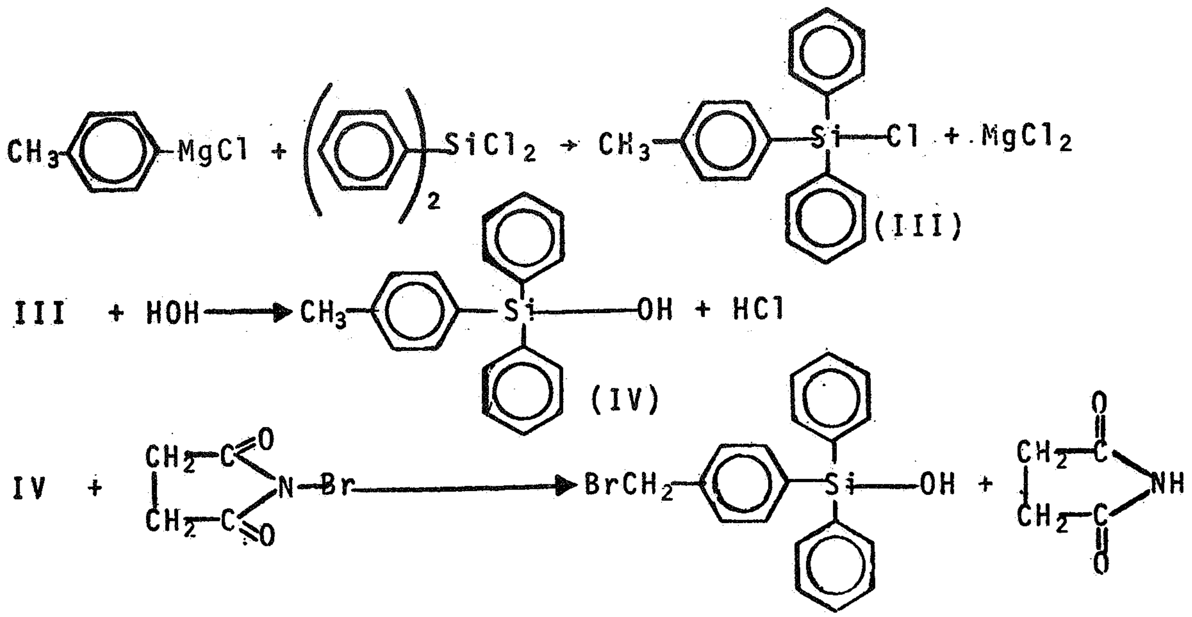
c. There are no volatile byproducts produced in the curing reaction;

d. The isocyanate group may improve the adhesive properties of the resin in aluminum adherends.

The reaction scheme used to produce such a polymer is as follows:



A stable silanol of structure I can be prepared and isolated when R is phenyl. We found that the dimethyl homolog, however, was too reactive; it condensed to its siloxane during isolation. p-Bromomethyldiphenylsilanol (I) was prepared by the following route:



The succinimide by-product in the last step was separated from the silanol by adsorption on silica gel from a benzene solution of the mixed products.

The stability of this silanol appears to vary with the degree of substitution, although the difference in stability we have found in these products could be the result of trace catalytic impurities (e.g., acid); product with 100% bromomethyl substituent appears to be stable at room temperature, but product with 87% substitution condensed to siloxane with evolution of HBr on standing over a weekend at room temperature. Partially substituted products could be stored at -10°C for short periods of time.

Prepolymers containing the bromomethyl group were prepared using our standard procedure for substitution of the siloxy groups on the polymer. Attempts to exchange the bromo group for an isocyanate group were only partially successful. Evidence of isocyanate on the polymer was seen in the infrared spectra of prepolymers after reaction with silver cyanate at 30°C in benzene, but exchange was incomplete.

Several variations of reaction conditions were used in an attempt to increase the degree of substitution by the isocyanate groups. These include:

a. Use of solvents for silver cyanate (e.g. dimethylformamide, benzene-acetonitrile);

b. Elevated temperature;

c. Addition of KI as activator;

d. KCNO in place of AgCNO;

e. Reaction on a column packed with AgCNO.

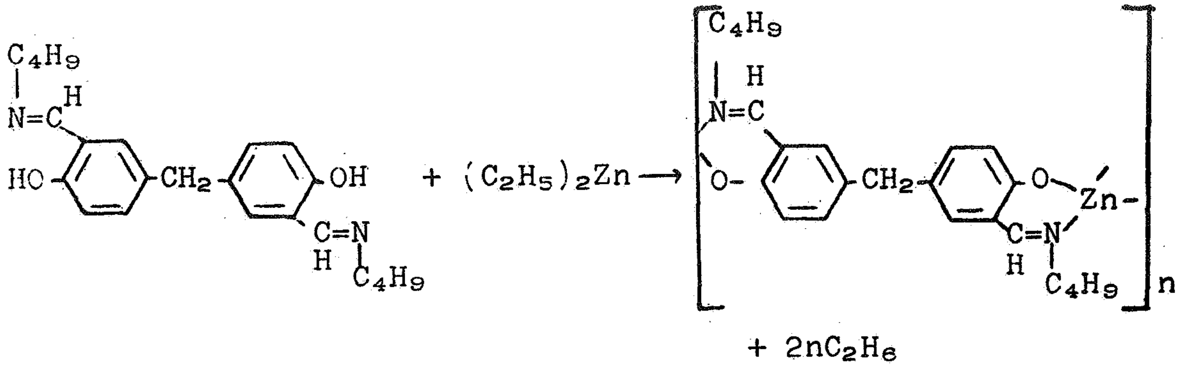
The extent of substitution of isocyanate in the products of these reactions was followed by analysis of their IR spectra. The optimal reaction condition found, based on these analyses, is the use of silver cyanate in dimethylformamide at 80°C. However, the products are not homogeneous and it is difficult to separate the silver salts from the product polymers. The bulk of product is insoluble, indicating that self-condensation is a possible side reaction.

Preparation of polymers with isocyanate substituents was deferred at this stage to complete crosslinking studies of the silanol polymers. The initial work, described above, indicates that to obtain a useful polymer with isocyanate substituents it will be necessary to: (1) improve the specificity of the isocyanate exchange reaction, i.e. $-CH_2Br \rightarrow -CH_2NCO$; and (2) use ligands with more flexible backbones, so that the prepolymers will have low melting ranges (under 170°C).

C. ZINC CHELATE POLYMERS

1. Polymerization Reaction Conditions

Our first goal in the development of a high temperature chelate polymer adhesive was the optimization of the reaction conditions for the condensation of a bis-bidentate ligand with an organometallic to yield a uniformly high molecular weight linear polymer. The condensation of 5,5'-bis(salicyl-N-butylimino)-methane with diethylzinc was used in this work because this ligand is easily prepared, and the resulting polymer is completely soluble in available solvents.



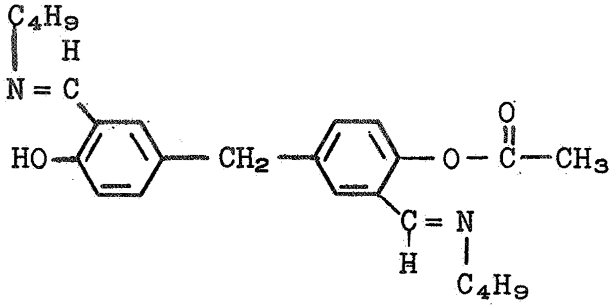
To optimize the procedure for the preparation of high molecular weight polymers we first purified all reagents, and adjusted stoichiometry to the best of our ability since accurate stoichiometry is the first requirement for the production of high molecular weight condensation polymers. Secondly, we studied the reaction variables to optimize the condensation reaction conditions. The reaction variables studied included reaction time and temperature, concentration of reactants and identity of reaction solvents.

a. Reactant Purity

The reactant purity and stoichiometry is of utmost importance to the preparation of high molecular weight chelate polymers. Therefore, in all of this work extreme care was exercised to insure the purity of all reactants and solvents.

(1) Ligand

The ligand, prepared as described in Section D.1, was found to be pure up to the limits detectable by IR, NMR, and VPC techniques (98% purity). NMR analysis of the bis-salicylaldehyde precursor to our ligand indicated that trace quantities of an acetylated material may have been present. This compound, if converted to the butylimine derivative, would be a chain-terminating group.



However, none of this compound was detected by analysis of the ligand. To eliminate this type of impurity, if present, a sample of the ligand precursor, 5,5'-methylene-bis-salicylaldehyde, was specially purified by treatment with aqueous sodium hydroxide. Samples of the n-butylimine ligand prepared from this purified batch were then polymerized with diethylzinc. No increase in molecular weight of polymer was obtained, however, thus indicating that this is not a cause of polymer termination. The relative viscosity of a 2% solution of this polymer in pyridine was 1.55.

(2) Diethylzinc

The diethylzinc used in this work was purified by fractional distillation in an anhydrous nitrogen atmosphere. Several possible methods of determining the absolute purity of the redistilled diethyl zinc were investigated. NMR and IR analyses of this material showed no detectable (<0.3%) impurities.

An even more sensitive test for purity is to determine the amount of oxygen present in the diethylzinc. Any oxygen would mean the presence of a partially hydrolyzed or oxidized species that would undoubtedly be a chain terminator. Oxygen can be determined by neutron activation analysis, and three samples of our redistilled diethylzinc were analyzed by this method. By comparing the relative intensity of the 6.13-Mev gamma-ray photopeak of N^{16} against an oxygen standard, the concentration of oxygen contaminant was caluclated. N^{16} is the product of the O^{16} (n,p)N^{16} reaction.

The results of this analysis showed that our distilled diethylzinc,contained an average of 23.2 ppm of oxygen. From this analysis, we can conclude that contamination of the diethylzinc by oxygen-containing molecules is not an important factor in causing the termination of the chelate polymer.

Termination of this type would be expected to occur less in a less basic solvent.

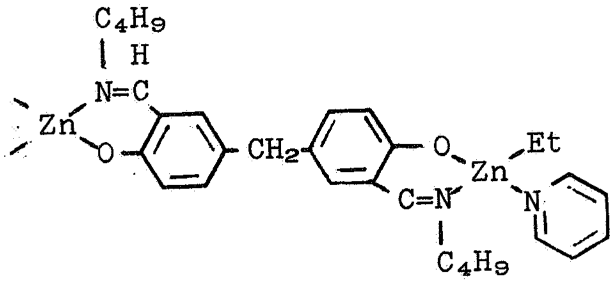
This statistical program required 27 experiments. A listing of the details of each of these experiments is given in the Experimental Section of this report. The relative molecular weights of the polymers were determined from the viscosity of 2% solutions in pyridine.

b. Statistical Study of Reaction Variables

A statistically designed program aimed at determining the optimum reaction conditions for the condensation of 5,5'-bis-(salicyl-N-butylimino)methane and diethylzinc was carried out in the three-variable, three-level program shown below. The three reaction variables were chosen as those having the greatest effect on the degree of polymerization (ref. 6).

Variables	Levels
1. Concentration of reactants	8%, 10%, 15%
2. Identity of solvents	Pyridine (pKa 5.17) Quinoline (pKa 4.8) 2-Chloropyridine (pKa 0.72)
3. Reaction times	1, 5, and 20 hours

Solvents for this study were chosen for two reasons. First, the polymer is soluble in each of these solvents. Second, these solvents represent a large range in donor properties. The donor strength of the solvent is important because the formation of a partially reacted organometallic group stabilized by a donor molecule such as that shown below may be one of the methods of polymer termination.



The data obtained in these tests were analyzed for variance using standard statistical procedures (ref. 7). The results of this analysis showed that:

(a) 2-Chloropyridine is superior to pyridine or quinoline as a reaction solvent.

(b) Varying the concentration of reactants from 8% to 15% does not affect the degree of polymerization.

(c) Variations in the reaction time over the range studied has little effect on the degree of polymerization. A slight effect is observed, however, that favors a longer reaction cycle (>5 hours).

A problem encountered in this work involved the use of high-boiling solvents such as quinoline. This solvent is many times more difficult to remove from the polymer than is either pyridine or 2-chloropyridine. In casting films of the polymers from pyridine and 2-chloropyridine, all the solvent can be removed by heating at 150°C/20 mm Hg for 4 hours. With quinoline, however, the solvent can only be removed if the semidried polymer is ground to a fine powder and then further heated at 150°C/1.0 mm Hg for at least 12 hours. Such a solvent removal problem could present a major difficulty in the use of these polymers as adhesives; therefore, high-boiling solvents were avoided.

As a result of our statistical program and our previous experience with chelate polymers of this type (ref. 6), the following tentatively optimized polymerization conditions were chosen:

(a) Reactant and solvent purity greater than 99.9 mole per cent.

(b) 2-Chloropyridine as reaction solvent.

(c) Ten per cent as the concentration of reactants.

(d) Organometallic compound to be added to a solution of the ligand at 90°C.

(e) Reaction time five hours.

A large scale condensation of 5,5'-bis(salicyl-N-n-butylimino)-methane with diethylzinc using the reaction conditions described above was run to obtain polymer for characterization.

All the reactants and the solvent used in this reaction were purified to the best of our ability. The 2-chloropyridine solvent was fractionally distilled and then dried by passing through a column of molecular sieves (Linde 4A). The ligand was recrystallized several times from both methanol and petroleum ether and was then dried under vacuum for 24 hours. The diethylzinc was freshly distilled. A complete description of the reaction scheme is given in the Experimental Section.

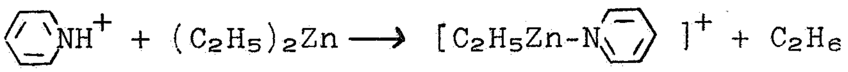
The polymer produced by this procedure had a relative viscosity of 1.63. This viscosity is equivalent to the best polymer produced in our statistical study. This polymer also showed a high softening point (range 190-222 °C, 383-432 °F). Films of this polymer cast on glass were similar in physical appearance to an unfilled phenolic resin.

The above described chelate polymer was then fractionated by first depositing the polymer on glass micro beads and then eluting with mixed solvents. The results of this fractionation are given in Table 4.

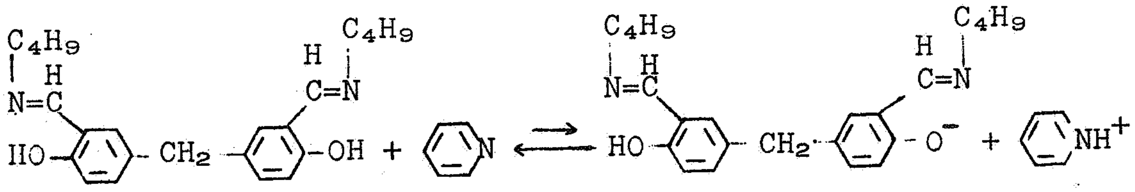
Two conclusions can be drawn from the results of this fractionation. First, this polymer has a more uniformly high molecular weight distribution than our original polymers. These data also show that in spite of the rigid control of reactant purity and stoichiometry, there is still a 5% fraction that has a low molecular weight. This led us to look for other sources of termination species.

c. Ionic Species as Chain Terminators

A possible method by which chain termination may occur in our present polymerization system is by the reaction of diethylzinc with a pyridinate ion to give a partially reacted species.



This species would then act as a chain terminating group. The hypothesized pyridinate ion might be produced in the following manner:



To eliminate, or at least minimize, this ionization we: (1) used solvents with less basicity, (2) radically increased the ratio of ligand to solvent, and (3) used a less acidic ligand.

Table 4

FRACTIONATION OF CHELATE POLYMERS FROM LARGE-SCALE PREPARATIONS

Fraction	Solvent (100 ml aliquot)	Wt % of Fraction*	Softening Point °C	Softening Point °F
1	Ethanol	5.15	70	158
2.	Acetonitrile	0.12	-	
3	3:1 Acetonitrile/ pyridine	0.45	-	
4	1:1 Acetonitrile/ pyridine	1.15	70-90	158-194
5	1:3 Acetonitrile/ pyridine	10.36	140-150	285-300
6	Pyridine	76.27	190-222	375-432
7	Pyridine	0		

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* The total recovery of polymer was 93.5%. The remaining 6.5% could not be accounted for. However, this small amount does not change the overall conclusions that can be drawn from this experiment.

The range of solvents that can be used in the polymerization of the chelate polymers is limited because these polymers are insoluble in most organic solvents. However, we found that the polymer has appreciable solubility in triphenylphosphine, dioxane, and tetrahydrofuran, all of which are less basic solvents than pyridine. Polymerizations in triphenylphosphine, tetrahydrofuran, dioxane, and mixed solvents did not, however, yield polymers of higher molecular weight than those obtained in pyridine solvents. Data are summarized in Table 5. Based on the softening points of these polymers, the highest molecular weight polymers were prepared in triphenylphosphine, triphenylphosphine-dioxane, and concentrated quinoline solvents. These polymers are, however, comparable to the best polymers prepared in pyridine and 2-chloropyridine solvents.

Table 5

EFFECT OF SOLVENT ON CHELATE POLYMERIZATION

Solvent	Ratio of Solvent to Ligand	Softening Point of Polymer, °C	Relative Viscosity of Polymer in 2% Solution of Pyridine
Triphenylphosphine	10:1	197	1.46
Triphenylphosphine	20:1	198-235(d)	1.34
1:1 Triphenylphospnine: Dioxane	33:1	189-230(d)	1.58
Dioxane	10:1	85-115*	1.09
Tetrahydrofuran	60:1	122-155, 105-170	-
Tetrahydrofuran	10:1	150-157	1.39
Pyridine	1:1	176-180	1.35
Quinoline	1:1	205-223	1.44

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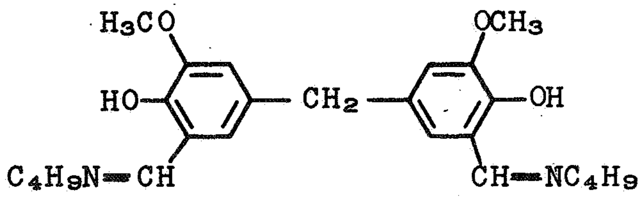
* Polymer precipitated during reaction

As detailed above, attempts to eliminate any chain termination by ionic species such as pyridinate ion both by decreasing the basicity of the solvent and by increasing the ratio of ligand-to-solvent used in the reaction did not give polymers with higher molecular weights. An alternate method of overcoming this problem was the use of a less acidic ligand. To test the effect of this type of ligand, 5,5'-bis(o-vanillinbutylimino)methane was prepared and polymerized with diethylzinc.



Bis(o-vanillinbutylimino)methane was polymerized in a pyridine solvent by the same procedure used for the unsubstituted ligand, except that reaction time was extended to 24 hours to compensate for the lesser activity of the phenolic hydrogen. The resulting polymers had a softening point of 225-275°C. Relative viscosity in 2% pyridine was 1.38 for one sample and 1.47 for the other. The polymers are more crystalline and have lower solubility in pyridine than polymers of the unsubstituted ligand.

Results of polymerizations in such a wide range of reaction conditions indicate that ionic species are probably not the cause of chain termination.

d. Polymerizations Using Dimethylcadmium

To insure that the degree of polymerization of our chelate polymer was not limited by side reactions involving zinc, we prepared chelate polymers from 5,5'-bis(salicyl-N-butylimino)-methane and dimethylcadmium. The procedure used was the same as that used for diethylzinc, except that the organometallic was added at 80°C instead of 90°C. Polymerizations using dimethylcadmium are slower than those using diethylzinc, and we found it necessary to heat the polymerization mixture at the reflux temperature of the pyridine solvent overnight to complete the condensation. The resulting polymers are completely soluble in pyridine.

Viscosity measurements of these polymers in 2% pyridine solution indicated that the polymer had about the same degree of polymerization as the zinc polymers. However, the softening point of the polymers is somewhat higher than comparable zinc polymers (270-280°C compared to 190-220°C).

Two other types of linear polymers containing cadmium were also prepared:

1. Dimethylcadmium condensed with 5,5'-bis(salicyl-N-hexylimino)-methane yielded a polymer with softening point of 180-203°C and comparable molecular weight.

2. Copolymerization of dimethylcadmium and diethylzinc in the ratio 1:3 with the standard n-butyl ligand yielded a polymer that softened in the range 178-195°C and had relative viscosity in 2% pyridine solution of 1.55.

In summary, the properties of the cadmium polymers are comparable to the zinc polymers except that softening points are higher.

e. Polymerizations Using Other Organo Zinc Compounds

The objective of this work was to determine whether less reactive organo zinc compounds would be superior sources of zinc for the polymerization of our bis-bidentate ligands.

Two organo zinc compounds, diphenylzinc and di-n-butylzinc, were reacted with 5,5'-bis(salicyl-N-butylimino)methane using our best polymerization technique. The polymers produced by both of these organometallics were, however, inferior to those obtained by using diethylzinc. The viscosities of 2% solutions were lower, and the films cast from these polymers were excessively brittle. We found that for these less reactive compounds, the condensation reaction must be carried out at an elevated temperature and over a longer period of time.

As a result of this work, our best linear chelate polymers now have a relative viscosity of approximately 1.70. Although this specific viscosity would not indicate a very high molecular weight material, we felt that it was sufficient to allow us to continue on to our crosslinking studies.

2. Ligand Structural Study

The second part of our program on zinc chelate polymers was aimed at determining the structural requirements of the ligand that lead to the optimum stability and tractability in the corresponding zinc chelate polymer.

The study of effects of structure on polymer tractability can be divided into two parts. The first part was aimed at determining the effect of the size of the ligand side group on the crystallinity and tractability of the corresponding polymer. This information is essential so that we may know the optimum size, shape, and type of side group to place on a chelate polymer so that the crystallinity of the polymer is sufficiently reduced to yield a tractable material without sacrificing thermal and oxidative stability. To accomplish this, the following imine derivatives of 5,5'-bis(salicylaldehydo)methane were prepared, purified, and polymerized.

a. 5,5'-bis(salicyl-N-ethylimino)methane

b. 5,5'-bis(salicyl-N-iso-butylimino)methane

c. 5,5'-bis(salicyl-N-tert-butylimino)methane

d. 5,5'-bis(salicyl-N-sec-butylimino)methane

e. 5,5'-bis(salicyl-N-cyclohexylimino)methane

f. 5,5'-bis(salicyl-N-4-methylbenzylimino)methane

g. 5,5'-bis(salicyl-N-n-hexylimino)methane

The polymers resulting from these ligands were, with the exception of the n-hexyl substituted ligand, more crystalline than polymers formed from the n-butyl ligand. The polymer formed from the n-hexyl substituted ligand was soluble and noncrystalline, as expected. Based on their softening point and relative solubilities in pyridine, the most crystalline polymers were those with t-butyl and cyclohexyl substituents; the least crystalline was the isobutyl-substituted polymer. Table 6 summarizes these results.

Table 6

CHARACTERISTICS OF CHELATE POLYMERS FROM VARIOUS SUBSTITUTED 5,5'-BIS(SALICYL-N-ORGANOIMINO)METHANE LIGANDS

Substituent on Imine	Softening Point of Polymer, °C	Film Characteristics
Ethyl	240-270(d)	Formed an insoluble fraction
Isobutyl	145-220	Extremely brittle
Sec-butyl	over 300	Extremely brittle
t-Butyl	over 315	Formed an insoluble fraction
Cyclohexyl	over 305	Formed an insoluble fraction
n-Hexyl	175-227*	Resinous
4-Methylbenzyl	215-232	Formed an insoluble fraction

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* Relative viscosity of 2% solution in pyridine was 1.44.

From the evaluation of these polymers and from our previous work on chelate polymers of this type, we can conclude that the side groups on the chelate polymers must be aliphatic and must be at least as long as an n-butyl group to yield a tractable resin.

In addition to determining the effect of ligand side groups on the crystallinity and tractability of our chelate polymers, it was also important to determine how various other bisbidentate ligands that contain either other flexible linkages or other aromatic ligand groups of potentially higher oxidative stability than salicylaldehydeimine affect the tractability of a zinc chelate polymer. To do this, the following bisbidentate ligands were prepared, purified, and polymerized.

a. 5,5'-bis(salicyl-N-butylimino)sulfone

b. 5,5'-bis(8-hydroxyquinolino)methane

c. 5,5'-bis-(7-hexanoxyl-8-hydroxyquinolino)methane

d. 5,5'-bis(4-hydroxy-3-octanoylphenyl)pentane

5,5'-Bis(salicyl-N-butylimino)sulfone was condensed with diethylzinc in pyridine by the standard polymerization procedure. The ligand gave a green solution. This color disappeared when the equivalent amount of diethylzinc was added to the reaction. The product precipitated during reaction and only 3% of product was found to be soluble in pyridine. The polymer softened in the range 270-300(+)°C.

The characteristics of this polymer indicate that the sulfone linkage is not suitable for incorporation into chelate polymers where solubility and tractability are required. The sulfone linkage may cause crystallinity and insolubility either by interaction of the oxygen atoms on the sulfone group with phenyl groups on adjacent polymer chains or, more probably, by simply decreasing the flexibility of the polymer chain.

Bis-(8-hydroxyquinolino)methane, polymerized using our best polymerization method with diethylzinc, gave an insoluble, intractable polymer, which did not soften up to 300°C.

This ligand, however, was copolymerized with 5,5'-bis(salicyl-N-n-butylimino)methane to yield a soluble polymer. To obtain a soluble polymer, the salicylaldehydeimine ligand must be first reacted with diethylzinc, and then the 8-hydroxyquinolino ligand added. This is necessary because if both ligands are present initially, two polymers are made. One is insoluble and crystalline, consisting of mostly quinolinate units, and the other is the soluble bis(salicylaldehydeimine) polymer. The 8-hydroxyquinolino ligand is much more reactive. The preparation of these polymers is given in the experimental section of this report.

The soluble copolymer that resulted from aligand charge of 1 part of 5,5'-bis(8-hydroxyquinolino)methane to 3 parts of 5,5'-bis(salicyl-N-butylimino)methane had a softening point of 273-282°C, about 50°C above that of the standard linear salicylaldehydebutylimine polymers.

Chelate polymers derived from the 8-hydroxyquinolino linkage have two advantages: (1) the chelate bond is strong; and (2) polymers derived from this chelate are extremely stable both thermally and oxidatively (ref. 8). Therefore, substituted bisbidentate ligands with 8-hydroxyquinoline sites, such as bis(7-hexanoyl-8-hydroxyquinolino)methane were made and polymerized to improve polymer tractability.

Condensation of 5,5'-bis(7-hexanoyl-8-hydroxyquinolino)methane with diethylzinc gave a crystalline, insoluble polymer that did not melt under 300°C. The infrared absorption of the carbonyl group was shifted in the polymer to 6.1 microns from 6.0 microns in the ligand, indicating that the zinc was coordinated to a carbonyl oxygen in preference to the quinoline nitrogen. This change in donor groups undoubtedly affected the steric blocking ability of the side group.

The ligand 1,5-bis(4-hydroxy-3-octanoylphenyl)pentane has both a very flexible connecting linkage and a bulky side group to protect the zinc atom. Zinc chelate polymers of 1,5-bis(4-hydroxy-3-octanoylphenyl) pentane were prepared in pyridine solution by the same procedure. The linear zinc polymers prepared from this ligand were soluble in pyridine and had low softening points.

Copolymers of this ligand and ligands containing the 8-hydroxyquinoline nucleus were also prepared and were found to have higher softening points. A description of the polymers prepared from this ligand is given in Table 7.

3. Crosslinking and Cure of Zinc Chelate Polymers

a. Precure of Zinc Chelate Polymers

A limited amount of work was done to precure linear zinc chelate polymers by crosslinking for use as adhesives in steel joints. Crosslinking was accomplished in pyridine solution by the following three general methods.

1. Incorporation of multiple site ligands such as tris(2-hydroxyphenyl)-s-triazine or low molecular weight methylene-linked 8-hydroxyquinoline polymers into the polymer.
2. Incorporation of trivalent metal ions into the prepolymer by ligand exchange with trisacetylacetonato or trishexafluoroacetylacetonato chelates.
3. Direct incorporation of trivalent metal ions into the polymer by reaction with triethylgallium or triethylaluminum.

Table 7

CHELATE POLYMERS PREPARED FROM 1,5-BIS-(4-HYDROXY-3-OCTANOYLPHENYL)PENTANE

Ligand$_1$ (L_1)	Ligand$_2$ (L_2)	Metal† (M)	Mole Ratio Charged L_1: L_2: M	Softening Point of Polymer °C
Oct.*	--	Zn	1:0:1	44-59
Oct.	--	Zn	1:0:1	29-66
Oct.	--	Zn	1.1:0:1**	40-53
Oct.	--	Ti	1:0:1	>285††
Oct.	--	Ti	1:0:1	125 over 230††
Oct.	Hex*	Zn	0.77:0.33:1	115-158
Oct.	Hex	Zn	0.49:0.51:1	210-239
Oct.	CH_2*	Zn	0.9:0.41:1**	138-172

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* Oct. = 1,5-bis-(4-hydroxy-3-octanoylphenyl)pentane
5,5'-bis(7-hexanoyl-8-hydroxyquinolino)methane
5,5'-bis(8-hydroxyquinolino)methane

† Zn reagent was diethyl zinc; titanium reagent was titanium tetrabutoxide

** Prepolymers prepared with excess ligand

†† High softening points indicate partial crosslinking through alkoxy substituents

These reactions generally gave mixtures of soluble, fusible and insoluble, infusible products. Since the products that were infusible at temperatures much above 250°C were also intractable and unusable as adhesives, this approach to curing the polymers was abandoned.

b. Low-Temperature *In Situ* Cure of Zinc Chelate Polymers

A series of these low-melting, linear, zinc chelate polymers were crosslinked with diamines in aluminum adherend joints. Tensile shear strength in the ranges of 800-1020 psi at room temperature and 204-270 psi at 260°C were obtained with these resins. The shear tensile specimens were prepared by melting finely ground powder mixes of the linear chelate polymer and diamine on the aluminum test strips at 170°C. Curing was then accomplished by heating at 170°C for periods of 24 to 96 hours. Pressures above 5 psi were required only for polymers that softened above about 140°C. For these, specimens were first compressed for 10 minutes at 170°C and 500 psi and then cured completely at 170°C and 3-5 psi pressure.

The results of this work, summarized in Table 8, led to the following conclusions. First, aliphatic diamines are more effective crosslinking agents than the corresponding aromatic diamines. Second, α-aminopropyltriethoxysilane also acts as an efficient crosslinking agent and the curing rate appears to be faster with this reagent. Stability of these polymers is limited by low oxidative stability of the Schiff base crosslinkage. Therefore, no further work was done in this series.

4. Evaluation of Adhesive Properties of Linear Chelate Polymers

The adhesive character of the linear chelate polymers was also measured on stainless steel. A large batch of the linear zinc 5,5'-bis(salicyl-N-butylimino)methane polymer was prepared for these evaluation tests. This batch of polymer was representative of the best of the linear polymers. Its relative viscosity in 2% pyridine was 1.75 and its softening point was 195-235°C.

Shear tensile strength values as high as 1300 psi were obtained. As would be expected, adhesive strength was highly dependent on the method used to fabricate the test specimens.

The best reproducibility and also the highest tensile shear strengths were obtained by first coating the specimens in an inert atmosphere with melted resin and then spreading the coating evenly over the surface with a doctor blade. The paired test specimens were then pressed together at 10 to 20 psi and allowed to cool.

Using this method, tensile shear strengths of 1230 ± 110 psi (25°C) were obtained with specimens coated with two different batches of linear chelate polymer. Other methods of coating gave poor reproducibility and lower shear strengths.

Table 8

TENSILE SHEAR STRENGTHS ON ALUMINUM OF ZINC CHELATE POLYMERS CURED *IN SITU* BY REACTION WITH DIAMINES

Test No.*	Polymer Composition			Crosslinking Agent	Conditions of Cure		Temp. of Test °F	Tensile Shear Strength, (psi)
	Ligand 1	Ligand 2	Ratio Ligands		Pressure (psi) for Initial 10 min	Cure Time (hr) at 170°C and 3 psi		
1	Oct.†	--	--	1,6-hexanediamine	--	92	r.t.	1020,668
2	Oct.	--	--	p-phenylenediamine	--	92	r.t.	337,263
3	Oct.	--	--	" (with polymer pre-coat on strips)	--	92	r.t.	325,390
4	Oct.	HQ	3/1	1,6-hexanediamine	500	18	r.t.	905,802
5	Oct.	OQ	4/1	A-1100	--	16	500	245,270
6	Oct.	HQ	3/1	1,6-hexanediamine	500	68	500	204,209
7	Oct.	HQ	3/1	1,6-hexanediamine	500	68	500	152,168
8	Oct.	HQ	3/1	1,6-hexanediamine	500	68	500	254,192
9	Oct.	HQ	3/1	1,6-hexanediamine plus aluminum filler	500	20	500	139, 62

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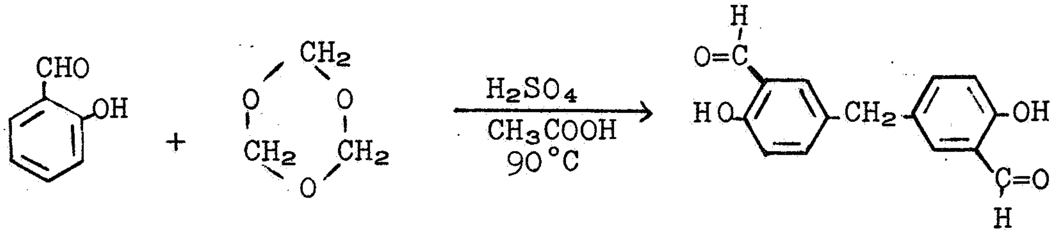
* Two specimens each test

† Oct. = 1,5-bis(4-hydroxy-3-octanoylphenyl)pentane
HQ = 5,5'-bis(7-hexanoyl-8-hydroxyquinolino)methane
OQ = 5,5'-bis(7-octanoyl-8-hydroxyquinolino)methane

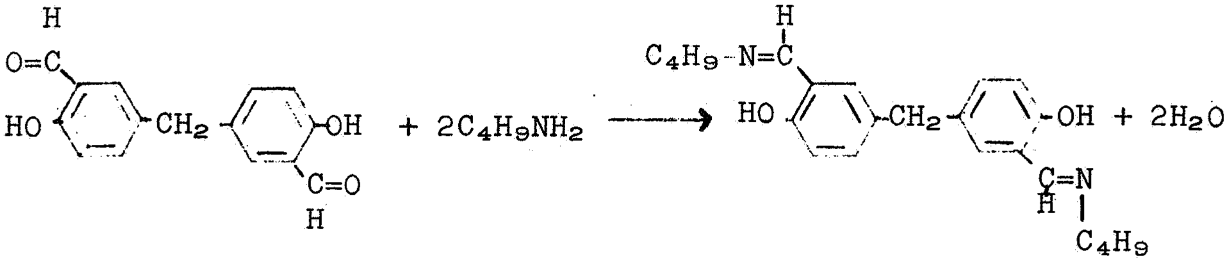
D. PREPARATION OF LIGANDS

1. Schiff Base Ligands

The bisbidentate ligand 5,5'-bis(salicyl-N-n-butylimino)-methane was used as a standard to develop the best preparation procedures for the various chelate polymers since it gave soluble, tractable chelate polymers (ref. 6) and was easily prepared. Highly purified 5,5'-bis(salicyl-N-butylimino)methane was prepared by a two-step procedure. First, 5,5'-bis(salicylaldehydo)methane was prepared by the procedure of Marvel, et al (ref. 9). This procedure involves the condensation of salicylaldehyde with s-trioxane in glacial acetic acid solvent.



The second step is the condensation of the bis(salicylaldehyde) with n-butylamine to form the dibutylimine derivative.

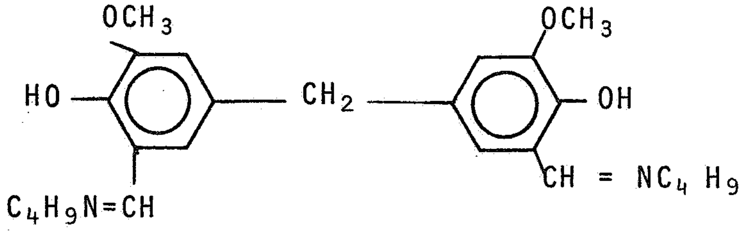


The formation of this Schiff base can best be carried out in refluxing benzene. The water formed in the reaction is removed by azeotropic distillation. The crude ligand is purified by multiple recrystallizations from petroleum ether.

Several other 5,5'-bis(salicyl-N-organoimino)methaneswwere prepared by the same general procedure using the following primary amines: ethyl, sec-butyl, iso-butyl, t-butyl, cyclohexyl, n-hexyl, γ-dimethylaminopropyl, and 4-methylbenzyl. These ligands were used to study the steric effect of the ligands on the tractability of zinc chelate polymers (Section C).

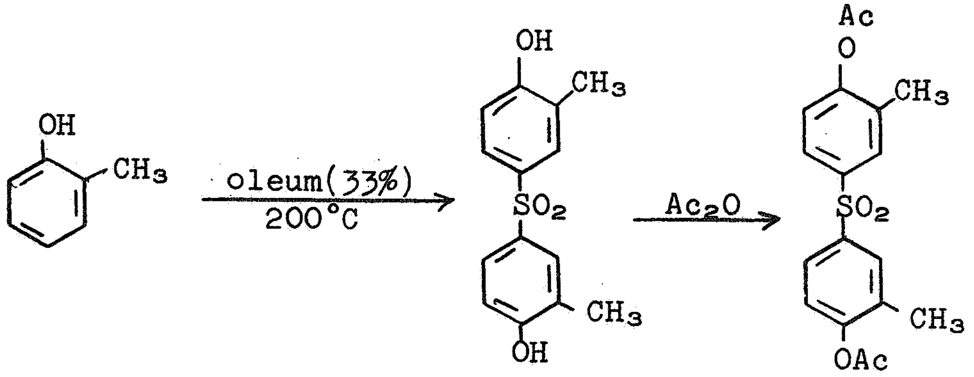
Several attempts were also made to prepare the pentafluoroaniline derivative of 5,5'-bis(salicylaldehydo)methane. Ligands containing this type of side group were of interest because of their increased thermal stability. Attempts to prepare this compound by conventional techniques using benzene, toluene, or xylene as solvent were not successful. Based on infrared analysis of the product, this ligand was prepared in small yields by the direct reaction of 5,5'-bis(salicylaldehydo)methane and pentafluoroaniline in a melt. However, the product was not successfully separated from starting materials in the purity needed for polymerization.

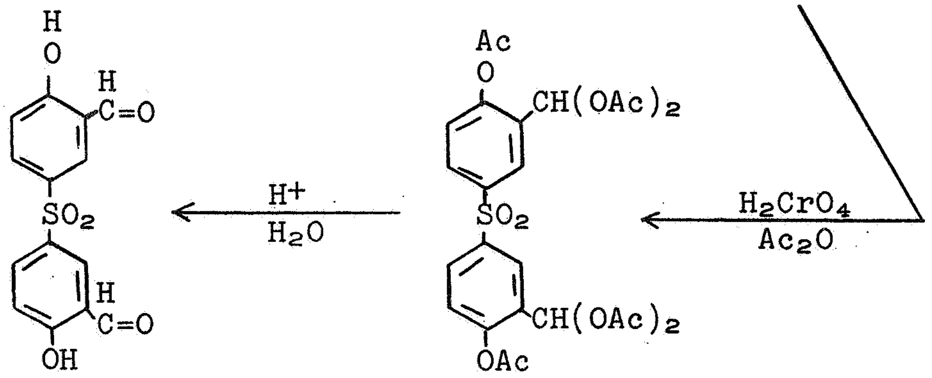
5,5'-Bis(3-methoxysalicyl-N-butylimino)methane was prepared to study the effect of decreasing the acidity of the ligand on the condensation reaction of ligand with diethylzinc.



We prepared this ligand by first preparing 5,5'-bis(3-methoxysalicylaldehydo)methane and then reacting this compound with n-butylamine to give the desired material. The precursor, 5,5'-bis(3-methoxysalicylaldehydo)methane was prepared by reacting o-vanillin with formaldehyde in a basic solution. The position of the methylene group in our product was not determined, but it was probably para to the hydroxyl substituents.

A bis(salicyl-N-n-butylimine) ligand with sulfone connecting linkage instead of methylene was also prepared. The intermediate 5,5'-bis(salicylaldehydo)sulfone was prepared by the method of Bailer, et al., (ref. 10). This method involves the condensation of o-cresol in fuming sulfuric acid to give 3,3'-dimethyl-4,4'-dihydroxydiphenylsulfone, which, on treatment with acetic anhydride, gives a corresponding diacetate. Oxidation of the diacetate with chromic acid in acetic anhydride then gives the hexa-acetate. Acid hydrolysis of the hexadiacetate yields the bis-salicylaldehyde. The overall yield was 12%.

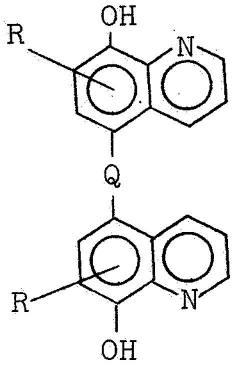




The butylimine derivative of this compound was prepared by a procedure identical with that previously described for 5,5'-bis(salicyl-N-butylimino)methane.

2. 8-Hydroxyquinoline Ligands

To increase the thermal and oxidative stability of the chelate polymers, bisbidentate ligands of 8-hydroxyquinoline were prepared:



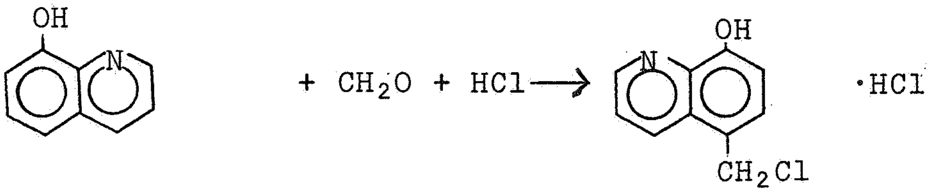
bis-8-hydroxyquinolines

Ligands of the above type with several different Q and R groups were prepared to vary the flexibility and the tractability of the product polymers. Ligands with low flexibility were used principally as crosslinking agents for the polychelatotitanosiloxanes; ligands with high flexibility were incorporated into the backbone of the chelate polymers.

Flexible bisbidentate 8-hydroxyquinoline ligands were not previously available. In our work, we found that flexible linkages could readily be inserted between the 8-hydroxyquinoline groups by reaction of diamines with 5-chloromethyl-8-quinolinol hydrochloride. The methods used to prepare this type of ligand and other bis(8-hydroxyquinolino) Q ligands used in the program are summarized below.

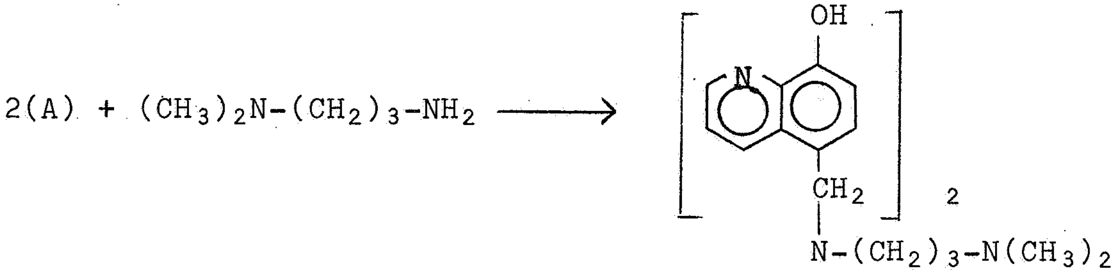
a. Ligands Derived from 5-Chloromethyl-8- quinolinol Hydrochloride

The intermediate 5-chloromethyl-8-quinolinol hydrochloride, (A), was prepared by the method described by Burckhalter and Leib (ref. 11).



(A)

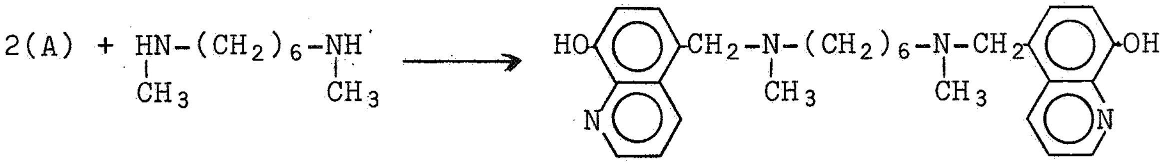
One bisbidentate ligand was prepared by reaction of γ-dimethylaminopropylamine with [A], as follows:



A procedure similar to that used by Burkhalter and Leib (ref. 11) for reaction of the chloromethyl compound with amine reactants was used. A detailed description of the preparation is in the experimental section. The product melts at 118-9°C and is soluble in benzene.

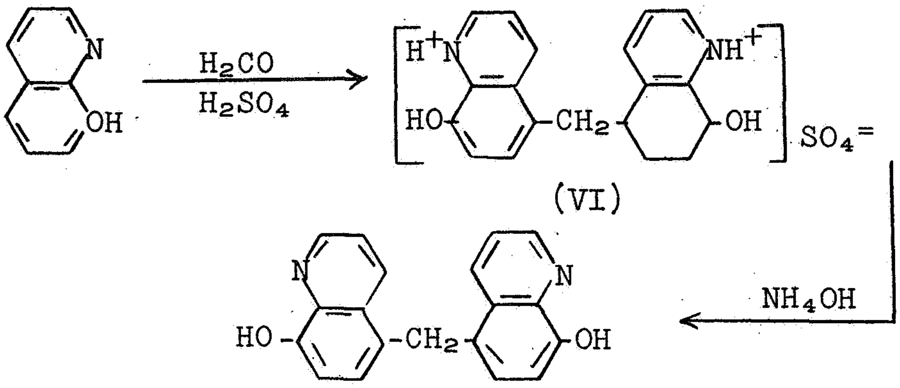
The n-butyl analog, N,N-bis(8-hydroxyquinolylmethyl)butylimine was prepared in the same way from butylamine and the hydrochloride.

A longer connecting linkage was inserted between the 8-hydroxyquinoline groups by using an α,ω-secondary diamine in a similar reaction, as follows:



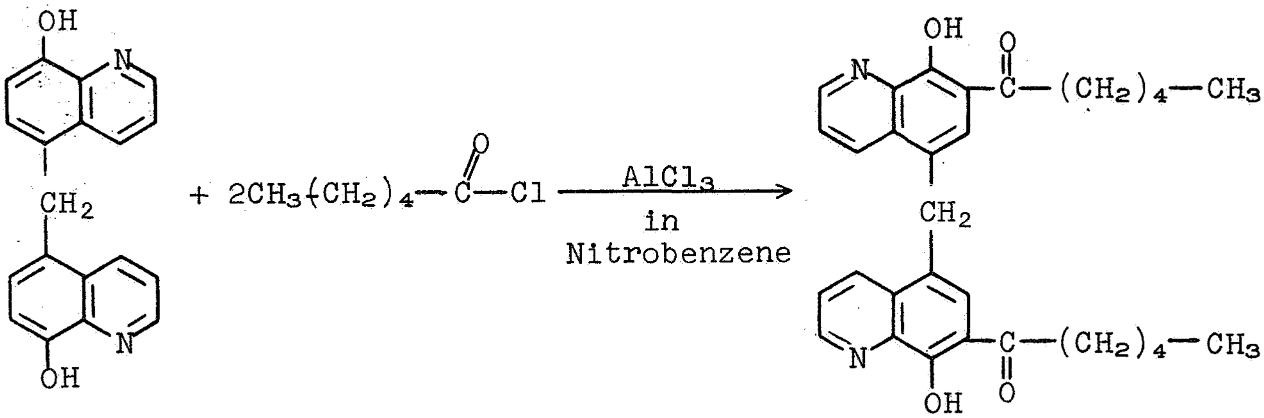
b. 5,5'-Bis(8-hydroxyquinolino)methane

5,5'-Bis(8-hydroxyquinolino) was prepared by a modification of the procedure of Schuller (ref. 12). This procedure involved the condensation of 8-hydroxyquinoline with formaldehyde in concentrated sulfuric acid at 0°C to yield 5,5'-methylene-bis-8-hydroxyquinoline sulfate. Decomposition of the sulfate by aqueous ammonia yielded the desired product. This ligand was purified by recrystallization from dimethylformamide as described by Korshak (ref. 13). The overall yields were about 25%.



c. 5,5'-Bis(7-alkanoyl-8-hydroxyquinolino)methane

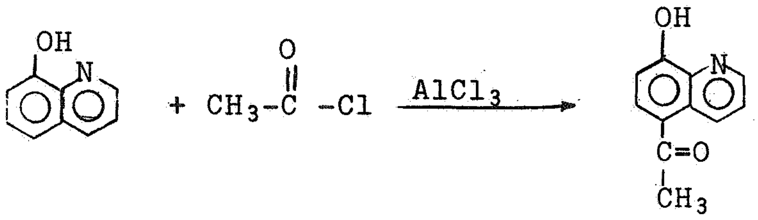
5,5'-Bis(7-hexanoyl-8-hydroxyquinolino)methane was prepared by the Friedel-Crafts reaction of hexanoyl chloride with 5,5'-bis(8-hydroxyquinolino)methane. This ligand has two sets of donating groups: (1) the nitrogen in the quinoline nucleus; and (2) the carbonyl oxygen. The long alkyl substituents are used to increase polymer solubility and tractability. The octanoyl analog was also prepared by the same method.



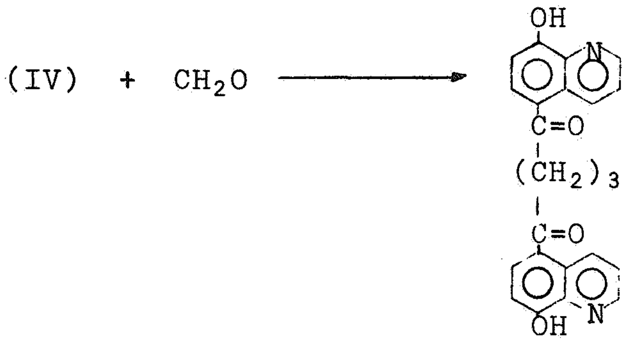
Two attempts to prepare 5,5'-bis(7-perfluorooctanoyl-8-hydroxyquinolino)methane were made. After reaction under conditions used to prepare the 7-octanoyl analog, only starting material was recovered. Reaction at a higher temperature (120°C) yielded mixed products that showed carbonyl substitution in their infrared spectra, but we were not able to separate any of the desired product from the mixture.

d. Attempted Preparation of 1,5-Bis(8-hydroxy-5-quinolyl)-pentane

Intermediates for the preparation of 1,5-di(8-hydroxy-5-quinoyl)pentane were prepared by the following reactions:



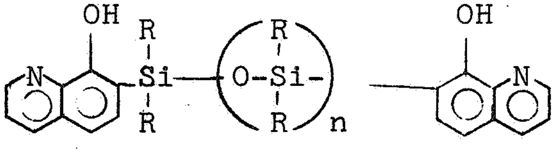
(IV)



Attempts to reduce carbonyl groups in (V) were not successful. No reduction occurred with hydrogen using Pd/$BaSO_4$ catalyst under the conditions reported by Rosenmond and Karst (ref. 14) for reduction of carbonyl substituents on the quinoline nucleus. When forcing conditions and $PdCl_2$ catalysts were used, partial reduction of the quinoline nucleus occurred. An attempt to reduce the carbonyl groups by the Clemmensen method was also unsuccessful.

e. Siloxane-linked 8-Hydroxyquinolines

We planned to use siloxanes as the Q-linkages between 8-hydroxyquinoline nuclei since the results of our study of the structural requirements of ligands with the 8-hydroxyquinoline group showed that both a flexible connecting linkage and a bulky side group were required to insure polymer tractability in polymers containing zinc atoms. The most direct way to obtain this was by use of 7-substituted connecting linkages that also have a bulky group, as for example:



where R is octyl or a siloxane group.

The intermediate α-ω-dichloropolydimethylsiloxanes were readily prepared by hydrolysis of dimethyldichlorosilane by adding a dioxane-water solution to an ether solution of the silane (ref. 15).

However, coupling of the siloxanes to the 8-hydroxyquinoline nucleus was not successful. Two approaches were taken. The first was direct reaction of 5-chloro-7-iodo-8-methoxymethyleneoxyquinoline via the Grignard reaction or coupling with sodium. Several variations in the Grignard reaction conditions were tried:

1. Solvents (ether and tetrahydrofuran).

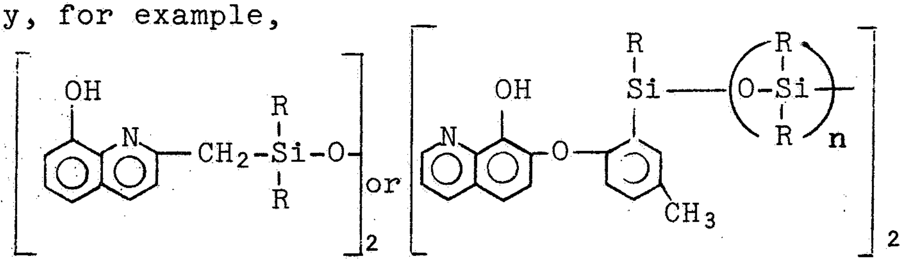
2. Order of addition of silane (initial or after Grignard reaction initiated).

3. Stoichiometry (calculated or excess Grignard component; a mole of methylmagnesium bromide was used in one run).

4. Elimination of iodide ion [it contributes to side reaction with tetrahydrofuran in the presence of Mg and chlorosilanes (ref. 16)].

The main problem appeared to be that these substituted quinoline compounds did not form a normal Grignard reagent although magnesium was consumed. The 5-chloro compound in tetrahydrofuran was reacted with magnesium in the absence of chlorosilanes in one run; 60% of the magnesium was consumed, but no carboxylic acid product could be isolated after carboxylation in Dry Ice.

The second approach was to substitute the siloxane bridges indirectly, for example,



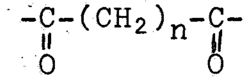
Reaction of 8-hydroxyquinaldine with two moles of butyllithium and one-half mole of dichlorotetramethyldisiloxane in tetrahydrofuran gave visual indication of formation of the colored $-CH_2Li$ salt and its dissappearance on addition of the chlorosiloxane, but starting material (the quinaldine) was recovered on isolation of products. The chlorosilanes apparently do not couple on the hydroxy group; products are isolated as lithium salts even when a mole of trimethylchlorosilane is included in the reaction sequence.

In the coupling reaction of 5,7-dibromo-8-hydroxyquinoline with silicon compounds via butyllithium, the direct alkylation reaction of butyllithium predominated.

An attempt to substitute the phenoxy group by reaction of potassium phenoxide with 5-chloro-7-iodo-8-hydroxyquinoline in the presence of copper gave a polymeric product.

3. α-Acylphenols

a. 1,5-Bis(4-hydroxy-3-octanoylphenyl)pentane

The reaction scheme shown in Figure 1 illustrates the routes taken to incorporate the octanoyl radical as R and  $-\underset{\underset{O}{\|}}{C}-(CH_2)_n-\underset{\underset{O}{\|}}{C}-$ and $-(CH_2)_n-$ as Q.

1,3-Bis(p-methoxybenzoyl)propane (A) was prepared readily by the Friedel-Crafts reaction of glutaryl chloride with anisole using the procedure of Lipp and co-workers (ref. 17). Initial attempts to prepare bis(p-hydroxybenzoyl)methane by reacting phenol with succinyl chloride and aluminum chloride was not successful. These reactions were carried out in nitrobenzene at 50-60°C to favor <u>para</u> substitution. However, even after prolonged reaction periods, large quantities of the starting material, phenol, and partially reacted materials soluble in sodium carbonate were recovered. The remaining products isolated were condensation products. Since intermolecular ring formation is a serious side reaction in this procedure, we abandoned this method in favor of the Friedel-Crafts reaction of anisole with glutaryl chloride, which was successful.

A Friedel-Crafts reaction of 1,3-bis(p-methoxybenzoyl) propane (A) with octanoyl chloride in carbon disulfide resulted in dimethylation of the methoxy group and yielded the ester, 1,3-bis(p-octanoyloxybenzoyl)-propane (B). Attempts to prepare the desired ortho-substitued acyl compound (D) by the Fries rearrangement of this ester in nitrobenzene were unsuccessful.

Therefore, in order to facilitate introduction of the octanoyl substituents, we reduced the carbonyls in (B) to give the hydrocarbon (C). This reduction step was difficult. Reduction by Martin's modification of the Clemmensen method (ref. 18) gave two products. The major product melts at 78-81°C, which is over 30°C above that of the expected product, and is low in alkyl hydrogens. Reduction of the diketone by hydrogen with $PdCl_2/PtCl_2$ catalyst in acetic acid at room temperature caused partial reduction of the phenyl rings. Reduction of dianisalacetone by the same procedure gave similar results. Platinum on carbon catalysts, however, were inactive under the same conditions with these compounds.

Two methods of reduction were found to give the desired product. The first method used was two-step reduction of dianisalacetone. Initial reductions with hydrogen at 2 to 3 atmos-

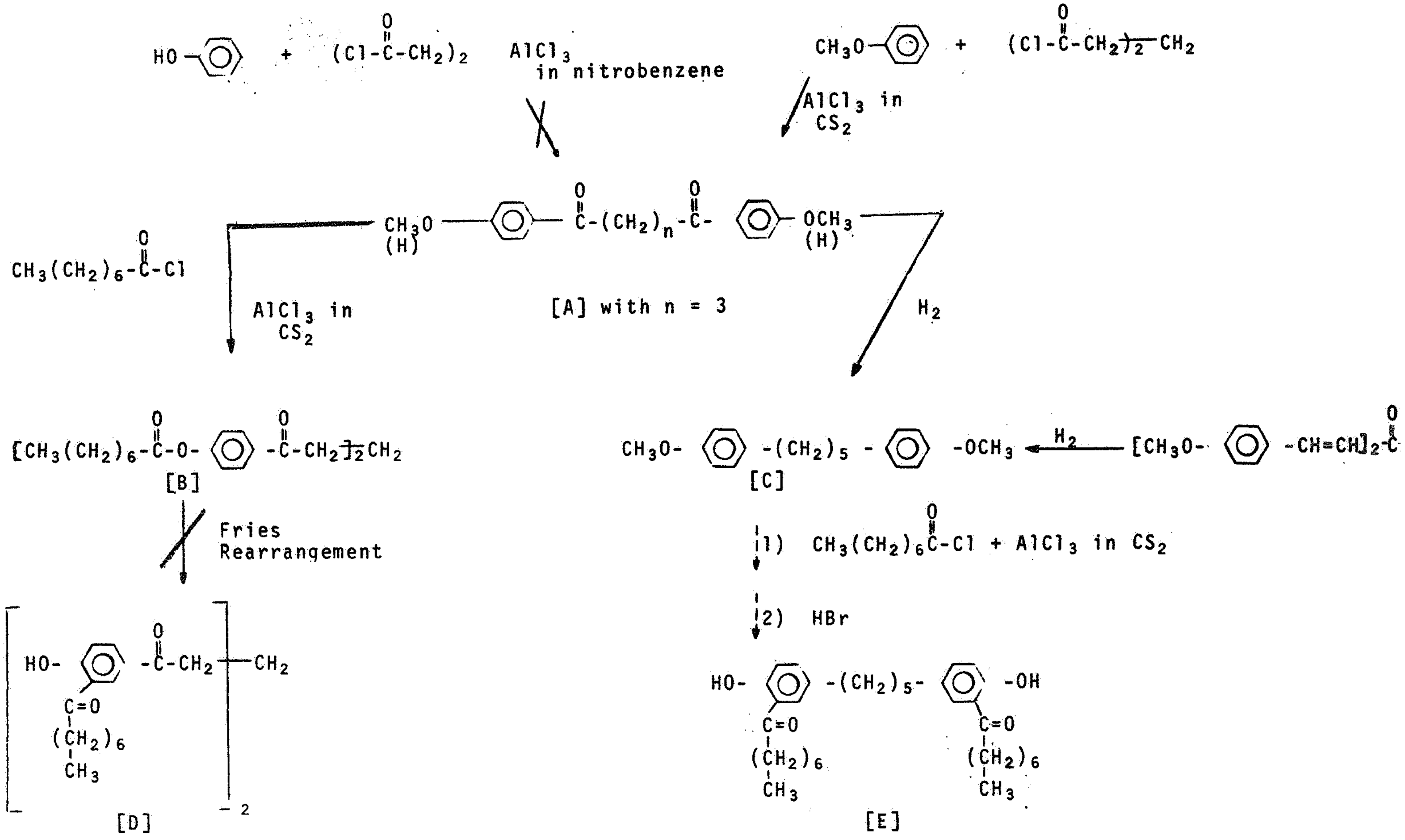


Figure 1. Preparation of Ligands Derived from α-Acylphenols

pheres pressure with Pd/$BaSO_4$ catalyst yielded a reproducible mixture of a partially reduced compound containing hydroxyl groups plus the desired completely reduced product. Reduction to the hydrocarbon was completed by the Clemmensen method.

The alternate route was by reduction of 1,3-bis(p-methoxybenzoyl) propane by hydrazine. Of the two methods, the first required slightly less working time.

The Friedel-Crafts reaction of 1,5-bis(4-anisoyl)pentane with octanoyl chloride proceeded normally. Partial demethylation occurred during reaction. Therefore, the mixed product was reacted directly without further purification with 50% HBr to complete the demethylation. This ligand has a melting point of 50-55°C.

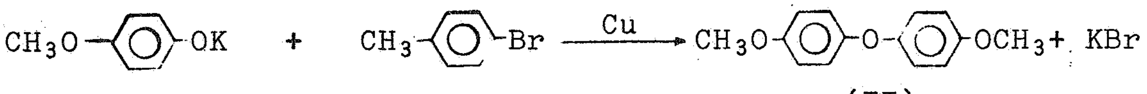
b. 1,5-Bis(4-hydroxy-3-perfluorooctanoylphenyl)perfluoropentane

A similar reaction sequence was followed in attempts to prepare the above perfluorinated analog of 1,5-bis(4-hydroxy-3-octanoylphenyl)pentane. Friedel-Crafts reaction of anisole with perfluoroglutaryl chloride yielded the intermediate 1,3-di(4-anisoyl) perfluoropentanedione-1,5. The carbonyl groups were then reacted with sulfur tetrafluoride using the procedure developed by Smith and co-workers (ref.19). It was necessary to conduct several test runs to find the proper conditions for substitution of the carbonyl groups by fluoride. The extent of reaction was followed by NMR and VPC analysis. Results of the tests indicated that yields were extremely sensitive to HF content. The best conditions found were 120°C for 20 hours with HF catalyst in a rotating bomb. Large amounts of ether-insoluble residue were produced in some runs at higher temperatures.

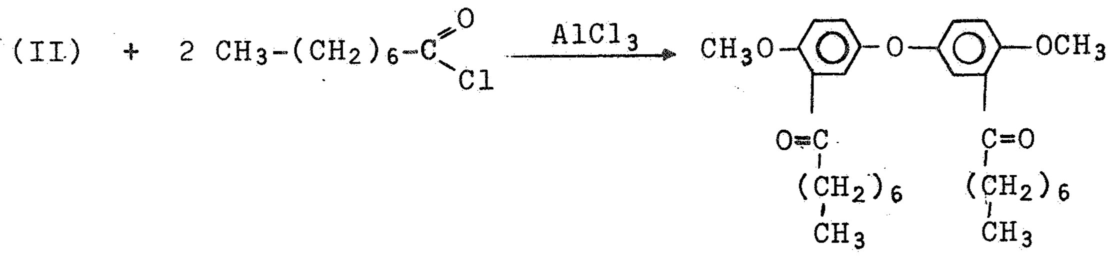
Attempts to substitute perfluorooctanoyl groups on 1,5-di (4-anisoyl)-perfluoropentane by Friedel-Crafts reaction in carbon disulfide and in ethylenedichloride did not yield the desired product. Two factors apparently made this reaction difficult: (1) the low solubility of perfluorooctanoyl dichloride, and (2) the electronic deactivating effect of the $-(CF_2)_5-$ linkage on the rings. Preparation of this ligand was deferred at this stage.

c. Bis(4-hydroxy-3-octanoylphenyl)ether

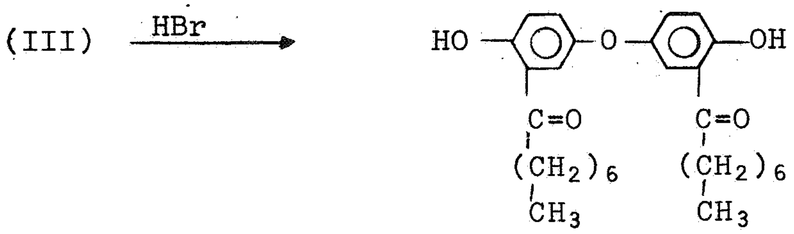
This ligand was prepared by the following reaction sequence. Both the coupling reaction and substitution reaction proceeded normally to give the desired product.



(II)



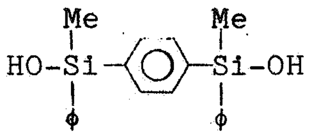
(III)



E. PREPARATION OF ARYLENESILANEDIOLS AND OTHER SILICON-CONTAINING REAGENTS

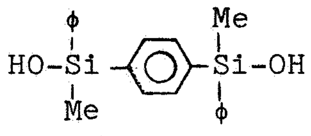
1. p-Arylenebis(diorganosilanols)

A series of p-arylenebis(diorganosilanols) was prepared for use as intermediates to prepare polychelatotitanosiloxanes, polytitanosiloxanes, and silanol-substituted titanium chelate polymers as well as for reactive plasticizers for the titanium chelate polymers. The general route for preparation involved substitution of chlorodiorganosilyl or ethoxydiorganosilyl groups on p-arylenes via Li, Na, or the Grignard reaction followed by hydrolysis of the chloro or ethoxy substituent to hydroxyl. Several variations in experimental procedure were used in these preparations. The most reliable general procedure was substitution of ethoxydiorganosilyl substituents via the Grignard reaction in tetrahydrofuran followed by hydrolysis of ethoxy to hydroxyl with sodium hydroxide in cold aqueous alcohol solution following a procedure of Popeleva (ref. 20). This general procedure is illustrated in the preparation of p-phenylenebis(methylphenylsilanol) in Section IV.C.2b. p-Phenylenebis(methylphenylsilanol) is obtained as a mixture of *cis* and *trans* forms.



cis-form

and/or



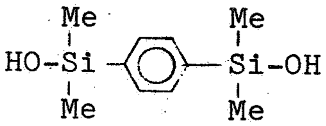
trans-form

These stereoisomeric forms have a d,l optically active racemic pair derived from the *trans*-form and an optically inactive *meso*-form derived from the *cis*-form. The white powdery crystals had a melting range of 135-145°C.

The specific procedures used to prepare other p-arylene-bis-(diorganosilanols) are discussed in the following paragraphs.

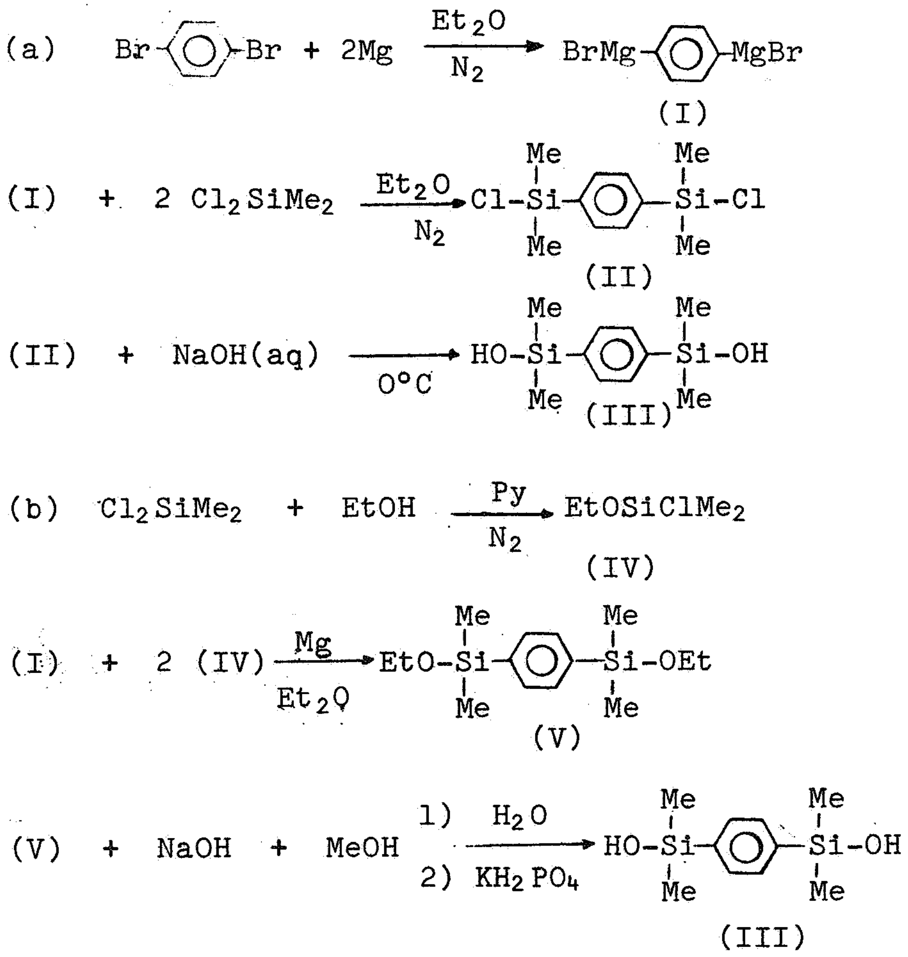
a. p-Phenylene-bis(diorganosilanols)

(1) p-Phenylene-bis(dimethylsilanol)



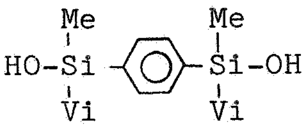
mp 133-134°C

The silanol was prepared via two routes: (1) the hydrolysis of p-phenylene-bis(chlorodimethylsilane), and (2) the hydrolysis of p-phenylene-bis(dimethylethoxysilane). The reaction sequences are as follows:

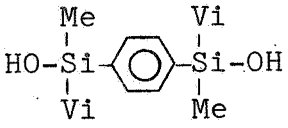


The white powdery crystals are rather reactive toward condensation with the elimination of water at elevated temperatures.

b. p-Phenylene-bis(methylvinylsilanol)



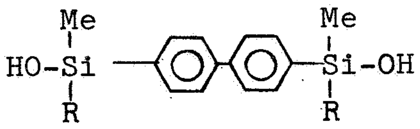
cis-form



trans-form

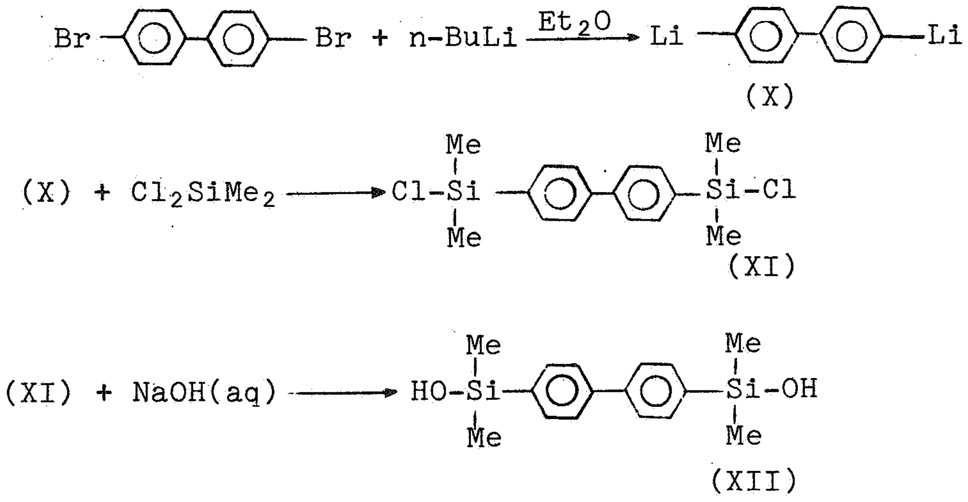
This monomer was prepared via the hydrolysis of p-phenylene-bis(ethoxymethylvinylsilane) and the procedure was essentially the same as for the preparation of the methylphenyl analog. As in the earlier cases, the methylvinyl analog can be divided into the same d, l-racemic pair and the optically inactive *meso*-form. However, the melting point range of this product is only 92-95°C.

c. 4,4'-Bis(diorganohydroxysilyl)biphenyl Monomers

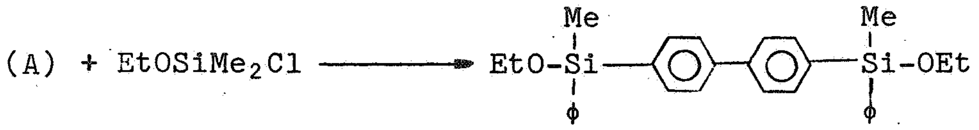


where R = Me, mp = 165-175°C
R = ϕ , mp = 102-105°C

The biphenyl systems were prepared to provide greater rigidity to polymers when properly incorporated into the backbone. The dimethyl monomer was easily prepared according to the procedure of Baum (ref. 21), as follows:

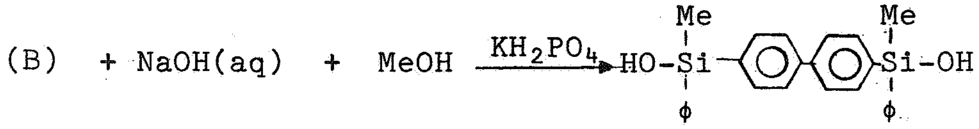


We were unsuccessful in preparing the methylphenyl analog by hydrolysis of the chlorosilyl intermediate. Instead, a procedure based on the preparation of a 4,4'-bis(ethoxymethylphenylsilyl)biphenyl intermediate was successful.

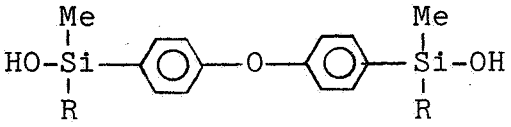


(B)

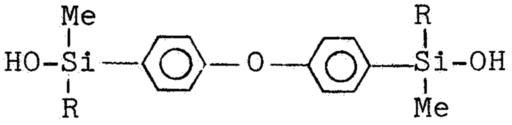
cis- and *trans*-forms



d. 4,4'-Bis(diorganohydroxysilyl)biphenyl Ether Monomers



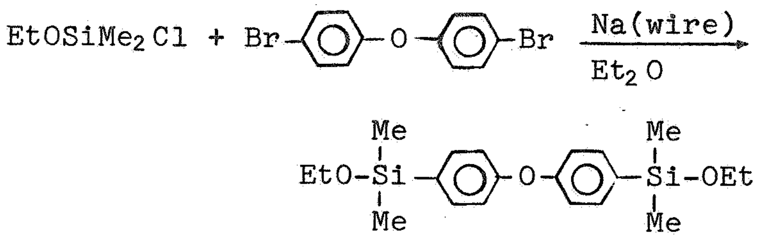
cis-form



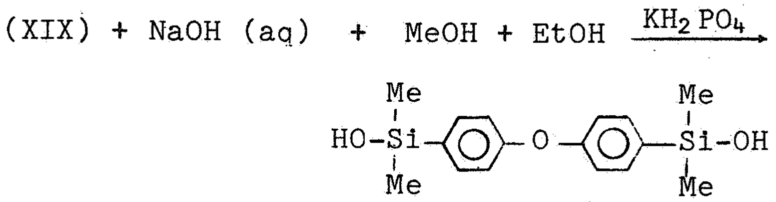
trans-form

when R = Me mp = 88-90°C
R = ϕ

These monomers were prepared to provide some flexibility to the backbone of the polymer chain in case the biphenyl backbone proved to be too rigid. The dimethyl-substituted monomer was prepared according to Breed et al., (ref. 22) in the following manner:



(XIX)



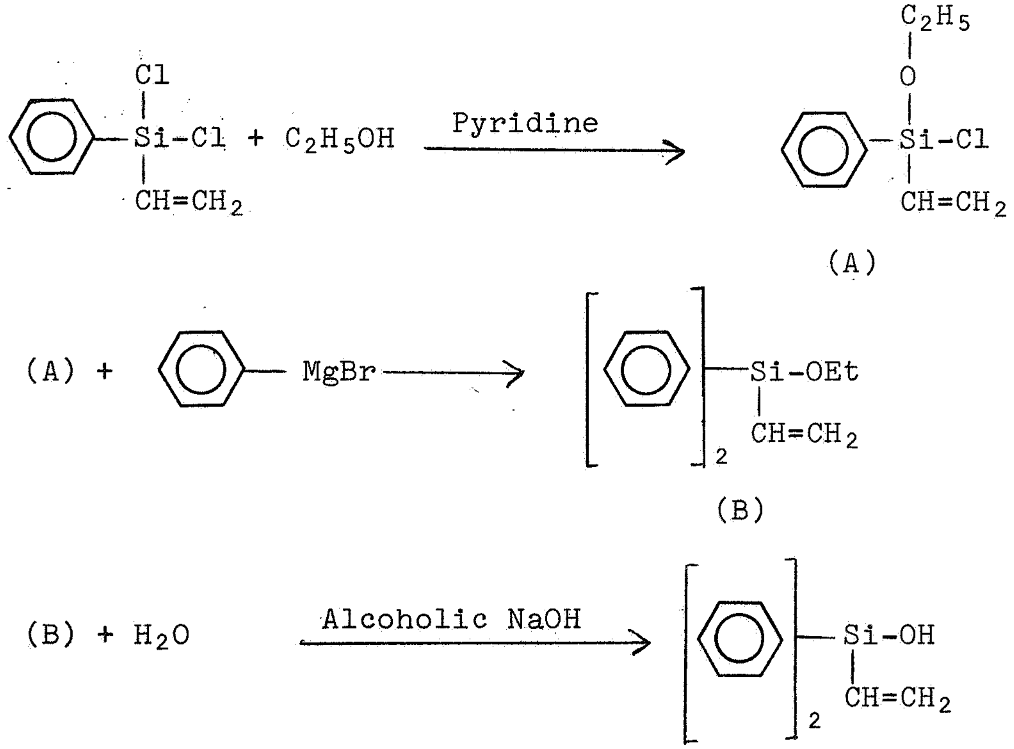
(XVI)

Two attempts to prepare this monomer through the hydrolysis of 4,4'-bis(chlorodimethylsilyl)biphenyl ether (prepared via the n-BuLi route) were unsuccessful.

Attempts to prepare the methylphenyl analog, 4,4'-bis(hydroxymethylphenylsilyl)biphenyl ether via the sodium coupling reaction were not successful. This disilanol was prepared via the Grignard reaction-ethoxyhydrolysis route used to prepare p-phenylene-bis-(methylphenylsilanol).

2. Diphenylvinylsilanol

Diphenylvinylsilanol was used to substitute the vinyl group on the titanium chelate polymers. It was prepared by the following route:



This silanol condensed to its siloxane when an attempt was made to purify it by distillation in vacuum. Therefore, the silanol was recovered by first cleaving the siloxane bond with alcoholic sodium hydroxide and then neutralizing the sodium salt of the silanol with acetic acid following a procedure developed by Hyde and coworkers (ref. 23). The NMR spectra of the original and recovered products were identical and were consistent for the structure of the silanol.

3. Phenylsilanetriol

Phenylsilanetriol was used as a crosslinking agent because of its high reactivity and trisubstitution. The triol readily condenses when heated and is also extremely sensitive to both acidic and basic catalysis.

Two methods were used to prepare samples of phenylsilanetriol. Takiguchi's method (ref. 24) involving hydrolysis of phenyltrichlorosilane in the presence of aniline gave the purest product. The product formed by this method had the correct proton count in its NMR spectra and very low absorption of the Si-O-Si linkage in its infrared spectra. We found that products formed by hydrolysis of phenyltriethoxysilane in the presence of acetic acid (ref. 25) were difficult to purify.

4. Alkoxysilanes

A crosslinking agent with reactive $SiOCH_3$ groups, namely, p-phenylene-bis(dimethylmethoxysilane), was also prepared. This reagent does not undergo self-condensation. Therefore, the sterically small methyl group substituents on silicon can be used to favor condensation with silanol groups on the polymers. p-Phenylene-bis(dimethylmethoxysilane) was prepared by reaction of the Grignard reagent of p-dibromobenzene with chlorodimethylmethoxysilane.

5. Silazanes and Aminosilanes

These reagents were prepared for use both in making polyphenylene-bis(methylphenylsiloxanes) and as crosslinking agents for silanol-substituted polymers. These reagents were chosen because they react with both dimethylphenyl- and triphenyl-substituted silanols (ref. 26) at a reasonable rate under 170°C.

Bis(methylamino)methylphenylsilane was prepared by reaction of methylamine with dichloromethylphenylsilane using the procedure developed by Breed (ref. 27). Because of the extreme sensitivity to hydrolysis of this aminosilane, fabrication of all samples with this curing agent was done in the dry box.

Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclorhexane was prepared by reaction of methylamine with 1,5-dichlorohexamethyltrisiloxane using the reaction conditions developed by Breed et al. (ref. 28). The dichlorosiloxane used in this preparation was prepared by controlled hydrolysis of dimethyldichlorosilane. The silazane analysis by VPC indicated 94% purity after distillation. A sample of this material was used in initial crosslinking studies. In all other tests, a redistilled sample having VPC purity of 99.3% was used.

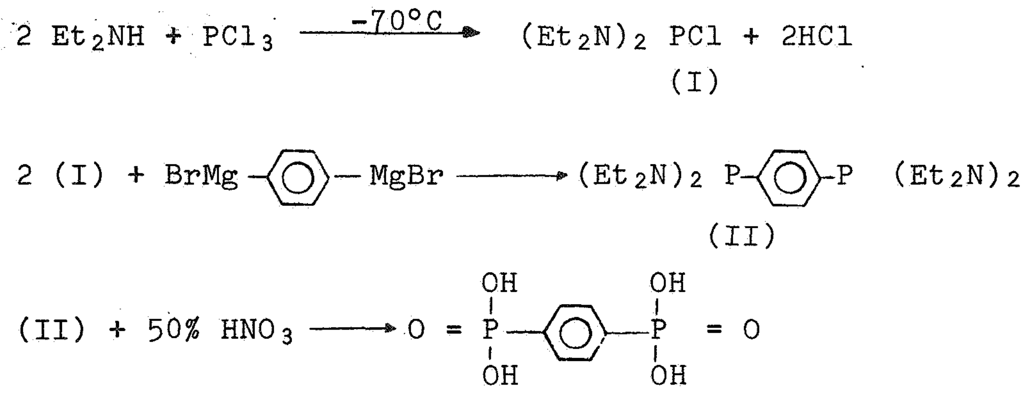
6. Polyphenylene-bis(methylphenylsiloxanes)

These polymers were used both as chain extenders for preparation of polychelatotitanosiloxanes and as fillers and/or plasticizers in adhesive formulations. Low molecular weight polymers with high silanol content were used as chain extenders. One sample of this type with average molecular weight of 3050 was prepared by reaction of p-phenylene-bis(methylphenylsilanol) with heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane in mole ratio 1 to 0.8.

Another sample of polyphenylenesiloxane with molecular weight of 13,500 was prepared by condensation of p-phenylene-bis(methylphenylsilanol) with bis(methylamino)methylphenylsilane in 1-to-0.85 mole ratio. This sample has been used as an adsorbent filler and carrier for the highly reactive crosslinking agents used with our titanium chelate polymers.

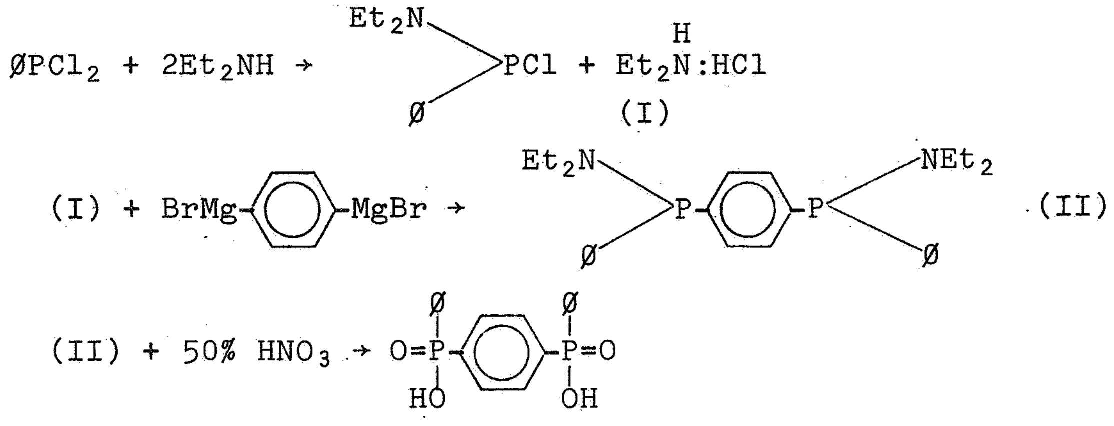
F. PREPARATION OF PHOSPHORUS-CONTAINING CROSSLINKING AGENTS

We first prepared p-phenylenediphosphonic acid according to the procedure of Cantrell, et al., (ref. 29). The reaction scheme is as follows:



(p-phenylenediphosphonic acid)

Unfortunately, this compound had no common solvents with our polydichelatotitanosiloxane prepolymer and its melting point was too high (285°C) for a melt polymerization reaction. We, therefore, synthesized p-phenylene-bis(phenylphosphinic) acid to obtain greater solubility in aromatics. This curing agent was prepared according to the following route:



p-phenylene-bis (phenylphosphinic acid)

This compound is soluble in pyridine and very slightly soluble in acetone. Details of both preparation methods are in the experimental section.

G. PREPARATION OF TITANIUM COMPOUND REAGENTS

1. Bischelatodialkoxytitanium Compounds

a. Bisacetylacetonato Compounds

Bisacetylacetonatodibutoxytitanium and bisacetylacetonatodiisopropoxytitanium were prepared by reaction of two moles of acetylacetone with the corresponding tetraalkoxytitanium compound following the method of Yamamoto and Kambaro (ref. 30). The products were purified by distillation in a molecular still.

b. Bis(8-hydroxyquinolino)diisopropoxytitanium

Bis(8-hydroxyquinolino)diisopropoxytitanium(IV), which has chelato substituents with higher stability than the acetylacetonato analog, was prepared by reaction of two moles of 8-hydroxyquinoline with one mole tetraisopropoxytitanium. The product was a solid that was soluble in benzene.

2. Tetrakis(dimethylamino)titanium(IV)

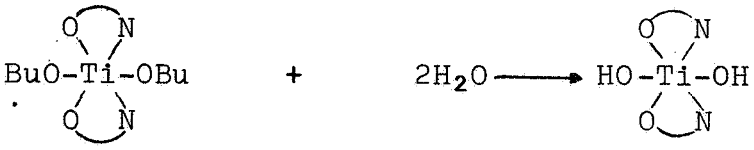
This polyfunctional reagent is very reactive with silanol groups, and therefore was used both as a curing agent for our titanium chelate polymers and as a reagent for extending the molecular weight of the polychelatotitanosiloxanes. A sample of tetrakis(dimethylamino)titanium was prepared using the procedures developed by Bradley and Thomas (ref. 31), as follows:

$$(CH_3)_2NH + C_4H_9Li \longrightarrow (CH_3)_2NLi + C_4H_{10}$$

$$4(CH_3)_2NLi + TiCl_4 \longrightarrow Ti[NCCH_3)_2]_4 + 4LiCl$$

3. Bis-chelatotitaniumdihydroxides

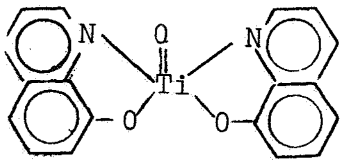
Andrianov (ref. 32) has reported the preparation of bis(8-oxyquinolino)dihydroxytitanium (IV) by the hydrolysis of the corresponding dibutoxide compound:



$$BuO\text{-}Ti(O\frown N)_2\text{-}OBu + 2H_2O \longrightarrow HO\text{-}Ti(O\frown N)_2\text{-}OH$$

where O⌒N is 8-hydroxyquinoline.

Several attempts were made to repeat this preparation. In all cases we did not obtain the dihydroxy species. Rather, the dehydration produced bis (8-oxyquinolino)oxotitanium (IV) as shown by IR and NMR analysis.

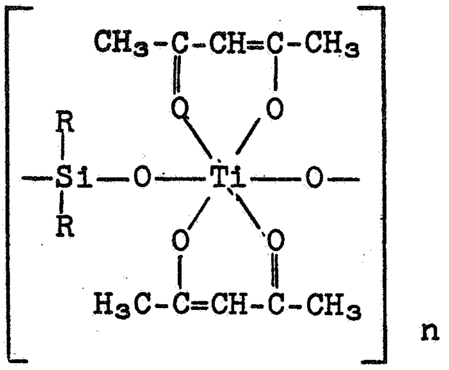


Andrianov reported only the elemental analysis for the compound he believed to be the dihydroxy species. This analysis would be the same for the mono aquo titanyl compound that we isolated. It appears that the dihydroxy metal chelate species, although originally formed, is highly unstable and quickly dehydrates to the titanyl species.

H. POLYDICHELATOTITANODIORGANOSILOXANES

1. Introduction

In 1961 Andrianov (ref. 33) reported a new type of polymer obtained by the cohydrolysis of organic dichlorosilane and bis(acetylacetonato)dichlorotitanium. This type of polymer was named "poly-organo-chelato-siloxane" and has the general structure shown below:



Polymers with molecular weights in the range 100,000 to 200,000 were reported. These polymers were chosen as starting materials to develop high temperature adhesives because of their thermal and mechanical properties were better than those of other polyorganometallosiloxanes, which characteristically were low molecular weight, infusible, glass-like solids with limited mechanical strength (ref. 13, 30, 34-39). However, this type of polymer softened in the range 50-65°C (120-150°F). Similar polymers with 8-hydroxyquinoline as the chelato substituent had similar softening points. Therefore, to develop these materials into usable high temperature adhesives, it was necessary to accomplish the following two tasks:

a. Determine methods of reliably preparing poly-(bis-acetylacetonotitanodimethylsiloxane) elastomers having a high Ti/Si ratio to give high potential degree of crosslinkage;

b. Develop methods of crosslinking these elastomers to render them infusible at temperatures up to 315°C.

We also prepared and crosslinked a series of methylphenyl- and methylvinyl-substituted poly(bisacetylacetonotitanodiorganosiloxane) elastomers to improve the adhesive properties and mechanical toughness of this type of polymer.

2. Polychelatotitanodimethylsiloxanes

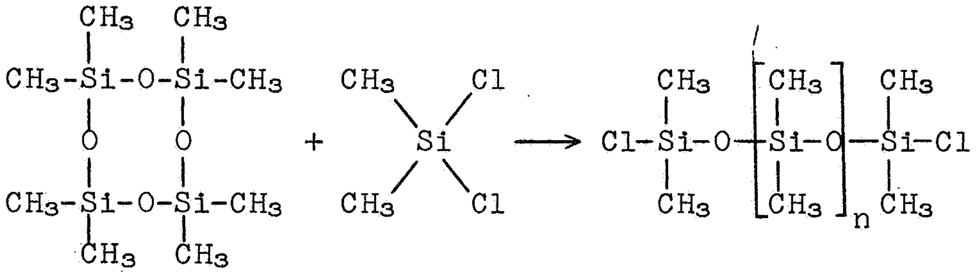
a. Low Molecular Weight Siloxane Oligomers

To prepare polychelatosiloxanes having a high Ti/Si ratio, it is first necessary to prepare low molecular weight α,ω-dihydroxypolydimethylsiloxanes.

Efforts were directed towards the preparation of low molecular weight α,ω-dihydroxypolydimethylsiloxanes through the decyclization of octamethylcyclotetrasiloxane. In this method, reported by Andrianov and his coworkers (ref. 37), dimethyldichlorosilane and octamethylcyclotetrasiloxane are mixed and reacted at 200°C for 3.5 hours. Using a ratio of 12.5 to 1 of octamethylcyclotetrasiloxane to dimethyldichlorosilane, the α,ω-dichloropolydimethylsiloxane prepared had a molecular weight of 3170.

This was then hydrolyzed in a water-acetone-benzene mixture containing $NaHCO_3$, followed by purification by fractional distillation at 3-4 mm Hg at temperatures up to 200°C. This dihydroxy oligomer had a molecular weight of 8200.

The reaction can be represented by the following sequence:



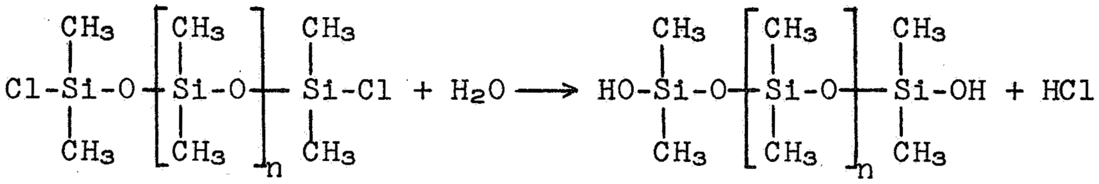
Following Andrianov's method but at one tenth the amount, we were able to prepare α,ω-dichloropolydimethylsiloxane with a molecular weight of 2800. Increasing the reaction temperature from 200°C to 300°C produced no great advantages. Therefore, subsequent reactions were run at 200°C for 3.5 hours.

It was found that a low yield of product followed every time the bomb was cleaned with chromic acid, and that subsequent runs had higher yields. This was due to the catalytic activities of $FeCl_3$ formed from the reaction of HCl on steel. Therefore, in future runs we added catalytic amounts of $FeCl_3$ to a thoroughly cleaned stainless steel bomb before each run.

The value of n in the above reaction sequence can be controlled to a degree by varying the ratio of the cyclic siloxane to the chlorosilane. Thus, a mole ratio of dimethyldichlorosilane and octamethylcyclotetrasiloxane at two to one gives average molecular weights as low as 300 after careful fractionation. Usually a series of dichlorodimethylsiloxane with molecular weights (NMR method) from approximately 200 (2 Si atoms) to approximately 350 (4 Si atoms) are produced in each bomb run and a high ratio of the chlorosilane to the cyclic siloxane increases the yield of lower molecular weight products.

In the NMR spectra of these compounds, the methyl hydrogen atoms that are attached to silicon atoms containing both chlorine and oxygen atoms show a different chemical shift than those methyl hydrogens attached to a silicon atom containing only silicon-oxygen bonds. A comparison of the two resonance peak areas allows us to calculate the number of silicon atoms in the oligomer. This method of determining the molecular weights of our oligomers was checked to within 10% against results obtained by standard ebulliometric methods. A molecular weight check with tetramethyldisiloxane-1,3-diol was exact.

The α,ω-dichloropolydimethylsiloxanes can then be hydrolyzed by water in an acetone-benzene-water mixture with sodium bicarbonate to act as hydrogen chloride scavengers to form the corresponding α,ω-dihydroxypolydimethylsiloxane (ref. 37).



$$Cl-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-Cl + H_2O \longrightarrow HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HCl$$

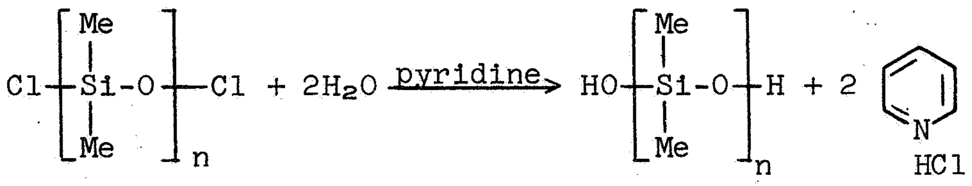
The hydrochloric acid thus produced was found to catalyze the cyclization of linear siloxanes. This is undesirable since cyclic siloxanes do not enter into condensation reaction with chelatotitano complexes to give the desired polychelatotitanodimethylsiloxane elastomers. The cyclic siloxanes are capable of being plasticizers and this reduces the elastomer's softening point. Therefore one of our primary aims was to lower the concentration of cyclic contaminants.

This hydrolysis reaction was carried out at 0°C by adding chlorosiloxane dropwise to a water-acetone-benzene mixture containing excess of sodium bicarbonate. We were able to prepare siloxane oligomer in the molecular weight range of 250-400 (3-5 Si atoms) with cyclic siloxane content less than two per cent.

In the course of this work, we also found that the dihydroxy oligomers undergo autopolymerization at room temperature. For example, a sample of this type oligomer that initially had a molecular weight of 2700 doubled its molecular weight after standing at room temperature for one week. However, molecular weight checks on these samples four weeks later showed that no further polymerization reaction occurred.

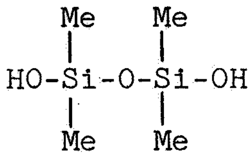
Low molecular weight (≈230) dihydroxy oligomers undergo autopolymerization reactions also at room temperature with the elimination of water. However, the average increase in molecular weight is only about 50%.

To reduce the formation of cyclic materials the hydrolysis reaction was carried out in the presence of pyridine.



This reaction was carried out to reduce cyclic contaminants by faster removal of byproduct HCl. Hydrolysis results showed, however, that considerable autopolymerization had taken place under these conditions.

The above-mentioned method would be inadequate to eliminate cyclic siloxane completely. Therefore, a method of preparing tetramethyldisiloxane-1,3-diol was found (ref. 38).



$$\mathrm{HO{-}\overset{Me}{\underset{Me}{Si}}{-}O{-}\overset{Me}{\underset{Me}{Si}}{-}OH}$$

In this method dimethyldichlorosilane was hydrolyzed in an excess of water at 0°C under pH controlled conditions (pH 8.5). The HCl produced in the hydrolysis was neutralized by bubbling NH_3 gas into the reaction mixture. After the addition of an excess of NaCl and extraction with hexane, a white crystalline product was obtained.

It was our hope to prepare a titanium elastomer completely free of cyclic siloxanes and with a Ti/Si ratio as high as 1/2 after condensation of this diol with bis-acetylacetonatodialkoxytitanium. Polymers having a limit of Ti/Si atom ratio of about 1/15 were obtained. It appears that some degree of siloxane polymerization takes place along with the condensation of the bis-acetylacetonatodiisoproposytitanium. The elastomers obtained by this procedure were slightly yellow and were less fluid than those made with α,ω-dihydroxypolydimethylsiloxane oligomers.

To clarify the polymerization reaction of this diol prior to condensation with bis-acetylacetonatodialkoxytitanium, the diol was dissolved in benzene and the temperature of the solution was gradually increased to 150°C. Then, at 10°C intervals, samples were taken and their molecular weights determined by the NMR method. Table 9 shows the increase of molecular weight at different temperatures.

Table 9

AVERAGE MOLECULAR WEIGHTS OF TETRAMETHYLDISILOXANE-1,3-DIOL AT DIFFERENT TEMPERATURES

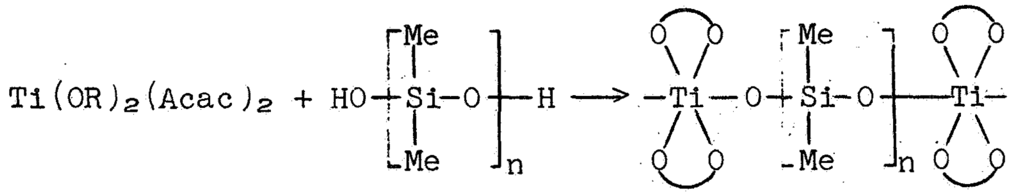
Temperature °C	Molecular Weight (NMR Method)
100	222
110	236
120	246
130	309
140	394
150	460

Since this method of preparation of elastomers has the advantage of yielding extremely low concentrations of cyclic contaminates, elastomer preparation by this method is preferred.

b. Preparation of Titanium Elastomers

Condensation of these oligomers with bis(acetylacetonato)-dialkoxytitanium (ref. 39) produced the desired poly(bis-acetylacetonotitanodimethylsiloxane) elastomer. These reactions are best carried out at ≈60°C under dry nitrogen. After the initial reaction is completed, the temperature is gradually increased to ≈200°C at a residual pressure of ≈1 mm Hg, with the simultaneous removal of alcohol by distillation. It was noted that in the early phase of the reaction the titanium complex underwent hydrolysis to a small extent even though the solvents (benzene, chloroform, alkylalcohol) were carefully dried and redistilled.

This hydrolysis results in the formation of a white precipitate in the reaction mass. Filtering of this precipitate with a glass fritted filter solved the problem and no further hydrolysis was noted at higher temperatures. The elastomers prepared by this procedure are light yellow and soften around 20°C. These elastomers are soluble in benzene or toluene. The reaction scheme is as follows:



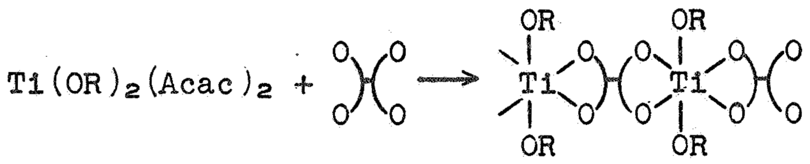
where O‿O is acetylacetone and R can be either isopropyl or butyl.

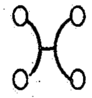
c. Crosslinking Via Ligand Exchange Reactions

To find a suitable reaction condition for crosslinking poly(acetylacetonotitano)dimethylsiloxanes, a series of crosslinking reactions was run using 5,5'-bis(salicylaldehydo)methane and 5,5'-bis(8-hydroxyquinolino)sulfone. These reactions were carried out by dissolving a mixture of the ligand and poly(bisacetylacetonotitanodimethylsiloxane) in a solvent (such as benzene or pyridine) and then removing the solvent by atmospheric distillation. The mixture of polymer and ligand was then heated at 250°C/1.2 mm Hg for 16 hours. This procedure is essentially a ligand exchange reaction that is carried out in the polymer met melt. Attempts to carry out this type of ligand exchange in a solvent were not successful.

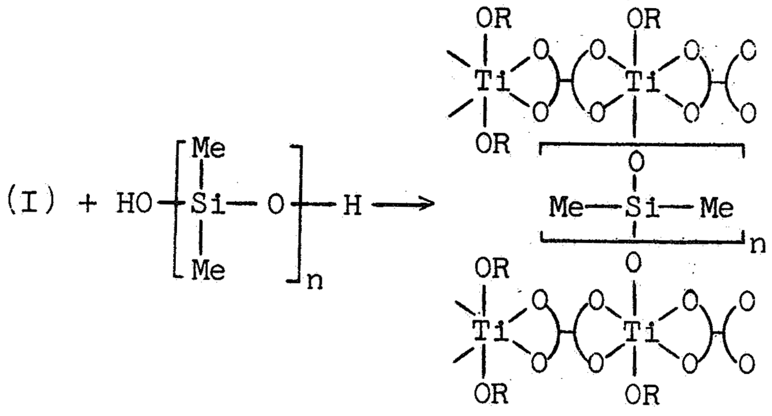
From these reactions, we established that a starting ligand-to-titanium ratio of 1:2 provided the best crosslinked characteristics in the elastomers.

Further ligand exchange reactions were carried out with 2,5-dihydroxy-p-benzoquinone, 5,8-dihydroxy-1,3-naphthoquinone (naphthazarin), 1,4-dihydroxyanthraquinone (quinizarin), 1,5-dihydroxyanthraquinone (anthrarufin). With these tetradentate ligands, two types of crosslinking reactions were tried. In the first case, these ligands were added to bis(acetylacetonato)diisoproposytitanium before the addition of α,ω-dihydroxypolydimethylsiloxanes. Presumably, structures of the following type were formed during the ligand exchange polymerization reaction:



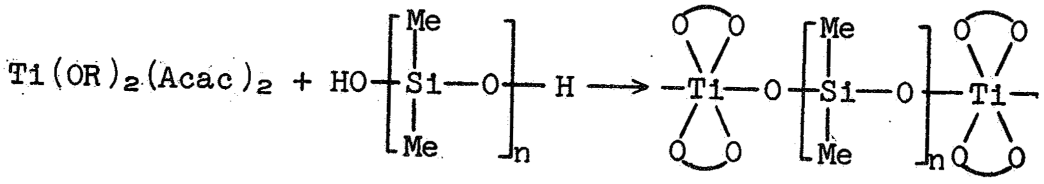
where  is a tetradentate ligand and R is isopropyl.

Crosslinking was effected by a polycondensation reaction with α,ω-dihydroxypolydimethylsiloxane at the titanium alkoxy site.

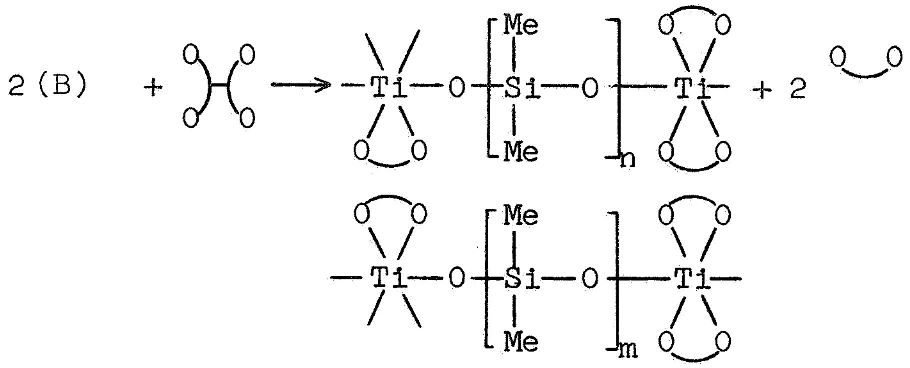


(A)

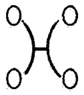
In the second case, crosslinking was effected after the polycondensation of bis(acetylacetonato)diisopropoxytitanium with α,ω-dihydroxypolydimethylsiloxane.



(B)



(C)

where  is an acetylacetone ligand and  is a tetradentate ligand, and R can be either butyl or isopropyl.

It is seen that structures (A) and (C) can be the same.

Experimentally, both methods have yielded crosslinked polymers with greatly improved softening point and increased physical toughness over noncrosslinked bis-acetylacetonotitanopolydimethylsiloxane elastomer when the tetradentate and bis-bidentate ligands were quinizarin, anthrarufin, and 5,5'-bis(8-hydroxyquinolino)-sulfone.

We did not obtain crosslinked polymers with 2,5-dihydroxy-p-benzoquinone probably because its extremely high chelating ability took up all six available coordinating sites on the metal titanium ions and effectively blocked further condensation reaction with siloxane oligomers.

In Table 10 we have summarized the data on crosslinked and noncrosslinked elastomers. It is seen that both methods for crosslinking at the titanium site produced up to five-fold increase in softening point. The data also corroborated our earlier belief that a higher Ti/Si atom ratio elastomer should have a higher softening point.

Table 10

SOFTENING POINTS OF CROSSLINKED AND NONCROSSLINKED ELASTOMERS

Crosslinking Agent		Ti/Si Ratio	Softening Point °C	Preparation Method*
1.	None	1/70	20	C
2.	Naphthazarin	1/70	25	A,C
3.	Quinizarin	1/70	90-100	A,C
4.	Anthrarufin	1/70	70-75	A,C
5.	None	1/20	80-90	D
6.	None	1/15	30-40	D
7.	None	1/14	55-65	D
8.	Quinizarin	1/16	270-290	B,D
9.	Anthrarufin	1/16	220-235	B,D
10.	None	1/15	30	-
11.	Quinizarin-2-sulfonic acid	1/15	80	B
12.	4,4'-Diamino-1,1'-dianthrimide	1/15	44	B
13.	4,4'-Dibenzamido-1,1'-dianthrimide	1/15	25	B
14.	4,5'-Dibenzamido-1,1'-dianthrimide	1/15	25	B
15.	Tris(2-hydroxyphenyl)-sym-triazine	1/15	160-180	B

---

* Preparation Methods:

A α,ω-Dihydroxypolydimethylsiloxanes added to chelatotitanium polymers

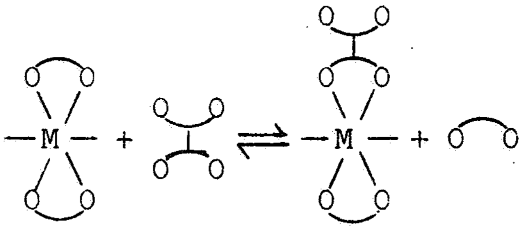
B Crosslinking agents added to polychelatotitanodimethylsiloxane elastomers

C Polychelatotitanodimethylsiloxanes prepared from α,ω-dihydroxypolydimethylsiloxane oligomer with molecular weight of 5,800

D Polychelatotitanodimethylsiloxane prepared from tetramethyldisiloxane diols

As can be seen in Table 10, four tetradentate ligands gave somewhat lower softening points for the elastomers than the others. For example, quinizarin-2-sulfonic acid was a less effective crosslinking agent than quinizarin. Even though the sulfonic acid group on quinizarin is an electron-withdrawing group, making the phenol group in the ortho position more acidic and more reactive, apparently this also decreases the electron-donating ability of the carbonyl oxygen, thus preventing the formation of a stable complex. In the case of 4,4'-diamino-1,1'-dianthrimide and the others, the R-NH-R linkage may be weaker than a methylene or a sulfo linkage. Also, a chelation with O and O may be preferred over one with N and O.

It should be realized that these ligand exchange reactions are equilibrium reactions, and that factors such as temperature, pressure, catalysis, concentration and steric effects, to name a few, can play very important roles in determining the final product.



3. Methylphenyl- and Methylvinyl-substituted Polychelatotitanodiorganosiloxanes

a. Methylphenyldisiloxanediol

Methylphenyldisiloxanediol was prepared by a procedure similar to that reported by Shoslakovskii (ref. 40). In this procedure, methylphenyldichlorosilane dissolved in Et_2O was added dropwise to an Et_2O-NaOH-water solution. The organic layer was separated from the aqueous layer and concentrated. The diols were crystallized by the addition of isopentane and cooling the solution in a Dry Ice-acetone bath. NMR analysis confirmed the product as being the methylphenyldisiloxanediol. The molecular weight as determined by the NMR method was 290.

b. Polychelatotitanomethylphenylsiloxane

A series of elastomers containing phenyl substituents was prepared to determine the optimum phenyl/methyl and Ti/Si ratios to give toughness in product polymer. Elastomers from condensation of bis(acetylacetonato)dibutoxytitanium (IV) with both 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol and mixtures of tetramethyldisiloxane-1,3-diol and diphenylsilanediol have been prepared. The bis(acetylacetonato)titanopolymethylphenylsiloxane elastomers prepared with reactant ratios of Ti/Si of 1/3.4, 1/8, and 1/10 were soluble in benzene and brown in color. The highest Ti/Si ratio produced the toughest elastomer.

Co-condensation of a mixture (1:0.8 Si atom ratio) of tetramethyldisiloxane-1,3-diol and diphenylsilanediol and bis(acetylacetonato)dibutoxytitanium (IV) produced a tough, brownish elastomer. A reactant ratio of 1/8.4 Ti/Si was used in this preparation.

c. Polychelatotitanodiphenylsiloxane

Condensation of diphenylsilanediol with bis(acetylacetonato) dibutoxytitanium (IV) produced a very brittle crystalline polymer that is soluble in organic solvents and has a softening point of 35°C. The Ti/Si atom ratio of the starting reagent was 1/5.

In another preparation, the starting Ti/Si atom ratio was 1/20 and the softening range was 55-60°C.

d. Polymethylvinylsiloxanediol

An oligomer with the vinyl substituent on the siloxane backbone was prepared to use in determining the characteristics of polymers crosslinked both through tetradentate ligands substituted on titanium sites and through the vinyl group. Polymethylvinylsiloxanediol was prepared using a procedure similar to that used for preparation of methylphenyldisiloxanediols above. The average molecular weight of this oligomer, as determined by NMR was 355.

e. Polychelatotitanomethylvinylsiloxanes

This elastomer was prepared to evaluate the advantage in physical properties of a crosslinked polymer at both the metallic and the silicon sites.

When methvlvinylsiloxanediol was condensed with bis(acetylacetonato)dibutoxytitanium (IV) in Ti/Si atom ratios of 1/14.8 and 1/8, an elastomer resulted with an appearance very similar to that of our lower Ti/Si ratio polychelatotitanodimethylsiloxanes. However, it was tougher than the dimethylsiloxane elastomer of similar Ti/Si ratio.

f. Crosslinking of Methylphenyl- and Methylvinyl-Substituted Poly(bis-acetylacetonatotitanodiorganosiloxanes)

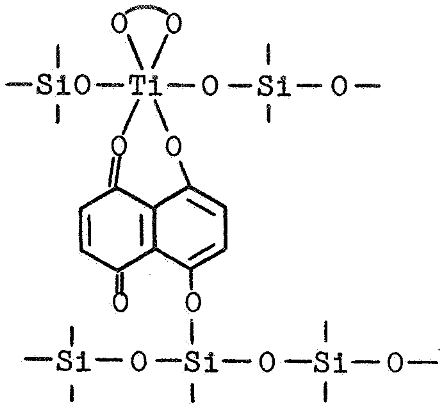
The elastomers just described were then reacted by our normal procedure with a series of bisbidentate ligands to yield crosslinked resins having higher softening points. These crosslink reactions yielded polymers that melted in the range of 100 to 150°C.

However, these higher melting crosslinked polymers failed to adhere well to aluminum. This lack of adhesion was due to the formation of small amounts of cyclic polysiloxanes, which tended to coat the metal and prevent good contact between the resin and the metal surface.

Subsequently our attention was turned to another class of polychelatotitanosiloxanes with the general name, polychelatometallo-p-arylene-bis(diorganosiloxanes). These polymers are described in Section I, following.

4. Attempted Preparation of Ligand Substituted Siloxane Oligomers

A second possible method of crosslinking our polychelatosiloxane elastomers to render them infusible is by placing ligand side groups on the siloxane oligomers. The ligand side groups could then interact with the titanium of an adjacent polymer chain to form a silicon-ligand-titanium crosslinking pattern such as that shown below.

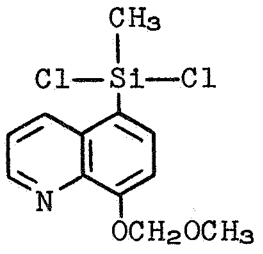


A literature search was undertaken to determine various methods of preparing siloxane oligomers having ligand-containing side groups. No specific examples of this type of compound were found. The best approach to their synthesis appears to be the following two-step procedure: (1) the preparation of a ligand containing dichlorosilane, and then (2) the use of this silane to open the octamethylcyclotetrasilane ring. This ring opening reaction would then yield an α,ω-dichloropolysiloxane containing ligand side groups.

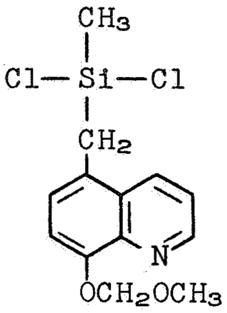
Several attempts were made to prepare methyldichlorosilanes containing a tridentate ligand group by reacting 5,8-dihydroxynaphthaquinone and 1,4-dihydroxyanthraquinone and their respective monopotassium salts with methyltrichlorosilane under various conditions. In addition, the reaction of methyldichlorosilane with quinizarin was attempted. However, no siloxane species corresponding to the desired products were obtained. In fact, the reaction of dichloromethylsilane with quinizarin did not produce hydrogen at all. This is probably due to the fact that the polarity of the Si^{+}-H^{-} bond is altered by the presence of the electron-withdrawing chlorine atoms.

The reaction of trichloromethylsilane with 5,5'-bis(8-hydroxyquinolino)methane and 5,5'-bis(salicyl-N-butylimino)methane yielded gummy reaction masses that contained silicon. No definite compounds could, however, be separated.

Several attempts were also made to prepare an alternate type of ligand containing a catalyst for opening the polysiloxane ring, in which the ligand is bonded directly to the silicon by a carbon-silicon bond. Examples of this type of compound are shown below.



5-(methyldichlorosilyl)-8-hydroxyquinoline methoxymethyl ether, and



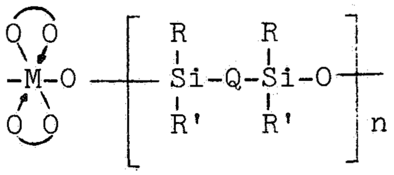
5-(methyldichlorosilylmethyl)-8-hydroxyquinoline methoxymethyl ether.

The following route was employed in attempts to prepare 5-(methyldichlorosilyl)-8-hydroxyquinoline methoxymethyl ether. The quinoline ring was metallated utilizing the reaction of n-butyllithium with 5-chloro-8-hydroxyquinoline methoxymethyl ether, and then this lithio substituted quinoline was reacted with methyltrichlorosilane. To prevent the hydroxyl group on the quinoline ring from reacting with the chloride substituents present on the silyl group, the hydroxyl group was first converted to an ether. Two metallation reactions employing 5-chloro-8-hydroxyquinoline methoxymethyl ether were carried out at -35°C and at 25°C. The products of these reactions, however, did not yield the desired compounds.

A complete description of the procedures used in the attempted synthesis discussed above is given in the experimental section of this report.

I. POLYDICHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANES)

1. Preparation of Prepolymers

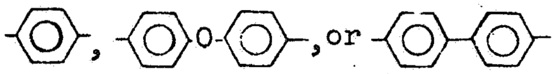


where M = metal

O O = bidentate ligand

R = Me, R' = Me, Vi, or Ø

R = Ø, R' = Ø, or Vi

Q = 

Polychelatotitanosiloxanes of this type were investigated because they have several characteristics that should give improved adhesive and mechanical properties compared to the simple poly(bis-chelatotitanodiorganosiloxanes), described in Section H. First, the arylene-bis(diorganosiloxanes) do not cyclize to give siloxane oil, which would interfere with the adhesion between the polymer and the metal. Second, Merker and Scott (ref. 41) reported that poly-p-phenylene-bis(methylphenylsiloxane) has far superior thermal and oxidative stability than polydimethylsiloxanes. Finally, Breed, et al., (ref. 42) reported that these arylene siloxanes readily condense with dichelatotitanoalkoxides.

A series of prepolymers were made by condensation of bis-(acetylacetonato)dibutoxytitanium with p-arylene-bis(diorganosilanols), where arylene (Q) was p-phenylene, p-biphenylene or p-biphenylene ether and diorgano (R) was dimethyl, methylvinyl or methylphenyl. The reagents were first mixed in benzene solution at 40°C or under to avoid homopolymerization of the disilanols that takes place at higher temperatures. After the initial condensation, the solvent was removed and the products were heated under vacuum to further condensation and remove the last traces of butanol. During this time, the temperature was kept under 120°C to avoid formation of high melting products, which result apparently from loss of acetylacetonato groups from the product at elevated temperatures. The exact reaction conditions, compositions, and properties of these polymers are summarized in Tables 11 and 12. The products from charges with Si:Ti ratios from 2:1 to 6:1 were clear or slightly opaque, hard solids with softening ranges from 30 to 130°C.

2. Characterization of Prepolymers with Varying Ti:Si Ratios

The structure of the products made by condensation of bis-(acetylacetonato)dibutoxytitanium with arylene-bis(diorganosilanols), unlike the structure of the simple polychelatotitanosiloxanes, varies with Si:Ti ratio. This is illustrated by analysis of a series of elastomers prepared from p-phenylene-bis(methylphenylsilanol) and its dimethyl homolog. Data are summarized in Table 13.

One significant difference in structure is the acetylacetone content of the various elastomers. The NMR analysis shows that the acetylacetonato groups on bis(acetylacetonato)dibutoxytitanium are displaced from titanium by any excess arylsilanol available after reaction with the alkoxy groups. Therefore, elastomers from the aryl substituted silanols having Si:Ti ratios above 2:1, react in our ligand exchange cure reactions largely by exchange of -Si-O- groups, whereas elastomers having a Si:Ti ratio of 2:1, react by exchange of acetylacetonato groups.

Table 11

PREPARATION AND PHYSICAL PROPERTIES OF HOMOPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

						Reaction Conditions		
	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Temp °C	Press. mm Hg	Time hr.
1	70194	$(Me_2SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	10 1	3.10 0.51	∿40	140	1.0	4.0
2	70195	" "	5 1	3.10 1.02	∿25	74	1.0	6.0
3	81129	" "	4 1	1.50 0.63	∿25	125	1.2	20
4	81105	" "	3 1	1.99 1.15	<25	120	1.0	3.0
5	77589	" "	2.5 1	1.64 1.15	∿25	120	0.6	1.5
6	81106	" "	2 1	0.86 0.75	<25	120		3.0
7	81141	" "	2 1	2.00 1.73	<25	80	9.0	20

Table 11 (Cont)

PREPARATION AND PHYSICAL PROPERTIES OF HOMOPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Reaction Conditions Temp °C	Reaction Conditions Press. mm Hg	Reaction Conditions Time hr.
8	87004	"	2	1.50	25-28	110	0.9	4.0
		"	1	1.31				
9	81178	"	2	2.00	45-70	110	1.0	1.0
		"	1	1.73				
10	93041	"	2	0.50	25-30	65	1.5	1.0
		"	1	0.43				
11	81160	"	2	2.00	38-48	130	2.0	1.0
		"	1	1.74				
12	81188	"	2	1.00	34-45	120	10.0	6.0
		"	1	0.87		120	1.5	2.0
13	81151	$(MeØSiOH)_2Ø$	3	3.00	30-46	130	0.3	2.0
		$Ti(OBu)_2(acac)_2$	1	1.03				
14	77598	"	2	1.00	48-80	110	0.8	2.0
		"	1	0.56				
15	81161	"	2	1.00	115-146	130	7.5	3.0
		"	1	0.56				

Table 11 (Cont)

PREPARATION AND PHYSICAL PROPERTIES OF HOMOPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

						Reaction Conditions		
	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Temp °C	Press. mm Hg	Time hr.
16	85255	$(\mathrm{Me}\phi\mathrm{SiOH})_2\phi$	2	1.50	65-118	120	0.3	3.0
		$\mathrm{Ti(OBu)_2(acac)_2}$	1	0.84				
17	85283	"	2	1.50	45-87	115	2.5	1.5
		"	1	0.84				
18	93003	"	2	2.50	50-68	a-80	0.8	1.0
		"	1	1.40	60-130	b-150	0.7	2.0
19	81121	$(\mathrm{MeViSiOH})_2\phi$	5	2.50	<25	120	1.0	1.5
		$\mathrm{Ti(OBu)_2(acac)_2}$	1	0.68				
20	85216	$(\mathrm{Me_2SiOH})_2\phi\text{-}\phi$	3	0.090	80-120	80	1.5	1.5
		$\mathrm{Ti(OBu)_2(acac)_2}$	1	0.039				
21	77580	"	3	0.120	240-280	100	--	2.0
		"	1	0.056				
22	85208	"	3	1.00	--	65	1.5	2.0
		"	1	0.43				
23	77578	"	1.4	0.40	∿150	190	--	1.0
		"	1	0.39				

Table 12

PREPARATION AND PHYSICAL PROPERTIES OF HETEROPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

						Reaction Conditions		
	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Temp °C	Press. mm Hg	Time hr.
24	85245	$(Me\phi SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	3 1	0.600 0.184	50-80	100	0.7	3.0
25	81162	$(Me_2SiOH)_2\phi\text{-}O\text{-}\phi$ $Ti(OBu)_2(acac)_2$	2 1	0.800 0.422	46-65	130	8.0	2.0
26	85207	" "	2 1	1.000 0.616	30-35	70	0.9	1.5
27	85242	$(Me_2SiOH)_2\phi$ $(Me\phi SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	1 1 1	0.346 0.654 0.602	45-60	73	0.2	2.0
28	85243	" " "	1.4 0.6 1	0.554 0.446 0.685	30-50	8.0	1.0	2.0
29	85244	" "	0.8 1.2 1	0.252 0.748 0.545	60-130	85	0.2	2.0
30	77599	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	3 7 5	1.50 2.06 2.03	65-101	100	5.0	2.0
31	77594	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	1.550 0.575 0.828	60	120	--	--
32	81143	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	1.000 0.575 0.826	~25	120	1.0	2.0

Table 12 (Cont)

PREPARATION AND PHYSICAL PROPERTIES OF HETEROPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

						Reaction Conditions		
	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Temp °C	Press. mm Hg	Time hr.
33	81181	$(\mathrm{Me_2SiOH})_2\emptyset$ $(\mathrm{Me_2SiOH})_2\emptyset\text{-O-}\emptyset$ $\mathrm{Ti(OBu)_2(acac)_2}$	7 3 5	0.623 0.377 0.774	40-50	105	1.7	1.0
34	81169	" " "	7 3 5	0.584 0.416 0.722	44-75	80	8.0	3.0
35	81180	$(\mathrm{Me}\emptyset\mathrm{SiOH})_2\emptyset$ $(\mathrm{Me_2SiOH})_2\emptyset\text{-O-}\emptyset$ $\mathrm{Ti(OBu)_2(acac)_2}$	7 3 5	1.080 0.420 0.866	49-65	115	1.5	.10
37	81192	$(\mathrm{Me_2SiOH})_2\emptyset$ $(\mathrm{Me_2SiOH})_2\emptyset\text{-O-}\emptyset$ $\mathrm{Ti(OBu)_2(acac)_2}$	1 1 1	0.415 0.585 0.722	50-65	125	1.0	3.0
38	81193	" " "	7 3 10	0.625 0.375 1.550	30-45	130	2.5	---
39	81194	" " "	3 2 5	0.519 0.481 1.500	30-37	125	0.9	1.0
40	81200	" " "	7 3 10	0.625 0.375 1.550	30-45	130	2.5	---
41	85203	" " "	7 3 5	0.584 0.416 0.722	30-42	75	1.0	2.0

Table 12 (Cont)

PREPARATION AND PHYSICAL PROPERTIES OF HETEROPOLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) PREPOLYMERS

	Sample	Intermediates	Mole Ratio of Intermediates	Weight of Intermediates Used, g	Melting Range of Prepolymers °C	Reaction Conditions Temp °C	Reaction Conditions Press. mm Hg	Reaction Conditions Time hr.
42	81153	$(Me_2SiOH)_2\phi$	7	1.308	30-55	120	2.0	2.0
		$(Me\phi SiOH)_2\phi$	2	0.580				
		$(Me_2SiOH)_2\phi-\phi$	1	0.250				
		$Ti(OBu)_2(acac)_2$	5	1.620				
43	81155	"	5	0.933	65-85	120	5.0	2.0
		"	3	0.869				
		"	2	0.500				
		"	5	1.620				
44	81195	$(Me_2SiOH)_2\phi$	2	0.130	45-60	115	1.5	1.0
		$(Me\phi SiOH)_2\phi$	3	0.300				
		$(Me_2SiOH)_2\phi-\phi$	2	0.173				
		$(Me_2SiOH)_2\phi-O-\phi$	3	0.272				
		$Ti(OBu)_2(acac)_2$	10	1.120				

Table 13

PROPERTIES OF PRODUCTS† OF REACTION OF BIS(ACETYLACETONATO)DIBUTOXYTITANIUM WITH p-PHENYLENE-BIS(DIORGANOSILANOL)

Ratio Charged Si:Ti	Substituents on Silicon	Softening Range°C	Ratio†† in Product AcAc:OC_4H_9:SiOH based on Si-CH_3 Ref.	Molecular Weight†††
2:1	CH_3,CH_3	r.t.-30	2:0:(0)	(1.01)
4:1	CH_3,CH_3	37-45	0.1:0:(0)	(1.02)
2:1	CH_3,C_6H_5	45-60	2:0:(0)	1240*
4:1	CH_3,C_6H_5	50-105	0.1:0:(0)	1260
8:1	CH_3,C_6H_5	38-46	0:0:3.2	930
2:1**	CH_3,C_6H_5	70-95	2:0:(0)	1730*

---

† Products as formed

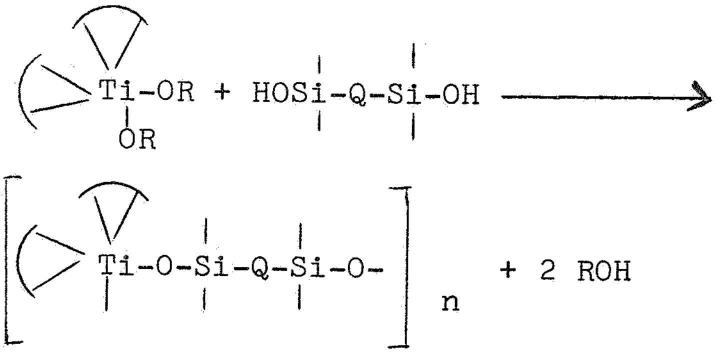
†† From NMR; (0) denotes analysis insensitive to amounts under about 0.2

††† By vapor phase osmometry; (   ) indicates relative viscosity at 30°C of 0.5% benzene solution

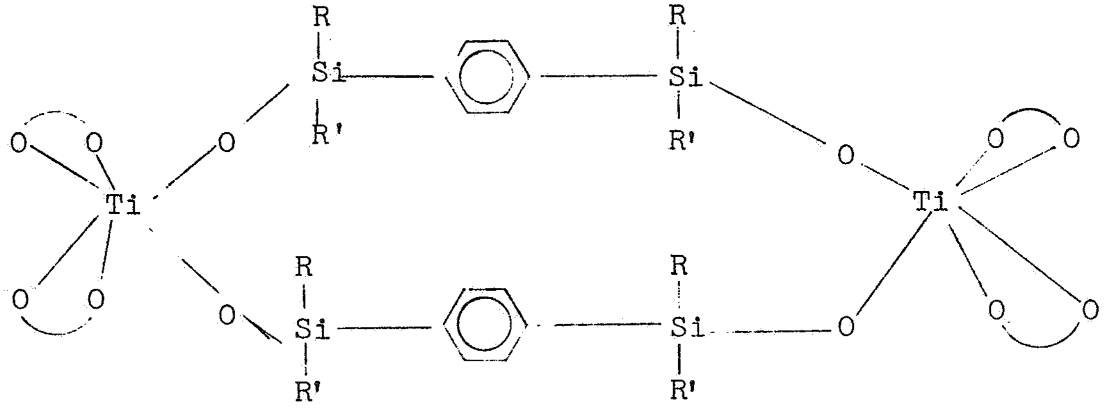
* Molecular weight of bridged driver is 1186.

** Product purified by washing with ethanol. Over 90% of product was insoluble in ethanol.

The data in Table 13 also show that molecular weights of condensation products are lower than expected for the high degrees of condensation that the product analysis for silanol and butoxy show. This indicates that the simple condensation reaction, shown below for the 2:1 Si:Ti charge is terminated by a major



side reaction. The fact that this side reaction must account for the disappearance of both butoxy and methanol groups, suggests that termination is by condensation to cyclic bridged structures such as the following:



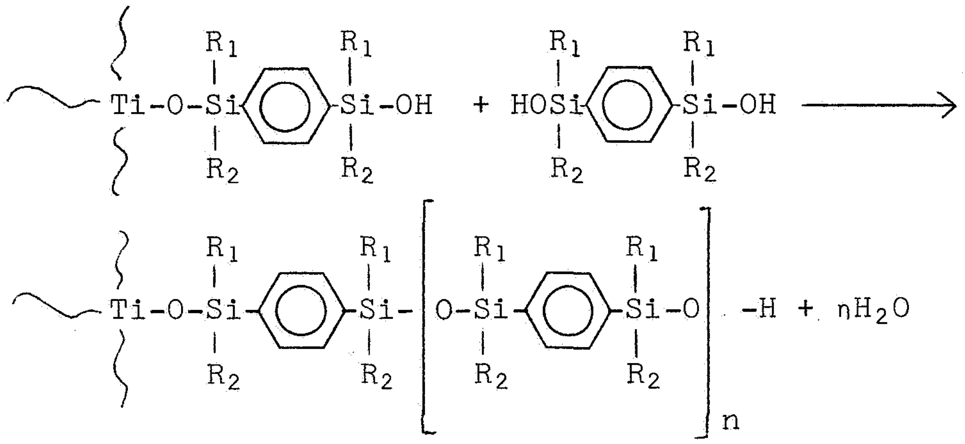
Steric requirements of these structures are very unfavorable, although molecular models suggest they are not impossible. Additional evidence that supports this mode of termination is as follows:

a. The acetylacetonato groups in titanium complexes are known to be stabilized in the *cis* position (ref. 43).

b. Elemental analysis for C, H, and Ti of one product from a 2:1 Si:Ti charge that was purified to remove unreacted silanediol by washing with ethanol was in agreement for a 1-to-1 condensation product:

Calc. for 1:1 product:	C, 60.6; H, 5.77; Ti, 7.07; Si, 9.49
Found:	C, 60.1; H, 5.58; Ti, 7.97; Si, (reproducible values not obtained 13.9 and 7.8).

The product initially isolated from charges with Si:Ti ratios of 6 to 1 or greater usually are mixtures containing unreacted silanediol. These silanediols presumably condense normally with the silanol groups on the titanium moiety during the later steps of reaction and during cure at a rate that depends on the substituents on the silicon:



3. Crosslinking of Prepolymers

a. Precure

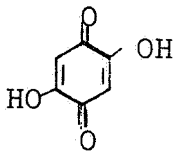
A preliminary series of crosslinking reactions by ligand exchange with the prepolymers described in section 1 above was done in reaction flasks for the following objectives:

(1) To find bisbidentate ligands that react with these prepolymers at low (under 170°C) temperatures in order to yield cured resins that do not soften below 250°C;

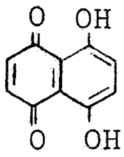
(2) To determine reaction conditions for the preparation of "B" stage resins consisting of partially crosslinked polymer with flow temperature below 150°C;

(3) To determine the reaction conditions necessary to complete the crosslinking reaction for the various prepolymer-ligand combinations. The crosslinking ligands that were used were as follows:

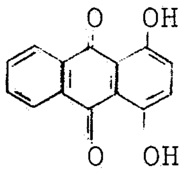
2,5-dihydroxybenzoquinone (2,5-DHBQ)



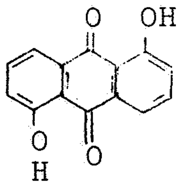
5,8-dihydroxynaphthaquinone (5,8-DHNQ)



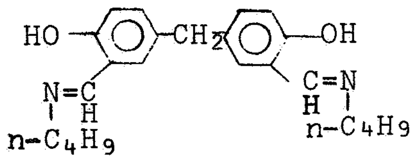
1,4-dihydroxyanthraquinone (1,4-DHAQ)



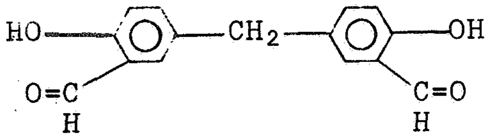
1,5-dihydroxyanthraquinone (1,5-DHAQ)



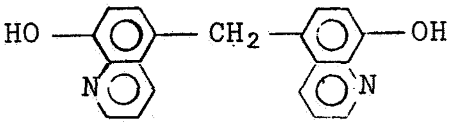
5,5'-bis(salicyl-N-butylimino)methane (5,5'-BSNBM)



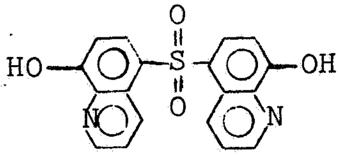
5,5'-bis(salicylaldehydo)methane (5,5'-BSAM)



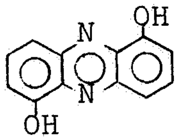
5,5'-bis(8-hydroxyquinolino)methane (5,5'-B8HQM)



5,5'-bis(8-hydroxyquinolino)sulfone (5,5'-B8HQS)



1,6-dihydroxyphenazine (1,6-DHP)



In the preliminary tests, the crosslinking ligands and prepolymers were mixed in benzene (or benzene-pyridine for benzene-insoluble ligands), the solvent was removed under vacuum, and the resin was heated for varying lengths of time under vacuum. Melting ranges of samples of the resin were taken periodically. The specific reaction conditions used, together with the melting ranges of the products from individual tests using prepolymers with varying Si:Ti ratios and with the different ligands, are summarized in Table 14. From these data, suitable precure times to give "B" stage resins for the different ligand-elastomer combinations are evident. It is preferable to use these partially cured "B" stage resins in the adhesive joint instead of the fresh reactants to minimize porosity in the coupled joint.

Although the melting points of the polymers given in Table 14 are for the partially cured resins, two conclusions can be drawn concerning the effects of the different variables on the physical properties of the cured resins.

Table 14

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Interme-diates	Melting Range of Prepolymer °C	Crosslinking Agent	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
1	70194 (-)*	$(Me_2SiOH)_2$Ø $Ti(OBu)_2(acac)_2$	10 1	~40			140	1.0	4.0	
2.	70195 (70197)	" "	5 1	~25	1,4-DHAQ	1/2	74 120	1.0 1.0	6.0 2.0	65-70
3.	81129 (81131)	" "	4 1	~25	5,5'-BSAM	1/2	125	1.2	20	yellow powder
4.	81105 (81108)	" "	3 1	<25	1,4-DHAQ	1/2.5	120 a-120 b-150 c-209	1.0 -- -- --	3.0 16 14 2	50-90 70-105 70-195
5.	77589 (77589)	" "	2.5 1	~25	1,4-DHAQ	1/2	120 160	0.6 0.5	1.5 16	135-150
6.	77589 (77590)	" "	2.5 1	~25	1,5-DHAQ	1/2	120 160	0.6 0.4	1.5 3.0	85-95
7.	81106 (81109)	" "	2 1	<25	1,4-DHAQ	1/3	120 110	0.7	3.0 16	85-105
8.	81141 (81142-a)	" "	2 1	<25	5,8-DHNQ	1/3	80 a-120 b-170	9.0 1.5	20 20	34-60 40-101
9.	81141 (81142-b)	"	2 1	<25	2,5-DHBQ	1/3	120 90	1.5 6.0	20 20	30-55
10.	87004 (81177)	"	2 1	25-28	5,5-BSNBM	1/1	110 115	0.9 1.0	4.0 4.0	80-116
11.	81178 (81179)	" "	2 1	45-70	(50%)5,5'-BSNBM (50%)5,5'-BSAM	1/2 1/2	110 120	1.0 1.5	1.0 1.0	70-110

Table 14 (Cont)

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Intermediates	Melting Range of Prepolymer °C	Crosslinking Agent	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
12.	93041 (93042)	$(Me_2SiOH)_2$Ø $Ti(OBu)_2(acac)_2$	2 1	25-30	1,4-DHAQ	1/2	65 117	1.5 0.9	1.0 1.5	90-150
13.	81160 (81166)	" "	2 1	38-48	1,4-DHAQ 1% $FeCl_3$	1/2	130 157	2.0 1.5	1.0 5.0	180-217
14.	81160 (81167)	" "	2 1	38-48	1,4-DHAQ 1% $AlCl_3$	1/2	130 130	2.0 8.0	1.0 4.0	95-160
15.	81188 (81190)	" "	2 1	34-45	1,4-DHAQ 1% $ZnCl_2$	1/2	120 120	10.0 1.5	6.0 2.0	81-167
16.	81188 (81191)	" "	2 1	34-45	1,4-DHAQ 0.5% $ZnCl_2$	1/2	120 120	10.0 0.9	6.0 2.0	55-158
17.	81151 (81151)	$(MeØSiOH)_2$Ø $Ti(OBu)_2(acac)_2$	3 1	30-46	5,8-DHNQ	1/2	130 a-117 b-200	0.3 5.0 0.1	2.0 2.0 5.0	67-104 110-145
18.	77598 (81149-a)	" "	2 1	48-80	1,4-DHAQ	1/2	110 110	0.8 0.2	2.0 16	168-180
19.	77598 (81149-b)	" "	2 1	48-80	5,8-DHNQ	1/2	110 125	0.8 0.2	2.0 16	175-192
20.	81161 (81176)	" "	2 1	115-146	5,5'-BSNBM	1/2	130 110	7.5 0.5	3.0 1.0	35-75
21.	85255	" "	2 1	65-118			120	0.3	3.0	
22.	85283	" "	2 1	45-87			115	2.5	1.5	

Table 14 (Cont)

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Interme-diates	Melting Range of Prepolymer °C	Crosslinking Agent	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
23.	93003 (93005)	(MeØSiOH)$_2$Ø Ti(OBu)$_2$(acac)$_2$	2 1	50-68 60-130	5,5'-BSNBM	1/1	a-80 b-150 129	0.8 0.7 2.5	1.0 2.0 2.0	
24.	81121 (77582)	(MeViSiOH)$_2$Ø Ti(OBu)$_2$(acac)$_2$	5 1	<25	1,4-DHAQ 1% Bz_2O_2	1/2	120 150	1.0 2.0	1.5 8.0	~130
25.	81121 (77583)	" "	5 1	<25	1,4-DHAQ	1/2	120 125	1.0 ---	1.5 16	75-130
26.	85216 (87005)	(Me$_2$SiOH)$_2$Ø-Ø Ti(OBu)$_2$(acac)$_2$	3 1	80-120	1,4-DHAQ	1/3	80 120	1.5 0.9	1.5 4.0	115-13
27.	77580 (77581)	" "	3 1	240-280	1,4-DHAQ	1/3	100 120	-- 1.2	2.0 1.0	250-295
28.	85208 (85212)	" "	3 1	--	5,8-DHNQ	1/4	65 135	1.5 1.0	2.0 16	70-135
29.	85208 (85213)	" "	3 1	--	5,5'-BSNBM	1/1	65 125	1.5 1.5	2.0 16	55-130
30.	77578 (77579)	" "	1.4 1	~150	1,4-DHAQ	1/2	190 150	-- --	1.0 2.0	>300
31.	85245	(MeØSiOH)$_2$Ø-Ø Ti(OBu)$_2$(acac)$_2$	3 1	50-80			100	0.7	3.0	
32.	81162	(Me$_2$SiOH)$_2$Ø-O-Ø Ti(OBu)$_2$(acac)$_2$	2 1	46-65			130	8.0	2.0	
33.	85207 (85209)	" "	2 1	30-35	5,5-BSNBM	1/1	70 115	0.9 0.7	1.5 1.5	55-78

Table 14 (Cont)

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Interme-diates	Melting Range of Prepolymer °C	Crosslinking Agent	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
34.	85207 (85210)	$(Me_2SiOH)_2\phi\text{-}O\text{-}\phi$ $Ti(OBu)_2(acac)_2$	2 1	30-35	5,8'-DHNQ	1/3	70 120	0.9 1.1	1.5 1.5	50-75
35.	85207 (85211)	" "	2 1	30-35	1,4-DHAQ	1/2	70 120	0.9 2.1	1.5 2.5	65-96
36.	85242	$(Me_2SiOH)_2\phi$ $(Me\phi SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	1 1 1	45-60			73	0.2	2.0	
37.	85243	" " "	1.4 0.6 1	30-50			80	1.0	2.0	
38.	85244	" " "	0.8 1.2 1	60-130			85	0.2	2.0	
39.	77599 (81152-a)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	3 7 5	65-101	5,8-DHNQ	1/2	100 196	5.0 --	20 20	67-116
40.	77599 (81152-b)	" " "	3 7 5	65-101	1,4-DHAQ	1/2	100 130	5.0 1.7	20 --	54-175
41.	77599 (81152-c)	" " "	3 7 5	65-101	5,5'-BSAM	1/1	100 120	5.0 1.0	20 --	190**
42.	77594 (81147-a)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	60	5,8-DHAQ	1/2	120 120	-- 0.15	-- --	113-135

Table 14 (Cont)

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Intermediates	Melting Range of Prepolymer °C	Crosslinking Agent	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
43.	77594 (81147-b)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi-\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	60	2,5-DHBQ	1/2	120 120	-- 1.0	-- --	86-131
44.	77594 (77595)	" "	7 3 10/3	60	1,4-DHAQ	1/2	120 170	-- 1.5	-- 20	80-110
45.	81143 (77596)	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi-\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	25	1,4-DHAQ	1/2	120 130	1.0 0.15	20 --	63-100
46.	81181 (81182)	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi-O-\phi$ $Ti(OBu)_2(acac)_2$	7 3 5	40-50	5,5'-BSNBM	1/1	105 120	1.7 1.7	1.0 --	66-101
47.	81169 (81189)	" " "	7 3 5	44-75	5,5'-BSNBM	1/1	$80^{\dagger}$ 110	8.0 0.3	3.0 6.0	50-80
48.	81180 (81185)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi-O-\phi$ $Ti(OBu)_2(acac)_2$	7 3 5	49-65	5,5'-BSNBM	1/1	115 115	1.5 1.5	1.0 16	140-167
49	81180 (81186)	" " "	7 3 5	49-65	5,5'-BSNBM	1/1	115 $115^{\dagger\dagger}$	1.5 1.2	1.0 16	93-125
50.	81192 (81196)	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi-O-\phi$ $Ti(OBu)_2(acac)_2$	1 1 1	50-65	5,5'-BSNBM	1/1	125 $115^{\dagger\dagger}$	1.0 1.5	3.0 20	60-110
51.	81193 (81197)	" " "	7 3 10	30-45	5,5'-BSNBM	1/1	130 $120^{\dagger\dagger}$	2.5 0.9	-- 20	50-75

Table 14 (Cont)

PHYSICAL PROPERTIES OF NONCROSSLINKED AND PARTIALLY CROSSLINKED POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE) POLYMERS

	Sample	Intermediates	Mole Ratio of Intermediates	Melting Range of Prepolymer °C	Crosslinking Agents	Ligand/Ti Mole Ratio	Temp °C	Press mm Hg	Time hr.	Melting Range After Cure °C
52.	81194 (81198)	$(Me_2SiOH)_2Ø$ $(Me_2SiOH)_2Ø$-O-Ø $Ti(OBu)_2(acac)_2$	3 2 5	30-37	5,5'-BSNBM	1/1	125 120	0.9 0.9	1.0 3.0	105-221
53	81192 (85201)	" " "	1 1 1	50-65	1,4-DHAQ	1/1	125 220++	1.0 3.0	5.0 2.0	50-150
54.	81200 (85202)	" " "	7 3 10	30-45	5,5'-BSNBM	1/2	130 125	2.5 1.5	-- 2.0	90-180
55.	85203 (85205)	" " "	7 3 5	30-42	5,5'-BSNBM	1/2	75 105	1.0 0.7	2.0 2.0	55-65
56	85203 (85206)	" " "	7 3 5	30-42	1,4-DHAQ	1/2	75 110	1.0 1.5	2.0 2.0	65-80
57.	81153 (81154)	$(Me_2SiOH)_2Ø$ $(MeØSiOH)_2Ø$ $(Me_2SiOH)_2Ø$-Ø $Ti(OBu)_2(acac)_2$	7 2 1 5	30-55	5,5'-R8HQM	1/2	120 110	2.0 2.0	2.0 16	110-195
58.	81155 (81158)	" " " "	5 3 2 5	65-85	2,5-DHBQ	1/2	120 120	5.0 2.0	2.0 1.5	120-150
59.	81195 (81199)	$(Me_2SiOH)_2Ø$ $(MeØSiOH)_2Ø$ $(Me_2SiOH)_2Ø$-Ø $(Me_2SiOH)_2Ø$-O-Ø $Ti(OBu)_2(acac)_2$	2 3 2 3 10	45-60	5,5'-BSNBM	1/1	115 100	1.5 1.5	1.0 2.0	150-250

* Numbers in parenthesis indicate crosslinking reference
** Decomposed
† Heated to 180°C for 5 min. first.
†† Melt crosslink

Higher melting points go with (1) a high Ti/Si ratio and (2) a more rigid crosslinking agent. For example, the more flexible 5,5'-BSNBM gave a crosslinked polymer with lower melting point than the cured polymer that was crosslinked with 5,8-DHNQ. The effect of the Ti/Si ratio can be seen by comparing the polymer with Ti/Si atom ratio of 1/6 and a decidedly lower melting point than the polymer with Ti/Si ratio of 1/4. Generally speaking, the series of crosslinking agents (2,5-DHBQ, 5,8-DHNQ, 1,5-DHAQ, 1,4-DHAQ) under similar crosslinking conditions produced polymers with increasing melting ranges. This was probably due to the fact that the chelating strength decreases within the series in the order given and that the strongest chelating agent (2,5-DHBQ) was able to form a tris-complex with the titanium atom thus breaking up the polymer backbone. The effect would then be similar to a low molecular weight polymer with a titanium chelate as filler. The 1,4-DHAQ, on the other hand, only undergoes ligand exchange reactions with the acetylacetone group, forming crosslinked polychelatotitano-p-arylene-bis-(diorganosiloxane) polymer.

In order to increase the rate at which our ligand exchange crosslinking reaction takes place, experiments were conducted in which Lewis acids were added at .5-1% by weight to the mixture of polymer and crosslinking ligand prior to use. Using polychelatotitano-p-phenylene-bis(dimethylsiloxane) and 1,4-DHAQ with $FeCl_3$, the melting range of the polymer was increased to 180-217°C after reaction at 157°C for 5 hours. This represents a 146°C increase in the softening temperature of the polymer, at a substantially faster rate of cure than the polymers cured without ferric chloride catalyst. The effect increases in the order $ZnCl_2 < AlCl_3 < FeCl_3$.

Another way to increase the melting ranges of these polymers is to increase the degree of crosslinking by increasing the available crosslinking sites. Thus, polychelatotitano-p-phenylene-bis(methylvinylsiloxane) prepolymers were prepared and crosslinked at the vinyl sites by the addition of 1% benzoylperoxide. However, the results show that instead of a melting range from 75-130°C the vinyl-crosslinked polymer has a rather sharp melting point at 130°C. The data in Table 12 also show that in general heteropolychelatotitano-p-arylene-bis(diorganosiloxane) polymers have high melting points. Many have melting points above the curing temperatures.

b. Cure *In Situ* in Aluminum Joints

Factors that are pertinent to the formation of a good adhesive joint have already been discussed in detail. In order to obtain good adhesive-adherent contact, the polymers were only partially cured in the reaction flask. Further curing of these resins was carried out in the adhesive joint. Prepolymers described above were melted between two 2011-T6 aluminum adherent strips and cured at 170°C. Their adhesive properties are summarized in Table 15. Most of these samples had tensile shear strengths of 1000 to 1100 psi at room temperature. Tensile shear strengths of samples cured with Lewis acids had somewhat lower strengths.

Table 15

ADHESIVE TESTS OF CROSSLINKED POLYCHELATOTITANOSILOXANE POLYMERS CURED *IN SITU* AT 170°C IN AN ADHESIVE JOINT

2011-T6 Aluminum Adherent

Sample	Intermediate	Mole Ratio of Intermediate	Crosslinking Agent	Ligand/Ti Mole Ratio	Melting Range Prior to Cure	Average Tensile Shear Strength, psi	
						Rate	150°C
(81142)	$(Me_2SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	2 1	5,8-DHNQ	1/3	40-101	1100	
(81179)	"	2 1	50% 5,5'-BSNBM 50% 5,5'-BSAM	1/2	80-194	648	155.
(81190)	" "	2 1	1,4-DHAQ 1% $ZnCl_2$	1/2	81-167	560	
(81191)	" "	2 1	1,4-DHAQ 0.5% $ZnCl_2$	1/2	55-158	525	
(81177)	" "	2 1	5,5'-BSNBM	1/1	60-170	945	
(81149-b)	$(Me\phi SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	2 1	5,8-DHNQ	1/2	175-190	1030	
(81147-a)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	5,8-DHNQ	1/2	150-185	1120	
(77595)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	1,4-DHAQ	1/2	175-215	800	
(77596)	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 10/3	1,4-DHAQ	1/2	145-200	1050	
(81182)	$(Me_2SiOH)_2\phi$ $(Me_2SiOH)_2\phi\text{-}O\text{-}\phi$ $Ti(OBu)_2(acac)_2$	7 3 5	5,5'- BSNBM*	1/1	95-150	1014	384
(81189)	" " "	7 3 5	5,5'-BSNBM	1/1	--	660	

Table 15 (Continued)

ADHESIVE TESTS OF CROSSLINKED POLYCHELATOTITANOSILOXANE POLYMERS CURED *IN SITU* AT 170°C IN AN ADHESIVE JOINT

2011-T6 Aluminum Adherent

Sample	Intermediate	Mole Ratio of Intermediate	Crosslinking Agent	Ligand/Ti Mole Ratio	Melting Range Prior to Cure	Average Tensile Shear Strength, psi	
						Rate	150°C
(81197)	" "	7 3 10	BSNBM*	1/1	68-105	790	
(81196)	" " " "	1 1 1	BSNBM*	1/1	70-120	1090	
(81185)	$(Me\phi SiOH)_2\phi$ $(Me\phi SiOH)_2\phi$-O-ϕ $Ti(OBu)_2(acac)_2$	7 3 5	BSNBM	1/1	160-195	527	
(81186)	$(Me\phi SiOH)_2\phi$ $(Me_2SiOH)_2\phi$-O-ϕ $Ti(OBu)_2(acac)_2$	7 3 5	BSNBM*	1/1	93-125	1055	

Sample	Intermediate	Mole Ratio of Inter-mediate	Cross-linking Agents	Ligand/ Ti Mole Ratio	Melting Range Prior to Cure	Tensile Shear Strength, psi		
						RT	150°C	-100°C
85205	$(Me_2SiOH)_2$Ø $(Me_2SiOH)_2$Ø-O-Ø $Ti(OBu)_2(acac)_2$	7 3 5	5,5'-BSNBM	1/2	55-65	1080	---	>1370
85206	" " "	7 3 5	1,4-DHAQ	1/2	65-80	790	270	>1250
85209	$(Me_2SiOH)_2$Ø-O-Ø $Ti(OBu)_2(acac)_2$	2 1	5,5'-BSNBM	1/1	55-78	1000	90^+	1170
85210	" "	1 1	5,8-DHNQ	1/3	50-75	---	---	310
85211	" "	1 1	1,4-DHAQ	1/2	65-96	---	---	900
85212	$(Me_2SiOH)_2$Ø-Ø $Ti(OBu)_2(acac)_2$	3 2	5,8-DHNQ	1/4	70-135	---	---	670
70197	$(Me_2SiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	4.25 1	1,4-DHAQ	1/2	75-145	640	---	---
70197	"	4.25 1	1,4-DHAQ	1/2	75-145	1280	---	---
77584	$(MeViSiOH)_2\phi$ $Ti(OBu)_2(acac)_2$	4 1	1,4-DHAQ 1% Bz_2O_2	1/2	~ 130	1040	---	---

* Melt crosslink

\+ = Melt Yield

5,5'-BSNBM = 5,5'-bis(salicyl-N-butylimino)methane

1,4-DHAQ = 1,4-dihydroxyanthraquinone

5,8-DHNQ = 5,8-dihydroxynaphthaquinone

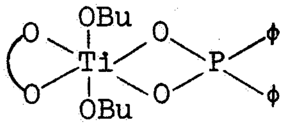
5,5'-BSAM = 5,5'-bis(salicylaldehydo)methane

5,5'-B8HQM = 5,5'-bis(8-hydroxyquinolino)methane

It is apparent that these polymers are good low- and room temperature adhesives, but their high temperature adhesive properties are limited by their melting range. To improve their high temperature properties, two methods of attack were used: (1) increase the molecular weight of the linear prepolymer, and (2) increase crosslinking sites as well as crosslinking rate.

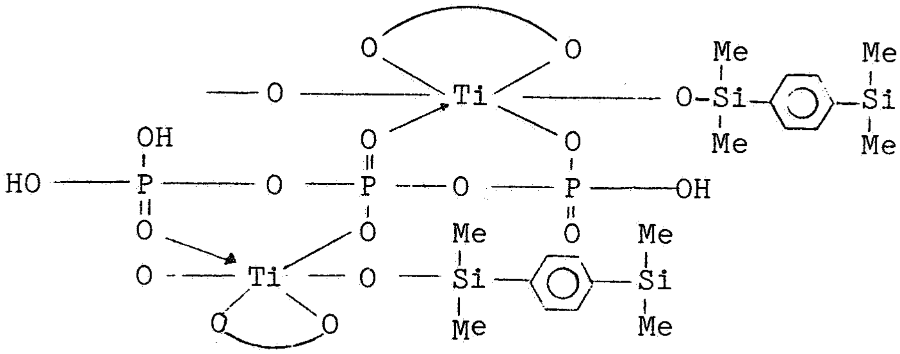
c. Cure with Phosphorus-Containing Ligands

We found that diphenylphosphonic acid can successfully undergo a ligand exchange reaction with bis(acetylacetonato) dibutoxy titanium (IV). In this case it was found that acetylacetone was preferentially displaced by the incoming diphenylphosphonic acid rather than the alkoxy group. This type of reaction should, therefore, lend to crosslinking rather than polymer chain cleavage should a diphosphosphonic acid be used instead.



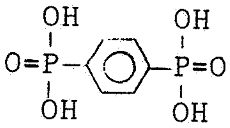
The diphenylphosphonic group also aided adhesion. For example, tensile shear strengths of over 1140 psi at room temperature was obtained with p-phenylene-bis(dimethylsilanol) and diphenylphosphonic acid chelated titanium compound crosslinked with 5,5'-bis (salicyl-N-butylimino)methane at 170°C for 20 hours. However, at 150°C the tensile shear strength dropped to 460 psi.

Following this successful ligand exchange reaction, we decided to use polyphosphates as crosslinking agents thereby eliminating the organic tetradentate ligands altogether. The P-O-P bonds should provide high thermal stability, and the chelating ability of the polyphosphates was well reported in the literature (refs. 44 and 45). The presence of phosphorus in the polymer chain should also serve to enhance the adhesive ability of this class of polychelatotitanosiloxane polymers.

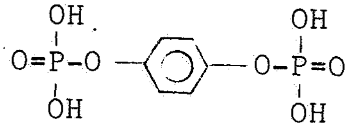


where O⌣O is acetylacetone.

We prepared several samples of free polyphosphoric acids from their sodium salts by passing aqueous solutions through an Amberlite IR-120H cation exchange resin. However, we had considerable difficulty in keeping the free acids from disproportionating into pyro- and metaphosphoric acids prior to reacting with the linear polychelatotitanosiloxanes. Consequently, our attentions turned to phosphates of the following structures that should have greater stabilities toward disproportionation:

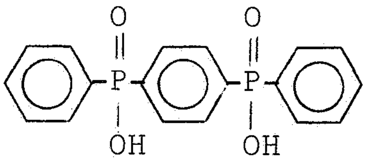


p-phenylenediphosphonic acid



p-phenylenediphosphoric acid

Unfortunately, we found that p-phenylene diphosphonic acid had no common solvents without polychelatotitanosiloxane prepolymers and its melting point was too high for a melt polymerization reaction. We therefore synthesized p-phenylene-bis(phenylphosphinic acid) to obtain greater solubility in aromatics:

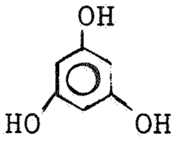


Resins that are infusible at 250°C were obtained with p-phenylene-bis(phenylphosphinic acid) as crosslinking agent. The rate of cure was faster than comparable resins with 5,5'-BSNM. However, tensile strengths of aluminum joints cured with these resins were low (150-250 psi at 250°C) because of poor wetting of substrate by the partially cured resins.

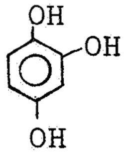
4. Chain Extension of Polychelatotitano-p-arylene-bis(diorganosiloxanes)

a. Via Trihydroxybenzenes

In our first approach, attempts were made to increase the molecular weight of the linear prepolymer by a condensation reaction with trihydroxybenzenes:

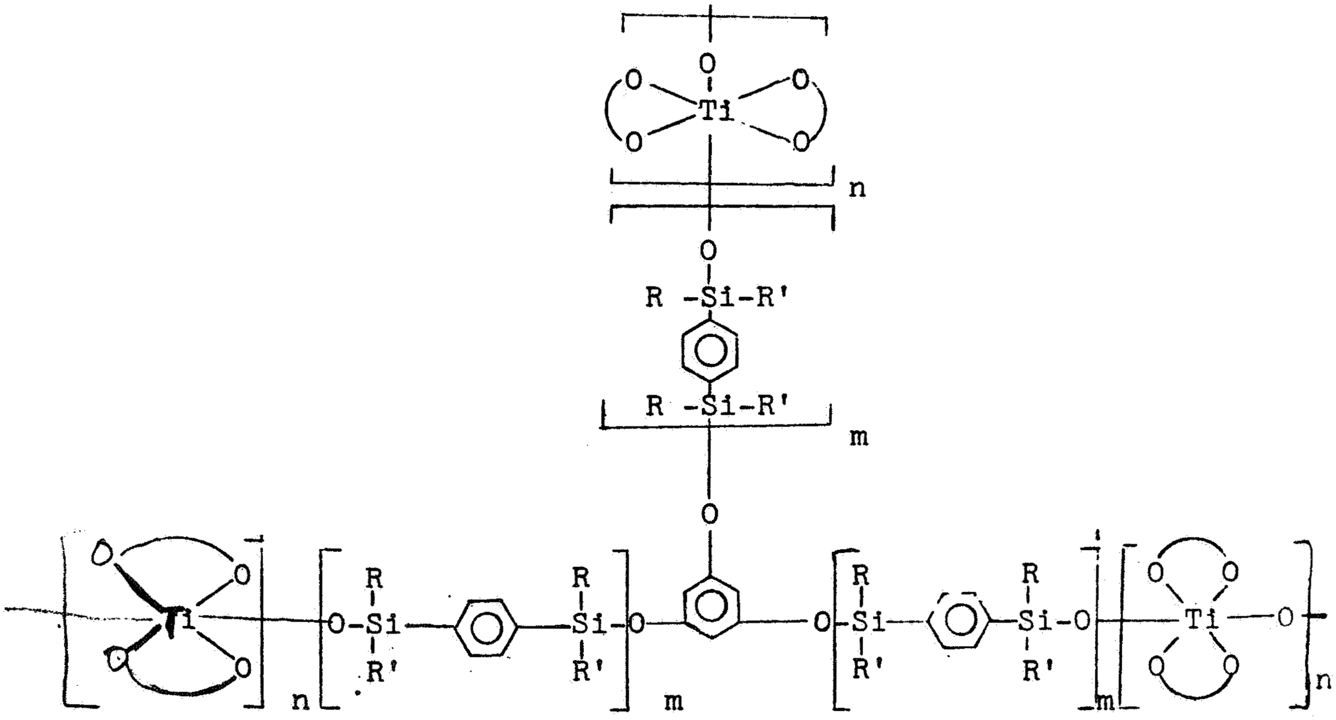


1,3,5-benzenetriol
(phloroglucinol)



1,2,4-benzenetriol

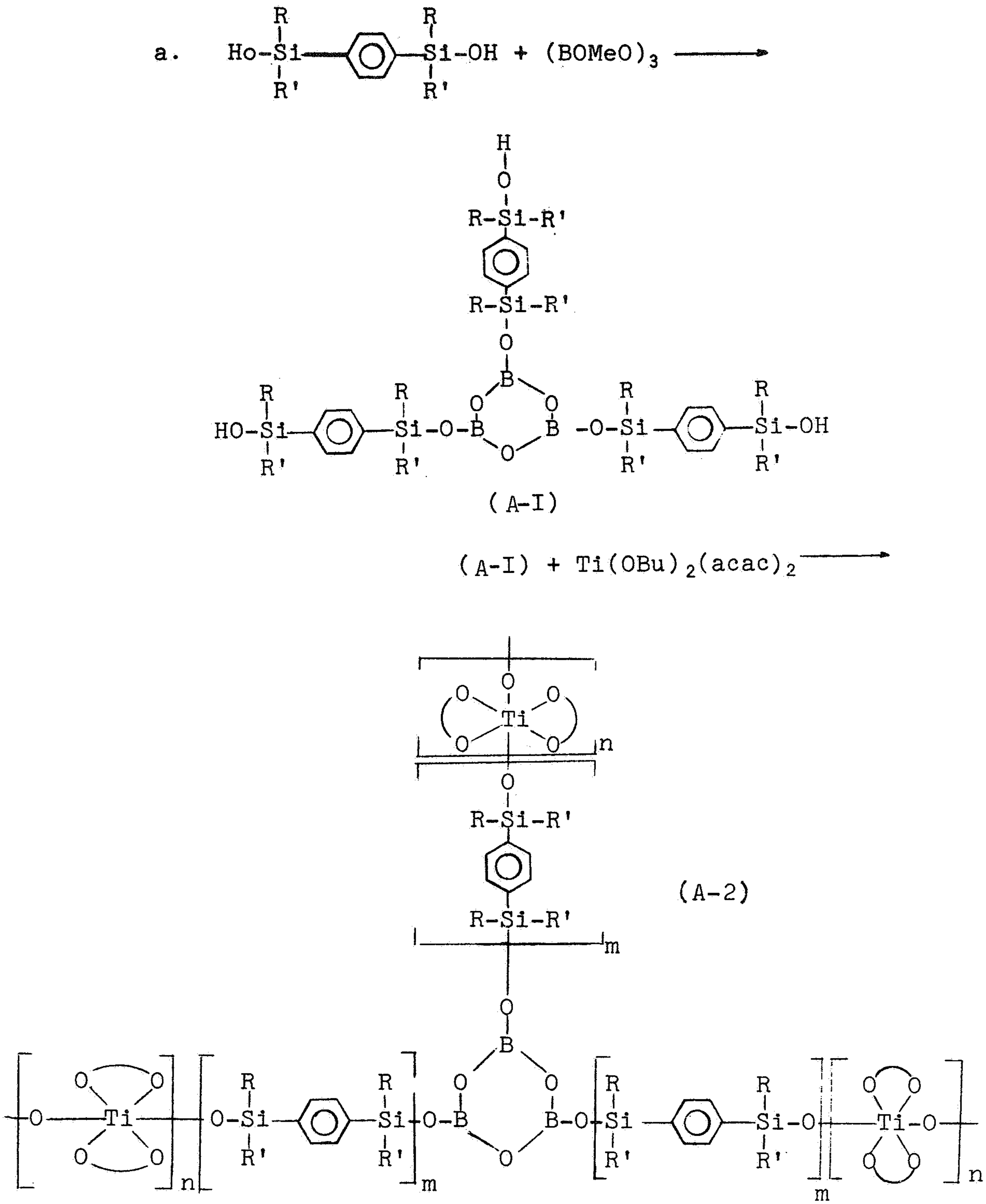
For example, bis-phenol-A has been found to condense with silanols to form a linear polymer with alternating phenylene and siloxane units. Under ideal conditions our proposed cross-linked polymer should have the following structure:



We reacted polychelatotitanosiloxane polymer containing silanol end groups with 1,2,4-benzenetriol in pyridine. The resulting dark maroon product did not show the expected increase in softening temperature. Further tests show that the pyridine destroyed the siloxane polymer backbone. Since these polyhydroxybenzenes are not soluble in an inert solvent, no further effort was spent on this part of the project.

b. Via Trimethoxyboroxin

The three condensation reaction sequences can be represented as follows:



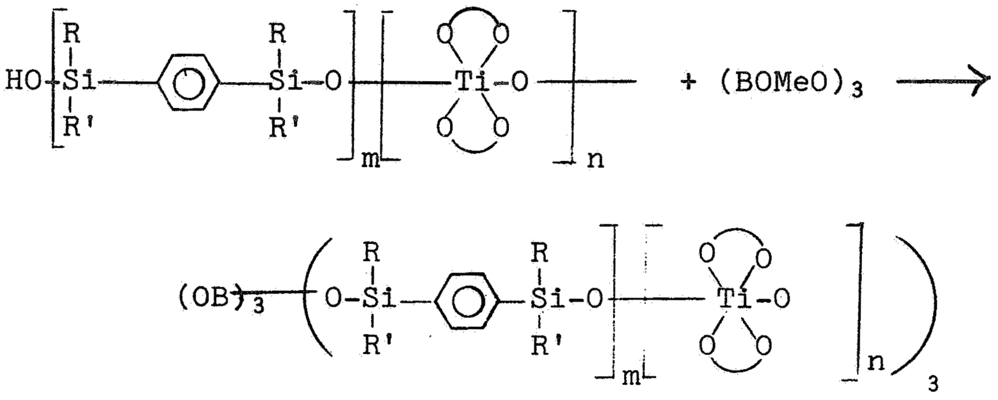
a.

(A-I)

(A-I) + $Ti(OBu)_2(acac)_2$ →

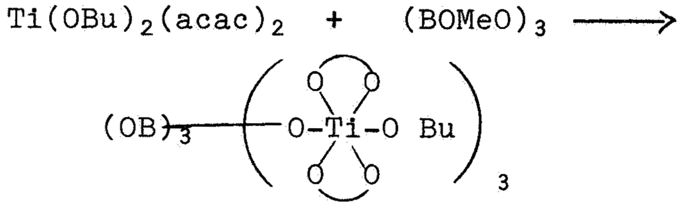
(A-2)

b.

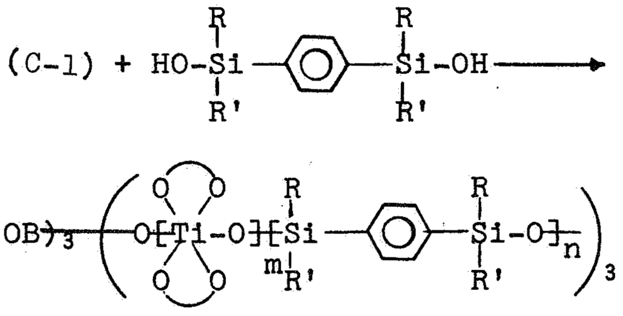


(B)

c.



(C-1)



(C-2)

where R and R' could be $-CH_3$ or C_6H_5 and O‿O is acetylacetone.

Product (A-1) (a white, crystalline material) shows a broad band at 7.5 μ indicating B-O stretch in the ring system and product (A-2) with melting range from room temperature to 28°C, has Ti-O-Si stretching band at 10.8 μ. Products (C-1) and (C-2) were not shown to be the expected products. This would be expected if the condensation reaction between dibutoxybis(acetylacetonato)-titanium and trimethoxyboroxin did not proceed under the experimental condition employed. A difficulty lies in the fact that bis(acetylacetonato)dibutoxytitanium(IV) decomposes at temperatures above 65°C at atmospheric pressure.

Compounds (A-2) and (B) were crosslinked with 1,4-dihydroxyanthraquinone (1,4-DHAQ), 5,8-dihydroxy-1,4-naphthoquinone (5,8-DHNQ), and 5,5'-bis(salicyl-N-butylimino)methane (BSNBM). Table 16 summarizes the results.

c. By Condensation with Bis(dimethylhydroxysilyl)-m-carborane Instead of Simple Arylenesilanediols

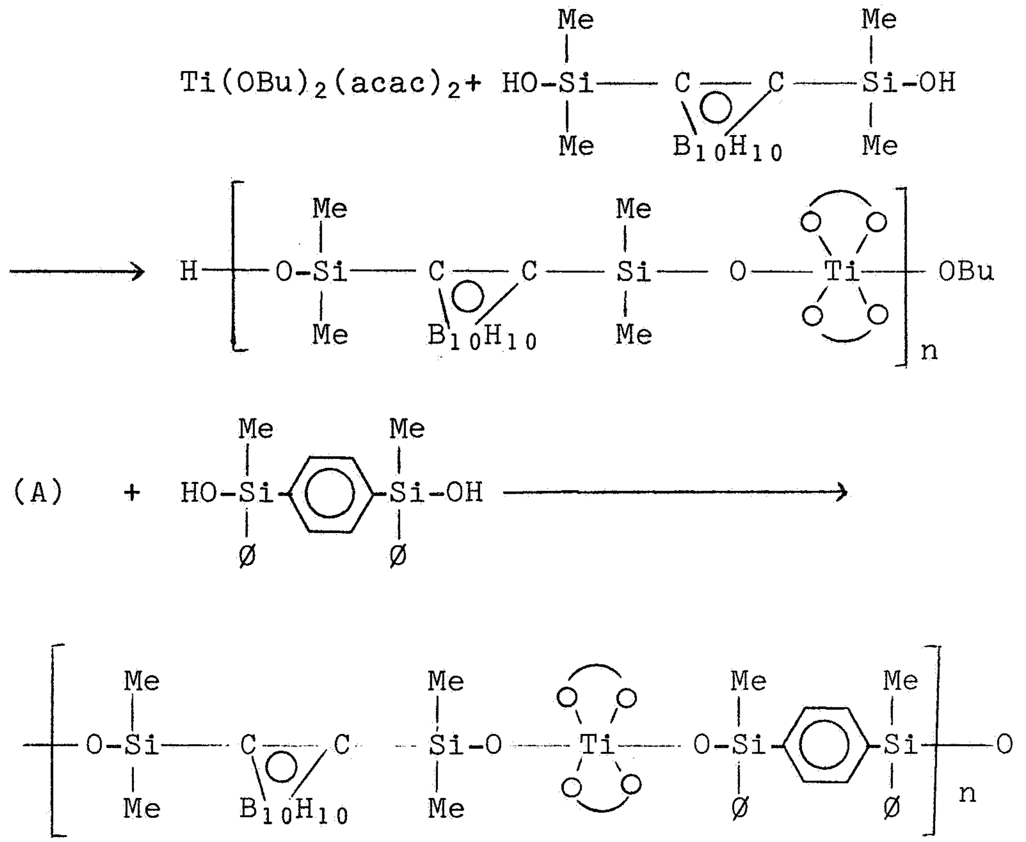
Bis(dimethylhydroxysilyl)-m-carborane was incorporated into the prepolymer backbone by two methods. In the first case, the carborane was dissolved with bis(acetylacetonato)dibutoxytitanium (IV) in benzene, then heated under reflux, and finally heated under vacuum at 120°C for 3 or 5 hours.

Table 16

PHYSICAL PROPERTIES OF CROSSLINKED BORON CONTAINING POLYCHELATOTITANO-p-PHENYLENE-BIS(DIORGANOSILOXANE) POLYMERS

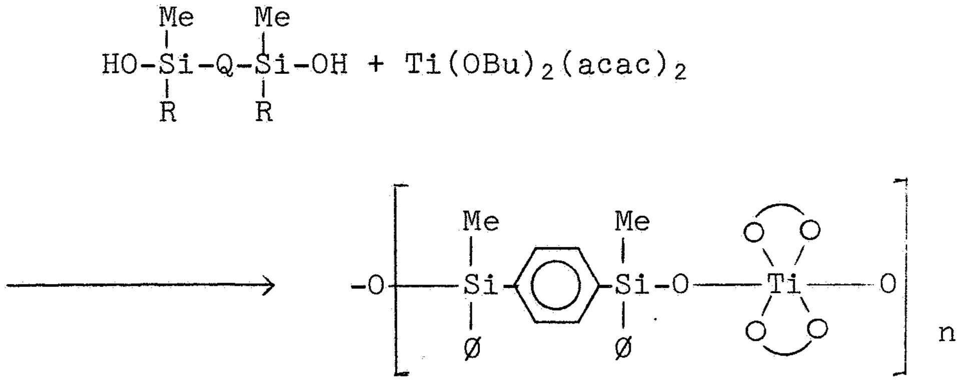
Sample	Intermediates	Mole Ratio of Intermediate	Crosslinking Agent	Ligand/Ti Mole Ratio	Reaction Condition Temp. °C	Reaction Condition Press mm Hg	Reaction Condition Time hr	Melting Range °C
85284	$\mathrm{Ti(OBu)_2(acac)_2}$	2	1,4-DHAQ	1/2	126	0.1	2.5	70-110
	$\mathrm{(OBOMe)_3}$	1	5,8-DHNQ	1/2	120	0.5	1.0	50-75
	$\mathrm{(Me\text{Ø}SiOH)_2\text{Ø}}$	4	5,5'-BSNBM	1/1	120	0.3	2.0	50-155
85285	$\mathrm{(Me\text{Ø}SiOH)_2\text{Ø}}$	3	1,4-DHAQ	1/2	120	0.2	2.0	40-75
	$\mathrm{(OBOMe)_3}$	1	5,8-DHNQ	1/2	123	4.0	1.0	58-75
	$\mathrm{Ti(OBu)_2(acac)_2}$	1.5	5,5'-BSNBM	1/1	118	2.0	1.0	68-140
85288	$\mathrm{(Me\text{Ø}SiOH)_2\text{Ø}}$	3	1,4-DHAQ	1/2	120	3.0	2.0	45-90
	$\mathrm{(OBOMe)_3}$	1						
	$\mathrm{Ti(OBu)_2(acac)_2}$	1.5	5,5'-BSNBM	1/1	120	2.5	1.0	70-140

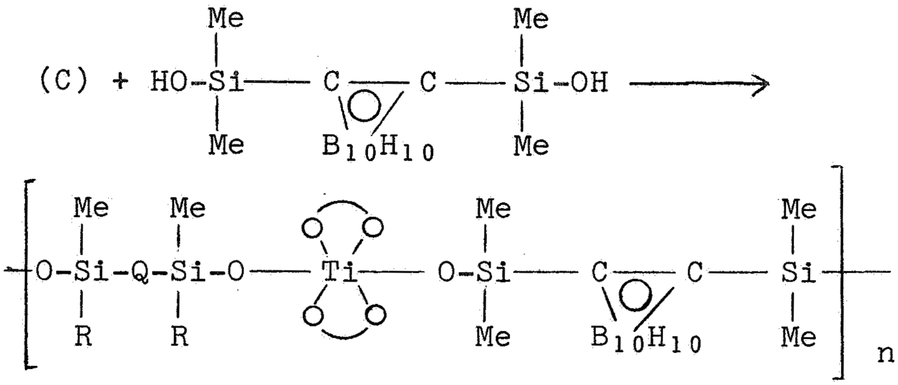
This product was then reacted with p-phenylene bis(methylphenylsilanol) at one-to-one mole ratio. The reaction sequence is as follows:


(A)

(B)

The second method for incorporating the bis(dimethylhydroxysilyl)-m-carborane onto the polymer backbone is by the reaction of polychelatotitanosiloxanes with the carborane as follows:

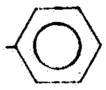
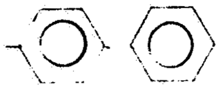

(C)



(D)

where

R can be methyl or phenyl

Q can be  or  or both

 is acetylacetone.

We synthesized polymers (B) and (D) and crosslinked them with a bisbidentate ligand such as 5,5'-bis(salicyl-N-butylimino) methane. The tensile shear strengths of this class of polymers at 250°C averaged 224 psi. Examination of the adhesive joints, after curing at 170°C for 76 hours, showed that there was considerable degassing of the adhesive material, so that the effective area covered by the adhesive is approximately 20%.

d. By Reaction with Silanediols with Extended Chain Lengths

The silanediols with extended chain lengths used in these reactions were prepared by either thermal condensation of the monomer, p-phenylene-bis(diorganosilanol), with sodium hydroxide catalysis, or by reaction of the disilanols with silizanes.

Silanediols, $\mathrm{HO-\overset{|}{\underset{|}{Si}}-Q-\overset{|}{\underset{|}{Si}}-OH}$, containing Q with extended lengths were used as reactants with bis(acetylacetonato)dibutoxytitanium. We expected that the steric configuration of the extended silanediols would minimize chain limitation caused by formation of bridged structures. Some chain extension was obtained with a silanediol (98460) of average molecular weight 3050 as reactant. The products (Table 17) were mixtures with a range of molecular weight that were fractionated according to solubility in ethanol. One fraction consisting of 34% product had a molecular weight of 6880. Its spectra in the infrared had a strong, broad absorption at 910 cm^{-1}, characteristic of the Ti-O-Si linkage.

Increasing the length of Q slightly from phenylene to biphenylene ether was not effective: reaction of bis(methylphenylhydroxysilyl)biphenyl ether with bis(acetylacetonato)dibutoxytitanium in 1:1 mole ratio did not give a polymer (98467 in Table 17).

e. By Condensation of Silanol End Groups on Prepolymers with Silizanes

Reaction of prepolymer with 8:1 Si:Ti ratio and molecular weight of 930 with heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane for 20 hours at 160°C resulted in a product with molecular weight of 3900 (Table 17). Similar condensations of prepolymers with Si:Ti ratios of 4:1 did not increase the molecular weight, apparently because there was not sufficient silanol functionality available for reaction on these prepolymrs.

Table 17

PROPERTIES OF POLYCHELATOTITANOSILOXANES WITH EXTENDED CHAINS

			Properties of Crude Product			Properties of Separated Product		
Reference	Reactant	Mole Ratio Si:Ti Charged	Soft Range °C	Molecular Weight	Treatment to Separate	Soft Range °C	Molecular Weight*	Wt. %**
98465	prepolymer 98460 (molec. wt. 3052)	2:1 of estimated SiOH to Ti	room temp.	3900	ethanol wash	----	6880	34
98466	prepolymer 98460	2:0.9 of estimated SiOH to Ti	room temp.	3000	ethanol wash	room temp.	4410	65
					second wash	----	----	34
98461	p-phenylenebis-(methylphenylsilanol)	6:1	40-50	780	ethanol wash	85-135	2320	71
98467	Bis(methylphenylhydroxysilyl)biphenyl ether	2:1	32-38	1720†	----	----	----	--
98490	p-phenylenebis-(methylphenylsilanol)	2:1	----	----	ethanol washes	70-95	1730	over 90
98488	"	3:1***	70-90	----	ethanol washes	----	2220	--
97549	"	8:1	37-46	930	----	----	----	--
----	1:1.05 of 97549 to heptamethyl-1-aza-3.5-dioxa-2,4,6-trisilacyclohexane	8:1	----	3900	----	----	----	--

---

* By vapor phase osmometry of benzene solutions of washed samples

** Weight % of crude sample that was insoluble after designated treatment

*** Reactant was tributoxyacetylacetonatotitanium

† Molecular weight of dimer with bridged structure is 1373

f. By Reaction of p-Phenylene-bis(methylphenylsilanol) with Acetylacetonatotributoxytitanium(IV)

An attempt to prepare a higher molecular weight polychelatotitanosiloxane by use of the tributoxy titanium compound was also made. This titanate and p-phenylene-bis(methylphenylsilanol) in 1:1 mole ratio were heated in benzene and then an equivalent mole quantity of triphenylsilanol was added. The solvent was removed and the residue was heated at 115°C overnight. The product consisted of ether-soluble and ether-insoluble fractions, both of which were soluble in benzene. Both had very low relative viscosity (0.5% in benzene gave 1.014 and 1.016), indicating very low molecular weight. A similar product from a ratio of 3:1 Si:Ti had molecular weight of 2216 (Table 17).

g. By Thermal Condensation of Polychelatotitanosiloxane in Higher Boiling Solvents

When a polychelatotitanosiloxane derived from bis-(acetylacetonato)dibutoxytitanium(IV) and p-phenylene-bis(methylphenylsilanol) was dissolved in xylene (bp = 140°C) and refluxed for 18 hours, the molecular weight increased to 3600. This represents a tetramer.

Another sample after refluxing in mesitylene (bp = 160°C) for 20 hours, gave a molecular weight of 1210, indicating that use of higher boiling solvents breaks the polymer chain rather than giving higher molecular weight.

h. By Condensation with Phenylsilanetriol in Place of Arylenesilanediols

The product from condensation of a 3 to 2 mole ratio of bis(acetylacetonato)diisopropoxytitanium with phenylsilanetriol had a molecular weight of less than 1500. It cured very rapidly with the ligand 5,5'-bis(salicyl-N-butylimino)methane with the result that it was not usable as an adhesive, because the resin became infusible before an aluminum joint could be wet and coupled.

J. POLYTITANOSILOXANES FROM TETRAISOPROPOXYTITANIUM(IV) AND p-ARYLENESILANEDIOLS

1. Preparation

Soluble polytitanosiloxanes with molecular weights as high as 23,500 were initially prepared by reaction of tetraisopropoxytitanium with p-phenylene-bis(methylphenylsilanol) in 1:2 mole ratio (4:1 Si:Ti). These polymers (Table 18) had molecular weights up to ten times higher than that of the product (molecular weight 1730) formed by reaction of this silanediol with bis(acetylacetonato)-dibutoxytitanium(IV).

Table 18

PROPERTIES OF POLYTITANOSILOXANES FROM TETRAISOPROPOXYTITANIUM

					Properties of Separated Product		
Reference	Silanediol	Reaction Conditions	Soft.Range, °C Crude Product	Treatment to Separate	Soft.Range °C	Molec. Weight**	Wt. %***
98468*	p-Phenylene-bis(methylphenyl-silanol)		35-45	3 ethanol washes	94-135	5700	48
98473	same as 98468		120-230	ether washes	---	23,500	97
98475	same as 98468		60-220	ethanol washes	---	7400	---
98492	same as 98468		---	ethanol washes	130-250	11,000	---
98493	p-Phenylene-bis(methylphenyl-silanol) and p-phenylenebis(methyl-vinylsilanol) in 9:1 ratio		110-250	ethanol washes	---	10,220	95
97058	Bis(methylphenyl-hydroxysilyl)bi-phenyl)ether		---	ethanol and ether washes	160-	insoluble in benzene	60
93493	9 $(Me,\phi SiOH)_2\phi$ to 1 $(Me,ViSiOH)_2\phi$	Reagents mixed in 5% conc. in benzene at 40°C. Benzene removed by freeze drying. Residue heated at 108°/-.4mm for 2 hrs.	110-250	3 ethanol washes	---	10,200	95
105622	Same as 98493	Same as 98493	---	"	85-130	8,050	87
98494	Same as 98493 in 3 to 2 ratio	Same as 98493	---	"	120->300	11,300	
105601	Same as 98493 in 3 to 1 ratio	Same as 98493 except residue heated 20 hrs.	---	"	100-185	14,800	82
105602	Same as 105601	Same as 105601 except conc. of solution was 0.5%.	---	"	90-165	9,500	80
105607	$(Me,ViSiOH)_2\phi$	Same as 105601	---	"	90->300	Polymer partially insoluble in benzene	
105619	$[(Me,\phi SiOH)_2\phi]_2O$	Same as 10561	---			Polymer insoluble	
105628	$1[(Me,\phi SiOH)_2\phi]_2O$ to $1(Me,ViSiOH)_2\phi$	Same as 98493	---	"	50-170	Polymer insoluble	

---

* Si:Ti ratio was 8:1 instead of 4:1
** By vapor phase osmometry of benzene soluble
*** Weight % of crude sample that was insoluble in ethanol

These polymers did not soften sufficiently below 170°C to wet aluminum joints well. Tensile shear strengths at 250°C of joints coupled with polymer 98473 were only 70-95 psi after 60 hours cure at 170°C. Stronger joints (up to 190 psi) were obtained in some cases, when the polymer was plasticized with 10 weight % bis(hydroxymethylphenylsilyl)biphenyl ether. However, some duplicate joints containing this formulation were soft at 250°C after cure at 170°C, indicating that the cured resin softens very near 250°C.

A similar polymer (97058 in Table 18) was also prepared by reaction of tetraisopropoxytitanium(IV) with bis(hydroxymethylphenylsilyl)biphenyl ether. This polymer precipitated from the benzene solution. A formulation of this polymer with 10 weight % bis(hydroxymethylphenylsilyl)biphenyl ether was cured for 60 hours at 170°C in aluminum joints. All the joints were infusible at 250°C, but they showed poor adhesive-substrate contact and, as a result, had low strengths.

These results showed that two improvements in these polymers were needed to make them usable as adhesives for aluminum in this program. First, it was necessary to plasticize them effectively to give good flow at 170°C. Secondly, a reactive site for cross-linking the resin to infusibility at 250°C was needed. Therefore, polymers containing vinyl substituents were made.

These polymers were prepared by condensation of tetraisopropoxytitanium(IV) with mixtures of methylphenyl- and methylvinyl-substituted phenylene-bis(diorganosilanols) with a Si:Ti ratio of 4:1. The properties of these polymers are also summarized in Table 18. Two modifications in reaction conditions were made to increase their molecular weight above the 10,000 range obtained. However, these modifications, [reaction in extremely dilute solution (105602 in Table 18), and increase in heat treatment of the crude polymer (105601 in Table 18)] did not effect the molecular weight of the products significantly.

2. *In Situ* Cure

Three types of curing reactions were tested with these polymers:

a. Condensation of silanol end substituents;

b. Coupling of vinyl substituents by silanes or of silane substituents by divinyl compounds;

c. Direct coupling of vinyl substituents using peroxide initiation.

The results of these tests can be summarized as follows:

a. The most effective cure method is the coupling of vinyl substituents on the prepolymer by reaction with diphenylsilane. In this type formulation, 15 to 25 wt-% p-phenylene-bis(methylphenylsilanol) was used as plasticizer and diphenylsilane was used as curing agent. The ratio of Si-H in the curing agent to C=C in the adhesive formulation was varied from 0.3 to 2.0. No definite trend in joint strengths with variation of this ratio was detected, however. The best strengths obtained were with formulations containing 25% plasticizer and a 0.45 to 0.60 mole ratio of Si-H to C=C. These strengths averaged 440 psi and had a maximum of 564 psi at 250°C after 68 to 115 hours cure at 170°C.

   The strengths of these joints appeared to be limited by their high porosity. This porosity was reduced, but not eliminated by precuring the formulation in open joints at 170°C for 3 to 10 minutes to allow escape of volatile byproducts. However, it was difficult to obtain reproducible joints by this method because of simultaneous loss of diphenylsilane during the precure period.

b. The porosity was successfully eliminated by first preparing prepolymers with Si-H substituents and then curing and crosslinking these polymers *in situ* with a vinyl-substituted plasticizer. The prepolymers with Si-H substituents were prepared by reacting the vinyl-substituted polytitanosiloxane polymers with diphenylsilane used in large excess to minimize crosslinking. Details of this preparation method are in the Experimental Section. These prepolymers were more difficult to plasticize than the vinyl-substituted polymers. Although several formulations were tested none had strengths above 300 psi at 250°C.

c. Arylenesilanediols are the best plasticizers for both the vinyl and silane substituted polymers. A 45:55 styrene-divinylbenzene solution gave partial plasticization of the silane-substituted polymers. Tetravinylsilane, tetramethyldivinyldisiloxane and bisphenol-A-dimethacrylate were poor plasticizers.

d. Polymers with 10,000 molecular weight that were plasticized to flow at 170°C in formulations containing 25% of 1:1 bis(methylphenylhydroxysilyl)biphenyl ether: phenylsilanetriol, cured to resins that were infusible at 250°C. However, their tensile strengths at 250°C were under 200 psi.

e. Peroxide cure was not effective at 170°C for formulations containing 1 to 2% di-t-butylperoxide or t-butylhydroperoxide and 10 to 20% phenylene-bis(methylvinylsilanol) with the vinyl-substituted polytitanosiloxanes. The effectiveness of the peroxides was probably limited by their extremely low half-lives at 170°C (under 20 min.). One resin had a tensile shear strength of 1040 psi at room temperature, but was soft at 250°C after 20 hours cure at 170°C. Resins cured at 120°C were also soft at 250°C.

IV. EXPERIMENTAL

A. PREPARATION OF LIGANDS

1. 5,5'-Bis(salicylaldehydo)methane

A mixture of 3.1 ml of concentrated sulfuric acid and 15.6 ml of glacial acetic acid was added slowly with stirring in a nitrogen atmosphere at 90-95°C to a solution of 500 g (4.09 moles) of redistilled salicylaldehyde in 313 ml of glacial acetic acid, in which 43.75 g (equivalent to 1.45 moles formaldehyde) of trioxane was dissolved. This temperature was maintained for 22 hours with continuous stirring. The reaction mixture was then poured into four liters of ice water and allowed to stand overnight. The deposited solid was filtered and extracted twice with 600 ml of petroleum ether (bp 30-60°C). The isolated solid was triturated three times with 500 ml portions of ether. The crude reaction product was recrystallized from acetone with activated charcoal three times to remove all traces of salicylaldehyde. After drying at 50°C under vacuum for several hours the product weighed 130 g. Yield: 36%; mp: (Corr.) 142-3°C; lit, 142-143°C.

2. Schiff Base Derivatives of 5,5'-Bis(salicylaldehydo)methane

a. 5,5'-Bis(salicyl-N-n-butylimino)methane

n-Butylamine (77 g, 1.05 moles) was slowly added to a mixture of 129.5 g (0.503 mole) of 5,5'-bis(salicylaldehydo)-methane in anhydrous benzene at reflux temperature. The solution was kept at reflux until the stoichiometric amount of water (18 ml) was collected by azeotropic distillation. The reaction mixture was then allowed to continue refluxing for one hour. At this time, 1750 ml of solvent was removed by distillation and the remaining reaction mixture allowed to cool to room temperature. To this was added 2 ℓ of petroleum ether (bp 30-60°C) and the solution cooled to -50°C in a Dry ice-acetone bath. The precipitated ligand was collected by filtration in a jacketed Buchner funnel that was cooled to Dry ice-acetone temperature. The crude reaction product was recrystallized twice from petroleum ether with activated charcoal as described above. The yield of yellow powder melting at 41-2°C (corr.) was 155 g (85%).

Anal. for $C_{23}H_{30}N_2O_2$: Calc., N = 7.7%; Found, N = 7.6%.

b. Others

Seven other Schiff base derivatives of 5,5'-bis(salicylaldehydo)methane were prepared in a manner similar to that described above. The melting points of these ligands are given below.

	Compound	mp, °C
1.	5,5'-Bis(salicyl-N-ethylimino)methane	86
2.	5,5'-Bis(salicyl-N-sec-butylimino)methane	48-50
3.	5,5'-Bis(salicyl-N-tert-butylimino)methane	178
4.	5,5'-Bis(salicyl-N-n-hexylimino)methane	68
5.	5,5'-Bis(salicyl-N-cyclohexylimino)methane	197
6.	5,5'-Bis(salicyl-N-4-methylbenzylimino)methane	130
7.	5,5'-Bis(salicyl-N-γ-dimethylaminopropylimino)methane	40-42

c. Attempted Preparation of 5,5'-Bis(salicyl-N-pentafluorophenylimino)methane

An initial attempt to prepare the imine by reacting 20.1 g (0.11 mole) of pentafluoroaniline with 12.8 g (0.05 mole) 5,5'-bis(salicylaldehydo)methane in benzene was not successful. Replacement of benzene solvent with xylene together with additions of catalytic amounts of the acetic acid and hydrochloric acid and refluxing the solution for several hours also did not yield the desired Schiff base.

Reaction of 6.7 g of pentafluoroaniline and 1.8 g of the above aldehyde in a melt at 145°C for 72 hours yielded a yellow solid. Its infrared spectra indicated that some of the product was the desired imine mixed with the unreacted aldehyde.

Another attempt was made to form the Schiff base by heating 22.9 g of pentafluoroaniline and 5.1 g of 5,5'-bis(salicylaldehydo)methane with 11 g of 4A Linde molecular sieves in a steel bomb at 150°C. After reaction for 142 hours at 150°C, the infrared spectra indicated that most of the carbonyl was unreacted.

3. 5,5'-Bis(3-methoxysalicyl-N-butylimino)methane

a. Preparation of 5,5'-Bis(3-methoxysalicylaldehydo)methane

The method used for the preparation was similar to that used by Garber (ref. 46) for the preparation of 5,5'-bis(3-methoxysalicylaldehydo)methane. A solution of 61 g (0.40 mole) purified o-vanillin and 18 g 35% aqueous formaldehyde (0.21 mole) in 100 ml water was heated and stirred at 100°C. A solution of 16 g sodium hydroxide in 300 ml water was added dropwise and the solution then refluxed for 3.5 hours, cooled to 30°C, and acidified with hydrochloric acid. An oil separated which hardened to a semi-solid. This product was separated from the aqueous layer, washed with water, and triturated with ethanol. The solid melted at 135-150°C. This crude product was recrystallized from 60% benzene-40% absolute ethanol and yielded 8 g (13%) bright yellow nugget crystals which melted at 162.5-163°C. A larger scale preparation using commercial grade o-vanillin resulted in a yield of 9% final product. The spectrum of the product in the infrared is consistent for 5,5'-bis(3-methoxysalicylaldehydo)-methane.

Anal. for $C_{17}H_{16}O_6$

Calcd: C, 64.6; H, 5.07

Found: C, 64.5, 64.8; H, 4.9, 5.0

b. Preparation of 5,5'-Bis(3-methoxysalicyl-N-butylimino)-methane

n-Butylamine (7.4 g, 0.044 mole) was added to a solution of 12.7 g (0.04 mole) 5,5'-bis(3-methoxysalicylaldehydo)-methane in benzene at reflux temperature. The water of reaction was removed as the azeotrope and then the solvent distilled. The residue when recrystallized three times from hexane yielded 12 g (70%) yellow product which melted at 78-78.5°C.

4. 5,5'-Bis(salicyl-N-butylimino)sulfone

a. 3,3'-Dimethyl-4,4'-dihydroxydiphenylsulfone

One hundred grams of distilled o-cresol was heated under reflux with a mixture of 12 ml of 98% sulfuric acid and 14 ml of 30% oleum for four hours. After that time, the reaction was poured into two liters of cold, dilute sodium hydroxide solution. The alkaline solution was extracted with ether, and the water layer acidified with concentrated hydrochloric acid and allowed to stand overnight. The crude product was isolated by filtration and washed with water. After recrystallization from 50% ethanol (charcoal), the product melted at 265-266°C.

b. 5,5'-Bis(salicylaldehydo)sulfone

Forty-three grams of 3,3'-dimethyl-4,4'-dihydroxydiphenylsulfone (0.155 mole) was heated under reflux with 430 ml of acetic anhydride for one hour. To the cold solution (5°C), a cold solution (16°C) of 430 ml of acetic acid and 60 ml of concentrated sulfuric acid was added slowly with stirring. The temperature of the mixture was kept at 5°C, and over a period of one hour, with vigorous stirring, 70 g (0.700 mole) of chromic acid was slowly added. Stirring was continued for an additional three hours. The mixture was then poured into about eight liters of ice water and allowed to stand overnight.

c. 5,5'-Bis(salicyl-N-butylimino)sulfone

The Schiff base was prepared in toluene using the procedure for preparation of 5,5'-bis(salicyl-N-butylimino)methane. The product was recrystallized from methanol and dried in vacuo (mp 135.5-136.5°C).

Anal. for $C_{22}H_{28}N_2O_4S$: Calc., N = 6.72%; Found, N = 6.83%.

5. 5,5'-Bis(8-hydroxyquinolino)methane

Seventy-two grams of 8-hydroxyquinoline (≈0.5 mole) was dissolved in 75 ml of conc. sulfuric acid, and the solution was cooled to 0°C in an ice bath. The cooled solution was stirred and 94 ml of a 38% formaldehyde solution was added slowly over a 3-hour period. After the addition was completed, the reaction mixture was allowed to stir at 0°C for 2 hours. The mixture was then poured into 2 liters of cracked ice whereupon a yellow solid precipitated. This material was recrystallized from pyridine. This product was then dissolved in 250 ml of dimethylformamide and treated with an excess of conc. ammonium hydroxide. The resulting mixture was concentrated to approximately 100 ml. On cooling to room temperature, a white powder precipitated. The material, recrystallized from dimethylformamide several times, melted at 274°C (decomp.). The yield was ≈25%. The IR and NMR spectra of this material were consistent for the desired 5,5-bis-8-(hydroxyquinolino)methane.

6. 5,5'-Bis(7-hexanoyl-8-hydroxyquinolino)methane

The procedure of Rosenmund and Karst (ref. 14) for acetylation of 8-hydroxyquinoline was used for dicaprolation of 5,5'-bis(8-hydroxyquinolino)methane. Hexanoyl chloride (24.3 g) was added with stirring to 21.2 g of 5,5'-bis(8-hydroxyquinolino)-methane in 100 ml nitrobenzene at 70°C yielding a bright yellow solid which reacted, yielding a green solution when 54.2 g $AlCl_3$ was added in portions. The solution was kept at 70°C overnight, then poured onto ice and the nitrobenzene was removed by steam distillation. On cooling, the product separated as a complex that was very difficult to dissociate. The final method used to isolate the product consisted of refluxing the complex in aqueous hydrochloric acid for several hours, separating the solid from dissolved aluminum salts, and triturating the solid in aqueous sodium bicarbonate.

The product, after two recrystallizations from benzene, melted at 212-213°C, and its NMR analysis was consistent for the disubstituted compound. The yield from this run was 8 g.

Analysis for $C_{31}H_{34}N_2O_4$:

Calc: C, 73.7; H, 6.86; N, 5.61.

Found: C, 73.5; H, 6.5; N, 5.2, 5.3; residue, none.

7. 5,5'-Bis(7-octanoyl-8-hydroxyquinolino)methane

Octanoyl chloride (28 g, 0.17 mole) was added with stirring to 20 g (0.066 mole) of 5,5'-bis(8-hydroxyquinolino)methane in 100 ml of nitrobenzene at 70°C. After 10 min, 52 g (0.39 mole) of $AlCl_3$ was added in portions while the temperature was kept at 70-75°C. The resulting solution was then heated at 75°C overnight. The product was poured on ice, the nitrobenzene was removed by steam distillation, and the residue was heated in 5-10% HCl for several hours.

The acid solution was decanted, fresh HCl was added to the residue, and the treatment was repeated twice. After the acid solution had been decanted, the residue was slurried in dilute sodium hydroxide, acetic acid was added to neutralize excess base, and the residue was filtered and extracted with benzene in a Soxhlet extractor. The product melted at 170-172°C. After recrystallization from benzene it weighed 8 g and had the following analysis: Calc.: C, 76.3; H, 7.63; N, 5.06; Found: C, 75.9; H, 7.73; N, 4.88.

A second preparation on a 1.5 scale yielded 23.6 g with melting point 177-180°C.

8. 5,5'-Bis(8-hydroxyquinolino)sulfone

a. 1,6-Dihydroxyphenazine

o-Anisidine (31.0 g, 0.24 mole), 70.0 g (0.46 mole) o-nitroanisole, and 70.0 g (1.23 moles) of KOH were added to 180 ml of dry benzene and refluxed for 7 hr with constant stirring. After cooling, the liquid organic layer was discarded and the solids were extracted with 200 ml of 15% HCl. The extractant was made basic with NH_3(aq) and the ppt washed in ethanol and recrystallized from ethanol-dioxane (1:1) mixture. The 1,6-dimethoxyphenazine thus obtained was yellow crystals with mp 248°C, yield 1.0 g (2%). The 1,6-dimethoxyphenazine was sealed in a glass bomb with 10 mole excess of H_2SO_4(7.3 g) and placed in a sand bath at 175°C.

The reactant turned purple on addition of H_2SO_4. The yellow crystals were recrystallized from benzene, mp 278°C. The IR spectrum was similar to that reported by Irie, et al., (ref. 47).

b. 5,5'-Bis(3-nitro-4-hydroxyphenyl)sulfone

Conc. HNO_3 (674 ml, 9.6 mole) was added to bis(4-hydroxyphenyl)sulfone (100 g, 0.56 mole) in a 1-liter beaker. This was stirred moderatley for 3-4 min until reaction became exothermic. It was then cooled in an ice bath for one hour, diluted with hot water (1300 ml) and dried overnight in 100°C oven. The yield of bis(3-nitro-4-hydroxyphenyl)sulfone was 86 g (93%) (mp 224°C).

c. Reduction of 5,5'-Bis(3-nitro-4-hydroxyphenyl)sulfone

Na (33.26 g) covered with a 1-cm layer of oil was placed in an 18-cm enameled dish. The Na was then melted on a hotplate. To the molten Na was added 2000 g of Hg, slowly at first, with constant stirring. The time for addition was ≈4 minutes. The amalgam was then cooled in an ice bath and broken up with a spatula.

Dry 5,5'-bis(3-nitro-4-hydroxyphenyl)sulfone (8.5 g, 0.11 mole) was added to a 3-necked, 1-liter Morton flask equipped with stirrer, nitrogen inlet and thermometer and containing the Na-Hg. Then 80 ml of NH_3 (aq) was added slowly and the temperature was kept at 0°C with an acetone-Dry Ice bath until the addition was completed. The temperature was allowed to rise to 38°C and then was allowed to subside to room temperature. Water (1000 ml) was added and the Hg was filtered off. The salt was neutralized with acetic acid, and the resulting straw-colored product was recrystallized from ethanol.

d. 5,5'-Bis(8-hydroxyquinolino)sulfone

5,5'-Bis-(3-amino-4-hydroxyphenyl)sulfone (6.3 g, 0.02 mole) was stirred into H_2SO_4 (13.9 g, 0.14 mole) keeping the temperature below 70°C. Glycerine (23.2 g, 0.25 mole) was added at the same temperature. This mixture was placed on a steam bath and kept at 70-80°C. 5,5'-bis(3-amino-4-hydroxyphenyl)sulfone (2.7 g, 0.009 mole) and 1 gram of $FeSO_4 \cdot 7H_2O$ were placed in a 1-liter 3-necked flask equipped with sealed stirrer, thermometer and reflux condenser and heating mantle. This was warmed to 120°C and the premix was poured into the reaction flask in four equal portions. It was allowed to reflux for 15 min after each addition and for another 4 hr at the conclusion of addition. The black mass was then transferred to a beaker, neutralized with 40% NaOH, and filtered, and the residue was extracted overnight with xylene in a Soxhlet extractor. The extract was concentrated, and orange colored crystals (mp 300°C) were recovered.

Analysis: Calc.: C, 76.3; H, 7.63; N, 5.06; Found: C, 75.9; H, 7.73; N, 4.88.

9. β,β'-(8-Hydroxy-2-quinoxyl)-p-divinylbenzene

Terephthalaldehyde (26.8 g, 0.2 mole) and 8-hydroxyquinaldine (63.6 g, 0.4 mole) were refluxed in 280 ml of acetic anhydride for 7 hours. The cooled mixture was poured into water and the precipitated ester was saponified by boiling for 1 hour in 20% NaOH. The ligand was isolated by neutralization of the basic solution with HCl and acetic acid to pH 5, washed well with water, and recrystallized from benzene-pyridine. The product melted at 213-218°C (ref. 48) reports 215°C).

10. 1,5-Bis(8-hydroxy-5-quinolyl)pentanedione

The procedure of Matsumura and Sone (ref. 49) was used. 5-Acetyl-8-hydroxyquinoline was first prepared by a procedure also reported by Matsumura (ref. 50). Acetyl chloride (50 g) was added to 87 g of 8-hydroxyquinoline in 600 ml of nitrobenzene at 70°C. Then 186 g of $AlCl_3$ was added in portions with stirring. The resulting solution was kept at 70°C for about 20 hours, was cooled, and ice and hydrochloric acid were added. Nitrobenzene was removed by steam distillation and the residue was cooled in ice and filtered. The solid was still largely the complex and another treatment with hot hydrochloric acid was required to break it up. The free acetyl compound was then isolated by adjusting the pH to 5 with sodium hydroxide and acetic acid and was recrystallized from water.

The coupling reaction was accomplished by adding 18.7 g of 5-acetyl-8-hydroxyquinoline with stirring to 150 cc of 37% aqueous formaldehyde solution containing 5 g of paraformaldehyde. The mixture was heated to reflux and refluxed for 3 hours and then cooled. The precipitated product was separated and recrystallized from nitrobenzene. Product melted at 338-341°C and had the following analysis.

Calc: C, 71.5; H, 4.7; N, 7.2.
Found: C, 71.8; H, 4.9; N, 7.1.

11. N,N-Bis(8-hydroxy-5-quinolylmethyl)butylamine

a. 5-Chloromethyl-8-hydroxyquinoline Hydrochloride

The method described by Burckhalter and Leib (ref. 11) was used in a preparation on a 3 mole scale. Product melted with decomposition at 278-280°C.

b. N,N-Bis(8-hydroxy-5-quinolylmethyl)butylamine

n-Butylamine (92 g, 1.25 mole) was added with stirring over a period of 45 minutes to a slurry of 115 g (0.5 mole) 5-chloromethyl-8-hydroxyquinoline hydrochloride in 1500 ml of ethyl acetate. The mixture was heated at 55-60°C for 1 hour and then filtered hot. The precipitate was washed with 400 ml of ethyl acetate and the solvent removed from combined filtrate. The residue was washed with ether and then recrystallized from benzene three times and dried overnight in a vacuum desiccator. The product (38 g) melted at 118-120°C. Its spectra in the NMR was consistent for the above named product and showed no impurities.

12. N,N-Dimethyl-N',N'-bis(8-hydroxy-5-quinolylmethyl)-1,3-propanediamine

To a solution of 47.9 g (0.42 mole plus 10% excess by weight) of γ-dimethylaminopropyl amine in 400 ml of ethyl acetate, was added 65.2 g (0.28 mole) of 5-chloromethyl-8-quinolinol hydrochloride. After the initial exothermic reaction subsided, the mixture was heated at reflux temperature for 18 hrs. The amine dihydrochloride by-product was removed by filtration and the ethyl acetate filtrate concentrated to give an oily material. This oil was taken up in acetone, and the solution was allowed to stand. The white precipitate, which formed, was filtered and washed with acetone. This solid after drying under vacuum at room temperature weighed 14.0 g (23.8% yield) and melted at 118-119°C. Its NMR spectrum had a proton count that was consistent with the sought-for compound.

13. Bis[N-methyl-N-(8-hydroxy-5-quinolylmethyl)]-1,6-hexanediamine

5-Chloromethyl-8-quinolinol hydrochloride (53.2 g, 0.23 mole) was added to a solution of 50.0 g (0.35 mole) of N,N'-dimethyl-1,6-hexanediamine in 400 ml of ethyl acetate. After an initial exothermic reaction, the mixture was heated at reflux temperature for 20 hrs. The reaction mixture was filtered. The ethyl acetate solution was concentrated and cooled to give a yellow precipitate. This precipitate was taken up in acetone and cooled. Only 0.9 g product, that was identified by its NMR spectra, precipitated. The remaining solid was mono-substituted amine. Therefore, the ethyl acetate insoluble portion was extracted with chloroform for 17 hr. From this extract, a solid was obtained that was recrystallized from chloroform. It consisted of 12.1 g (22.9% yield) of the sought-for compound that melted at 159-161°C.

14. Attempted Preparation of Siloxane-Coupled 8-Hydroxyquinolines

a. 5,7-Dibromo-8-hydroxyquinaldine

This compound was prepared by the method of Senn (ref. 51). Bromine (32 g, 0.2 mole) was added with stirring to quinaldine (15.9 g, 0.1 mole) dissolved in 150 ml of 90% formic acid while the temperature was maintained at 0 ± 5°C. Product was isolated by pouring the mixture into water, and was recrystallized from ethanol. Its melting point was 126-127°C (ref. 50 gives 125-126°C).

b. α,ω-Dichloropolydimethylsiloxanes

The procedure described in example 1 of Brit. Pat. 631,018 (ref. 15) was used. A solution of 33 ml (1.83 moles)of H_2O in 33 ml of dioxane was added dropwise through a funnel with its stem below the surface of a solution of dimethyldichlorosilane (471 g, 3.65 moles)in an equal volume of anhydrous ether, while stirring vigorously under a Dry Ice-cooled condenser. After the addition, the condenser was replaced with a simple head and most of the ether was distilled. The residue was then distilled through a 12 x 1 in. column packed with 1/8 in. glass helices.

Among the cuts of this fractionation were one of dichlorotetramethyldisiloxane of 91.5% purity (VPC) and one of dichlorohexamethyltrisiloxane of 83.9% purity. The composition of the products included 42.7 g recovered dimethyldichlorosilane and 88.2 g, 83.1 g, 39.5 g, 17.5 g and 4.8 g, of the linear di-, tri-, tetra-, penta- and hexa- siloxanes. Cyclic products were minor by-products.

c. Reaction of 5,7-Dibromo-8-Hydroxyquinaldine with Butyllithium and Dichlorotetramethyldisiloxane

A hexane solution of butyllithium (9.3 ml of 15.2% solution, 0.015 mole) was added to a stirred solution of 5,7-dibromo-8-hydroxyquinaldine (4.75 g, 0.015 mole) in about 150 ml dry tetrahydrofuran under nitrogen. Then trimethylchlorosilane (1.6 g, 0.015 mole), butyllithium (9.3 ml, 0.015 mole) and dichlorotetramethylsiloxane (1.02 g, 0.0075 mole) were added after intervals of 5, 20, and 3 min respectively. The solution was stirred for two hours and then most of the tetrahydrofuran was distilled and water added to the residue. The product was separated into hexane-soluble, hot ethanol-soluble, and hot ethanol-insoluble portions. The insoluble portion (a lithium salt) was treated with acetic acid and precipitated with water. Analysis of the hexane-soluble portion (0.8 g) by VPC and IR indicated mostly siloxanes not coupled to quinoline rings. The residue from the acetic acid treatment (0.9 g) contains both siloxane and quinoline components.

Mostly unreacted dibromo compound was recovered from a similar reaction in ether.

15. Bis(4-hydroxy-3-octanoylphenyl)ether

a. Bis(4-methoxyphenyl)ether

p-Methoxyphenol (181.6 g, 1.5 moles) was added to toluene (75 ml) in a 3-necked, one-liter flask equipped with a Dean-Stark trap. Potassium hydroxide (38.2 g, 0.6 mole)was added slowly, the mixture was heated to reflux and the water of reaction was distilled as an azeotrope.

Copper powder (0.5 g) and a solution of p-bromoanisole (100 g, 0.54 mole) in toluene (50 ml) was added, the toluene was distilled and the reaction then heated to 200°C. The Dean-Stark trap was removed and the reaction was refluxed overnight at a pot temperature of 218°C.

The reaction mixture was cooled and 50 ml of water was added at 120°C. At 80°C, the contents were poured into 300 ml of water and then chilled. The solid was filtered off, taken up in one liter of toluene, and then extracted with 500 ml of 10% sodium hydroxide.

The toluene was washed twice with water and then flash evaporated leaving a brown, crystalline solid. This was recrystallized from hot methanol yielding 69.2 g of a light tan crystalline solid [mp 95-97°C; lit. (ref. 52). reports 101-102°C].

b. Bis(4-methoxy-3-octanoylphenyl)ether

Aluminum chloride (11.8 g, 0.088 mole) was added slowly to a solution of octanoyl chloride (14.3 g, 0.088 mole) dissolved in 150 ml of carbon disulfide. A solution of bis(4-methoxyphenyl) ether (9.2 g, 0.04 mole) in 100 ml of carbon disulfide was added dropwise at room temperature over 40 minutes. Acidic vapors evolved during refluxing, which was continued for 16 hours.

The carbon disulfide was distilled off and the resulting solid was decomposed with 100 g of ice and 100 ml of hydrochloric acid. This was then steam distilled. An oil separated on chilling and was washed with 200 ml of 5% sodium carbonate and then washed twice with water. The oil was dissolved in ether and dried, and the ether was flashed off yielding an oil (14.3 g). This was demethylated without further purification.

c. Demethylation of Crude Bis(4-methoxy-3-octanoylphenyl)-ether

Acetic acid (52 g) and constant boiling 48% hydrobromic acid (20 g) were added to crude bis(4-methoxy-3-octanoylphenyl) ether (14.3 g, 0.03 mole) and refluxed (112°C) over a weekend.

The reaction was cooled and the contents were poured into a mixture of 100 g of ice and 100 ml of water. This produced an oil, which was dissolved in ether, washed with water, and dried. Then the ether was flashed off. A solid was filtered off when the oil was dissolved in ether and chilled in a Dry Ice-methanol bath. The solid was washed with methanol and dried (mp 36-37.5°C). The NMR spectrum was consistent for the product.

16. 1,5-Bis(4-hydroxy-3-octanoylphenyl)pentane

a. 1,3-Bis(4-methoxybenzoyl)propane

The procedure reported by Lipp and co-workers was followed (ref. 17).

Aluminum chloride 78 g (0.59 mole) was added slowly to 81 g of anisole (0.75 mole) in 400 ml of carbon disulfide while the temperature was kept below 30°C. Glutaryl chloride (60 g, 0.35 mole) was then added dropwise over 40 min. The red reaction mixture was heated with a water bath to reflux for 2 hr. Most of the carbon disulfide was blown off in an air stream, leaving a dark-red, tarry solid. This was poured into a mixture of 400 ml of concentrated hydrochloric acid and 400 g of ice with stirring, and the mixture was steam-distilled to remove the remaining carbon disulfide and anisole. The aqueous phase was then decanted from the cooled mixture, and the residue was washed with two 250-ml aliquots of 5% sodium carbonate and one 250-ml aliquot of water. The orange solid was recrystallized from 3 liters of methanol, yielding 64 g of a slightly orange solid (mp 95-97°C). (ref. 18 gives mp 99°C). The IR and NMR spectra were consistent for the desired 1,3-bis-(4-methoxybenzoyl) propane. The compound was found to exist in two crystalline forms with different spectra in the infrared. The lower melting form could be converted to the higher melting form by heating in the KBr pellet.

b. Reaction of 1,3-Bis(p-methoxybenzoyl)propane with Octanoyl Chloride

(1) In Carbon Disulfide

Octanoylchloride (14.3 g, 0.088 mole) was added dropwise over a period of 10 min to 12.5 g of 1,3-bis(4-methoxybenzoyl)-propane (0.04 mole) in 500 ml of carbon disulfide. The reaction flask was heated to 33°C, and 23.5 g of aluminum chloride (0.176 mole) was added slowly. The resulting red-brown mixture was refluxed overnight.

Most of the carbon disulfide was distilled off, leaving a dark-red, sticky residue. This was stirred into a mixture of concentrated hydrochloric acid (500 ml) and cracked ice (500 g), and the mixture was steam-distilled to remove carbon disulfide and octanoyl chloride. The residue was cooled and filtered, and then was washed with two 200-ml aliquots of 5% sodium carbonate and one 200-ml aliquot of water. The residue was then recrystallized from 1200 ml of methanol and was dried under vacuum. The product weighed 8.5 g and melted at 102.5-103.5°C. The characteristic adsorption bands in the infrared (1678 cm^{-1} and 1757 cm^{-1} for carbonyl and ester groups) together with the nmr spectrum of this product indicated it to be the ester, 1,3-bis(p-octanoylbenzoyl) propane.

(2) In Nitrobenzene

1,3-Bis(p-methoxybenzoyl)propane (25 g, 0.08 mole) was dissolved in 400 ml of nitrobenzene, and 28.6 of octanoyl chloride (0.176 mole) was added dropwise to the solution. The reaction mixture was heated, and 47 g of aluminum chloride (0.352 mole) was added slowly, starting at 60°C. The reaction was exothermic, and final addition brought the temperature up to 140°C. The reaction was then heated overnight at 135°C.

The dark-brown mixture was stirred into 500 ml of concentrated hydrochloric acid and 500 g of ice and the nitrobenzene was steam-distilled. The reaction mixture was filtered, and the residue was washed with two 400-ml portions of 5% sodium carbonate and then once with 400 ml of water.

The dark-brown solid was extracted twice with a total of 600 ml of hot methanol. The remaining solid was given another treatment with hydrochloric acid and ice, and was then washed with sodium carbonate and water and extracted with a total of 300 ml of hot methanol. The methanol extractions were combined and flash-evaporated, leaving a dark-red, sticky residue that could not be characterized by IR spectrum and NMR.

c. Attempted Fries Rearrangement of 1,3-Bis(p-octanoyloxybenzoyl) Propane

1,3-Bis(p-octanoyloxybenzoyl)propane (8 g, 0.015 mole) in 200 ml of nitrobenzene was heated to 80-90°C, and aluminum chloride (4.4 g, 0.033 mole) was added slowly. The mixture was reacted overnight at 92°C.

The reaction mixture was poured into 300 ml of concentrated hydrochloric acid and 300 g of ice with stirring. The nitrobenzene was then steam-distilled. The residue was washed with two 200-ml portions of 5% sodium carbonate and once with 200 ml of water. The solid was then recrystallized from 100 ml of methanol. A dark-red solid was present whose IR spectrum did not conform to the desired structure.

d. Dianisalacetone

This compound is available commercially, but because of its high cost, it was prepared in the laboratory following a procedure reported by Conard and Dolliver (ref. 53) for preparation of dibenzolacetone.

Sodium hydroxide (50 g) dissolved in 500 ml of water and 400 ml of ethanol was cooled and maintained at 20-25°C during the reaction. With rapid stirring, one-half of a mixture of anisaldehyde (68.1 g, 0.5 mole) and acetone (14.6 g, 0.25 mole) was added and reacted for 30 minutes, then the remainder was added and reacted for an additional hour.

The yellow solid formed was filtered off, washed with water until free of alkali, and then recrystallized from hot acetic acid yielding 50 grams (67%) of yellow plates melting at 125-127°C. Reported melting point is 129-130°C.

e. 1,5-Di-p-anisoylpentane

This preparation was carried out in two steps from dianisalacetone.

(1) Step 1. Hydrogenation of the Ethylenic Double Bonds

Palladium on barium sulfate (3 g) catalyst was added to dianisalacetone (29.6 g, 0.10 mole) dissolved in 200 ml of glacial acetic acid. This was placed under hydrogen (40 psig) in a Parr shaker overnight at room temperature.

The catalyst was filtered off and the acetic acid evaporated, leaving a light yellow oil. A VPC of the oil shows it to be a 50-50 mixture of the ketone and the intermediate alcohol, both of whose ethylenic double bonds were hydrogenated.

(2) Step 2. Modified Clemmensen Reduction

The Clemmensen reduction was best accomplished by the method described by Bachmann and Kloetzel (ref. 54).

Mossy zinc (200 g) was amalgamated by using mercuric chloride (5 g) in 200 ml of water and 20 ml of concentrated hydrochloric acid. Occasional stirring for 20 minutes was sufficient. The aqueous layer was decanted and the zinc was washed twice with water.

To the amalgamated zinc was added 200 ml of water, 200 ml of concentrated hydrochloric acid, and 200 ml of ethanol. The yellow oil from step 1 was then added with rapid stirring and refluxed briskly for three days.

The reaction mixture was then extracted with a total of 250 ml of toluene. This was filtered and then distilled off. The residue distilled at 208-211°C/1.5 mm Hg to give 18.4 g (64.8% yield) colorless 1,5-di-p-anisoylpentane.

f. 1,5-Bis(4-methoxy-3-octanoylphenyl)pentane

Aluminum chloride (23.4 g, 0.176 mole) was added slowly to a solution of 1,5-di-p-anisoylpentane (22.8 g, 0.08 mole) dissolved in 400 ml of carbon disulfide. Octanoyl chloride (28.6 g, 0.176 mole) was added over 20 minutes to the red reaction mixture at 30°C. This was then refluxed overnight.

The carbon disulfide was distilled off leaving brown chips. This residue was stirred into 400 ml of concentrated hydrochloric acid and 400 grams of ice and then was steam-distilled. The yellow mixture was chilled, separating the oil, which was then washed with two 200-ml portions of 5% sodium carbonate and two 200-ml portions of water. The oil was then dissolved in 400 ml of hexane, dried with magnesium sulfate, and filtered. The hexane was flashed off leaving a brown oil, which solidified.

IR and NMR spectra of the product indicate a mixture of the desired product, 1,5-bis(p-4-methoxy-3-octanoylphenyl) pentane and the demethylated compound.

g. Demethylation of Crude 1,5-Bis(4-methoxy-3-octanoylphenyl) Pentane

The brown product (32.4 g) from the reaction of 1,5-di-p-anisoylpentane and octanoyl chloride was refluxed for 22 hours at 114°C in glacial acetic acid (78 g) and constant boiling hydrobromic acid (30 g).

The reaction mixture was poured, with rapid stirring, into 150 g of ice and 150 ml of water. The resulting oil was dissolved in ether, dried with anhydrous magnesium sulfate, and filtered. The ether was flashed off leaving a dark brown oil which was recrystallized from ether. It melted at 50-53°C.

An NMR spectrum of the product was consistent with the desired product, 1,5-bis(4-hydroxy-3-octanoylphenyl)pentane.

h. Wolff-Kishner Reduction of 1,3-Bis(4-methoxybenzoyl)-propane

The general procedure of Huang and co-workers was followed (ref. 55).

Triethanolamine (100 ml) was added to 1,3-bis(p-methoxybenzoyl) propane (10 g) with stirring. Then hydrazine hydrate (95%, 20 ml) was added. This was heated at reflux (101°C) for 1 hr. and 45 min.

At this point, an aliquot was removed. When diluted with water and filtered, this aliquot yielded a solid with an IR spectrum identical to that of the starting diketone.

An additional 20 ml of hydrazine hydrate was added and the reaction allowed to reflux overnight. A similar aliquot was then removed and this showed the absence of the carbonyl bands.

Potassium hydroxide (11 g) was dissolved in 20 ml of water and added to the reaction flask at 25°C. This was refluxed for minutes at 111°C. Then distillation took place until the pot temperature reached 201°C. The reaction was refluxed at this temperature for 5 hours.

The contents were poured into 200 ml of water forming a milky green, oily mixture. This was extracted with two 100-ml portions of ether, and the ether was washed with water. The ether was dried over magnesium sulfate, separated, and flashed off, yielding 4.4 g of a slightly green oil. Analysis of this oil by VPC and NMR indicated it to be approximately 35% of 1,5-bis(4-methoxy-3-octanoylphenyl)pentane and 65% 1-(4-methoxy-3-octanoylphenyl)-5-(4-hydroxy-3-octanoylphenyl)-pentane.

The remaining basic fraction was acidified and the precipitate formed was filtered off. The ethanol-soluble portion was flash evaporated yielding 4 g of 1,5-bis(4-hydroxy-3-octanoylphenyl)-pentane.

17. 1,5-Di-p-anisoylperfluoropentane

a. 1,3-Bis(4-methoxybenzoyl)perfluoropropane

The general procedure used by Lipp and co-workers for similar compounds was followed (ref. 17).

Aluminum chloride (78 g, 0.59 mole) was added slowly to a solution of anisole (81 g, 0.75 mole) in 400 ml of carbon disulfide while the temperature was kept near 30°C. Then perfluoroglutaryl chloride (98.5 g, 0.35 mole) was added dropwise over 45 minutes. The blue-purple mixture was refluxed for 20 hours. The carbon disulfide was then distilled off leaving a purple, tarry mass, which was poured into a total of 450 g of ice and 450 ml of concentrated hydrochloric acid with stirring. This mixture was then steam-distilled to remove the remaining carbon disulfide and anisole. After chilling, the aqueous layer was decanted leaving a tarry mass, which was washed with three 200 ml aliquots of 5% sodium carbonate and one of water.

The tarry semi-solid was recrystallized from ethanol-water to give 69 g of a light brown solid melting at 35-43°C. A VPC showed one component, and the IR and NMR spectra were consistent for the desired 1,3-bis(4-methoxybenzoyl)perfluoropropane.

It had the following analysis:

Calc: C, 54.3; H, 3.36; F, 27.12; found: C, 55.3; H, 3.55; F, 26.45.

b. Reaction of 1,3-Bis(4-methoxybenzoyl)Perfluoropropane With Sulfur Tetrafluoride

The method reported by Hasek and co-workers was followed (ref. 19).

1,3-Bis(p-methoxybenzoyl)perfluoropropane (8.4 g, 0.02 mole), was placed in a 150-ml stainless steel bomb. Sulfur tetrafluoride (20 g, ∿0.2 mole) and a catalytic amount of HF was then added using the usual vacuum techniques.

Several bomb runs were reacted for different periods at temperatures from 120 to 200°C. Products were divided into ether-soluble and ether-insoluble fractions. Ether-soluble products were analyzed by VPC and were found to consist of the desired product plus starting material and partially fluorinated product.

Ether-soluble fractions from runs at 180°C for reaction periods of 20 hours contained totally converted product in 99% purity, but in some runs large amounts of insoluble, polymeric by-product were also produced. Reactions at 120°C for 20 hours gave higher yields. Reaction products consisted of about 10% starting and partially fluorinated material and about 40 to 50% of ether-insoluble residues in addition to the desired product.

The NMR spectrum of the product was consistent for the structure of 1.5-di-p-anisoylperfluoropentane. Its melting point is 48.5-49.5°C.

18. Sym-bis(salicyloxymethyl)tetramethyldisiloxane

This compound was prepared using the procedure of Merker and Scott (ref. 56) by dissolving 19.2 g (0.1 mole plus 20% excess) of salicylic acid sodium salt and 11.6 g (0.05 mole) of bis-(chloromethyl)tetramethyldisiloxane in 50 ml of N,N-dimethylformamide and refluxing for 3 hours.

The sodium chloride formed was removed by filtration. The filtrate was mixed with an equal volume of benzene, and washed with five 50-ml aliquots of water to remove the dimethylformamide and excess sodium salicylate. The benzene fraction was dried over anhydrous magnesium sulfate and the benzene was then distilled off at atmospheric pressure. The residue was recrystallized at 0°C three times from 95% ethanol, yielding 8.2 g of product (38% yield, mp 36.5-37°C). After drying at room temperature, the purity as checked by IR, VPC and NMR was excellent.

B. PREPARATION OF TITANIUM COMPOUND REAGENTS

1. Preparation of Bis(acetylacetonato)diisopropoxytitanium(IV)

Tetraisopropoxytitanium (IV) (56.9 g, 0.20 mole) was mixed with 40.0 g (0.40 mole) of acetylacetone in an ice bath. 2-Propanol was separated out with a rotating evaporator at 50°C. The product was further purified in a molecular still at ∿20 μ pressure and ∿80°C.

2. Preparation of Bis(dibenzoylmethano)diisopropoxytitanium(IV)

Dibenzoylmethane (25.74g, 0.115 mole) was added with stirring under nitrogen to 16.31g (0.0574 mole) of tetraisopropoxytitanium. Then, 100 ml of dry benzene was added to the mixture and heated until homogeneous. The solution was cooled and the precipitate that formed was collected and recrystallized from diethyl ether. The product weighed 12.8g (36.6% yield) and melted at 173-177°C. Its NMR and infrared spectra were consistent for the above named product.

3. Preparation of Bis(8-hydroxyquinolino)diisopropoxytitanium(IV)

Tetraisopropoxytitanium (4.915g, 0.0173 moles) was added dropwise under nitrogen to 5.022g (0.0346 moles) 8-hydroxyquinoline in 150 ml dry, refluxing benzene. Most of the solvent (130ml) was distilled and the residue was dried in vacuum, triturated with petroleum ether (30-60°C) and redried. The product melted at 178-180°C. Its NMR spectra was consistent for the above named product.

4. Preparation of Acetylacetonatodibutoxydiphenylphosphinatotitanium(IV)

To a 500-ml, 3-necked flask (magnetic stirrer, distilling head, Dry Ice-acetone traps, thermometer, and N_2 bleed) was added 5.0 g (0.013 mole) of bis(acetylacetonato)dibutoxytitanium(IV) and 2.8 g (0.013 mole) of diphenylphosphinic acid in 300 ml of toluene. The solids dissolved at 52°C and the reactants were kept at 59°C for 20 hours. Devolatilization at 60°C (1 mm Hg) produced 4.6 g of the product. NMR spectra was consistent with the structure.

5. Preparation of Tetrakis(dimethylamino)titanium(IV)

Dimethylamine was added with stirring to 625 ml of a 1.6 molar solution of n-butyl lithium in hexane contained in a dry flask, while the reaction temperature was kept at -10°C by cooling with a Dry Ice bath. A solution containing 45 g (0.24 mole) titanium tetrachloride in 60 ml dry benzene was then added to the mixture at 0 to 10°C. This mixture was heated at reflux overnight. The precipitated lithium chloride was removed by filtration and the filtrate was distilled. The yellow liquid that distilled at 58-74°C/0.6 mm. was redistilled. The fraction boiling at 50.8-52.0°C/0.35 mm. [lit. 50°C/0.05 mm. (ref. 28) and 56-68°C/0.30-0.50 mm. (ref. 57)] weighed 21 g.

C. PREPARATION OF SUBSTITUTED ARYLENEDISILANOLS AND OTHER SILICON-CONTAINING REAGENTS

1. p-Phenylene-bis(dimethylsilanol)

a. Via Hydrolysis of p-Phenylene-bis(chlorodimethylsilane)

(1) p-Phenylene-bis(chlorodimethylsilane)

An etheral solution (250 ml) of 59.0 g (0.25 mole) of p-dibromobenzene was added to 24.3 g (1.0 mole) of Mg in a four-necked, one-liter flask fitted with stirrer, thermometer, condenser, N_2 inlet, and dropping funnels. After the Grignard reaction was started (0.5 hr) 129 g (1.0 mole) of dichlorodimethylsilane was added dropwise concurrently with the dropwise addition of the rest of the p-dibromobenzene. The temperature of the reaction was maintained at reflux by the rate of the addition of the p-dibromobenzene. The reaction mixture was refluxed at 40°C for another 22 hours after the addition of reagents. The magnesium salts were filtered off under N_2 atmosphere, and the filtrate was distilled. White crystals (31.5 g, 48.0% yield) with a melting point of 50°C were collected. In another preparation (85246) 65g (54%) was collected.

(2) Hydrolysis of p-Phenylene-bis(chlorodimethylsilane)(81150)

p-Phenylene-bis(chlorodimethylsilane) (31.5 g, 0.12 mole) in about 300 ml of ether was added dropwise to a stirring solution of 9.6 g of sodium hydroxide in 160 ml of water maintained at 0°C over a period of 15 minutes. The mixture was then kept at -15°C for 18 hr, and the ethereal layer was separated from the aoueous layer. The etheral washings of the aqueous layer was combined with the original etheral layer and evaporated at room temperature (1 mm Hg). The yield was 28.3 g of crude product. Recrystallization from cyclohexane-ether mixture yielded 15.1g (55.5% yield) of white powder (mp 133-134°C). In another preparation (85247) 37.8 g (60.3% yield) of white powder (mp 133-136°C) was collected.

b. Via Hydrolysis of p-Phenylene-bis(dimethylethoxysilane)

(1) Chlorodimethylethoxysilane

In a one-liter flask fitted with stirrer, condenser, thermometer, and a dropping funnel was placed 181 g (1.41 moles) of dichlorodimethylsilane in about 500 ml of anhydrous ether. Anhydrous ethanol (64.5 g, 1.41 moles) and 110 g (1.41 moles) of dried pyridine were mixed in the dropping funnel and added dropwise to the silane solution at 0°C over a period of about 1 hour. The white precipitate was filtered off and the excess solvents were distilled from the filtrate. The yield of product was 112 g (0.81 mole), 57.5%.

(2) p-Phenylene-bis(dimethylethoxysilane)

A flame-dried 4-necked, one-liter flask containing 14.6 g (0.6 mole) of Mg was fitted with two dropping funnels, a thermometer, a stirrer, a N_2 inlet, and a condenser. About 50 ml of a solution made up of 64.3 g (0.27 mole) of p-dibromobenzene and 200 ml of ether was added. After the Grignard reaction was started, 84 g (0.6 mole) of chlorodimethylethoxysilane in about 250 ml of ether was added dropwise concurrently with the dropwise addition of p-dibromobenzene-ether solution.

The rate of addition of p-dibromobenzene was governed by the refluxing temperature. After this addition, the reaction mixture was refluxed for 16 hours and the salt was filtered off in a drybox. Distillation gave 64.2 g of a liquid crude product.

(3) p-Phenylene-bis(dimethylsilanol)

A solution made up of NaOH (27.14 g, 0.68 mole), MeOH (158.7 ml), and H_2O (22.6 ml) was added to a solution of 64.2 g of crude p-phenylene-bis(dimethylethoxysilane). After 5 minutes 27.1 g (0.68 mole) of NaOH in 180 ml of water was added with stirring. After one hour the mixture was poured into an ice-cold solution of 233.6 g (1.73moles) potassium dihydrogen phosphate in about 1700 ml of water. The mixture was left at -15°C for 16 hours and then filtered. A solid was recrystallized from benzene and petroleum ether in 11% yield (6.2 g, mp 133°C). IR and NMR spectra are consistent with the desired product.

2. p-Phenylene-bis(methylphenylsilanol)

a. Via Hydrolysis of p-Phenylene-bis(chloromethylphenylsilane)

(1) p-Phenylene-bis(chloromethylphenylsilane)

Recrystallized p-dibromobenzene (38 g, 0.16 mole) in about 350 ml of ether was added to 15.1 g (0.64 mole) of Mg turnings in 200 ml of tetrahydrofuran. After the Grignard reaction was started the rest of the p-dibromobenzene was added dropwise concurrently with 123 g (0.64 mole) of methylphenyldichlorosilane. After addition, the reaction mixture was heated to 40°C and stirred for 16 hours. The magnesium salts were filtered under N_2 atmosphere. The solvents were distilled off and the residue was distilled through a Claisen head. The 30.9 g (50% yield) fraction (210-320°C/0.5 mm Hg) was identified by IR and NMR spectra to be the major portion of the desired product.

(2) p-Phenylene-bis(methylphenylsilanol)

Crude p-phenylene-bis(chloromethylphenylsilane) (30.9 g, 0.08 mole) in about 250 ml of ether was added to a cooled (0°C) aqueous solution of sodium hydroxide made up of 6.4 g (0.16 mole) sodium hydroxide in 110 g water over a 15-min period. The etheral layer was separated and combined with ether washings of the aqueous layer. After evaporation of the ether, white powdery crystals were collected. Recrystallization from toluene-petroleum ether gave 4.06 g (14.5% yield) of white powder (mp 135-145°C). IR and NMR spectra were consistent with the structure.

b. Via Hydrolysis of p-Phenylene-bis(ethoxymethylphenylsilane)

(1) Chloroethoxymethylphenylsilane

A mixture of anhydrous ethanol (368 g, 8 moles) and anhydrous pyridine (632 g, 8 moles) was added dropwise to a constantly stirred solution of methylphenyldichlorosilane (1528 g, 8 moles) in 3 liters of anhydrous diethyl ether maintained at 10°C. The mixture was stirred for an additional 30 minutes and then the pyridine hydrochloride was collected on a filter and washed twice with 600 ml portions of anhydrous diethyl ether. The combined filtrate and washings were stripped of solvent. Distillation of the residual liquid yielded the major fraction of product (1169 g, 73% yield) which boiled at 58-59°C/1.55 mm Hg.

(2) p-Phenylene-bis(ethoxymethylphenylsilane)

Separate solutions of chloroethoxymethylphenylsilane (828 g, 4.12 moles) in 500 ml of anhydrous tetrahydrofuran and p-dibromobenzene (436 g, 1.85 moles) in 1000 ml tetrahydrofuran were added dropwise at a rate sufficient to maintain reflux into a 12 liter, three-necked, round-bottomed flask containing magnesium turnings (100.2 g, 4.12 g-atm) in 500 ml anhydrous tetrahydrofuran. The reaction mixture was refluxed overnight, and then cooled to room temperature. Addition of 1 liter of anhydrous ether precipitated magnesium salts, which were filtered by suction and washed three times with 600 ml of ether. The combined filtrate and washings were stripped of solvent and the residue was distilled using a 7-inch Vigreux column. The product, a colorless liquid, (bp 204-205°C/0.55 mm Hg, n_D^{25} 1.5545) was obtained in 50% yield (376.6 g).

(3) p-Phenylene-bis(methylphenylsilanol)

A solution of sodium hydroxide (110.8 g, 2.77 mole) in 775 ml methanol and 119 ml water was added with stirring to p-phenylene-bis(ethoxymethylphenylsilane)(376 g, 0.924 mole) in 525 ml ethanol. After standing for five minutes, the mixture was treated with an additional amount of sodium hydroxide (110.8 g, 2.77 mole) in 800 ml water. After standing for one hour with intermittent stirring, the mixture was neutralized with a saturated aqueous solution of potassium dihydrogen phosphate at 5°C. The reaction mixture was allowed to stand for three hours then it was filtered and air dried. Trituration of the crude solid with a minimum amount of cold diethyl ether yielded 130 grams of white solid with a melting range of 148-157°C. Concentration of the ether filtrate yielded 85 g of solid (mp 127-132°C, [lit. (ref. 57) mp 128-140°C]). Both fractions were dissolved in acetone, filtered, and recovered by removal of solvent. The purified product had the same mp range and had a combined weight of 162 g (50% yield).

3. p-Phenylene-bis(methylvinylsilanol)

a. Chloroethoxymethylvinylsilane

By a procedure similar to that described in section IV. B. 3. b. (1), 196.5 g (1.39 moles) of methylvinyldichlorosilane in 100 ml dry ether was converted to 109 g (1.26 moles, 90% yield) of chloroethoxymethylvinylsilane.

b. p-Phenylene-bis(ethoxymethylvinylsilane)

About 50 ml of an ethereal (400 ml) solution of 98.4 g (0.417 mole) of p-dibromobenzene was added to 30.5 g (1.26 g-atoms) of Mg and 75 ml of dry tetrahydrofuran in a four-necked, one-liter flask fitted with stirrer, thermometer, condenser, N_2 inlet and dropping funnels. After the Grignard reaction was started, 109 g (1.26 moles) of chloroethoxymethylvinylsilane was added dropwise. The temperature of the reaction was maintained at reflux by the rate of addition of the etheral solution of p-dibromobenzene.

The reaction mixture was allowed to reflux for 60 hours after the addition of p-dibromobenzene and chloroethoxymethylvinylsilane. The magnesium salts were filtered off, and the filtrate was distilled. The fraction (bp 130-150°C/0.05 mm) was collected and identified by NMR to be the desired product (95.3% pure by VPC). The yield was 38.23 g (0.125 mole, 30%).

c. p-Phenylene-bis(methylvinylsilanol)

p-Phenylene-bis(ethoxymethylvinylsilane) (38.23 g, 0.13 mole) in 25.6 ml of absolute ethanol was added slowly to a cooled (0°C) methanol solution of sodium hydroxide and water (77 ml, 15.4 g, 12.2 ml, respectively). Upon neutralization with potassium dihydrogen phosphate, white crystals were formed (mp 84°C). Recrystallization from benzene yielded 17.95 g (57% yield) of white powder (mp 92-95°C). NMR and IR spectra were in accord with the structure.

4. 4,4'-Bis(dimethylhydroxysilyl)biphenyl

a. 4,4'-Bis(chlorodimethylsilyl)biphenyl

4,4'-Dibromobiphenyl (24.47 g, 0.081 mole) dissolved in a mixture of 150 ml of toluene and 50 ml of benzene was placed in a one-liter, four-necked flask fitted with a condenser, stirrer, dropping funnel, N_2 inlet, and thermometer. The flask was flushed with nitrogen and 118 ml (0.26 mole) of a hexane solution of n-butyllithium in a sealed dropping funnel was added slowly with rapid stirring. The reaction temperature was kept at 30°C.

After the addition, the reaction mixture was refluxed at 78°C for 0.5 hour. After cooling, the above reaction mixture was added with rapid stirring to 52.3 (0.41 mole) of redistilled dichlorodimethylsilane, and this was refluxed for another 2.5 hours at 78°C under N_2 flush. It was then cooled and stirred under N_2 for 20 hours. After filtration of the salts under N_2 evaporation of the solvents yielded 24.9 g (0.0735 mole, 91%) of crude product. In another preparation 35 g (0.11 mole. 51.5% yield) of purified product was obtained.

b. 4,4'-Bis(dimethylhydroxysilyl)biphenyl

4,4'-Bis(chlorodimethylsilyl)biphenyl (24.9 g, 0.0735 mole) in 300 ml of ether was added dropwise to a rapidly stirring, cooled (0°C) solution of 5.88 g (0.15 mole) of NaOH in 100 ml of water over a period of 15 minutes. The aqueous layer was separated and washed with ether (150 ml), and the wash was combined with the ether layer. The ether was evaporated off, and the residue was washed with acetone and dried. A white solid (mp 174-175°C) was obtained. Its IR spectrum was similar in most respects to that obtained for p-phenylene-bis(dimethylsilanol) except for two medium intensity bands at 1000 cm^{-1}. These bands can be attributed to the biphenyl. The yield was 1.5 g (7.3%). In another preparation 6.62 g (0.022 mole, 22% yield) of the purified white powder (mp 165-173°C) was obtained.

5. 4,4'-Bis(hydroxymethylphenylsilyl)biphenyl

a. 4,4'-Bis(ethoxymethylphenylsilyl)biphenyl

4,4'-Dibromobiphenyl (63 g, 0.2 mole) dissolved in 150 ml of toluene and 50 ml of benzene was placed in a one-liter, four-necked flask fitted with a condenser, stirrer, dropping funnel, N_2 inlet, and thermometer. The flask was flushed with N_2, and 261 ml (0.61 mole) of a hexane solution of n-butyllithium in a sealed dropping funnel was added dropwise with rapid stirring. After the addition the reaction mixture was refluxed at 78°C for 0.5 hr under N_2.

After cooling, the above reaction mixture was added with rapid stirring to 201 g (1.01 moles) of chloroethoxymethylphenylsilane under N_2, and the reactants were refluxed at 78°C for another 2.0 hr. The mixture was then cooled and stirred under N_2 for 20 hours. After filtration, the residue was washed three times with 100-ml portions of hot benzene and combined with the filtrate. The solvents were then devolatilized. Claisen distillation yielded 70 g (0.145 mole, 72%) of crude product.

b. 4,4'-Bis(hydroxymethylphenylsilyl)biphenyl

Sodium hydroxide (17.4 g, 0.435 mole) in 121.8 ml of water was added dropwise to a rapidly stirring mixture composed of 70 g (0.145 mole) of 4,4'-bis(ethoxymethylphenylsilyl)biphenyl, 300 ml of dry ether, 17.4 g (0.135 mole) sodium hydroxide, 104.4 ml methanol, and 16 ml H_2O. After the addition, the mixture was neutralized with potassium dihydrogenphosphate and kept at -15°C for 16 hr. After filtration the solid and the aqueous layer were washed with dry ether and then separated. After devolatilizing the ether, a tan oil was left, and no solids precipitated after adding a 50-50 petroleum ether (bp 30-60°C) and toluene mixture. Similarly, the addition of benzene produced no solids. The oil was left in petroleum ether for 6 days. After the evaporation of the ether, addition of toluene produced 3.5 g (4.1% yield) of white powder (mp 102-105°C). IR and NMR spectra were consistent with the structure.

6. 4,4'-Bis(dimethylhydroxysilyl)biphenyl Ether

a. 4,4'-Bis(dimethylethoxysilyl)biphenyl Ether via Grignard Reaction

This compound was prepared via a Grignard reaction with the following stoichiometry:

260 g (1.88 moles) of chlorodimethylethoxysilane.
45.68 g (1.88 moles) of Mg turnings.
235.18 g (0.72 moles) of bis-(p-bromophenyl) ether in
400 ml THF.

The procedure is essentially the same as that for the preparation of 4,4'-bis(ethoxymethylphenylsilyl)biphenyl ether. Fractional distillation gave 63 g (24% yield) of gold colored liquid (bp = 186-192/9.6 mm, n_D^{25} 1.5185).

b. 4,4'-Bis(dimethylethoxysilyl)biphenyl Ether via Sodium

A mixture of 45.47 g (0.14 mole) of bis(p-bromophenyl) ether 42.4 g (0.36 mole) of chlorodimethylethoxysilane (81157), 14.1 g (0.61 g-atom) of sodium wire (0.5 mm), and about 500 ml of ether was refluxed with rapid stirring for 60 hours. The fine suspension was centrifuged off and the supernatant was devolatilized at 25°C/ 1 mm Hg. Fractional distillation gave 28.6 g (54.8% yield) product.

c. 4,4'-Bis(dimethylhydroxysilyl)biphenyl Ether

4,4'-Bis(dimethylethoxysilyl)biphenyl ether (18.1 g, 0.048 mole) in 70 ml of EtOH was added slowly with stirring to NaOH (9.95 g) in 3.9 ml of MeOH. After 10 minutes, 9.95 g of NaOH in 45 ml of H_2O was added slowly to the reactants. After one hour the reactants were added dropwise with stirring to 51.1 g (0.38 mole) of KH_2PO_4. A white precipitate was filtered from the water after the reactants were left stirring for one hour. After repeated recrystallization from acetone-petroleum ether mixture, 2.1 g (13.6%) of white solids (mp 88°C) were obtained. IR and NMR spectra agreed with the structure. In another preparation a white powder with mp 90°C and a yield of 24.8% was obtained. An attempt to prepare the compound through hydrolysis of 4,4'-bis(chlorodimethylsilyl)biphenyl ether was unsuccessful.

7. 4,4'-Bis(hydroxymethylphenylsilyl)biphenyl Ether

a. 4,4'-Bis(ethoxymethylphenylsilyl)biphenyl Ether

Mg turnings (41.97 g, 1.69 moles) were placed in a 3-liter, 4-necked flask fitted with stirrer, thermometer, condenser, dry N_2 inlet, and dropping funnels. After flushing the flask with N_2 for 15 minutes, approximately 200 ml of the chloroethoxymethylphenylsilane solution (338 g, 1.69 mole in 180 ml of THF) was added. The Grignard reaction was started with ethylbromide, after which 20 ml of the bis(p-bromophenyl) ether solution (208 g, 0.643 mole in 400 ml of THF) was added rapidly. With stirring the temperature was raised to 71°C, where the rest of the silane was added rapidly. The rest of the bis(p-bromophenyl) ether solution was added slowly to maintain a gentle reflux without stirring. At the end of the addition, stirring was commenced, with an ice bath to control the reaction temperature. The reactants were reacted at 71°C for an additional

16 hours, cooled and then filtered. The filtrate was combined with the washings and solvent were devolatilized. Fractional distillation yielded five fractions. The last fraction weighed 95.7 g(from 283-295°C/0.2 mm) Yield of a second preparation was 95 g from 0.32 mole dibromo compound.

b. Hydrolysis of 4,4'-Bis(ethoxymethylphenylsilyl)biphenyl Ether

4,4'-Bis(ethoxymethylphenylsilyl)biphenyl ether (95.7 g, 0.192 mole) was added to 109 ml of absolute ethanol in a 4-liter beaker. To this solution was added slowly with stirring an alcoholic solution (23 g, 0.576 mole of NaOH in 162 ml of methanol and 24.8 ml H_2O) of NaOH. After 5 minutes, an aqueous solution (23 g, 0.576 mole of NaOH in 167 ml of water) of NaOH was added slowly with stirring. After one hour, an ice cold saturated potassium dihydrogen phosphate solution was added until the mixture became neutral. After 16 hours at room temperature, repeated recrystallization from 50:50 toluene and ligroin (60/90°) failed to produce a crystalline product. NMR spectrum of the clear gum was consistent with the desired product. After 30 days the gum was redissolved in ether and the solution added to n-hexane cooled to -70°C. The product separated as a white powder (mp 40°C).

8. p-Phenylene-bis(dimethylmethoxysilane)

a. Chloromethoxydimethylsilane

A mixtureof 80.8 ml (2.0 moles) of absolute methanol and 160.7 ml (2.0 moles) of pyridine was added slowly with stirring to 258 g (2.0 moles) of dichlorodimethylsilane in 300 ml of dry ether in a 2-liter flask previously flushed with dry N_2, at 15°C. Stirring was continued at room temperature for one hour after addition. The mixture was filtered and the white pyridine hydrochloride was washed with several portions of dry ethyl ether. The filtrate and washings were combined and distilled. The yield of chloromethoxydimethylsilane (bp 71-78°C) was 92.9 g (0.75 mole, 38%).

b. Grignard Reaction with p-Dibromobenzene

A solution of 80 g (0.34 mole) of p-dibromobenzene and 92.9 g (0.75 mole) of chloromethoxydimethylsilane in 300 ml of dry tetrahydrofuran was added to 18.23 g (0.75 mole) of Mg in 150 ml of dry tetrahydrofuran at a rate to maintain reflux after first initiating the reaction with ethyl bromide. The mixture was refluxed overnight under nitrogen, cooled to room temperature, and filtered. Additional salts, precipitated by addition of ether to the filtrate, were filtered, and washed with ether. The clear filtrate was fractionally distilled. The fraction collected at 78-81°C/0.25 mm eluted as a single peak on VPC analysis, and the trapped peak had an infrared spectrum consistent for the product. NMR analysis of a hydrolyzed sample was consistent for the corresponding siloxane.

9. Phenylsilanetriol

a. From Phenyltrichlorosilane

The procedure developed by Takiguchi (ref. 24) was followed. Phenyltrichlorosilane, (31.7g, 0.15 mole) in 210 ml of diethyl ether was added to 8.1g of H_2O (0.45 mole) and 41.9g of aniline (0.45 mole) dissolved in 750 ml of diethyl ether while the temperature was kept at 0°-5°C. The reaction mixture was filtered and the insoluble aniline hydrochloride by-product was washed with ethyl acetate. The filtrate was concentrated to precipitate a white solid, which was filtered and washed with petroleum ether (30-60°C). The solid weighed 10.2 g (43.6% yield) after drying under vacuum at room temperature, and melted at 134-137°C. Its NMR spectrum gave a proton count that corresponded exactly to the desired compound. Its infrared absorption spectrum also gave bands consistent with the desired product (ref. 25).

b. From Phenyltriethoxysilane

A method similar to reference 25 was used, except that phenyltriethoxysilane rather than phenyltrimethoxysilane was used as the reactant.

Phenyltriethoxysilane, 25.0g (0.104 mole), was stirred with 23.0g of H_2O (1.25 mole, 4X theoretical), containing 0.5% acetic acid as a catalyst. The temperature was kept at 0°C. A heterogeneous mixture was still present after 16 hours of stirring.

The emulsion was extracted with 60 ml of diethyl ether and the ether insoluble fraction was evaporated to dryness. The resulting white solid 1.05 g (6.5% yield) gave an infrared absorption spectrum similar to that given by reference 4 and it softened at 125°C, but did not melt. Its NMR spectrum gave a low proton count for OH.

In a second reaction on the same scale, a 1.0% acetic acid solution was used as the catalyst. The product weighed 0.5g (3.2% yield), had a melting point of 124-128°C, and had an infrared absorption spectra identical to the first product.

10. Diphenylvinylsilanol

a. Phenylvinylethoxychlorosilane

A solution containing 68.3 g (1.48 mole) ethanol and 117.2 g (1.48 mole) pyridine in 130 ml ether was added with stirring to a solution of 300 g (1.48 mole) phenylvinyldichlorosilane in 330 ml ether at -5°C under a blanket of nitrogen. The pyridine hydrochloride was removed by filtration and washed with 1ℓ of ether, and the ether was then distilled from the filtrate at atmospheric pressure. The residue weighed 232 g (1.09 mole, 73%).

b. Diphenylethoxyvinylsilane

Solutions containing 232 g (1.09 mole) phenylvinylethoxychlorosilane in 100 ml tetrahydrofuran and 152 g (0.97 mole) bromobenzene in 300 ml tetrahydrofuran were added simultaneously under nitrogen to 26.5 g (1.09 mole) magnesium turnings in 200 ml tetrahydrofuran at a rate to maintain reflux. The mixture was refluxed for 16 hrs and then cooled. Ether (1ℓ) was added to precipitate magnesium salts and the mixture was filtered. The filtrate was distilled and the fraction boiling at 121°C/0.5 mm collected (146 g).

c. Diphenylvinylsilanol

A solution of 34.3 g (0.858 mole) of sodium hydroxide and 23.3 ml water in 180 ml methanol was added with stirring to 146 g (0.57 mole) diphenylethoxyvinylsilane in 250 ml ethanol. Five minutes later 34.3 g NaOH in 186 ml of water was added and stirring was continued for 1 hour. The solution was neutralized with saturated aqueous potassium dihydrogenphosphate, precipitating an oil. The aqueous solution was extracted with 1ℓ ether, the ether solution was combined with the oil, and the ether was removed from the product at 25 mm pressure. The NMR spectra of the product was consistent for the silanol.

11. Dimethyl-p-tolylsilanol

a. Dimethyl-p-tolylchlorosilane

A solution of 253 g (2 moles) of p-chlorotoluene and 10 g of ethyl bromide in about 100 ml of anhydrous tetrahydrofuran was added dropwise to 58.6 g (2.25 moles) of Mg in 400 ml of tetrahydrofuran under nitrogen while stirring vigorously and heating at 60°C. An exothermic reaction occurred during which the temperature rose to 95°C. After the reaction subsided, the mixture was heated overnight at 45°C. The Grignard solution was transferred to an addition funnel under nitrogen and added dropwise at 65°C to a stirred solution of 420 g (3.26 mole) of dimethyldichlorosilane in 200 ml of anhydrous ether. The mixture was refluxed for 1 hr, and filtered. The filtrate was distilled, yielding 250 g (68%) of dimethyl-p-tolylchlorosilane that boiled at 55°C/0.9 mm. (n_D^{25} 1.506).

b. Tetramethyldi-p-tolyldisiloxane

Dimethyl-p-tolylchlorosilane (120 g, 0.65 mole) was added with vigorous stirring to 644 g of water-ice mixture at 0°C. The mixture was stirred for 30 min. at 0°C and then extracted with two 400-ml portions of ether. The ether extract was washed with water several times, treated with sodium bicarbonate and filtered. Removal of ether by flash evaporation left 104.6 g (100%) of the disiloxane.

c. Dimethyl-p-tolylsilanol Sodium Salt

The procedure of Hyde (ref. 58) for preparation of the sodium salt of dimethylphenylsilanol from the disiloxane was followed. This sodium salt, which was extracted from insoluble solids in petroleum ether, melted at 65°C. The first crop of sodium salt obtained from 70 g of disiloxane weighed 28 g. Repeated treatment of the insoluble residue with boiling methanol yielded more product.

d. Dimethyl-p-tolylsilanol

The sodium salt of the above silanol (28 g, 0.15 mole) was added with rapid stirring at 4°C to a mixture of 12.6 ml of glacial acetic acid, 150 ml of ether, and 300 ml of water. The ether layer was separated, washed with two 250-ml portions of water, and distilled. Product collected at 84°C/0.9 mm weighed 17.9 g.

e. Attempted Hydrolysis of Dimethyl-p-tolylchlorosilane to Dimethyl-p-tolylsilanol

A solution of 113 g (0.614 mole) of chlorodimethyl-p-tolylsilane in 300 ml of ether was added with stirring to a mixture of 24.6 g of NaOH in 300 ml of water and 200 ml of ether at -2°C to 0°C. Then the ether layer was separated and washed with water. Product was isolated by distillation at 0.2 mm. and identified as tetramethyl-di-p-tolyldisiloxane from its boiling point and by its infrared spectra.

f. Bromomethylation of Dimethyl-p-tolylsilanol

N-Bromosuccinimide (19.2 g, 0.108 mole) was added to a stirred solution of 17.95 g (0.108 mole) of dimethyl-p-tolylsilanol in 300 ml refluxing carbon tetrachloride under nitrogen. After refluxing for 20 hours, an aliquot of the mixture liberated iodine from KI. About 0.05 g of azo-bis-isobutyronitrile was added and white light was shown on the refluxing mixture. After 3 hours, the KI test was negative. Succinimide was removed by filtration and volatiles were distilled. The bulk of the product did not distill below 200°C at 0.7 mm.

Infrared and NMR analysis showed the product to be a mixture of tetramethyl-di-p-bromomethylphenyldisiloxane and tetramethyl-1-(p-tolyl)-3-(p-bromomethy-phenyl)disiloxane in a ratio of about 7 to 6.

12. p-Bromomethylphenyldiphenylsilanol

a. Chlorodiphenyl-p-tolylsilane

Tolylmagnesium chloride was prepared by adding dropwise 200 g (1.58 moles) of p-chlorotoluene in 150 ml of dry THF to 38.4 g (1.58 moles) of magnesium in 350 ml of dry THF at 68°C in a three-liter flask equipped with stirrer, thermometer, condensor, and nitrogen inlet. Twenty minutes after addition was completed the mixture gradually turned deep brown. The reaction flask was left for sixteen hours at 68°C.

The tolylmagnesium chloride (≈ 1.58 mole) was added quickly from a 2000-ml separatory funnel to 600 g(2.37 moles) of diphenyldichlorosilane in a three-liter flask equipped with condenser, thermometer, and nitrogen inlet. The temperature rose gradually during addition to 65°C, where it maintained itself for five minutes following addition. A heating mantle was applied to maintain reflux of the reaction mixture at 68°C for two hours.

The mixture was filtered under nitrogen and the solid was washed with several 250-ml portions of dry ethyl ether. The filtrate was devolatilized at 60°C/10 mm, and then fractinated to yield 0.84 mole (53%) of a yellow solid boiling at 171-183°C/0.45mm and melting at 58-62°C (Ref59 reports bp. 175-185°C/0.2 mm).

b. p-Tolyldiphenylsilanol

p-Tolyldiphenylchlorosilane 258.7 g (0.84 mole) was dissolved in 1000 ml of dry ethyl ether and placed in a separatory funnel. The silane was shaken with successive 500-ml portions of water until the water was neutral to pH paper. The ether was removed at 40°C/10 mm yielding a white, oily solid. The solid was washed with several portions of petroleum ether (30-60°C). This left 164.4 g (35.8%) of p-tolyldiphenylsilanol, melting range 90-95°C (reported by ref. 59, 94-95°C). Its NMR spectrum was consistent for the product.

c. Bromomethylation of the Silanol

N-bromosuccinimide (11.8 g, 0.066 mole) was added to 15.62 g (0.060 mole) diphenyl-p-tolylsilanol in 250 ml of carbon tetrachloride, and the mixture was heated to 60°C and irradiated with ultraviolet light for 1.5 hours. An insoluble fraction of the succinimide by-product was collected on a filter, and the solvent was removed from the filtrate by flash evaporation. The residue was dissolved in ether and cooled to -70°C, and another fraction of succinimide was collected on a filter. The ether was then removed, and the residue was dissolved in benzene. The benzenesolution was removed from the eluent. The infrared and NMR spectra of the resulting product indicated that it was free of succinimide and that 100% of the methyl groups were brominated.

In two similar runs with less N-bromosuccinimide, products with 67% and 85% bromomethylation were obtained.

13. 1,7-Dichlorohexamethyltrisiloxane and 1,9-Dichlorooctamethyltetrasiloxane

Dimethyldichlorosilane (464.5g, 3.60 moles) was hydrolysed in ether with 32.5 ml (1.80 mole) water in an equal volume of dioxane following the procedure of Patnode and Wilcock (ref. 60). Fractional distillation of products yielded 41 g trisiloxane (99.2% purity by VPC) and 39 g tetrasiloxane (97.5% purity).

14. Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

The procedure described in ref. 28 was followed with 40.5 g (0.146 mole) 1,7-dichlorohexamethyltrisiloxane. The product collected at 63-64°C/22 mm was 94.2% pure by VPC analysis. Further distillation gave 99.3% purity.

15. Bis(methylamino)methylphenylsilane

Dichloromethylphenylsilane (76.4 g, 0.4 mole) was reacted with methylamine at 5°C following the procedure described in ref. 27. Distillation yielded a 50 g fraction boiling at 117.5°C/19 mm that had n_D^{26} 1.5094. VPC analysis showed one peak and NMR spectra was consistent for the above named product. Addition of a drop of water to the NMR sample caused complete disappearance of $N-CH_3$ protons.

D. PREPARATION OF PHOSPHOROUS-CONTAINING CROSSLINKING AGENTS

1. p-Phenylenediphosphonic Acid

a. Bis(diethylamino)chlorophosphine

Two liters of 30/40°C petroleum ether was added to a 3-liter, 4-necked flask fitted with stirrer, thermometer, and dropping funnel, and cooled to -70°C. Phosphorus trichloride (137.5 g, 1.0 mole) was added slowly, maintaining the temperature of the reactants at -70°C. A petroleum ether solution [292 g (4 moles) of diethyl amine, and 400 ml of 30/40° petroleum ether] was added slowly over a period of 3.5 hours. After the reactants reached room temperature, the amine hydrochloride was filtered off and washed with several portions of petroleum ether. The washings and the filtrate were combined and devolatilized at 45°C/10 mm. Fractional distillation yielded only one fraction (115 g, 54.5%; 52°C/0.2 mm; $n_D^{26.5}$ 1.4862, reported $n_D^{19.5}$ 1.4932).

b. p-Phenylene di-Grignard Reagent

Mg turnings (36.0 g, 1.5 moles) in 100 ml of THF were placed in a 2-liter, 3-necked flask fitted with stirrer, condenser, nitrogen inlet, dropping funnel and thermometer. Approximately 100 ml of the p-dibromobenzene solution (177.0 g, 0.75 mole in 375 ml of THF) was added with rapid stirring. Ethyl bromide was used as starter for the Grignard reaction. The rest of the p-dibromobenzene was added dropwise to maintain a gentle reflux. After the addition, the mixture was refluxed for 17 hours.

c. p-Phenylene-bis(tetraethylphosphorous Diamide)

Bis(diethylamino)chlorophosphine (115 g, 0.546 mole) in 100 ml of petroleum ether (80/100°) was placed in a 3-liter, 4-necked flask fitted with stirrer, thermometer, condenser, N_2 inlet, and dropping funnel. Approximately 0.75 mole of the Grignard reagent in 500 ml of THF and 500 ml of petroleum ether (80/100°) were added. The phosphine was then added slowly with rapid stirring under N_2 atmosphere and the temperature was raised to 70°C where the reagents turned brownish in color. The reagents were refluxed for an additional 18 hours and then were filtered while hot. All solids were washed with boiling petroleum ether (80/100°) and combined with the filtrate. White crystals appeared after devolatization of the solvents. After washing with ethanol and water, the crystals were dried in a vacuum desiccator (yield 39 g (38%); mp 100°C).

d. p-Phenylenediphosphonic Acid

The p-phenylene-bis(tetraethylphosphorous diamide) was added in small portions to 50% nitric acid over a two-hour period. Violent reaction occurred. The resulting pale yellow solution was refluxed for 5 hours and cooled. White crystals precipitated. After filtration and washing with acetone they gave 10 g of product (mp — 283-285°C).

2. p-Phenylene-bis(phenylphosphinic Acid)

a. Diethylaminophenylchlorophosphine

Two liters of 30/40° petroleum ether was added to a 3-liter, 4-necked flask fitted with stirrer, thermometer, and dropping funnel, and cooled to -70°C. Dichlorophenyl phosphine (179 g, 1.0 mole) was added slowly, maintaining the temperature of the reactants at -70°C. A petroleum ether solution [146g (2 moles) of diethyl amine, and 200 ml of 30/40° petroleum ether] was added slowly over a period of 3.5 hours. After the reactants reached room temperature, the amine hydrochloride was filtered off and washed with several portions of petroleum ether. The washings and the filtrate were combined and devolatilized at 45°C/10 mm. Fractional distillation yielded only one fraction (90 g, 39%; 95-96°C/0.6 mm).

b. p-Phenylene di-Grignard Reagent

Mg turnings (27.2 g, 1.08 moles) in 200 ml of THF were placed in a 3-liter, 4-necked flask fitted with stirrer, condenser, N_2 inlet, dropping funnel and thermometer. Approximately 100 ml of the p-dibromobenzene solution (127.4 g, 0.54 mole in 400 ml of the THF) was added with rapid stirring. The rest of the p-dibromobenzene was added dropwise to maintain a gentle reflux. After the addition the mixture was refluxed for 23 hours.

c. p-Phenylene-bis(phenyldiethylaminophosphine)

Approximately 0.54 mole of the Grignard reagent in 500 ml of THF and 500 ml of petroleum ether (80/100°) were placed in a 3-liter, 4-necked flask fitted with stirrer, thermometer, condenser, N_2 inlet, and dropping funnel. After heating the Grignard reagent to 70°C, 90.0 g (0.39 mole) of diethylaminophenylchlorophosphine, in 300 ml of petroleum ether (60-110°), was added slowly with rapid stirring under N_2. The reaction mixture was refluxed for an additional 23 hours and then filtered after cooling. The petroleum ether washings of the solids were combined with the filtrate. After devolatilization of the solvents, a yellow viscous liquid remained. Petroleum ether was added to the oil. It solidified after standing overnight and was recrystallized from 1:1 ethanol:hexane. The white solid product melted at 163-171°C. NMR analysis was consistent for the product and indicated purity of about 85-90%.

d. p-Phenylene-bis(phenylphosphinic Acid)

p-Phenylene-bis(phenyldiethylaminophosphine) (25 g 0.058 mole) was added in small portions to 189.7 ml 37% HNO_3. A violent reaction occurred, resulting in an insoluble brown gum that was refluxed in acid for seven hours. After cooling and filtering the mixture, the yellow solid was washed with 200 ml of acetone, recrystallized from ethanol and dried in a vacuum desiccator for 16 hours at room temperature. The solid did not melt below 315°C. NMR analysis was consistent for the product.

Analysis Calc'd:	C, 60.3; H, 4.48; P, 17.26.
Found:	C, 60.1; H, 4.68; P, 17.08.

E. TITANIUM CHELATE POLYMERS WITH ALKOXY SUBSTITUENTS

1. Condensations of Tetraalkoxytitanium Compounds with Bis-bidentate Ligands Using Ti-to-Ligand Ratio of 1 to 1

a. Condensation of 5,5'-Bis(salicyl-N-butylimino)methane with Tetrabutoxytitanium

5,5'-Bis(salicyl-N-butylimino)methane (5.316 g, 0.0145 mole) in 170 ml of dry pyridine in a dry flask under oxygen-free nitrogen was stirred and refluxed, and 50 ml of pyridine was distilled into a Dean-Stark trap. The solution was cooled to 100°C, and 4.94 g, (0.0145 mole) of tetrabutoxytitanium dissolved in 10 ml of dry pyridine was added quickly. The solution was heated at 100°C for 1 hour and at reflux for 2 hours during which time 50 ml of pyridine was distilled. Solvent and product butanol were then removed under vacuum leaving a tough, light amber colored resin that softened at 90-110°C and solidified on exposure to moist air at 100-120°C to a bright red, infusible (over 300°C) solid.

b. Large-Scale Condensation of 5,5'-Bis(salicyl-N-butylimino)methane with Tetrabutoxytitanium

Tetrabutoxytitanium (24 886 g, 0.0709 mole) was added dropwise to a pyridine solution of 26.798 g (0.0709 mole) of 5,5'-bis-(salicyl-N-butylimino)methane in a dried apparatus under nitrogen at 90°C. The reaction was heated for 2 hrs. at 90°C and then was refluxed for 5 hrs, slowly distilling off the pyridine. The remaining solvent was removed under vacuum (0.05 mm Hg 110°C for 3 hr). The dried yellow amber resin softened at 110-125°C.

c. Condensation of Tetrabutoxytitanium with 5,5'-Bis-(salicyl-N-butylimino)methane and Triethylsilanol 88512

Tetrabutoxytitanium (4.974 g, 0.0146 mole) was added dropwise to a pyridine solution of 5,5'-bis(salicyl-N-butylimino) methane in a dried apparatus under N_2 at 100°C. The reaction was heated at reflux for 3 hours, slowly removing 100 ml of pyridine by distillation. Triethylsilanol (1.932 g, 0.0146 mole) was added dropwise after cooling to 80°C, heated at 80°C for 1 hour and then refluxed for 5 hours. Most of the solvent was stripped off by distillation. The remaining solvent was removed under vacuum and the bright yellow polymer was dried at 110°C, 0.01 mm Hg for 5 hours. This polymer has a softening point of 105-130°C before crosslinking.

d. Condensation of 5,5'-Bis(8-hydroxyquinolino)methane with Tetraisopropoxytitanium

A solution containing 4.26 g (0.0141 mole) of 5,5'-bis(8-hydroxyquinolino)methane and 2.65 g (0.0282 mole) of phenol in 200 ml of dry quinoline was heated to 130°C for 30 minutes under dry nitrogen. The mixture was then cooled to 110°C and 4.00 g (0.0141 mole) tetraisopropoxytitanium was added. The solution was heated at 130°C for 2 hours and at reflux for 3 hours during which time 100 ml of quinoline was distilled. On cooling, a small amount of solid separated, but the bulk of product was soluble. The polymer condensed when heated in moist air at 80°C in quinoline solution to a gel that yielded an infusible solid on removal of solvent.

e. Condensation of Bis-(4-hydroxy-3-octanoylphenyl)ether with Tetrabutoxytitanium

The above ligand (4.2768 g, 0.009408 mole) in 200 ml dry pyridine in a dry flask under oxygen-free nitrogen was stirred and refluxed and 100 ml pyridine was distilled into a Dean-Stark trap. The solution was cooled to 95°C, 3.202 g (0.009408 mole) tetrabutoxytitanium was added and the solution reheated to reflux. Some insoluble polymer precipitated during reflux overnight. Solvent was then removed first by distillation at atmospheric pressure and then by heating at 120°C/0.10 mm. The resin did not melt below 300°C.

f. Condensation of sym-Bis(salicyloxymethylene)tetramethyldisiloxane with Tetrabutoxytitanium

The procedure was the same as in e above with 8.688 g (0.020 mole) this ligand and 6.807 g (0.0200 mole) tetrabutoxytitanium. The polymer isolated was black and softened starting at about 30°C.

2. Condensations of Diethylzinc and Tetrabutoxytitanium with Bisbidentate Ligands

a. Condensation of 5,5'-Bis(salicyl-N-butylimino)methane with Diethylzinc and Tetrabutoxytitanium

(1) Mole Ratio Zn/Ti of 1:1

A dry pyridine solution (190 ml) containing 14.102 g (0.0384 mole) of 5,5'-bis(salicyl-N-butylimino)methane was stirred and refluxed in a dry flask under oxygen-free nitrogen, and 40 ml of pyridine was distilled into a Dean Stark trap. The solution was cooled to 90°C and 2.376 g (0.0192 mole) of redistilled diethylzinc in 10 ml of anhydrous pyridine was added. After one-half hour at 90°C, 6.480 g (0.0192 mole) of redistilled tetrabutoxytitanium in 20 ml of dry pyridine was added, and the resulting red solution was refluxed for 3 hours. During this time 100 ml of pyridine was distilled. An amber resin was recovered after complete removal of solvent in vacuum.

(2) Mole Ratio Zn/Ti of 3.3:1

Condensation was carried out in the manner recorded above except that 3.217 g (0.0260 mole) of redistilled diethylzinc and 2.626 g (0.0077 mole) of redistilled tetrabutoxytitanium were reacted with 12.376 g (0.03377 mole) of 5,5'-bis(salicyl-N-butylimino) methane. A pale amber resin was obtained after drying in vacuum.

(3) Mole Ratio Zn/Ti of 3:1

Fifty ml pyridine was distilled into the trap from a solution of 300 ml pyridine containing 36.620 g (0.1000 mole) of the above ligand. The solution was cooled to 90°C, and 9.1158 g (0.0739 mole) of diethylzinc was added. After 2 1/2 hours at 90°C, 8.883 g (0.0261 mole)of tetrabutoxytitanium in 60 ml of pyridine was added. About 60 ml of pyridine was distilled over a period of 4 hours. Then the solution was kept at 110°C overnight and solvent was removed by distillation the next day. Final drying of the polymer was at 120°C/0.20 mm Hg. The polymer softened at 138°C, but did not flow freely below 300°C.

(4) Mole Ratio Zn/Ti of 1:1.33

This polymer was prepared exactly as in paragraph(3) above with 29.296 g (0.0800 mole) of ligand, 4.2386 g (0.03435 mole) of diethylzinc, and 15.540 g (0.04565 mole) of tetrabutoxytitanium. The polymer solution was separated into two parts. One part was kept for solution applications to adhesive specimens and the other part was distilled to remove all solvent. Dry polymer isolated from the second part softened at 148°C but did not melt completely below 300°C.

b. Condensation of Bis(4-hydroxy-3-octanoylphenyl)ether with Diethylzinc and Tetrabutoxytitanium

The above ligand (18.183 g, 0.0400 mole) in 200 ml pyridine in a dry flask under oxygen-free nitrogen was stirred and 50 ml pyridine was distilled into a Dean-Stark trap. The solution was cooled to 90°C, 2.3208 g, (0.01870 mole) diethylzinc was added, and the solution refluxed two hours. Then 7.2478 g (0.02130 mole) tetrabutoxytitanium was added and the solution refluxed overnight. The polymer, part of which was insoluble in boiling pyridine, was isolated as above. The resin softened at 210°C but did not melt below 300°C.

F. TITANIUM CHELATE POLYMERS WITH SILANOL- OR VINYL-SUBSTITUENTS

1. Condensation of Tetraisopropoxytitanium with 5,5'-Bis(salicyl-N-butylimino)methane and Phenylene-bis(methylphenylsilanol)

a. Ti-to-Si Ratio 1:4 (88554)

Tetraisopropoxytitanium (1.345 g; 0.0047 mole) was condensed with (1.737 g; 0.0047 mole) of 5,5'-bis(salicyl-N-butylimino)-methane by dropwise addition of the titanium compound to a refluxing benzene solution (200 ml) of the ligand over a period of one-half hour. The benzene was distilled off until about a 20% solution of the prepolymer remained. Then 3.323 g, (0.0095 mole) of phenylene-bis(methylphenylsilanol) was added in 100 ml of benzene to the prepolymer solution at room temperature. The reaction was then warmed to 40°C and held at 40-45°C for 20 hours. The solvent was distilled off under reduced pressure, and the polymer was dried at 50°C/0.01 mm Hg for 3 hours. Its softening range was 80-90°C.

The dried polymer was triturated with two 150-ml portions of ethyl ether and the washings were evaporated to dyrness. Approximately 22% of the crude polymer (1.345 g) was soluble in ether.

The purified ether-insoluble portion softened at 250-280°C and was soluble in benzene. Its intrinsic viscosity was 1.29.

b. Ti-to-Si Ratio 1:12 (88547)

Tetraisopropoxytitanium (1.327 g, 0.00467 moles) was added to 1.711 g (0.00460 mole) of 5,5'-bis(salicyl-N-butylimino)-methane, in a refluxing benzene solution, and the benzene was distilled off until about a 10% solution of polymer remained. Phenylene-bis(methylphenylsilanol) (9.816 g, 0.0280 mole) was dissolved in 150 ml of warm (45°C) benzene and the above polymer solution was added to it with stirring. The resulting solution was heated at 45-50°C for 3 hours and then was stirred overnight at room temperature. The benzene was distilled off at reduced pressure (35-40°C) and the dried polymer was redissolved in benzene and evaporated to dryness a second time with final drying of the polymer at 40°C/0.01 mm Hg for 2 hours.

The dried polymer was triturated with two 150-ml portions of ethyl ether, and the ether solution was evaporated to dyrness. The weight of extracted material was 9.63 g. The material that was insoluble in ether was redissolved in benzene (most of the ether-insolubles were soluble), and the benzene solution was filtered and evaporated to dryness yielding a clear yellow amber resin softening at 80-90°C. A sample of the polymer was triturated with ethyl ether. About 20% of the polymer was soluble in ether. The yellow resinous material that was insoluble in ether had a softening range of 260-290°C.

c. Ti-to-Si Ratio 1:4 on 0.36 Mole Scale (108984)

A solution of tetraisopropoxytitanium (102.430 g, 0.3604 mole) in 310 ml of dry benzene was added to 5,5'-bis(salicyl-N-butylimino)-methane (132.141 g, 0.3604 mole) in 7770 ml of dry benzene with stirring at reflux temperature under a nitrogen atmosphere. After the addition, 4250 ml of benzene was distilled off at atmospheric pressure (5% polymer solution). Then p-phenylene-bis(methylphenylsilanol) (252.662 g, 0.7208 mole) was added as a slurry in a total of 2 liters of dry benzene at 30°C. This formed a gel initially but dissolved completely after 2 hours. The resulting solution was stirred for 17 hours. The solvent was vacuum distilled and the yellow residue dried under vacuum, yielding 405 g of product. This was triturated 5 times with anhydrous diethyl ether, filtered, and vacuum dried for 36 hours. The ether-insoluble fraction weighed 260 g.

2. Condensation of 5,5'-Bis(salicyl-N-γ-dimethylaminopropylimino)-methane, Tetraisopropoxytitanium, and p-Phenylene-bis(methylphenylsilanol)(88596)

Tetraisopropoxytitanium (3.87 g, 0.0014 mole) was added dropwise to a refluxing solution of 5,5'-bis(salicyl-N- -dimethylaminopropylimino)methane (5.78 g, 0.0014 mole) in dry benzene over a period of 30 minutes. The benzene was distilled off until a solution of ≈10% concentration remained. After cooling to 40°C, p-phenylene-bis(methylphenylsilanol) (9.54 g, 0.0027 mole) in 100 ml of dry benzene was added and the reaction was stirred 18 hours at 40-50°C. Crude polymer was recovered by removing solvents under reduced pressure. It was fractionated by dissolving in 250 ml of warm benzene, cooling the solution to room temperature, and collecting the precipitated (presumably higher molecular weight) fraction on a filter. This solid was washed with two 100 ml portions of ethyl ether and dried for 5 hours at 0.05 mm Hg at room temperature. Its softening range was 150-180°C.

3. Condensation of N,N-Dimethyl-N',N'-bis(8-hydroxy-5-quinolylmethyl)-1,3-propanediamine with Tetraisopropoxytitanium and p-Phenylene-bis(methylphenylsilanol)

Thirty ml of a dry benzene solution containing 5.1303 g (0.01805 mole) tetraisopropoxytitanium was added under nitrogen to 400 ml refluxing benzene solution containing 7.5187 g (0.01805 mole) of the above ligand. After the addition, 320 ml of benzene was distilled. A yellow solid precipitate that did not redissolve when 100 ml benzene was added and the mixture warmed to 40°C. A slurry of 12.6534 g (0.03610 mole) p-phenylenebis(methylphenylsilanol) in 50 ml dry benzene was added. Complete solution occurred at this point.

The solution was kept as 39°C for 15 hrs. after which time a yellow solid was present. The solvent was vacuum distilled and the residue dried under vacuum. The yellow-colored polymer was triturated four times with anhydrous ether and dried to give 14.5 g of product that softened at 205°C. The polymer is insoluble in benzene and pyridine.

4. Condensation of 5,5'-Bis(7-octanoyl-8-hydroxyquinolino)-methane with Tetraisopropoxytitanium (100285)

A solution of tetraisopropoxytitanium (2.6535g, 0.00934 mole) in 30 ml of dry benzene was added to 5,5'-bis(7-octanoyl-8-hydroxyquinolino)methane (5.1810g, 0.00934 mole) in 300 ml of dry benzene with stirring at reflux temperature under a nitrogen atmosphere. After the addition, 200 ml of benzene was distilled. This was then stirred for one hour without any appearance of a precipitate. A slurry of p-phenylene-bis(methylphenylsilanol) (6.5479g, 0.01868 mole) in 200 ml of benzene was added and the resulting solution was stirred for 17 hours.during which time the polymer remained in solution. The solvent was vacuum distilled and the yellow residue dried under vacuum, yielding 11.3g. This was triturated with anhydrous diethyl ether four times and filtered. The ether insoluble fraction weighed 2.5 g and was insoluble in benzene and pyridine.

The ether soluble fraction was triturated with absolute ethanol four times and filtered. The insoluble fraction weighed 4g and was insoluble in benzene and pyridine. Its softening range was 220°C-295°C.

5. Condensation of Bis[N-methyl-N-(8-hydroxy-5-quinolylmethyl)]-1,6-hexanediamine with Tetraisopropoxytitanium and p-Phenylene-bis(methylphenylsilanol)

a. In Benzene Solution

A solution of 2.0672 g (0.00727 mole) of tetraisopropoxytitanium in 10 ml of dry benzene was added to 3.3356 g (0.00727 mole) of the above pure ligand in 100 ml of dry benzene at reflux temperature under an N_2 atmosphere. First, 130 ml of benzene was distilled from the reaction at atmospheric pressure and then a solution of 5.0988 g (0.01455 mole) of p-phenylene-bis(methylphenylsilanol) in 150 ml of dry benzene was added.

The solution was stirred for 63 hr. at room temperature under an N_2 atmosphere. The solvent was distilled under vacuum and the yellow solid residue was dried under vacuum at 40°C. The isolated solid, 7.40 g, was triturated four times with anhydrous diethyl ether and filtered. The ether insoluble fraction weighed 1.68 g, was insoluble in benzene and softened at 195°C. The ether soluble part weighed 4.29 g, softened at 73°C, hardened by 125°C, and resoftened at 155°C. The ether soluble fraction was stirred in 350 ml of ethanol and filtered. The 1.20 g of ethanol insoluble solid softened at 185°C. All isolated solids had essentially the same IR spectra.

A second similar preparation was done with 6.88 g of ligand that contained a small amount of benzene-insoluble impurity. The products isolated were similar to those in the smaller scale run. The ethanol insoluble fraction had a molecular weight of 1800 by vapor phase osmometry.

b. In Pyridine Solution

A solution of 4.510 g (0.0159 mole) of tetraisopropoxytitanium in 30 ml of dry pyridine was added with stirring to 7.282 g(0.0159 mole) of the above ligand in 380 ml dry pyridine at reflux in a nitrogen atmosphere. About 400 ml of solvent was distilled at atmospheric pressure and then 180 ml pyridine followed by a solution of 11.125 g (0.0317 moles) of p-phenylene-bis(methylphenylsilanol) in 195 ml pyridine was added to the residue. The solution was stirred for 60 hours at room temperature and then the solvent was removed by vacuum distillation. The residue was triturated four times with ether. The washed product weighed 6.3 g and did not soften below 270°C.

6. Condensation of N,N-Bis(8-hydroxy-5-quinolylmethyl)butylamine with Tetraisopropoxytitanium

a. In Toluene (100272)

A solution of tetraisopropoxytitanium (4.2442g, 0.01493 mole) in 30 ml of dry toluene was added to N,N-bis(8-hydroxy-5-quinolylmethyl)butylamine (5.7848g, 0.01493 mole) in 320 ml of dry toluene with stirring at reflux temperature under a nitrogen atmosphere. About 280 ml of solvent was distilled from the flask at atmospheric pressure and on cooling a yellow precipitate resulted. A slurry of p-phenylene-bis(methylphenylsilanol) (10.4668g, 0.02986 mole) in 300 ml of dry benzene was added and the mixture was heated to 45°C. Everything dissolved and then another precipitate formed as the solution was stirred for 17 hours at room temperature.

The solvent was removed by vacuum distillation, leaving a yellow residue weighing 15.1g. This was triturated four times with anhydrous diethyl ether and filtered. The ether insoluble fraction, after vacuum drying, weighed 9.9g. This product had a softening range of 210-250°C and was insoluble in benzene and pyridine.

b. In Toluene and Xylene (100281)

The same procedure was followed as in IV.F.6.a. on a 0.015 mole scale, except that after removal of the toluene in the first reaction step, 250 ml of xylene was added to the prepolymer. The prepolymer solution was heated at reflux for one hour and the xylene then distilled at atmospheric pressure. Then the xylene addition, heating and removal was repeated once more. The silanediol was added and the procedure used in IV.E.6.a. resumed. The product weighed 11.4 g, softened from 220 to 275°C, and was insoluble in benzene and pyridine.

7. Condensation of N,N-Bis(8-hydroxy-5-quinolylmethyl)butylamine" with Tetrakis(dimethylamino)titanium(IV)(100281)

A solution of tetrakis(dimethylamino) titanium (IV), (4.1317g, 0.01843 mole) in 30 ml of dry benzene was added to N,N-bis-(8-hydroxy-5-quinolylmethyl)butylamine (7.1409g, 0.01843 mole) in 400 ml of dry benzene with stirring at reflux temperature under a nitrogen atmosphere. During the addition a precipitate formed, and dimethylamine evolved. A portion (130 ml) of the solvent was distilled, the reaction mixture was allowed to reflux for 40 minutes and then an additional 70 ml of solvent was distilled. A slurry of p-phenylene-bis(methylphenylsilanol) (12.9205g, 0.03686 mole) in 350 ml of dry benzene was added and heated for 2 hours and then stirred at room temperature for 63 hrs during which time the product remained insoluble.

The solvent was removed by vacuum distillation leaving a yellow residue weighing 20.2g, after drying under vacuum. This was triturated four times with anhydrous diethyl ether and filtered. The ether insoluble fraction, after vacuum drying, weighed 14.6g. It was insoluble in benzene and pyridine and had a softening range of 185-260°C.

8. Condensation of 5,5'-Bis(salicyl-N-butylimino)methane with tetraisopropoxytitanium and diphenylvinylsilanol

a. Standard Procedure (106634)

A solution of 6.389 g (0.0225 mole) tetraisopropoxytitanium in 30 ml dry benzene was added with stirring to a solution of 8.240 g (0.0225 mole) of the ligand in 475 ml benzene at reflux under nitrogen. About 220 ml of solvent was distilled from the flask at atmospheric pressure leaving an orange, viscous solution. An additional 250 ml of dry benzene was added to dilute the polymer. Then a solution of 10.692 g (0.0450 mole plus 5% excess by wt.) of phenylvinylsilanol in 200 ml of benzene was added and the solution was stirred for 17 hrs at room temperature. The solvent was removed by vacuum distillation to leave 17.70 g of solid. This solid was triturated five times with diethyl ether, leaving 11.65 g of solid. The product softened at 140-185°C and had a relative viscosity in 1% benzene solution of 1.03. Another product weighing 2.4 g separated from the ether on standing. It softened at 235-270°C and the relative viscosity of 0.9% solution was 1.02. A second preparation with 7.5 g ligand yielded a similar product.

b. In Toluene (106673)

A similar preparation was carried out in toluene. The ether insoluble product softened in the range 135-215°C and had a molecular weight of 1660 by vapor phase osmometry. Its spectrum in the NMR was correct for a 2:1 mole ratio of diphenylvinylsiloxy to ligand in the product.

c. With Tetrakis(dimethylamino)titanium(IV) in Place of Tetraisopropoxytitanium (106684)

A similar preparation on 0.0288 mole scale was carried out with tetrakis(dimethylamino)titanium (IV) in benzene solution. The products were insoluble in hexane, soluble in benzene and fractionated by ether. Molecular weights of ether insoluble and soluble fractions were 1720 and 1635, respectively. The NMR spectra were also similar to the product obtained in toluene from tetraisopropoxytitanium.

d. Reverse Addition (100290)

A solution of 5,5'-bis(salicyl-N-butylimino)methane (1.9801g, 0.005401 mole) in 100 ml of dry benzene was added to tetraisopropoxytitanium (3.0701g, 0.010802 mole) in 750 ml of dry benzene at reflux temperature with stirring and under a nitrogen atmosphere. After the addition, 355 ml of solvent was distilled and the reaction cooled to room temperature. A solution of diphenylvinylsilanol (4.8900g, 0.021604 mole) in 300 ml of dry benzene was added and stirring continued for 45 minutes. This was heated to reflux and 380 ml of solvent distilled. An addition of 200 ml of dry benzene was then made and 100 ml more of the solvent distilled. A solution of 5,5'-bis(salicyl-N-butylimino)-methane (1.9801g, 0.005401 mole) in 300 ml of dry benzene was then added at reflux, 425 ml of the solvent distilled, and stirring continued at room temperature for 63 hours.

The solvent was distilled and the yellow residue vacuum dried at 40°C for 17 hours yielding 8.2g. This was triturated with petroleum ether (30-60°C) four times and decanted. The vacuum dried residue weighed 7.1g and was soluble in benzene. It had a molecular weight of 1900 by vapor phase osmometry.

e. High Ligand Concentration (108814)

A solution of 3.805g (0.01338 mole) tetraisopropoxytitanium in 5 ml dry benzene was added, under nitrogen, with stirring to 4.904 g (0.01338 mole) 5,5'-bis(salicyl-N-butylimino) methane in 6 ml dry benzene at 40°C. Four successive 10 ml portions of benzene were added and then distilled. Then to the cooled viscous solution was added 6.057 g (0.02676 mole) of diphenylvinylsilanol in 50 ml benzene. The viscous mass was left standing overnight at room temperature and then the solvent was removed by vacuum distillation. The dried residue weighed 10.4 g. It was triturated four times (mortar and pestle) with diethyl ether, leaving 7.5 g of yellow powder. This product was 81.5% soluble in benzene and softened in the range of 93°-140°C. The benzene-soluble fraction had a molecular weight of 2900 by vapor phase osmometry.

9. Condensation of 5,5'-Bis(salicyl-N-butylimino)methane with Tetraisopropoxytitanium, Diphenylvinylsilanol and p-Phenylene-bis(methylphenylsilanol)

A solution of 4.4128g (0.01553 mole) tetraisopropoxytitanium in 30ml dry benzene was added, under nitrogen, with stirring to 5.6925g (0.01553 mole) 5,5'-bis(salicyl-N-butylimino)methane in 335ml dry benzene at reflux. About 220ml of solvent was distilled from the flask at atmospheric pressure and a slurry of 5.4437g (0.01553 mole) p-phenylene-bis(methylphenylsilanol) in 100ml dry benzene was added simultaneously with a solution of 3.5152g (0.01553 mole) diphenylvinylsilanol in 150ml dry benzene. This was heated slightly to dissolve the silanols and then stirred at room temperature for 63 hrs.

The solvent was removed by vacuum distillation leaving a yellow residue weighing 13.5g. This was triturated with diethyl ether four times and filtered. The ether insoluble fraction, after vacuum drying, weighed 10.3g, softened from 170 to 280°C and was insoluble in benzene.

10. Condensation of 5,5'-Bis(salicylaldehydo)methane with Tetraisopropoxytitanium (100289)

A solution of tetraisopropoxytitanium (2.7560g, 0.00970 mole) in 30 ml of dry benzene was added to 5,5'-bis(salicylaldehydo)-methane (2.4856g, 0.00970 mole) in 350 ml of dry benzene with stirring at reflux temperature under a nitrogen atmosphere. The solution immediately became cloudy. The mixture was chilled to 28°C and a solution of diphenylvinylsilanol (4.3912g, 0.01940 mole) in 50 ml of dry benzene was added. This was stirred at 28°C for 35 minutes, and then heated to reflux and 320 ml of solvent distilled. Two additions of 250 ml of dry benzene were made and each distilled. Another 250 ml of benzene was made and stirring was continued for 63 hours. At this time there was an orange precipitate present. The solvent was distilled and the yellow residue vacuum dried, yielding 6.1g. This was triturated four times with anhydrous diethyl ether and filtered. The ether insoluble fraction weighed 5.2g and was insoluble in benzene and pyridine.

11. Condensation fo 5,5'-Bis(salicyl-N-butylimino)methane with Diethylzinc, Tetraisopropoxytitanium and p-Phenylene-bis-(methylphenylsilanol)

a. Mole Ratio Zn:Ti of 4:1 (108917)

Diethylzinc (2.9482g; 0.02387 mole) was added with stirring to a solution of 10.9965g (0.0300 mole) 5,5'-bis(salicyl-N-butylimino) methane dissolved in 540 ml of dry pyridine at 85°C in an oxygen-free nitrogen atmosphere. This was stirred at 85°C for 20 minutes and then heated at reflux for 1 hour. Tetraisopropoxytitanium (1.7433g; 0.00613 mole) in 20 ml of pyridine was added at reflux. Then about 300 ml of solvent was distilled at atmospheric pressure leaving a viscous orange-red solution which was cooled to room temperature. A solution of 4.2975g (0.01226 mole) p-phenylene bis(methylphenylsilanol) in 250 ml dry pyridine was added and the solution stirred for 16 hours.

The solvent was distilled under vacuum with slight heat leaving a residue weighing 16.7g. This was triturated five times with diethyl ether and filtered. The ether insoluble fraction, after vacuum drying, weighed 14.0g, softened from 135°C to 160°C, and was soluble in pyridine. Its relative viscosity in a 0.5% pyridine solution was 1.04.

b. Mole Ratio Zn:Ti of 19:1 (108923)

The same procedure was followed as in a above, except that 3.4997g (0.02834 mole) diethylzinc was added to 10.9965g (0.0300 mole) 5,5'-bis(salicyl-N-butylimino) methane. After this reaction, tetraisopropoxytitanium (0.4718g, 0.00166 mole) was added at reflux. During the early stage of the distillation at atmospheric pressure a precipitate separated, which did not redissolve when the p-phenylene bis(methylphenylsilanol) (1.1638g, 0.00332 mole) was added.

After 16 hours of stirring, the solvent was distilled leaving a residue of 11.4g, which was triturated four times with anhydrous diethyl ether and filtered. The ether insoluble portion, after vacuum drying, weighed 10.2g and softened from 130°C to 160°C. It was insoluble in pyridine.

12. Condensation of 5,5'-bis(salicyl-N-butylimino)methane with Diethylzinc, Tetraisopropoxytitanium and Diphenylvinylsilanol (108920)

The procedure described in IV.F.11, a was followed except that the following reagents were used:

	10.9965g	(0.0300 mole)	of 5,5'-bis(salicyl-N-butylimino) methane;
	2.9502g	(0.02389 mole)	of diethylzinc;
	1.7366g	(0.00611 mole)	of tetraisopropoxytitanium;
and,	2.7660g	(0.01222 mole)	of diphenylvinylsilanol.

After the solvent was distilled under vacuum, a residue weighing 14.0g remained. This was triturated five times with diethyl ether and filtered. The ether insoluble fraction, after vacuum drying, weighed 11.2g and softened from 135°C to 160°C. This product was initially soluble in pyridine but separated from solution on standing.

G. SUBSTITUTION OF ISOCYANATE GROUPS ON TITANIUM CHELATE POLYMER

1. Direct Substitution

Tetraisopropoxytitanium (3.1259 g, 0.011 mole) in 200 ml of dry benzene was added dropwise to a refluxing solution of 4.0315 g, (0.011 mole) of 5,5'-bis(salicyl-N-butylimino)methane in 370 ml of dry benzene. The polymer solution was cooled to room temperature after distilling of 300 ml of benzene. p-Tolyldimethylsilanol (3.66 g, 0.022 mole) was added in 100 ml of dry benzene and the reaction was stirred for 1 hour. Then the benzene was vacuum-distilled off. The polymer was dried at 40°C/0.005 mm Hg for 2 hours and then redissolved in 200 ml of dry benzene.

N,N'-Dibromodimethylhydantoin (2.516 g, 0.0088 mole) was added in 50 ml of dry benzene, and the mixture was stirred at room temperature under ultraviolet light for 45 min, and then filtered under nitrogen. Silver cyanate (4.642 g, 0.0211 mole) was added to the cloudy filtrate at room temperature. After stirring overnight (18 hr) the reaction mixture was filtered in the drybox and the filtrate evaporated to dryness under reduced pressure. The filtrate yielded a rubbery material that had a softening range of 115-120°C, and showed a pair of absorption peaks in the infrared that are characteristic of isocyanate (4.42μ, 4.60μ).

2. Substitution of the p-Bromomethylphenyldiphenylsilanoxy Group on the Titanium Chelate Polymer

A solution containing 4.099 g (0.0144 mole) of tetraisopropoxytitanium in 10 ml of anhydrous benzene was added to a refluxing solution of 5.285 g (0.0144 mole) of5,5' bis(salicyl-N-butylimino)methane in 250 ml of anhydrous benzene. Benzene was slowly distilled over a 4-hour period, during which 200 ml was collected. The polymer solution was then cooled to room temperature and a benzene solution containing 10.65 g (0.0288 mole) of p-bromomethylphenyldiphenylsilanol was added. The resulting solution was stirred for 18 hours and then the solvent was removed under reduced pressure. The crude polymer was washed with ether, and the ether insoluble fraction was redissolved in benzene.

H. ZINC CHELATE POLYMER PREPARATIONS

1. Statistical Study

Purified 5,5'-bis(salicyl-N-n-butylimino)methane (5.1000 g, 0.0139 mole) was dissolved in the solvent of choice under a dry nitrogen atmosphere. With a pyridine solvent, 30 ml was removed by distillation, and then the solution was cooled to 90°C. For quinoline and 2-chloropyridine, the solution was heated to 120°C for 45 minutes and then cooled to 90°C.

To the resulting solution at 90°C, 1.72 g (0.0139 mole) of redistilled diethylzinc was added over a two-minute period. After the addition was complete, the reaction mixture was allowed to stir at 90°C for either 1, 5, or 20 hours. The polymer was isolated from the solvent by heating at 150°C under a vacuum ($\approx$15 mm Hg) for 4 hours.

Table 19 outlines the combination of concentration, solvent, and reaction times used in each of the 27 experiments and gives the relative viscosity of the product polymer found for 2% solutions of polymer in pyridine at 25°C.

Analysis for variance by the standard procedure (ref. 7) showed that effects of solvent, concentration, and a solvent-concentration interaction were significant (99% confidence

Table 19

CONDITIONS FOR ZINC CHELATE POLYMERIZATIONS AND VISCOSITIES OF POLYMER PRODUCTS

Run No.	Combination*	Relative Viscosity
1	3 B b	1.467
2	3 A a	1.524
3	2 A b	1.290
4	1 C c	1.519
5	2 C a	1.376
6	1 C b	1.407
7	2 B b	1.245
8	3 B a	1.440
9	1 B a	1.393
10	2 B a	1.374
11	1 A a	1.469
12	1 A c	1.524
13	2 C c	1.482
14	1 A b	1.366
15	3 C c	1.438
16	3 C b	1.456
17	3 A b	1.356
18	1 B c	1.374
19	2 C b	1.437
20	2 A c	1.365
21	2 B a	1.300
22	3 A c	1.388
23	3 C a	1.404
24	3 B c	1.426
25	2 A a	1.314
26	1 B b	1.347
27	1 C a	1.527

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*Concentrations: 1 = 15%
2 = 10%
3 = 8%

Solvents: A = pyridine
B = quinoline
C = 2-chloropyridine

Reaction Time: a = 1 hour
b = 5 hours
c = 20 hours

level). The solvent effect showed that 2-chloropyridine was the best solvent. Average values for relative viscosities in the three solvents were:

Solvent	Average Relative Viscosity
2-Chloropyridine	1.449
Pyridine	1.399
Quinoline	1.374

The variations caused by concentration changes were small and there was a concentration-solvent interaction. In 2-chloropyridine there was a very slight advantage at high concentration:

Concentration, %	Average of 3 Tests in 2-Chloropyridine
15	1.484
10	1.432
8	1.433

2. Large-scale Chelate Polymer Preparation in 2-Chloropyridine

Distilled 2-chloropyridine (310 ml) was dropped through a 12 x 1 in. column packed with 1/16-in. Linde 4A molecular sieves into the reaction flask containing 32.7595 g (0.0895 mole) of purified 5,5'-bis(salicyl-N-n-butylimino)methane in a dry nitrogen atmosphere. The solution was stirred and heated at 120°C for 45 min., then cooled to 90°C and 11.0394 g (0.0895 mole) of diethylzinc was added. Two additional 0.033-g portions of diethylzinc were made at 1-hour intervals and the solution finally heated at 150°C for 3 hours. The polymer was isolated from the solvent by heating at 150°C under vacuum.

Relative viscosities of 2% solutions of the polymer in pyridine were:

After Initial Addition of Diethyl Zinc	After Second Addition
1.566	1.631

The polymer gave a negative Beilstein test for chlorine.

The above described chelate polymer was fractionated by first depositing the polymer on glass micro beads and then eluting with mixed solvents.

3. Polymerization in Triphenylphosphine

Triphenylphosphine, recrystallized from ethyl ether and dried in a vacuum desiccator over P_2O_5, and the ligand were added to the reaction flask under a dry nitrogen atmosphere and heated to 120°C for 45 min. Diethylzinc was added with stirring after cooling the solution to 95°C. Additional 0.3% portions of diethylzinc were added 1 hour after the initial charge and the reaction then held at 140°C for about 2 hours. One run was carried out with 10% reactant concentration on a 0.03 mole scale. Another run with 5% reactant concentration was on a 0.01 mole scale. Polymer was isolated by precipitation from benzene and purified by continuous extraction with benzene in a Soxhlet extractor.

4. Polymerization in 1:1 Triphenylphosphine:Dioxane

The procedure was the same as with triphenylphosphine above. The concentration of reactants was 3% and the scale was 0.01 mole.

5. Polymerization in Dioxane

Spectro-grade dioxane, dried over molecular sieves was used. The solution of ligand in dioxane was heated for 45 min and then cooled to 90°C, and an equilmolar amount of diethylzinc was added. Twenty drops of pyridine were added when a small amount of polymer started to precipitate. The solution was heated for about 3 hours and product isolated from benzene.

6. Polymerization of Substituted Imine Derivatives of 5,5'-Bis(salicylaldehydo)methane

Conditions for each of the ligands were:

1. 10% concentration reagents.
2. Pyridine solvent.
3. Scale approximately 0.014 mole.
4. Reaction temperature 90°C.

Solutions of the ligand in pyridine were refluxed on a Dean-Stark trap under oxygen-free nitrogen and then cooled to 90°C. An equimolar amount of diethylzinc was added. The product was isolated by distilling off most of the solvent under nitrogen and adding benzene to the residue to precipitate polymer. The polymer was extracted in a Soxhlet with benzene for several hours to insure removal of pyridine and dried in a vacuum oven.

The products were yellow powders. With the exception of the product from the n-hexyl-substituted ligand, none of this series of ligands gave a polymer that dissolved in pyridine to give a 2% solution, even after extended periods of heating. The product from the isobutyl-substituted ligand was most soluble and also had the lowest softening point.

7. Polymerizations Using Alternate Organo Zinc Compounds

a. Dibutylzinc

A solution of 3.64 g 5,5'-bis(salicyl-N-n-butylimino)methane in 20 ml dry 2-chloropyridine was heated under nitrogen to 120°C for 40 min. Then 1.7940 g (0.0145 mole) of dibutylzinc was added and the solution was raised to 170°C and kept there for 5 hours. The polymer was isolated by removing the solvent at 150°C under vacuum.

b. Diphenylzinc

Diphenylzinc in 10 ml of pyridine was added slowly to 3.495 g of 5,5'-bis(salicyl-N-n-butylimino)methane in 89 ml of pyridine under nitrogen at 120°C. The reaction solution was maintained at 120°C for 5 hours, and then the polymer was isolated by removing the solvent under vacuum at 120°C.

8. Polymerizations with Dimethylcadmium

The polymerizations were run in 10% pyridine. The dimethylcadmium was added at 80°C, and the solution maintained at 80°C for 2 hours, and then heated to reflux and refluxed overnight. In one run with 5,5'-bis(salicyl-N-butylimino)methane polymer isolated at this stage had a softening point of 270-285°C, and a relative viscosity in 2% pyridine solution of 1.33. Addition of 0.01 g excess dimethylcadmium to the reaction mixture at 80°C, followed by reflux overnight, yielded a polymer with relative viscosity of 1.38. A duplicate polymerization yielded polymer with softening point of 193-273°C and a relative viscosity of 1.21 at stage one. Two additions of 0.02 g excess dimethylcadmium, each followed by reflux overnight, gave only slight improvement in the polymeric product.

	Softening Point, °C	Relative Viscosity
Stage 2	204-265	1.26
Stage 3	200-286	1.31

The same procedure was used for condensation with 5,5'-bis(salicyl-N-hexylimino)methane.

Copolymerization with diethylzinc and dimethylcadmium was with a mole ratio of 4 Zn to 1 Cd. Diethylzinc was added to the ligand first, followed immediately by dimethylcadmium.

9. Polymerization of 5,5'-Bis(8-hydroxyquinolino)methane with Diethylzinc

Diethylzinc was added to a solution of 5 g of 5,5'-bis-(8-hydroxyquinolino)methane in 3.5% concentration in pyridine solvent at 90°C. Polymer started to precipitate after about one-half the stoichiometric amount of diethylzinc had been added. The mixture was heated to reflux and then the pyridine was distilled off and replaced with quinoline to make a 3.5% solution. The polymer remained insoluble after refluxing overnight at 237°C. The polymer did not soften under 300°C.

10. Copolymerizations of 5,5'-Bis(8-hydroxyquinolino)methane and 5,5'-Bis(salicyl-N-n-butylimino)methane with Diethylzinc

In the first preparation, both ligands were dissolved in a 10% solution of pyridine and the diethylzinc added at 90°C. For this run, 2 g of the above hydroxyquinoline and 3 g of the above salicylaldehydeimine ligands were used. A polymer precipitated which did not redissolve on heating overnight at reflux.

The insoluble polymer was isolated and the soluble portion recovered by evaporation of the solvent in a vacuum oven. The insoluble fraction weighed 1.88 g, did not soften under 300°C, and its adsorption spectra in the infrared was very similar to the spectra of the polymer resulting from 5,5'-bis(8-hydroxyquinolino)methane. The soluble polymer weighed 3.89 g and softened at 220-236°C. Viscosity of a 2% solution in pyridine was 1.35. This polymer was a copolymer but with only a small amount of the quinoline ligand incorporated in it.

Soluble copolymers were obtained by forming a prepolymer by reaction of excess diethylzinc with 5,5'-bis(salicyl-N-butylimino)methane and then adding the stoichiometric amount of 5,5'-bis(8-hydroxyquinolino)methane to complete the polymerization. A copolymer formed from 25% 5,5'bis(8-hydroxyquinolino)methane and 75% 5,5'-bis(salicyl-N-butylimino)methane had a softening point of 273-282°C and its relative viscosity in 2% concentration pyridine was 1.43.

11. Crosslinking of Chelate Polymers with Aluminum

A solution of 20.2100 g of 5,5'-bis(salicyl-N-n-butylimino)-methane in 350 cc of dry pyridine was heated in the standard polymerization reaction flask under dry, oxygen-free nitrogen and 100 ml of pyridine was distilled off. The solution was cooled to 90°C and one-half of a solution of 5.0297 g of diethylzinc in 20 cc of pyridine was added. The solution was refluxed for 30 min, and cooled to 90°C, and 0.8191 g of triethylaluminum was added. The solution was refluxed 60 min, cooled to 90°C, and the remaining diethylzinc added. Then the solution was refluxed overnight. The solution was brought to peak viscosity (a gel) by adding a pyridine solution of diethylzinc dropwise. (The polymer solution at this stage is not hydrolytically stable.) A pyridine solution containing 0.2418 g of decanedioic acid was added. This caused the solution first to become fluid and then slowly to increase in viscosity on heating, which was done first at 120°C overnight, and then at 237°C overnight when the pyridine was replaced with quinoline. The polymer was isolated in two batches. The first was isolated by evaporation of solvent in a vacuum oven at 150°C/10 mm and softened at 170-204°C. The second was precipitated by adding the quinoline solution to benzene. The solid was washed with benzene. This batch softened at 190-260°C.

12. Condensation of sym-Bis(salicyloxymethyl)tetramethyldisiloxane with Diethylzinc

Two condensations on approximately 0.01 mole scale were carried out in pyridine solution. The stoichiometric amount of diethylzinc dissolved in dry pyridine was added over a period of about 15 min. to the disiloxane compound in dry pyridine at 90°C in an oxygen-free, nitrogen atmosphere. The solutions were refluxed overnight, solvent was distilled, and the residue extracted with ethanol (run 1) or benzene (run 2) and dried in a vacuum oven at 90°C. The insoluble residues did not melt below 300°C. A residue determination with isolation of the zinc component as the chloride and sulfide confirmed the presence of zinc in the polymer.

I. POLYCHELATOTITANODIORGANOSILOXANES

1. Low Molecular Weight α,ω-Dichloropolydimethylsiloxane

Dimethyldichlorosilane (116 g, 0.90 mole), octamethyltetracyclosiloxane (134 g, 0.45 mole), and ≈0.1 g of $FeCl_3$ were mixed well and sealed in a 300-ml stainless steel bomb. The reactants were heated at 200°C for 4 hours, and the α,ω-dichloropolydimethylsiloxane was distilled off immediately after cooling under a N_2 atmosphere. The major fraction had MW = 250 (NMR method). The yield was 80 g.

2. Low Molecular Weight α,ω-Dihydroxypolydimethylsiloxane

Freshly prepared α,ω-dichloropolydimethylsiloxane was hydrolyzed slowly at 0°C after completion of distillation. $NaHCO_3$, H_2O (a four-times mole excess of each with respect to the dichlorosiloxane), benzene and acetone (1 liter of each per mole of $NaHCO_3$) were placed in a 3000-ml Morton flask with stirrer. Dichlorosiloxane in a dropping funnel was added dropwise over a 3/4-hour period at 0°C. At the end of hydrolysis, the benzene-acetone-water mixture was distilled off. The major fraction of the diol had a MW = 320-350 (NMR method).

3. Tetramethyldisiloxane-1,3-diol

Following a procedure described in ref. 38, water (3756 ml, 209 moles) was placed in a 5-liter Morton flask equipped with dropping funnel and stirrer. The flask was placed in a methanol-Dry Ice bath to keep the exothermic reaction at 0°C. NH_3 gas was bubbled into the water as 321 g (2.48 moles) of dimethyldichlorosilane was added slowly until the reddish-blue end point (pH 7.5-8.0) of bromthymol blue and phenolphthalein was reached. This pH was maintained throughout the reaction. After all the dimethyldichlorosilane was added, the stirring was stopped, and 1300 g of NaCl was added to precipitate the dimer. The reaction mixture was cooled at -15°C for 24 hours. White needles (73 g; 45% yield) were obtained from boiling n-hexane extractions and recrystallization (mp 66°C).

To test for autopolymerization, benzene or chloroform as solvent was added to duplicate samples of dimer (0.2 g) in test tubes. The tubes were heated to drive off the solvents and then heated again to 140°C for 5 minutes. Molecular weights were determined by the NMR method.

4. Hydrolysis of α,ω-Dichloropolydimethylsiloxane in Pyridine

α,ω-Dichloropolydimethylsiloxane (66 g) was slowly added to a mixture of 151.6 g (1.82 moles) of pyridine and 34.6 g (1.82 moles) of water. The reactants were kept at 0°C with a methanol-Dry Ice bath. The excess pyridine was distilled off and the remaining diol was kept in a brown bottle. This diol polymerized into a thick fluid within a week.

5. Preparation of Poly(bis-acetylacetonatotitano)dimethylsiloxane Elastomer

To 8.30 g (0.05 mole) of tetramethyldisiloxane-1,3-diol in an Erlenmeyer flask was added ∿50 ml dried 2-propanol and 2.42 g (0.0067 mole) of bis(acetylacetonato)diisopropyltitanium(IV). The mixture was heated to 70°C where slight cloudiness occured. The mixture was filtered through "M" glass fritted filter, and the filtrate was poured into a 3-necked flask with a N_2 atmosphere.

The excess 2-propanol was slowly distilled off under reduced pressure. Then the pot temperature was gradually increased to 125°C where the reaction byproduct, 2-propanol, was distilled off at 0.5 mm Hg pressure. The temperature was kept at 125°C/ 0.5 mm Hg pressure for three hours. The yield was 12.6 g (65.9%).

6. Crosslinking of Poly(bis-acetylacetonato)titanodimethylsiloxane Elastomers

Samples of elastomers weighing about 1 g were placed in 60-ml test tubes with ligands and heated to 140°C in a sand bath for 16 hours.

Ligand	Weight of Elastomer, g	Weight of Ligand, g
Quinizarin	0.970	0.071
Anthrarufin	1.230	0.090

7. Crosslinking of Titanium Polymer with α,ω-Dihydroxypolydimethylsiloxane

Bis(acetylacetonato)diisopropoxytitanium(IV) (0.406 g, 0.0011 mole) was added to each of five 60-ml test tubes. The stoichiometric amount of tetradentate ligands was added to respective tubes to give a Ti/ligand ratio of 2. Benzene (10 ml) was added to each tube and was then placed in a preheated sand bath at 50°C for 16 hours. At the end of this polymerization, 8 g (0.00138 mole) of α,ω-dihydroxypolydimethylsiloxane oligomer was added. The sand bath was heated to 100°C at 15 mm Hg for 2.5 hours, then was heated to 160°C at 1 mm Hg for 65 hours. A control tube was run, but without the addition of any crosslinking ligands.

Ligand	Weight of $Ti(Oipr)_2(Acac)_2$, g	Weight of Ligand, g
2,5-Dihydroxy-p-benzoquinone	0.406	7.75×10^{-2}
Naphthazarin	0.406	1.05×10^{-1}
Quinizarin	0.406	1.32×10^{-1}
Anthrarufin	0.406	1.32×10^{-1}
None (control)	0.406	-

In another run five samples of 1.70 g (0.005 mole) of bis(acetylacetonato)dibutoxytitanium(IV) were used in place of the diisopropoxytitanium complex.

Ligand	Weight of Ligand, g	Weight of α,w-Dihydroxypoly-dimethylsiloxane, g
1,4-Dihydroxyanthraquinone	0.901*	2.7
1,5-Dihydroxyanthraquinone	0.901*	3.0
5,5'-Bis(8-hydroxyquinolino)methane	0.151**	4.0
None (control	- **	3.0

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* Benzene as solvent

** Pyridine as solvent

The appropriate amounts of bis(acetylacetonato)dibutoxytitanium(IV), the ligands, and the solvents in each tube were mixed and heated gradually to 70°C in a sand bath under a N_2 atmosphere. The pressure was reduced in order to distill off the solvents. When most solvents were distilled off, the pot temperature was raised to 75°C for 30 minutes and then cooled. The appropriate amounts of dihydroxypolydimethylsiloxane were added to each tube and the reaction temperature was kept at 100°C and ∿2.5 mm Hg to distill off the reaction byproduct, n-butanol. The temperature was then raised to 135°C and kept there for six hours. The products were grainy and broke up easily. No softening points were taken.

8. Crosslinking of Elastomer with Tetradentate Ligands

Elastomer with Ti/Si ratio 1/15 (0.8 g) and 2.4×10^{-4} mole of ligand were dissolved in ≈5 ml of pyridine under a N_2 atmosphere. The solutions were heated gradually to 100°C under vacuum (0.2 mm Hg). The temperature was gradually raised to ≈150°C after all pyridine was distilled off. The reactants were kept at ≈150°C for five hours. At the end of this period, the polymers were removed and their softening points determined. A control was also run, but without the addition of any crosslinking ligand.

Ligand	Weight, g
Quinizarine-2-sulfonic acid	0.077
4,4'-Diamino-1,1'-dianthrimide	0.111
4,4'-Dibenzamido-1,1'-dianthrimide	0.161
4,5'-Dibenzamido-1,1'-dianthrimide	0.161

9. Crosslinking of Elastomer with the Ligand Tris(2-hydroxyphenyl)-sym-triazine

The titanium elastomer (1.5 g) with Ti/Si ratio 1/15 in toluene was refluxed for 25 hours prior to addition of 0.178 g (0.0005 mole) of ligand to give a Ti/ligand ratio ∿2. This reaction mixture was refluxed for three hours at 112°C. Then the toluene was distilled off and the temperature of the reaction flask was raised to 220°C for 16 hours. The softening range was 160-180°C.

10. Co-condensation of Tetramethyldisiloxane-1,3-diol and Diphenylsilanediol with Bis(acetylacetonato)dibutoxytitanium(IV)

Tetramethyldisiloxane-1,3-diol (4.0 g, 0.024 mole) and diphenylsilanediol (8.34 g, 0.038 mole) to give a phenyl-methyl ratio of 0.8/1 were condensed with bis-(acetylacetonato) dibutoxy titanium(IV) (4.04 g, 0.0103 mole) in ≈150 ml of benzene to give a starting Ti/Si ratio of 1/8.4. The benzene-water azeotrope was first distilled off at reduced pressure. Then the reaction flask was heated to 150°C at 0.5 mm Hg, where the elastomer started to congeal. The temperature was reduced to 145°C at 0.5 mm Hg, and was left at this temperature for 16 hr. The yield was 11 g (74%).

11. Condensation of Diphenylsiloxanediol with Bis(acetylacetonato)-dibutoxytitanium(IV)

Diphenylsiloxanediol (21.63 g, 0.1 mole) 7.84 g (0.02 mole) of bis(acetylacetonato)dibutoxy titanium(IV) and approximately 180 ml of benzene in 500 ml three-necked flask was gradually warmed to 85°C. During gradual warm-up, the water-benzene azeotrope was distilled off, followed by benzene. At 100°C and 0.7 mm Hg all reaction by-product butanol was distilled off. Upon cooling, the reaction hardened to a hard, reddish-orange resin (softening point 35-45°C). Continued heating to 235°C turned the resin to dark brownish orange. This resin is very soluble in common organic solvents. (Ti/Si - 1/5 for starting reagents.)

In another preparation a starting Ti/Si ratio of 1/20 was used and the product has a softening range of 55-60°C.

12. Condensation of Polymethylvinylsiloxanediol with Bis(acetylacetonato)dibutoxytitanium(IV)

a. Preparation of Polymethylvinylsiloxanediol

To fifty grams (0.35 mole) of 99.9% pure (by VPC) methylvinyldichlorosilane in 670 ml of ether was added, with constant stirring over a period of 10 min, a mixture of 29.4 g of NaOH in 539 ml of water and 134 ml of ether. After concentrating the ether and discarding the excess water, an oily product with an average NMR molecular weight of 355 was obtained.

b. Preparation of Elastomer

A mixture of 5 g (0.0144 mole) of polymethylvinylsiloxanediol (0.055 g-atom Si) and 2.60 g of bis(acetylacetonato)dibutoxy titanium(IV) (0.0068) g-atom Ti) was prepared, giving a starting Ti/Si ratio of 1/8 in ∿80 ml benzene. The mixture was heated to 40°C under reduced pressure and the benzene-water azeotrope was distilled off. After all benzene were distilled off, the reactants congealed at 85°C/0.7 mm Hg. The reaction was continued for another hour. A transparent, light yellowish-colored elastomer was obtained. The yield was 5.32 g (∿81%).

In another preparation a starting Ti/Si ratio of 1/14.8 was used and the reaction was run at 110°C for one hour.

13. Preparation of Polychelatotitanomethylphenylsiloxane Elastomer

a. Preparation of Methylphenyldisiloxanediol

Methylphenyldichlorosilane (98.6 g, 0.52 mole) in 750 ml of dry Et_2O was added slowly (3.5 hr) at room temperature to a mixture of 43.4 g (1.09 moles) of NaOH, 800 ml of water, and 200 g of Et_2O in a one-liter Morton flask fitted with stirrer and thermometer. The organic layer was separated and concentrated with air at room temperature and then kept at -15°C for 24 hrs. White crystals were obtained after the addition of isopentane and then were chilled in an acetone-Dry Ice bath. Pure crystals were obtained by recrystallization from benzene-isopentane. Yield was 26.18 g (17.1%) (mp 64-98°C).

b. Preparation of Elastomer

Appropriate amounts of crystalline 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol and bis(acetylacetonato)dibutoxytitanium (IV) (Table 20) in ≈ 150 Ml of benzene each were placed in three-necked, round-bottomed flasks. The benzene was distilled off first under slight vacuum. The temperature was increased to ∿125°C and at this temperature the reaction by-product butyl alcohol was distilled off (∿0.5-1.5 mm Hg). At 165°C the polymers started to congeal and began to turn darker in color. The elastomers were heated for another 2 hours.

Table 20

MOLE RATIOS OF TITANIUM COMPLEXES AND DIOL USED IN THE PREPARATION OF DIFFERENT Ti/Si ELASTOMERS

Ratio Ti/Si	Sample	Amount of Diol		Amount of $Ti(OBu)_2(acac)_2$	
		Weight,g	Moles	Weight,g	Moles
1/4	(77546)	10	0.0401	7.84	0.0200
		(MW = 249.32)			
1/8	(77543)	8.43	0.0290	2.85	0.00726
		(MW = 290.12)			
1/10	(77541)	10	0.0344	2.70	0.00344
		(MW = 290.2)			

14. Crosslinking of Chelatotitanodiorganosiloxane Elastomers

a. With 1,4-Dihydroxyqnthraquinone and 1,5-Dihydroxyanthraquinone

(1) First Method

Two samples of polychelatotitanomethylphenylsiloxane elastomer (1/10 Ti/Si ratio, 4.6 g), in ≈150 ml of redistilled and dried benzene, were refluxed for 2 hr and 0.068 of ligand was added to each to give a Ti/ligand ratio of 2.0. A distilling head was added and the benzene was distilled off. The reaction flasks were heated gradually. At 100, 120, 140, 160 and 180°C, respectively, samples were taken, and their softening ranges and melting points determined.

(2) Second Method

Two samples of 2.6 g each of the copolymers (Me/Ø = 1/0.8 polychelatotitanodimethylsiloxane and polychelatotitanodiphenylsiloxane) were crosslinked with the above two tetradentate ligands (ligand/Ti ratios were all 1/5). The procedures were the same as above except that 0.114 g of ligand was used in each case.

b. With 1,4-Dihydroxyanthraquinone

The following preparations were carried out by essentially the same procedure as those described above. The stoichiometrics are listed in Table 21.

Table 21

Sample No.	Starting Elastomer (Ti/Si)		Weight of Elastomer, g	Weight of Ligand, g	Ligand/Ti Ratio
77546 (70164)	Me, Ø	(1/4)	4.95	0.72	1/2
70166 (70168)	Me, Vi	(1/14.8)	2.51	0.19	1/2
70173 (70174-a)	Me, Vi	(1/8)	2.66	0.21	1/3
70173 (70174-b)	Me, Vi*	(1/8)	2.66	0.21	1/3

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*0.027 g benzoyl peroxide added to reactants.

c. With 5,5'-Bis(8-hydroxyquinolino)sulfone

Polychelatotitanodimethylsiloxane elastomer (1/100 Ti/Si ratio, 1.75 g), dissolved in 150 ml benzene was reacted with 0.16 g of the above bisbidentate ligand dissolved in 50 ml of pyridine to give a Ti/ligand ratio of 1/2. After all solvents were distilled, the reaction flask was gradually heated to 165°C at 1 mm Hg and was kept there for 16 hours. The crosslinked polymer had a softening point of 115°C.

d. With 1,6-Dihydroxyphenazine

Polychelatotitanodimethylsiloxane elastomer (1/15 Ti/Si ratio, 1.5 g) was crosslinked with 1,6-dihydroxyphenazine 0.0782 g, 0.000388 mole). The reaction procedure was the same as with 1,4-dihydroxyanthraquinone.

e. Attempted Crosslinking of Chelatotitanodiphenylsiloxane Elastomer with 1,4-Dihydroxyanthraquinone

1,4-Dihydroxyanthraquinone (0.96 g, 0.0004 mole) was added to 20 g of the above resin after it was dissolved in benzene. The reactants turned deep blue. After all benzene and acetylacetone were distilled, the reactants were allowed to remain at 115°C and 0.5 mm Hg for 16 hours. The product, when cooled was a hard, rather crystalline resin (softening point 45-50°C, mp 50-55°C).

J. LIGAND SUBSTITUTED SILOXANE OLIGOMERS

1. Attempted Preparation of Hydroxyanthraquinone Substituted Dichlorosilane

a. Reaction of Quinizarin with CH_3SiCl_3 in Pyridine

Methyltrichlorosilane was purified by distillation (bp obtained 66.2-67.0, literature 66.4/760 mm). Quinizarin recrystallized from acetic acid (3.0, 0.0125 mole) was placed in a 250-ml flask equpped with thermometer, stirrer and reflux condenser. Dry benzene (50 ml) and dry pyridine (10 ml), and HCl scavenger, were added. CH_3SiCl_3 (1.9 g, 0.0125 mole) in 50 ml of benzene was then added slowly to the above-mentioned mixture. A slight warming of the mixture was noted. After the addition of methyltrichlorosilane was complete, the reaction mixture was refluxed for four hours.

The solvent was then evaporated off under vacuum at 80°C and 0.1 mm pressure to remove all benzene and unreacted CH_3SiCl_3. A brown solid remained. NMR and IR spectra showed the presence of pyridimium chloride. However, no $CH_3-\overset{|}{\underset{|}{Si}}-$group was detected by NMR.

b. Reaction of Quinizarin with CH_3SiCl_3 in Xylene

Quinizarin (6.66 g) in 150 ml dry xylene and methyltrichlorosilane (6 ml) in 50 ml xylene were mixed in a flask under dry nitrogen. The reaction mixture was brought to a slow refluxing of the solvent (137°C), and heating was continued for seven hours. Slow evolution of HCl was noted during heating. The solvent and volatiles were removed under vacuum at 40°C/0.1 mm. A brownish solid remained. IR and NMR spectra of this solid did not show the presence of the desired product.

c. Reaction of Monopotassium Salt of Quinizarin with Methyltrichlorosilane

The monopotassium salt of quinizarin was prepared by reacting quinizarin with $KOCH_3$ in methanol, and was used as such after removing all solvent. A slight excess of quinizarin was used to eliminate excess base in the subsequent reactions.

To 13 g of quinizarin in 200 ml of absolute methanol was added 50 ml of 0.1004M $KOCH_3$ in benzene solution under constant stirring. The color of the solution became dark red. No temperature rise was noted during this addition. The solvent was then removed by distilling off at 64°C and then applying full vacuum at 80-90°C for two hours. Complete removal was effected by allowing the resulting solid to remain overnight at 25°C/0.1 mm. Small amounts of quinizarin sublimed on the walls of the distillation apparatus.

To this salt (0.0542 mole of quinizarin) was added 200 ml of dry ether. The mixture was stirred under N_2 for 20 minutes. The solution was then cooled with ice to 15°C, and 6.0 ml (0.050 mole) of the CH_3SiCl_3 in 50 ml of ether was added dropwise over a 10-minute period. Finally, the reaction mixture was refluxed for four hours.

The solvent was removed by distillation and freed of traces of ether by pumping under vacuum. The remaining red solid was not soluble in any solvents for NMR investigation. The IR spectra showed the presence of the starting solid only with two additional bands at 9.2 and 9.9 μ.

d. Reaction of Methyldichlorosilane with Quinizarin

To 150 ml of dried diglyme in a 1-liter flask containing 6 g (0.050 mole) of quinizarin was added slowly 6 ml of methyldichlorosilane, CH_3SiHCl_2, in 50 ml of dried diglyme. No heating of the reaction mixture was noted during the addition of the chlorosilane or during the evolution of gas. The reaction mixture was heated to 40°C for two hours. After cooling, the ether was removed at 50°C/0.1 mm. A brown solid remained, which was shown by IR to be unreacted quinizarin.

e. Reaction of Quinizarin with Excess CH_3SiCl_3

Three grams of quinizarin that was purified by recrystallization from toluene, was placed in a 250-ml round-bottomed flask equipped with condenser, stirrer, and dry nitrogen inlet. To this, 50 ml of CH_3SiCl_3 was added and the mixture was brought to the refluxing point of CH_3SiCl_3 (bp 67°C). Gaseous HCl evolved constantly. Some of it might have been CH_3SiCl_3 swept out by the nitrogen stream. Refluxing was continued for six days. The excess CH_3SiCl_3 was swept off with N_2, and the red-brown solid that remained behind was freed of volatiles under vacuum. The IR spectrum of this solid showed it to be mainly quinizarin with possible contamination by material containing Si-O bonds.

2. Attempted Preparation of Hydroxynaphthoquinone Substituted Dichlorosilane

a. Preparation of Naphthazarin

Naphthazarin is no longer commercially available. Following a thorough literature search to find the best method of preparing this ligand the procedure of Zahn and Ochwalt (ref. 61) was selected. The reagents, 20 g of maleic anhydride and 22 g hydroquinone, were added to a melt consisting of 200g anhydrous $AlCl_3$ and 40 g NaCl at 180°C and the melt held at 180 to 220°C for one hour. After cooling, it was added to water and HCl added to precipitate crude product. This was extracted into benzene, then extracted back into a Na_2CO_3 solution. It was finally separated out of water after acidification with HCl, and then dried. About 4 g were obtained by this method.

b. Reaction of 5,8-Dihydroxy-1,4-naphthoquinone with CH_3SiCl_3 in $CHCl_3$

Naphthazarin (9.5 g, 0.050 mole) in 200 ml of dried $CHCl_3$ was stirred under N_2 for two hours. Then, 6.0 ml (0.050 mole) of CH_3SiCl_3 in 50 ml of $CHCl_3$ was added slowly at room temperature to the naphthazarin mixture. The temperature of the reaction mixture was brought to 57°C (bp of $CHCl_3$), and was refluxed for four days, during which time evolution of HCl was noted.

The solvent was distilled off under vacuum, leaving a purple colored solid soluble only in acetone. NMR and IR spectra showed it to be decomposition product only.

c. Reaction of the Monopotassium Salt of Naphthazarin with CH_3SiCl_3

The monopotassium salt of naphthazarin was prepared as follows: 11 ml of 1.004 m $KOCH_3$ solution, diluted to 50 ml with benzene, was added slowly to 2.220 g of naphthazarin in ≈50 ml DMF. The mixture turned purple with the appearance of a similarly colored solid which separated out of solution. The solid was then freed of DMF and benzene by distillation under vacuum at 75°C/0.5 mm. Final drying of the potassium salt was accomplished by direct pumping at 25°C/0.1 mm overnight. Dry ether (150 ml) and then 2 ml CH_3SiCl_3 in 50 ml ether was added to 3.05 g of this salt under N_2. The resulting solution was refluxed for five hours and solvent was evaporated. The IR spectra of the residue was identical to that of the potassium salt of naphthazarin.

3. Reaction of the Monosodium Salt of Bis(8-hydroxyquinolino)methane with CH_3SiCl_3

Three grams of the sodium salt of bis(8-hydroxyquinolino)methane was prepared as follows: 2.96 grams of ligand was placed in 100 ml of dry DMF and 82.0 ml of 0.1222N $NaOCH_3$ (0.01 mole) added to the DMF mixture under stirring. The yellow color became stronger, indicating salt formation. The yellow solid was filtered off, washed with DMF and ether and dried at 30°C under vacuum for three hours.

To this solid in a 500-ml round-bottomed flask was added 150 ml of dry ether. To this mixture was added slowly 10 ml of CH_3SiCl_3 in 50 ml of ether while the mixture was constantly stirred. A whitish precipitate formed along with the yellow solid. No heating of the mixture was noted during the addition. Stirring was continued for 12 hours. The volatiles were pumped off under vacuum at 50°C.

The IR spectra of the free ligand, its monosodium salt, and the product in question were taken. The spectrum of the product was not very much different from that of the ligand. However, no Si-O band was observed in the 9-10 micron region. The insolubility of this product in several solvents made it impossible to free it from the NaCl that might have formed during the reaction. Product was shown by IR to be the result of decomposition of starting material.

4. Attempted Preparation of Bis(salicyl-N-butylimino)methane Silicon Modified Ligand

Three different reactions were carried out. Two employed the sodium salt of the ligand, and one the free ligand itself.

a. First Method

Bis(salicyl-N-butylimino)methane (7.33 g) was dissolved in benzene and 0.78 g of NaH-Nujol dispersion was added to the mixture. After stirring for one hour, the small amount of precipitate that had formed was filtered and the bright yellow solution was transferred to another flask. To this, 3.0 g (2.4 ml) of CH_3SiCl_3 in 200 ml of dried benzene was added, whereupon an immediate precipitate formed. Stirring of the reaction mixture was continued overnight.

The precipitate was filtered off, washed with benzene, and dried in a vacuum. The IR spectrum of the solid showed a band at 3.5μ due to imine hydrochloride and bands at 8μ ($Si-CH_3$) and 9-10μ (Si-O).

Some of this solid was treated with pyridine to decompose any amine hydrochlorides. It was then evaporated to dryness and extracted with benzene. The IR spectrum of this material showed a band at 9-10μ for Si-O, but was radically different from that of the Schiff base.

b. Second Method

A second experiment involved adding the CH_3SiCl_3 to the sodium salt of the Schiff base all at once. For this, 7.33 g of the Schiff base was employed and was reacted with 0.778 g of NaH-Nujol dispersion in 150 ml of benzene. A yellow precipitate formed. To this, 3.14 g (5.0 ml) of CH_3SiCl_3 in 50 ml of benzene was added quickly. A precipitate formed immediately. After filtration, washing with benzene, and drying under vacuum it had the same spectrum as that obtained by the first method, above.

c. Third Method

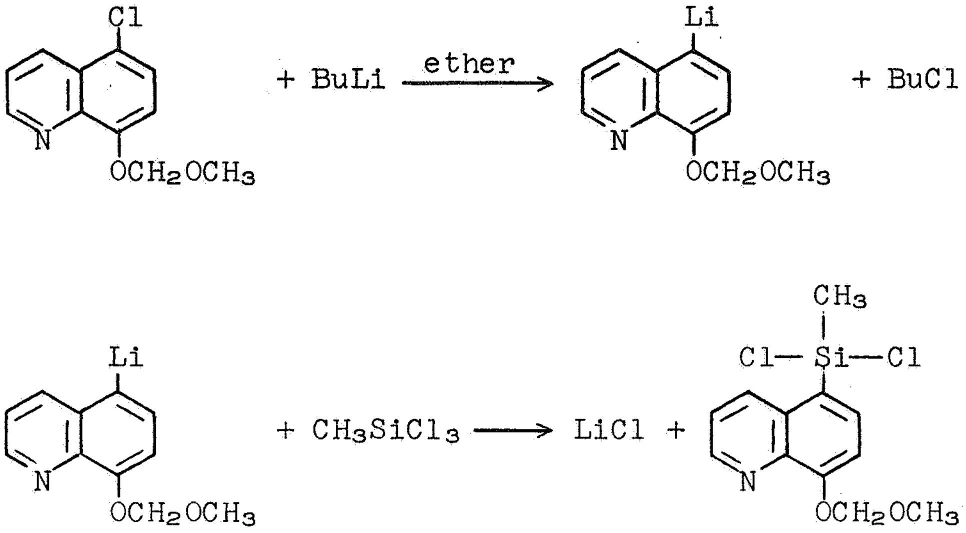
A third experiment utilized the free ligand instead of its sodium salt. For this, 7.33 g of Schiff base was dissolved in 250 ml of dried benzene, and 3.0 g (2.4 ml) of CH_3SiCl_3 dissolved in 50 ml of benzene was added to the solution under constant stirring. A yellow, gummy precipitate formed at the walls of the reaction flask along with a copious precipitate. The precipitate was filtered off and washed with benzene. Its IR spectrum after drying was similar to that obtained by both previous methods, above.

This precipitate after treatment with pyridine was evaporated to dryness. Treatment with benzene gave a benzene-soluble fraction. The insoluble fraction showed an amine hydrochloride band at ≈3.5μ and might be the hydrochloride undecomposed with pyridine.

The benzene-soluble fraction, after being taken to dryness, was extracted with hexane. The hexane-soluble material, after removal of the solvent, had an IR spectrum similar to that of the free Schiff base ligand. The hexane-insoluble portion had a broad band at 9-10 μ, which could be due to formation of polymer containing Si-O bands.

In addition, the gummy material that had originally formed on the walls of the reaction flask after drying was shown to have IR bands at 3.5 μ due to $\equiv NH^+Cl^-$ and at 9-10 μ due to Si-O.

5. Attempted Preparation of Methyldichlorosilyl-8-hydroxyquinoline Methoxymethyl Ether



a. Reaction 1

n-Butyl lithium (3.2 g) in hexane was added to 400 ml of sodium-dried ether cooled to -40°C by means of a CO_2-acetone external bath. When 5-chloro-8-hydroxyquinoline methoxymethyl ether (11.2 g) in 150 ml of ether was added to the above-mentioned solution, a dark red color developed. The temperature was maintained between -40 and -35°C. Then, 5.8 ml of CH_3SiCl_3 in 25 ml of ether was added quickly with vigorous stirring. A yellow precipitate formed as the mixture was allowed to reach -10°C. Then the temperature was allowed to reach 25°C. The solvent was evaporated off under vacuum. The product of this reaction was very soluble in the most common solvents. NMR spectra indicated, however, that the product did not contain the silicon-quinoline linkage.

b. Reaction 2

An additional reaction like the one described above was run, but all steps were carried out at 25°C instead of at -40°C. A brownish solid was obtained, very soluble in solvents, but again the desired product was not obtained.

6. Preparation of Heptamethylsalicyloxymethylcyclotetrasiloxane

a. Preparation of Heptamethylchloromethylcyclotetrasiloxane

This compound was prepared using the procedure of Krieble and Elliott (ref. 62) by bubbling dry chlorine into 251.9 g (0.85 mole) of octamethylcyclotetrasiloxane in a nitrogen atmosphere in a one-liter, three-necked flask cooled by an ice bath and equipped with a large magnetic egg for stirring, a gas inlet tube extending to the bottom of the flask, a reflux condenser and thermometer, and a large center neck which held a quartz tube and a G.E. 4-watt germicidal lamp. The effluent from the condenser led to a hydrogen chloride scrubber containing water.

The chlorine flow rate was adjusted so that the maximum temperature was 36°C. After reacting for 30 minutes, the system was flushed with dry nitrogen for 10 minutes. The reaction mixture showed a 22.9 g gain in weight.

The reaction mixture was washed and centrifuged with two 200-ml aliquots of water and clarified with Fuller's earth. The mixture was then distilled under reduced pressure using a one-foot column packed with glass helices. After recovering 89.1 g of starting material, 56.1 g of product was recovered at 70°C/3.0 mm Hg pressure.

Analytical results showed a purity of 91.5% by VPC with no starting material present. NMR and IR were consistent with the structure.

b. Preparation of Heptamethylsalicycloxymethylcyclotetrasiloxane

The procedure of Merker and Scott (ref. 56) for preparation of sym-bis(salicyloxymethyltetramethyldisiloxane) was used. A solution of heptamethylchloromethylcyclotetrasiloxane (33.1 g) in 50 ml of dimethylformamide was added to sodium salicylate (17.5 g) in 50 ml of dimethylformamide, and the solution was heated at reflux for about 3 hours. Sodium chloride was removed by filtration, an equal volume of benzene was added to the filtrate, and the solution was washed with five 50-ml portions of water. The benzene layer was dried over $MgSO_4$ and solvent was evaporated. The residue was an oil that did not distill below 125°C/0.25 mm. The oil was cooled and treated with sodium carbonate solution by stirring for one hour, taken up in benzene, and recovered by removing solvent. The NMR analysis and infrared spectrum of the oil indicated the expected product. A VPC of the oil showed 3 major peaks of 47.2, 31.4 and 7.7%. These data indicated that the oil is a mixture of three cyclic siloxanes with the salicylate substituent on each.

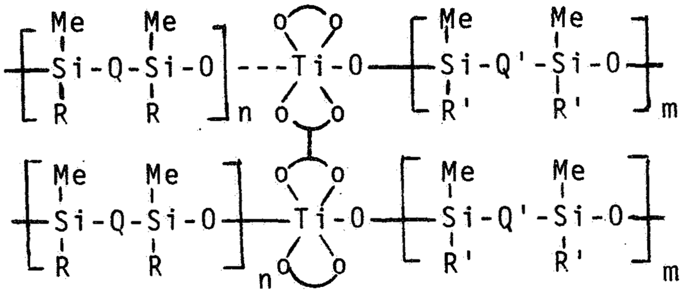
A sample of heptamethylchloromethylcyclotetrasiloxane was refluxed in dimethylformamide overnight and recovered by the same procedure used above. The VPC of the recovered product was unchanged, indicating no isomerization.

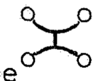
K. CONDENSATION OF p-ARYLENE-BIS(DIORGANOSILANOLS) WITH BIS-(ACETYLACETONATO)DIBUTOXYTITANIUM

1. General Procedure

The general procedure for the preparation of this class of polymers is as follows: The weighted amount of p-arylene-bis(diorganosilanol) monomer was dissolved in approximately 75 ml of dry benzene. Then the appropriate amount (depending on the desired Ti/Si atom ratio) of bis(acetylacetonato)dibutoxy titanium (IV) was added. The reactants were allowed to reflux from 1-2 hr. Then the solvents were distilled off at temperatures no greater than 80°C under vacuum. The reactants were then heated at ∿120°C under vacuum from 1-3 hr. The products were generally light yellow or faint green, crystalline materials melting from below room temperature to over 100°C. Table 21 summarizes the results.

2. Crosslinking of Polychelatotitano-p-arylene-bis(diorganosiloxane)



where  is a bis-bidentate ligand or a tetradentate ligand capable of undergoing ligand exchange reaction.

The ligand exchange crosslinking reactions were carried out by first dissolving the polychelatotitano-p-arylene-bis(diorganosiloxane) in dry benzene. Then the appropriate amount of crosslinking ligand was added. After refluxing from 1-20 hours, the solvent was distilled off *in vacuo* and the reactants heated to 120°C for 1-20 hours. Table 22 summarizes the reaction conditions, stoichiometry, and the melting range of these crosslinked polymers.

3. Preparation of Phosphorus Containing Polychelatotitanodiorganosiloxane and Crosslinking of Same

The condensation as well as the crosslinking reactions were carried out as described for previous polymer systems.

In a 3-necked, 250-ml flask, fitted with distilling head, and thermometer, was added 4.6 g (0.00904 mole) of acetylacetonatodibutoxydiphenylphosphinatotitanium (IV), 4.08 g (0.0181 mole) of p-phenylene-bis(dimethylsilanol), and ∿100 ml of anhydrous benzene. The reactants were heated to reflux temperature (82°C) until dissolved. The solvents were then distilled off and the reactants left at 80°C at 0.5 mm for 2 hours. The yield was 7.13 g (97%) (mp 35-48°C).

Table 22 summarizes the crosslinking of these polymers.

4. Preparation of Boron-Containing Polychelatotitano-p-Arylene-bis(diorganosiloxane)

a. Reaction of p-Phenylene-bis(methylphenylsilanol) and Trimethoxy Boroxin

To 2.00 g (0.00572 mole) of p-phenylene-bis(methylphenylsilanol), dissolved in ∿100 ml of dry benzene under N_2 flush in a 3-necked flask, was added from an eye dropper 0.332 g (0.00191 mole) of trimethoxy boroxin. The reactants were heated to reflux temperature for 2 hr. The solvent was then removed under reduced pressure, and the temperature was raised to 118°C/0.15 mm Hg for 1.75 hours. The product was white crystalline material with melting range of 27 to 34°C. The yield was 2.02 g (66.7% of theoretical yield).

b. Reaction of Polychelatotitanosiloxane with Trimethoxy Boroxin

To 0.935 g of polychelatotitanosiloxane polymer, containing 0.00154 g-atom Ti, dissolved in ∿150 ml dry benzene in a 3-necked flask, was added 0.089 g (0.000513 mole) of trimethoxy boroxin from an eye dropper. The solution immediately turned light orange. After the solvent was distilled off, the temperature was raised to 95°C/0.3 mm Hg for 3 hr.

The yield of the orange product was 1.01 g (∿99%) (mp 44-85°C).

Table 22

CROSSLINKING AND PHYSICAL PROPERTY OF PHOSPHORUS CONTAINING POLYCHELATOTITANO-p-PHENYLENE-BIS(DIORGANOSILOXANE)

Sample	Wt of Polymer Used, g	Crosslinking Agent	Wt of Crosslinking agent used, g	Ligand/Ti Mole Ratio	Reaction Condition Temp. °C	Reaction Condition Press mm Hg	Reaction Condition Time hour	Melting Range, °C
85229	0.50	1,4-DHAQ	7.44×10^{-2}	1/2	112	0.3	3.0	70-145
85230	0.50	1,4-DHAQ	1.49×10^{-1}	1/1	100	0.4	1.5	-165
85231	0.50	5,5'-BSNBM	2.26×10^{-1}	1/1	110	0.14	3.0	70- 96
85232	0.50	"	1.70×10^{-1}	0.75/1	110	1.0	1.5	45- 94
85233	0.50	5,5'-B8HQM	4.52×10^{-2}	1/4	110	1.1	4.0	75-126
85234	0.50	5,8-DHNQ	5.9×10^{-2}	1/2	115	1.5	3.0	71-110
85237	0.50	5,5'-BSAM	1.59×10^{-1}	1/1	115	1.0	5.0	94-155
85238	0.50	"	7.9×10^{-2}	1/2	112	0.15	3.0	77-110

c. Reaction of Bis(acetylacetonato)dibutoxy Titanium(IV) and Trimethoxy Boroxin

To 2.00 g (0.00512 mole) of bis(acetylacetonato)dibutoxy titanium (IV) dissolved in hot benzene under N_2 was added 0.44 g (0.00256 mole) of trimethoxy boroxin from an eye dropper. The reactants were warmed gradually to reflux temperature and kept there for 16 hr. The solvent was then distilled off, and the reactants left at room temperature at 1.9 mm Hg for 8 hr. The product was an amber-colored, viscous liquid.

d. Crosslinking of Boron-Containing Polychelatotitanosiloxane Polymers

The procedure for the crosslinking reaction is the same as reported earlier. Table 23 summarizes the results.

5. Polymerization of p-Phenylene-bis(methylphenylsilanol) with Bis(acetylacetonato)dibutoxytitanium(IV)

a. First Reaction

p-Phenylene-bis(methylphenylsilanol) [2.5 g (0.00715 mole) in ≈ 100 ml of benzene was placed in a 250-ml, 3-necked flask fitted with distilling head, thermometer, and Teflon sleeves. After complete dissolution of the silanol, 1.395 g (0.00358 mole) of bis(acetylacetonato)dibutoxy titanium (IV) was added. The benzene was then distilled off under reduced pressure and the reactants were left at 80°C/0.8 mm for one hour. The yield was 2.95 g (87.5%) and the melting range of the product was 50-68°C.

b. Second Reaction

The above product (0.5 g) was dissolved in hot xylene and refluxed for 18 hours at 136°C. The solution became copper colored at reflux temperature and deep brown at the end of 18 hours. Its molecular weight by vapor phase osmometry was 3600.

c. Third Reaction

The remaining product was further polymerized at 150°C/0.7 mm for 16 hours. The melting range was increased to 60-130°C. It had both a benzene soluble and a benzene insoluble fraction.

Table 23

CROSSLINKING OF BORON CONTAINING POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANSILOXANE)

								Reaction Condition			
Sample	Intermediate	Mole Ratio of Intermediate	Weight of Intermediate used, g	Cross-linking Agent	Ligand/Ti Mole Ratio	Weight of Polymer Used, g	Weight of Ligand Used, g	Temp. °C	Press. mm Hg	Time, Hr	Melting Range, °C
85292 (85285)*	(MeØSiOH)$_2$Ø	3	2.00								
	(OBOMe)$_3$	1	0.33	1,4-DHAQ	1/2	0.60	0.068	120	0.15	2	40-75
	Ti(OBu)$_2$(acac)$_2$	1.5	1.12								
85294 (85285)*	"	"	"								
	"	"	"	5,8-DHNQ	1/2	0.60	0.054	123	4.00	1	58-75
	"	"	"								
85293 (85285)*	" "	"	"								
	"	"	"	5,5'-BSNBM	1/1	0.60	0.207	118	2.00		68-40
	"	"	"								
87018 (87016)*	(Me$_2$SiOH)$_2$Ø	6	1.70								
	Ti(OBu)$_2$(acac)$_2$	3	1.47	1,4-DHAQ	1/2	0.86	0.197	82	1.00	4	80-160
	(OBOMe)$_3$	1	0.09								
85295 (85288)*	(Me$_2$SiOH) Ø	3	2.0								
	(OBOMe)$_3$	1	0.51	1,4-DHAQ	1/2	0.60	0.088	120	3.00	2	45-90
	Ti(OBu)$_2$(acac)$_2$	1.5	1.75								
85296 (85288)*	"	"	"								
	"	"	"	5,5'-BSNBM	1/1	0.60	0.269	120	2.50		70-140
			"								

Table 23

(Continued)

CROSSLINKING OF BORON CONTAINING POLYCHELATOTITANO-p-ARYLENE-BIS(DIORGANOSILOXANE)

Sample	Intermediate	Mole Ratio of Intermediate	Weight of Intermediate used, g	Cross-linking Agent	Ligand/Ti Mole Ratio	Weight of Polymer Used, g	Weight of Ligand Used, g	Reaction Condition Temp, °C	Reaction Condition Press. mm Hg	Reaction Condition Time, Hr	Reaction Condition Melting Range, °C
85287 (85284)*	Ti(OBu)$_2$(acac)	2	1.00								
	(OBOMe)$_3$	1	0.22	1,4-DHAQ	1/2	0.60	0.069	126	0.10	2.5	70-110
	(MeØSiOH)$_2$Ø	4	1.79								
85291 (85284)*	"	"	"								
	"	"	"	5,8-DHNQ	1/2	0.60	0.056	120	0.50	1.0	50-75
	"	"	"								
85289 (85284)*	"	"	"								
	"	"	"	5,5'-BSNBM	1/1	0.60	0.214	120	0.30	2	50-155

*Prepolymer

6. Condensation of Polychelatotitanosiloxane with Bisphenol-A

a. Co-polymerization of Polychelatotitanosiloxane with Bisphenol-A

Polychelatotitanosiloxane (Ti/Si = 1/4), 3.29 g (containing 0.00348 g-aton Ti), was dissolved in hot benzene then 0.863 g (0.00121 mole) of bisphenol-A was added. After refluxing for 1.5 hours, the solvents were distilled off under reduced pressure. The reactants were kept at 90°C/0.7 mm for 1.5 hours. Melting range of the polymer is 30-55°C.

b. Crosslinking of Polychelatotitanosiloxane-bisphenol-A Copolymer

To 1.0 g (0.000838 g-atom Ti) of the above copolymer (dissolved in hot benzene), was added 0.0983 g(0.000409 mole) of 1,4-dihydroxyanthroquinone. After refluxing for 1.0 hour, the solvents were distilled off and the reactants left at 120°C/0.4 mm for 2.5 hours. Melting range of the product is 40-140°C.

7. Polychelatotitanosiloxanes with 1,7-Bis(dimethylhydroxysilyl)-m-carborane

a. Condensation of 1,7-Bis(dimethylhydroxysilyl)-m-carborane with Bis(acetylacetonato)dibutoxytitanium(IV)

1,7-Bis(dimethylhydroxysilyl)-m-carborane (0.5 g, 0.0017 mole) and bis(acetylacetonato)dibutoxytitanium (IV) (0.67 g, 0.0017 mole) were dissolved in benzene at reflux temperature. After 15 minutes, the solvent was removed under reduced pressure, and the reactants were heated to 120°C/0.9 mm for 3.5 hours. The yield was 1.07 g (≈100%; melting range = 25 - 40°C).

b. Condensation of Polychelatotitanosilylcarborane with p-Phenylene-bis(methylphenylsilanol)

Polychelatotitanosilylcarborane (1.07 g containing 0.0017 g-aton Ti) was dissolved in hot benzene with p-phenylene-bis(methylphenylsilanol) (0.598 g, 0.0017 mole). After refluxing for 15 minutes, the solvents were removed under reduced pressure and the reactants were heated to 110°C/0.7 mm for 4 hours. The yield was 0.97 g, and the melting range was 30 - 40°C.

c. Crosslinking of Polychelatotitanosilylcarborane with 1,4-Dihydroxyanthraquinone

The above polymer (0.485 g, 0.00086 g-aton Ti) was dissolved in hot benzene. 1,4-Dihydroxyanthraquinone (0.103 g, 0.0004 mole) was added. After refluxing for 15 minutes, the solvent was removed under reduced pressure, and the reactants were heated to 115°C/0.8 mm for 1.5 hours. The melting range was 25 - 64°C.

d. Condensation of Polychelatotitanosiloxane with 1,7-Bis-(dimethylhydroxysilyl)-m-carborane

Polychelatotitanoheterosiloxane (0.2 g, 0.00022 g-aton Ti), prepared from a four-to-six mole ratio of p-phenylenebis(methylphenylsilanol) and 4,4'-bis(hydroxymethylphenylsilyl) biphenyl, was dissolved in hot benzene. 1, 7-Bis-(dimethylhydroxysilyl)-m-carborane (0.013 g, 0.000044 mole) was added and the solvent was removed under reduced pressure after refluxing for 15 minutes. The reactants were heated to 117°C/0.7 mm for 1 hour, 10 minutes.

e. Crosslinking of Polychelatotitanoheterosilylcarborane with 5,5'-Bis(salicyl-N-butylimino)methane

The procedure is the same as reported previously for other crosslinking reactions. The product polymer from (93091), containing 0.00022 g-atom Ti, was dissolved in hot benzene with 0.0797 g (0.00022 mole) of 5,5-bis(salicyl-N-butylimino)methane. After refluxing for 15 minutes, the solvent was removed under vacuum. The reactants were then heated to 121°C/0.8 mm for 1 hr. The melting range was 70-80°C.

8. Condensation of Bis(acetylacetonato)dibutoxytitanium(IV) with p-Phenylene-bis(methylphenylsilanol), Si:Ti = 8:1

Bis(acetylacetonato)dibutoxytitanium (1.622 g, 0.0041 moles) in 20 ml dry benzene was added dropwise to a refluxing solution of 5.798 g (0.0165 moles) p-phenylenebis(methylphenylsilanol) in 125 ml benzene. The solvent was distilled and the residue was heated at 125°C/0.07 mm for 1.5 hours.

9. Condensation of Polyphenylene-bis(methylphenylsiloxanes) with Bis(acetylacetonato)dibutoxytitanium(IV)

a. By Reaction of p-Phenylene-bis(methylphenylsilanol) with Bis(methylamino)methylphenylsilane

p-Phenylene-bis(methylphenylsilanol) (5.215 g, 0.0149 mole) and 2.294 g (0.0127 mole) bis(methylamino)methylphenylsilane were dissolved in dry benzene under nitrogen. The benzene was then removed by freeze-drying and the residue was heated at 75°C/0.5 mm. for 2 hours. The molecular weight of the residue was determined by vapor phase osmometry in benzene and found to be 13,500.

b. By Reaction of p-Phenylene-bis(methylphenylsilanol) with Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane

A benzene solution of 7 g (0.02 mole) p-phenylene-bis(methylphenylsilanol) and 3.76 g(0.016 mole) heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane was heated to reflux and the benzene was distilled. The residue was heated at 150°C overnight and then at 150°C/0.2 mm for 1.5 hrs. The product was a liquid that had 3050 molecular weight by vapor phase osmometry.

c. Reaction of Silanediol Prepolymer No. 98460 with Bis(acetylacetonato(dibutoxytitanium(IV)

A 2.36 g sample of 98460 prepolymer and 0.273 g bis(acetylacetonato)dibutoxytitanium(IV) were dissolved together in benzene. The solvent was distilled and the residue left at 120°C/0.2 mm for 2 hrs. Properties of this polymer are given in Table 17. Polymer 98465 was also prepared by this method.

L. PREPARATION OF POLYTITANOSILOXANES BY REACTION OF TETRAISOPROPOXYTITANIUM WITH SILANEDIOLS

1. Direct Reactions

a. With p-Phenylene-bis(methylphenylsilanol)

A dry benzene solution containing 1.302 g (0.00458 mole) tetraisopropoxytitanium was added with stirring to 3.206 g (0.00916 mole) p-phenylene-bis(methylphenylsilanol) dissolved in 150 ml benzene and under nitrogen. The benzene was removed by freeze-drying and the residue was heated at 80°C/0.2mm for 2 hours. The residue softened at 120-230°C. It was washed with ether to remove low molecular weight fractions. The ether insoluble fraction was 97% of the crude product; it was completely soluble in benzene and had a molecular weight of 23,500.

Similar preparations on a double scale yielded polymers with molecular weights of 7400 (98475) and 11,000 (98492).

b. With Bis(hydroxymethylphenylsilyl)biphenyl Ether

A procedure similar to a, above, was used with 1.6108 g tetraisopropoxytitanium and 5.0002 g bis(hydroxymethylphenylsilyl)biphenyl ether. The polymer started to precipitate slowly after the reagents were mixed. It did not redissolve when the mixture was heated to reflux. The mixture was left at room temperature overnight and then the polymer was isolated as above. Less than 5% of the crude product was soluble in benzene.

c. With p-Phenylene-bis(methylvinylsilanol)

A dry benzene solution containing 3.9490 g (0.01389 mole) tetraisopropoxytitanium was added to a stirred benzene solution of 0.6958 g (0.02778 mole) p-phenylene-bis(methylvinylsilanol) and 8.7650 g (0.0250 mole) p-phenylene-bis(methylphenylsilanol) at 40°C. The benzene was removed by freeze-drying and the residue heated at 108°C/0.35 mm for 2 hours. The properties of the product are given in Table 18.

d. With Excess p-Phenylene-bis(methylphenylsilanol)

Tetraisopropoxytitanium (1.842 g, 0.00646 moles) was added with stirring to a solution of 4.646 g p-phenylene-bis(methylphenylsilanol) in dry benzene under nitrogen. The benzene was removed by freeze-drying at 0.2 mm and the residue was heated at 75°C/0.2 mm for 2 hrs. The crude product (3.0 g) was pulverized and washed with three successive portions of ethanol. The first wash contained 1.15 g, the second 0.06 g and the last 0.17 g.

2. Polychelatotitanosiloxane from the Condensation of p-Phenylene-bis(methylphenylsilanol) with Tetraisopropoxytitanium and Bis(acetylacetonato)diisopropoxytitanium(IV)

A solution of 1.2262g (0.00431 mole) tetraisopropoxytitanium in 5 ml dry benzene was added rapidly, under nitrogen, with stirring to 5.039g (0.01437 mole) p-phenylene-bis(methylphenylsilanol) in 100 ml benzene at 50°C. To this was added rapidly a solution of 0.4088g (0.00144 mole) tetraisopropoxytitanium and 1.0474g (0.00287 mole) bis(acetylacetonato)diisopropoxytitanium in 10 ml benzene. After distilling about three-quarters of the benzene at atmospheric pressure, the remainder was removed by vacuum. The dried solid weighed 6.1g. After triturating four times with diethyl ether, the dried solid weighed 4.5g and had a softening range of 190-205°C. This solid was completely soluble in benzene. Its molecular weight was 4390 by vapor pressure osmometry.

3. Polychelatotitanosiloxane from Bis(acetylacetonato)diisopropoxytitanium(IV) and Phenylsilanetriol

a. Condensation Reaction

Bis(acetylacetonato)diisopropoxytitanium (10.9290g, 0.0300 mole) in 30 ml dry benzene was added to a stirred slurry of phenylsilanetriol (3.1244g, 0.0200 mole) in 200 ml dry benzene at room temperature. After stirring for 3 hours, the benzene was removed under vacuum from the resulting clear yellow solution. The dried solid product weighed 10.0g and was soluble in absolute ethanol.

A portion of this product (6.0g) was refluxed in dry benzene for 3 hours. The benzene was distilled at atmospheric pressure and the residue was dried under vacuum for 16 hours. The residue was 5.5g of yellow solid that softened between 90-120°C. It had a molecular weight of 1010 by vapor phase osmometry and was soluble in benzene and ethanol.

b. Ligand Exchange Reactions

5,5'-Bis(salicyl-N-butylimino)methane (1.0997g; 0.003 mole) and polymer 108929 (1.0450g; 0.003 g-atom Ti) were dissolved in 50 ml of dry benzene and heated to reflux. The benzene was distilled over 30 minutes and the residue dried *in vacuo*. It did not soften up to 300°C.

Polymer 108929 (0.5225g; 0.00015 g-atom Ti) and 5,5'-bis(salicyl-N-butylimino)methane (0.5499g; 0.0015 mole) were dissolved in 15 ml dry benzene and freeze-dried for 16 hours. This yielded a homogeneous solid that initially softened at 45 to 80°C and then rehardened above about 85°C.

4. Preparation of Polytitanosiloxanes with SiH Substituents

The general procedure used to prepare these polymers is illustrated using polymer 105622, as follows. A 1.5 g sample of 105622 and 1.0 g diphenylsilane were dissolved in 125 ml of anhydrous benzene. The benzene was distilled at atmospheric pressure and then the residue was heated at 60°C at 0.5 mm pressure for 22 hours to remove excess diphenylsilane. The infrared spectra of the residue has a large absorption at 2130 cm^{-1} that is characteristic of the SiH group. The absorption characteristics of the vinyl group have about 10% of their initial intensity.

M. TEST METHOD AND SPECIMEN PREPARATION FOR DETERMINATION OF ADHESIVE STRENGTH OF RESINS

1. Test for Tensile Shear Strength

Test specimens of resins on either 321 stainless steel or 2014-T6 aluminum were prepared and tested to conform to test method ASTM D1002-64. An Instron Tensile Tester, Model TT-C with self-aligning grips, was used at a rate of 0.05 inch per minute (1400 psi/min.). Tests at -100, 150, 200, and 250°C were done in a temperature-controlled chamber fitted to the Instron.

2. Cleaning Treatments

a. Standard Aluminum Etch

Aluminum strips previously degreased by immersion in trichloroethylene were cleaned by immersion for 10-15 min. at 65-70°C in a bath consisting of:

> 30 parts by weight distilled water; 10 parts by weight H_2SO_4 (sp gr 1.84); 1 part by weight sodium dichromate.

The strips were then rinsed in running distilled water for 10 minutes and dried at room temperature.

b. Titanium Acid Etch

Titanium strips were dipped in a solution having the composition 37% HCl/85% H_3PO_4/49% HF (20:2:1 by volume) for 120 seconds at ambient temperature. Residual acid was wached from the strips with distilled water and ether.

c. Titanium Surface Treatment with Chlorine Trifluoride

These strips were supplied by Dr. S. P. Terpko who prepared them by the procedure described in ref. 5.

3. Fabrication of Adhesive Test Specimens

a. Optimized Titanium Chelate Polymer Formulations

(1) Standard Cure

(a) Dissolve 71 parts by weight of plasticized titanium chelate polymer [A]* and 29 parts by weight phenylsilanetriol in 400 parts by volume of acetone.

(b) Remove the acetone quickly by evaporation at about 1 mm pressure in a vacuum desiccator.

(c) Preheat the freshly etched aluminum samples to 170°C and immediately coat both joint surfaces, using 0.1 g of formulation per square inch. The formulation melts and can be smeared evenly over the surface with a flat spatula.

(d) Precure the open surfaces 3 minutes at 170°C. Couple the joints and press at 1500 psi for 30 minutes at 170°C. Complete the cure at 170°C for 65 hours.

(2) Accelerated Cure

(a) Mix 71 parts by weight of plasticized titanium chelate polymer [A]*, 29 parts by weight phenylsilanetriol, and 1 part by volume of a 3% benzene solution of A-1100 in 400 parts by volume of acetone.

(b) Remove the acetone quickly as in 2 above and use immediately.

(c) Coat aluminum surface as quickly as possible as in 3 above.

(d) Couple the joints immediately and press at 170°C at 2500 psi for 30 minutes. Complete the cure at 170°C for 24 hours.

b. Solution Application of Titanium Polymers

The crosslinking agent was dissolved in an 10% solution of "B" stage resin. The resultant blend was applied as a thin film to the aluminum test specimens on a hot plate, a layer of resin and crosslinking agent being built up by 2-5 coats of blend. After the solvent was removed, the test strips were paired and cured in the Carver press at 160°C.

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*[A] is 80 parts by weight titanium chelate polymer derived from 5,5'-bis(salicyl-N-butylimino)methane and p-phenylene-bis-(methylphenylsilanol) and 20 parts by weight 4,4'-bis(methylphenylhydroxysilyl)biphenyl ether.

c. Powder Application of Titanium Polymers

Weighed quantities of resin and crosslinking agent were mixed and ground together in a glass mortar. Approximately 0.1 g of mix was applied to the test area of one Al strip held in the sample jig. The second Al strip was placed on top, and the pair was then cured in the heated Carver press at 160°C.

d. Application of Zinc Chelate Polymers

Test specimens of zinc chelate polymers were prepared on 321 stainless steel. Two methods of coating specimens were used. In one method, the specimens were heated in an inert atmosphere, and resin powder was melted on their surface. The resin was spread with a doctor blade, and specimen pairs were joined and cooled under slight pressure.

In the second method, specimens were precoated with resin from a pyridine solution. After solvent was evaporated, specimen pairs were joined and heated to the melting point of the resin under pressure and finally cooled under pressure.

e. *In Situ* Crosslinking of Polychelatotitanosiloxanes

The general procedure used is illustrated by the crosslinking reaction (1), below. The prepolymers were then applied to aluminum substrates and the aluminum joints coupled and cured at 170°C in an oven.

(1) Polymer (2.00 g) with Si:Ti ratio of 2:1 prepared from p-phenylene-bis(methylphenylsilanol) and melting at 50-60°C was dissolved in benzene and 0.508 g of 5,5'-bis(salicyl-N-butylimino)methane was added. After refluxing for 15 min the benzene was removed and the residue was left at 120°C/0.6 mm for 2 hours. The crude product softened under 110°C. It consisted of 0.29 g ether soluble and 1.77 g ether insoluble (mp 80-210°C) fractions.

(2) Use of procedure (1) with p-phenylene-bis(phenylphosphinic acid) in pyridine yielded products with softening points above 150°C. Therefore, elastomer and crosslinking agent were mixed by either grinding together the two powders or by depositing the crosslinking agent onto the elastomer from an acetone solution. The mixes so obtained were then cured *in situ* on aluminum at 170°C.

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